

FIRE SAFETY CONSIDERATIONS RELATED TO THE LARGE SCALE USAGE OF SODIUM

By G. H. BULMER, A.M.I. Fire E.†

Sodium is reactive chemically with the majority of the substances which are in general use as fire-fighting media. Its ignition temperature varies between ambient and around 400°C. When burning, the effects of temperature and radiant heat are less for sodium than for combustion of an equivalent volume of carbonaceous materials. However, fires involving this metal are characterized by the copious evolution of caustic fume which reduces visibility quickly and makes fire-fighting by manual means difficult, if not impossible. Fire safety is achieved by a combination of good plant design and an automatically operating installation. Support facilities are required for decontamination work and for waste disposal. Preplanning and safety control is necessary if injury to personnel engaged in these activities is to be avoided.

Introduction

Fire safety engineering practice in respect of any chemical process is based on an understanding of the properties of the materials involved, under the conditions of use specified by the plant project team. Sodium is no different from any other substance in this respect and fire safety problems arising from its use are quantifiable and capable of resolution.

Some Chemical and Physical Properties of Sodium

Textbook accounts of the chemical and physical properties of sodium will be found in References 1 and 2. Some chemical and physical properties of sodium having a relevancy to fire safety are summarised below.

Air. In atmospheres containing 5% or more oxygen by volume, sodium reacts readily and will ignite.

Nitrogen. Sodium at 800°C is inert to nitrogen at 1000°C.³ Azide⁴ or nitride⁵ are formed in the presence of activated nitrogen.

Noble gases. Sodium is inert.

Carbon dioxide. Gaseous carbon dioxide is decomposed by burning sodium. A mixture of solid carbon dioxide and sodium is explosive when impacted.⁶

Steam. Sodium reacts quietly with dry steam to form hydroxide and hydrogen.

Ammonia gas. Gaseous ammonia passed through molten sodium forms sodamide and hydrogen.⁷

Halogens. Sodium will ignite spontaneously with fluorine at ambient temperature and with chlorine around 100°C.

Water. Sodium reacts violently with water liberating hydrogen which in air forms a mixture which explodes when the metal ignites. In the absence of air and under specified conditions the reaction is non-explosive.

Alcohols. With low molecular weight alcohols, sodium reacts to liberate hydrogen more slowly than with water. In general, the reaction rate decreases as the alcohol molecular weight increases.

† U.K. Atomic Energy Authority, Safety and Reliability Directorate, Risley, Warrington, Lancs.

Hydrocarbons. It is reported⁸ that some types of kerosene can be heated safely in the presence of sodium whilst other types are less desirable.

Sodium organo compounds formed under specified conditions, ignite spontaneously in air.⁹

Chlorinated hydrocarbons. Sodium may detonate when in contact with chlorinated hydrocarbon liquids, e.g., carbon tetrachloride⁶ chloroform¹⁰ trichloroethylene¹¹ and the recently developed fire extinguishing media such as B.C.F. (Bromochlorodifluoromethane).

Ammonia liquid. Sodium is partly soluble in liquid ammonia and in the presence of a catalyst such as iron, sodium amide is formed.²

Mineral acids. Sodium explodes on contact with hydrochloric acid and ignites spontaneously in contact with nitric acid of S.G. exceeding 1.056. With sulphuric acid, the violence of the reaction is inversely proportional to the normality of the acid.¹

Physical properties of interest are:

Melting point 97.8°C boiling point 882.9°C

Density 0.9684 g/cm³ at 20°C

Vapour pressure in mmHg for various temperatures is:
400°C—1; 548°C—10; 696°C—100; 752°C—200 and
815°C—400

Ignition of Sodium

In common with other metals which are reactive chemically, there is no fixed ignition temperature for sodium in air as the onset of combustion is very dependent upon a number of variables. For example, sodium in finely divided form is pyrophoric, whilst a pool of metal may not commence burning until its temperature reaches 400°C or higher. There are many factors which contribute to this wide difference in ignition temperature the most important of which are:

Surface to Volume Ratio. Particles of metal arising from condensed vapour or sodium in the 1 to 10 micron range obtained from a dispersion prepared in an organic liquid, have a very high specific surface and are pyrophoric, that is they ignite immediately on exposure to air at ambient temperature.

An escape of liquid metal in droplet form from a closed system is likely to ignite immediately if it is in contact with atmosphere. A solid stream of liquid metal of comparatively low surface area issuing from a fractured pipe or vessel may not ignite unless the sodium is at or above a temperature of about 200°C.

Pool ignition temperatures vary widely. When metal at a temperature of 200°C escapes from a system and collects as a pool under circumstances which favour the retention of heat, immediate ignition is likely. However, environmental factors such as the geometry of the pool, cooling, local ventilation and the mode of heating of the metal are all of importance and the ignition temperature will be a characteristic of the particular system involved.

Mode of Heating. The ignition temperature of sodium varies with the mode of heating and at around 120°C is lowest when air is excluded from contact until the metal has liquefied. When sodium at ambient temperature is heated in air, oxide accumulates on the surface and inhibits ignition until temperatures in the 275 to 425°C range are attained. When the layer of surface oxide is disturbed the ignition temperature falls to about 200°C.

Atmospheres of Reduced Oxygen Content. Ignition temperatures increase when the oxygen content of the atmosphere is decreased significantly. The effect is shown in the following table which is based on work at Atomic International.^{1,2}

TABLE I.—Effect of Atmosphere Composition on Ignition Temperature
Atmosphere Composition
(1 bar pressure)

Oxygen % (v/v)	Nitrogen % (v/v)	Humidity (g H ₂ O/kg air)	Sodium geometry	Ignition temperature (°C)
6.5	93.5	0.427	Pool	427
4.6	95.4	0.427	Pool	538
4.8	95.4	20	Pool	538
5.2	94.8	20	Pool	538
5.0	95.0	0.427	Spray	538

Comment

From the fire safety point of view the absence of a fixed ignition temperature is unfortunate since experience shows that changes in the environmental or the process conditions which lower the ignition temperature are not always appreciated until after an outbreak of fire has occurred.

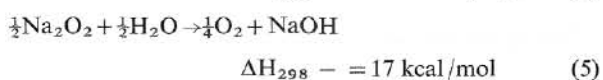
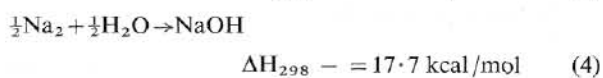
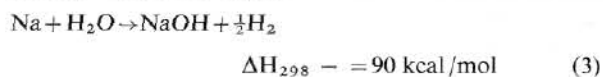
Combustion of Sodium

The thermochemical data for the principal reactions which occur when sodium is burning in air are as follows:

Reaction with oxygen



Reaction with water vapour



Since the water content in the air is small with respect to the oxygen, the reactions represented by equations (3) to (5) play a subordinate part in heat release.

The reaction which occurs in accordance with equation (1) represents the combustion of sodium to sodium oxide in a cell or other form of containment where there is an excess of metal. Under conditions where oxygen is available freely to support combustion, the formation of sodium peroxide (equation (2)) is favoured up to 650°C. Above this temperature the peroxide decomposes into sodium oxide and oxygen.

A summary of experimental work^{1,3} has shown that the burning rate of sodium varies between 2 to 45 g/s/m² of reacting metal surface (1.4 to 33 lb/h/ft²). Assuming the metal goes to the peroxide this corresponds to a heat output of between 2.3×10^4 to 5.1×10^5 J/s/m² (19 to 44 Btu/s/ft²).

It is reported^{1,4} that two-thirds of the combustion reaction of sodium occurs in the vapour phase with the balance taking place at the liquid surface. The reaction rate is determined by the vaporisation rate of the metal controlled by the rate of transport (including diffusion) of oxygen into the combustion zone. Sodium fires can therefore be subdivided into those occurrences where the metal burns as a pool and those where the metal is ejected in spray form from a leak or rupture in plant. In general the pool fire is characterised by a much slower rate of burning than in the spray fire due to limited access of oxygen to the reaction zone.

Typical sodium fires are shown in Figs 1 and 2 from which it will be seen that they are much less spectacular than are those involving many hydrocarbon and cellulosic type materials. It helps put sodium fire safety problems in perspective if its heat of combustion is compared with a few typical fire hazardous materials, for example:

Sodium	11.3×10^6 J/kg	(4 850 Btu/lb)
Timber, approx.	18.6×10^6 J/kg	(8 000 Btu/lb)
Methyl alcohol	22.3×10^6 J/kg	(9 600 Btu/lb)
Coal, bituminous	32.5×10^6 J/kg	(14 000 Btu/lb)
Petrol, approx.	47.8×10^6 J/kg	(20 600 Btu/lb)

Other significant differences of sodium combustion compared to that of hydrocarbons and cellulosic materials are:

Volume of combustion products. A volume of air which has reacted with sodium is decreased by the amount of oxygen which forms oxides. A volume of air reacting with hydrocarbons or cellulosic compounds is increased due to the formation of carbon dioxide and water vapour.

Flame height. Sodium flames rarely attain a height of more than a few centimetres. Flames from hydrocarbons may extend several metres above the liquid surface.

Convection currents. The convection currents produced by sodium fires are of smaller volume and lower velocity than those arising from the combustion of an equivalent amount of organic or cellulosic materials.

Radiant heat. The radiant heat flux from a sodium fire is much less intense than that arising from burning carbonaceous materials.

The net result of these differences is that the temperature at a distance of a metre or more above the burning sodium surface and the radiant heat incident upon the area surrounding the fire, are both lower than for a fire of equivalent size involving carbonaceous materials. There is also a reduction in building pressurisation effects.

The effects of sodium fires should not however be underrated as they can be serious. The metal burning as a spray, or as a pool of large surface area or high temperature may

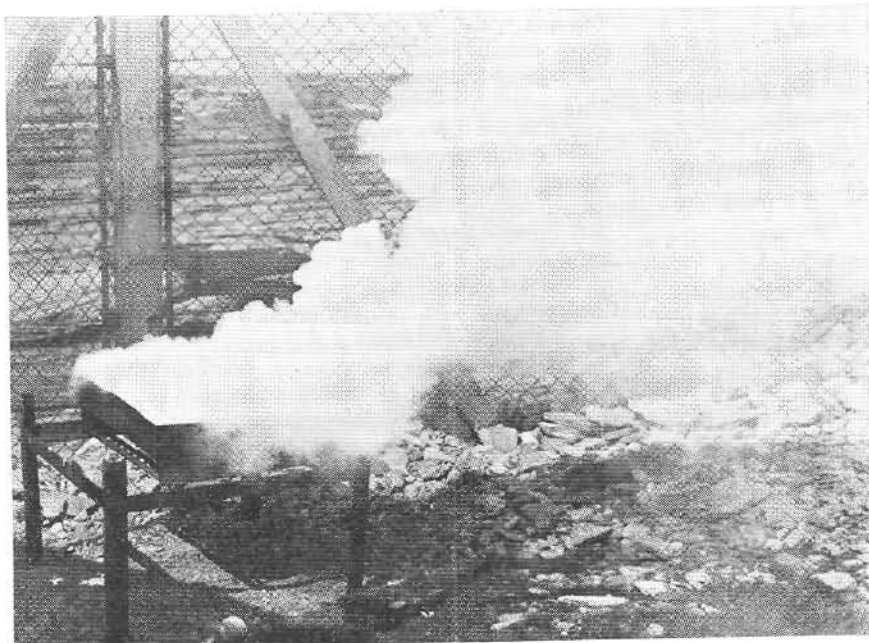


Fig. 1.—A sodium fire produced by heating metal bricks of the metal in contact with air. The large surface area of the tray available for cooling limits the equilibrium temperature and hence, the burning rate

pressurise and damage a building. Sodium and corrosion products arising from combustion can impair equipment severely. The fume evolved from a sodium fire of comparatively small size, quickly reduces visibility to a metre or less. The caustic and irritant nature of the combustion products make them unpleasant to remain in and personnel are likely to regard their own safety as being of greater importance than any shut-down or other remedial procedure which the fire demands. An appreciation of the fume hazard will be gained from the following table.

TABLE II.—*Sodium Fume Hazard*

Concentration of fume in air	Effect
2 mg/m ³	Acceptable for continuous exposure
50 mg/m ³	Tolerable for 2.5 min. Visibility reduced to under 15 metres
100 mg/m ³	Eye and lung discomfort. Serious loss of visibility, conditions intolerable
200 mg/m ³	Visibility nil

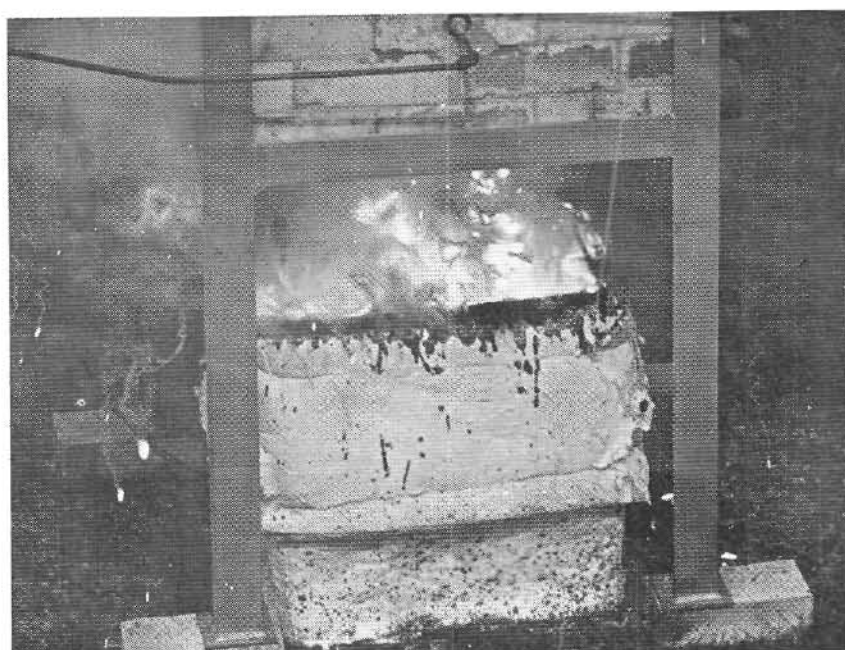


Fig. 2.—A sodium fire produced by heating metal to a temperature of 500°C+ in an argon atmosphere and then releasing it into a container which is thermally insulated. The sodium quickly reached boiling point and the burning rate is at maximum for a pool fire

Fire Safety

Introduction. The guide lines for fire safety in a plant handling significant quantities of sodium can only be determined satisfactorily following a hazard assessment whilst proposals are in the planning stage. Some of the many factors which need consideration against a background of appropriate legislation and suitable advisory documents are indicated briefly below.

Site suitability. Check that sufficient space is available for present needs and for expansion. There should be no possibility of flooding or an exposure hazard from adjacent plant or buildings. The site should have good road and telephonic communications.

Plan layout. Check that the layout provides adequate spacing to avoid congestion and that individual sites allocated for storage, processes, decontamination and waste disposal are segregated. Good access for emergency services should form part of the site layout.

Structures. Check that proposals for fire separation, ventilation (normal and emergency) and for fume scrubbing are adequate.

Chemical hazard. Establish the nature and magnitude of the fire, health and associated safety problems which are credible during normal and emergency conditions.

Materials handling. Examine proposals for handling and storing sodium and for transferring it through the plant. Arrangements for decontaminating equipment and for disposal of residues should be assessed.

Plant design. Check that provision has been made to reduce the incidence of fires and minimise the effects of those which are unavoidable.

When the fire safety assessment is complete detailed planning in respect of fire-prevention, fire-protection, and fire-fighting can commence. Some of the options open to management responsible for formulating a safeguards scheme are as follows:

Fire prevention. It should be ensured that all plant or facilities which handle sodium are not hazarded by a fire, or by the effects of fire, or by fire-fighting activities elsewhere.

Limiting sodium leakage. For plant handling significant quantities of metal at elevated temperature it is not normally justifiable, economically, to attempt to guarantee that leakage or spillage cannot occur. Good design can however reduce the probability of failure and limit the amount of sodium which escapes in the event of failure. For example, containment should be manufactured from sodium compatible materials and where recirculatory closed circuits are involved, cold trapping and gettering techniques used to limit internal corrosion damage. Double containment of pipework may be employed and the annulus monitored continuously to indicate leakage. Irrespective of whether double containment is used, provision should be made for the automatic detection of a sodium leak and for notification of the event to supervisory staff. In addition, the plant design should provide for draining the maximum quantity of metal from the circuit as rapidly as is practicable through heated pipework to one or more drain tanks. On large or complex plant it may be desirable to arrange for the remote operation of drain valves automatically.

Limiting the effects of leaking sodium. The hazard to plant, structure, operatives and the environment, resulting from a sodium leak can be minimised by pre-planning and good design. Sodium at elevated temperatures or when

burning will spall damp or uncured concrete explosively,¹⁵ react exothermically with asbestos and shatter materials containing hydrated compounds. It follows therefore that only sodium compatible materials should be used in the construction of a sodium facility. Granolithic concrete screed finishes should be avoided as quartz and other granitic materials tend to shatter when heated. In particular, concrete should be adequately sealed against in-leakage of water. In locations where concrete forms part of a system to direct or contain spills it should be well dried and cured. It is reported¹⁶ that fire resistant concretes made with cement of high alumina content have proved to be resistant to soaking and penetration by molten metals. No cable trenches or openings through which sodium can penetrate should be located below plant, nor should expensive equipment or important power supply or control circuits be positioned so that they are hazarded by leaking or burning metal. No service piping conveying materials which are incompatible with sodium should be routed through the plant area unless adequate protection against all credible emergency conditions is provided.

To protect personnel, vessels, pipework, test rigs, or laboratory apparatus which contain liquid sodium should be enclosed by a suitable screen in a manner which prevents escape of metal into the working area. Observation ports should be provided and shielded by a pivoted metal screen. Controls for both normal and emergency operation of equipment are required so far as is practicable, to be located on the outside of the screens.

As mentioned previously, the rate of burning of sodium varies widely and is determined largely by environmental factors. Where significant quantities of sodium are at risk, conditions should be created which control and confine leakage of metal in a manner which limits combustion, for example, a 16% reduction approximately in heat output is obtained if conditions restrict oxidation to sodium oxide instead of the peroxide (equations (1) and (2)).

The general pattern of such control is to arrange for small quantities of leaking metal to be channelled to honeycombed spill trays, or for larger quantities to containers, thereby limiting the surface area. A sump container is described, which it is reported¹⁷ collected and extinguished a simulated leak of burning sodium/potassium alloy. A grid or mesh positioned a few centimetres above the collecting pans is beneficial in restricting air flow to the volume enclosed below. It is recommended³⁰ that the area of perforation in such floors should be less than 30% of the free surface area.

When a large spill of burning metal which has collected on a floor or in open pans is extinguished, the danger of re-ignition remains until the metal pool temperature falls to around 200°C. An inert gas supply is an aid to cooling and spill containers should be designed to permit the free passage of gas around them in order to encourage heat transfer, for example, have fins welded to the base and sides.

A large spill of metal at a temperature of 500°C or more may also hazard structural steelwork. The aim should be to deflect leaking sodium away from steel stanchions or equipment supports. Safeguards include measures such as sloping floors away from sensitive areas and use of vermiculite or perlite concrete insulation. An alternative arrangement is to enclose stanchions or supports to a safe height above spill level by a metal sleeve which leaves an air gap for cooling by convection. In the latter case, entry of metal into the sleeve must be prevented by a deflector plate, alternatively, the space between the protected member and the sleeve may be filled with vermiculite or perlite granules.

Sodium leaking from an elevated position can cause damage in its descent due to effects such as corrosion and the shorting-out of electrical or instrument circuits. In addition, the fume

logging of the environment is encouraged. Where practicable, spill pans should be provided at intermediate levels. On large plant there would be merit in connecting individual pans to a low-level container by means of a heated pipe.

The use of an inert gas of low moisture content for cooling metal spills may, where practicable, be extended to provide a protective atmosphere for the whole sodium plant, thereby inhibiting combustion. Alternatively, a reduced oxygen content atmosphere may be employed. Longton¹⁸ has reported upon the mode of reaction of sodium at different levels of water vapour and oxygen. He has also compared the reactivities of water vapour and hydrogen upon the oxygen/metal reaction.

Table I shows the relationship between atmosphere composition and the ignition temperature of sodium. It follows that the metal cannot burn until sufficient oxygen is present¹² and the effect of varying atmosphere compositions is shown in Table III.

From the data in Table III it will be seen that in oxygen free atmospheres the main considerations are the temperature and pressure transients caused by heating of the inert gas. The rate of introduction of the metal, the duration of the fault condition and the degree of dispersion of the sodium will determine the severity of the transient. In atmospheres containing oxygen the same considerations will apply, augmented by the energy release from chemical reactions. As the oxygen percentage increases above 5% the combustion reaction becomes the dominant factor in determining the magnitude of a pressure transient.

A good ventilation system can help mitigate the effect of sodium fires by reducing building pressure, delaying the deterioration in visibility and lessening the site or district hazard. A scrubber or precipitation system of high efficiency is necessary as filtration units become blocked quickly by fume and particulate matter causing prohibitive back pressures to develop.

Fire detection. In plant which is manned continuously, operatives should become aware of the onset of fire or accident conditions at a sufficiently early stage to assess the fault in the few minutes available before visibility is lost. For other plant, an early warning of fire, or of conditions likely to lead to fire is an essential part of a fire protection scheme. Reference to Table III shows that the oxidation of sodium produces fumes even though incandescence is absent. This fume is detectable by conventional "smoke", or "products-of-combustion" type sensors which are available commercially. For plant

working in air or in an oxygen depleted atmosphere this is the preferred means of detection. Thermally operated sensors may have an application for detecting and locating spill fires, but in general they are too insensitive for monitoring buildings of large volume. In a vacuum or an inert atmosphere a flame photometer is suitable for detecting the presence of sodium vapour and thermally operated sensors or "spark plug" type detectors can be used to signal the presence of leaking metal.

An automatic fire detection system should be considered as an integral part of the safeguards scheme. There are rules¹⁹ and British Standard publications^{20 21} which give guidance on acceptable installations. There is a legal requirement²² that a fire warning system be provided in a works sodium plant and it is often advantageous economically to combine this with a scheme for automatic fire detection.

When planning an automatic fire detection system there are many variables to consider and, in addition to the guidance referred to in the previous paragraph, References 23 to 25 will be found useful. It is often necessary to use a signal from a smoke sensor to trigger relays which will operate protective devices, but the average instrument available commercially is not sufficiently reliable for this purpose. For example, consider a sodium plant facility which is monitored by fire smoke sensors wired in a single circuit and reconditioned annually. The arrangement is such that a signal from any one detector, cuts the power supply, operates a dump valve and discharges a fire protection system. A reliability assessment estimates the probability of a spurious alarm from any one of the sensors, as once in two years. In practice, faults in the control circuit and those due to other factors may well increase the likelihood of an alarm. Clearly such a high probability of a fault condition is unacceptable. A superior arrangement is that of triplicating the detection circuits and sensors and providing for control by a majority voting logic, two-out-of-three system. The probability of a spurious alarm is then diminished to one in about six years and by reducing the proof test interval to six months a further diminution to one fault in 26 years approximately results. In such a system there is an important bonus of improved sensitivity and reliability of detection.

Where a computerised alarm system is used to interrogate, process and display chemical plant data, signals from fire detection sensors may with advantage be integrated into the system to supplement the information available from other monitoring units. On smaller plant, a shared component installation for fire detection, security, equipment monitoring and other controls can be beneficial, economically.

TABLE III.—Effect of Atmosphere Composition on Combustion

Atmosphere Composition (1 bar pressure)			Sodium geometry and temperature (°C)	Observations
Oxygen % (v/v)	Nitrogen % (v/v)	Humidity (g H ₂ O/kg air)		
0.10	99.90	0.427	Pool, 427	No smoke
0.13	99.87	0.427	Pool, 538	Silvery surface; slight smoke
0.50	99.50	0.427	Pool, 427	Haze starting to appear
0.50	99.50	20	Pool, 538	Some smoke
0.50	99.50	0.427	Spray 538	Some smoke
2.00	98.00	0.427	Pool, 538	Heavy smoke
2.50	99.50	20	Pool, 538	Slight glow of oxide film
3.10	96.90	20	Pool, 538	Dense smoke, no incandescence
4.60	95.40	0.427	Pool, 538	Surface covered with nodules burning vigorously. Temperature increase to 693°C
5.00	95.00	0.427	Spray 538	Incandescence; dense smoke and rapid pressure increase
5.20	94.80	20	Pool, 538	Burning
6.50	93.50	0.427	Pool, 427	Burning nodules appeared

Since fire detection is often the king-pin on which plant safety depends, it is recommended strongly that the services of an independent qualified fire safety consultant be obtained. He should be required to survey the plant and prepare a scheme which provides an acceptable standard of protection and meets management's wishes with regard to reliability and sensitivity.

Control and Extinguishment of Sodium Fires

Introduction. Sodium fires are controlled and extinguished by excluding oxygen and by cooling. In general the same method is employed for extinguishing fires involving cellulosic and organic material fires, though there is a marked difference in fire-fighting techniques and in the extinguishants employed. To put problems of sodium fire control in perspective they are compared briefly with fires involving non-metals.

Cellulosic materials. Water is the medium employed to cool large quantities of burning cellulosic materials thereby reducing the rate at which flammable vapours are evolved and lessening the effects of the energy feedback from the flames. Eventually, the temperature of the materials falls below that at which sufficient vapour is evolved to sustain combustion. In practice, difficulties are encountered when water fails to penetrate a deep-seated fire and days may elapse before extinguishment is complete. Under these circumstances the danger of re-ignition remains until all the material involved has been exposed and cooled. The same problem of re-ignition arises when small quantities of burning cellulosic materials are extinguished by means of gaseous, vaporising or powdered materials, due to their inability to cool.

Flammable liquids. Re-ignition can occur when a liquid which has been involved in fire remains at a temperature above that at which the vapours will ignite spontaneously in air. Failure of the protective foam covering, or a lessening in the concentration of gas or vapour used to extinguish the flames, can result in re-ignition. Extinguishants in powdered form are characterised by their extremely rapid rate-of-flame knock-down but they have little cooling effect and the vapours may re-flash. Following a fire involving liquid hydrocarbons contained in storage tanks or vessels, the application of water sprays for cooling over a lengthy period is often necessary before the danger of re-ignition is passed.

Sodium. Metal fires follow the same pattern as that outlined for the non-metals and sodium can re-ignite whilst its temperature remains above 200°C approximately. The properties which make sodium attractive as a heat transfer medium create difficulties when a large spill of metal at high temperature occurs and provision for emergency cooling has not been made. The problem is aggravated by the fact that water cannot be used, (see equation (3)) also the quantity of heat contained in a pool of sodium at an elevated temperature may be significantly higher than that of an equal volume of a flammable liquid.

Sodium fire extinguishing media. There are a number of desirable characteristics which an extinguishing agent for sodium fires should possess. Some of the more important of these are:

- (1). It should be non-reactive chemically with sodium at high temperatures.
- (2). It should have a density less than that of high temperature sodium so that when it is applied, an oxygen-excluding seal can be formed on the metal surface.

- (3). It should have a good heat absorbing capacity.
- (4). It should be non-corrosive.
- (5). It should be non-toxic in the temperature range of use.
- (6). It should be non-hygroscopic, easy to store and be of reasonably low cost.

Scores of materials and combinations of materials have been investigated^{12 26} but no single substance meets all the above criteria. Some of the merits and demerits of the more suitable ones are:

Inert gases. Dry argon or nitrogen can be used for extinguishing a sodium fire but these gases are suited best to inerting to prevent fire. Changing an atmosphere from air to an inert gas of low oxygen content requires the through-put of a volume of argon or nitrogen many times that of the enclosure before this is achieved. Since the cooling effect of inert gas is low, the protective atmosphere has to be maintained until the metal cools below its ignition temperature. The gas supply may therefore have to be sufficient for a lengthy application, possibly exceeding 24 hours and the total volume required may be so high as to make the method impracticable. When inert gases can be used they have the advantage of being clean and non-corrosive.

Powdered materials. Metal fire extinguishants in powder or particulate form are good general purpose media with a wide range of application. When the combustion of sodium occurs at low temperatures, some of the oxides evolved remain on the surface and this effect, plus that of surface tension of the liquid metal forms a "raft" which will support extinguishants having a density greater than that of the sodium. As temperatures increase, the oxide covering diminishes and above 650°C approximately, the "raft effect" for all practical purposes, disappears. In practice this means that unless the extinguishant fuses and forms an oxygen-excluding skin on the metal, it is ineffective on deep pools of high temperature sodium unless the containment geometry permits an increase in level to be accommodated. When this is possible, cooling occurs as the powdered material sinks and the fire is controlled and eventually, extinguished. For example, it is reported¹² that small hollow spheres of aluminium oxide reduced the temperature of 5 lb of burning sodium, by 223°C in three minutes and extinguished the fire when they built up above the surface.

In general, test results show that dry inert materials such as sodium chloride and proprietary powders based upon it, ternary chloride eutectic,²⁷ anhydrous sodium carbonate (soda ash) and coarse grained vermiculite are the most successful extinguishants. All tend to permit sodium to burn through and further applications are necessary to maintain a seal. Brief comments on each, follow.

Sodium chloride and sodium chloride based extinguishants. The bulk density of these materials is a little over 1 g/cc. It is reported²⁶ that a sodium fire involving some 46 kg (100 lbs) of metal at a temperature of 732°C was extinguished in 3.5 minutes using about 36 kg (80 lbs) of a proprietary extinguishant based on sodium chloride. The hygroscopic nature of sodium chloride and its tendency to cake when stored are disadvantages. Manufacturers have attempted to improve the performance of the powders by using protective coatings and including flow additives. Some extinguishants contain an organic material to help create a seal on the burning metal surface.



Fig. 3.—The wicking action of burning sodium is shown by the several points at which the metal is burning on the surface of the vermiculite extinguishant

Sodium chloride powder ejected as a high velocity spray may be used for the control of combined flammable liquid/sodium fires. The density of the powder makes it suitable for use as a bund material to stem the flow of metal.

Sodium chloride powders are relatively inexpensive.

Austenitic stainless steels are susceptible to stress corrosion from compounds containing chloride ions.

*Ternary eutectic chloride.*²⁷ This powder is a mixture of sodium, potassium and barium chlorides, and its melting point is 555°C approximately. Its bulk density is about 1.2 g/cm³. It is reported²⁶ that a sodium fire involving some 236 kg (500 lb) of metal at a temperature of 760°C was extinguished in four minutes using 46 kg (100 lb) of TEC.

In general, TEC has the same advantages and disadvantages as sodium chloride, it is however more hygroscopic and more expensive. Dust masks should be worn by personnel handling the material, for example, filling fire extinguishers.

Soda ash. This material varies in bulk density between 0.5 to 1 g/cm³ dependent on grade. It finds application as an extinguishant for medium to low temperature sodium fires. Its use on metal near its boiling point is not advised as there is some doubt about the stability of the carbonate radical when in contact with high temperature sodium. Soda ash is very hygroscopic and double containment is necessary for its storage. Hydrated sodium carbonate flashes and decrepitates when applied to burning sodium. Though the material is relatively cheap, rather more is required than if sodium chloride were used.

Vermiculite. This material has a density of 0.2 g/cm³ approximately. In coarse granular form it will float on sodium and it will rise to the surface of liquid metal which flows onto it.

When applied to sodium burning at high temperature it reduces immediately the rate at which metal vapour is evolved and there is a noticeable lessening in flame intensity. Since vermiculite is a thermally insulating material there is no reduction in the sodium pool temperature. In practice, due to an adventitious moisture content in the extinguishant there is sometimes a slight rise in temperature accompanied by free flaming until the chemical reaction has ceased. Com-

bustion and other chemical reactions which continue are confined largely to the voids within the vermiculite layer but some wicking action often occurs, permitting sodium to burn as nodules on the surface (see Fig. 3). These spots must be covered with further vermiculite or the fire will re-establish itself. The interstices in the vermiculite layer become clogged in time with metal, oxides and other compounds which form a frit. A reasonably effective seal is thus formed which denies free access of oxygen to the metal surface. Figure 4 shows a sample cut from such a frit, the density of which is 0.32 g/cm³. Unless the metal can be cooled, it is likely to remain above its ignition temperature for a day or more. Vermiculite is inexpensive, non-corrosive, and easily handled.

Plastics materials. A number of plastics materials have been tested and of these, polyurethane foam appears the most promising though it requires further development. A sodium fire involving 46 kg (100 lb) of metal at a temperature of 427°C was extinguished in 8 min.²⁶ Fires burning at a higher temperature could not be controlled. Some success is claimed in the sealing of small leaks of metal.

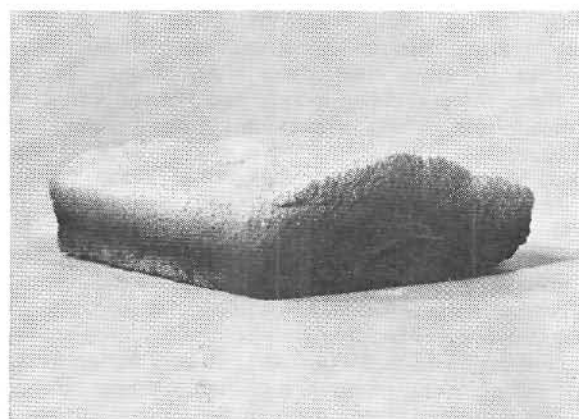


Fig. 4.—A section cut from the protective frit covering formed when vermiculite is applied to burning sodium metal at a pool temperature of 550°C

Fire-fighting

The time available for corrective action to be initiated before sodium fire conditions worsen markedly, is critically dependent upon the type of fire and, apart from metal burning as sprayed droplets, upon the prior arrangements made for cooling. When a stream of sodium at high temperatures escapes and collects under conditions which favour heat retention, the metal is likely to attain its boiling point very quickly. The situation which then confronts fire-fighters is so serious that it is very unlikely that corrective action of an improvised nature is practicable. When sodium collects as a pool under conditions which encourage cooling, either fortuitously or by design, the burning rate of the metal will be comparatively low and the fire is unlikely to attain its equilibrium temperature for tens of minutes. Under these more favourable circumstances fire-fighting by manual means is only practicable when an extinguishant in sufficient quantity can be applied to the burning metal. Where no means of transporting fire-fighting material mechanically has been provided, the amount that can be man-handled by men wearing full protective clothing, working in conditions of nil visibility, is very limited. As a guide, the work capacity of a man under these conditions may be taken as about 25% of what it would be normally. An operation of this type is only likely to be successful therefore when the fire is of limited size, within a reasonable distance of a fresh-air base and located at a point which can be reached by a straightforward unobstructed route.

There is no clearly defined relationship between the amount of sodium burning and the amount of material required to extinguish it. Under test conditions, ratios of extinguishant to metal vary between 0.2 to 1^{26} and 6 to 1.¹² In practice, under conditions of nil visibility much of the powder applied will be wasted and tens of kilogrammes of extinguishant may be required for each kilogramme of metal which is burning. Similarly, a vast amount of fire-fighting powder may be used when attempts are made to control metal leaking from an elevated position.

Protective clothing. Personnel entering a sodium fire area must be protected against caustic fume and against contact with burning metal. Respiratory protection is best afforded by self-contained breathing apparatus of the compressed air type as the filters of respirators are quickly clogged by fume. Clothing is a problem, as many materials are penetrated by burning sodium within seconds, for example, woollens and many synthetic fibres. The better materials such as chrome leather and aluminised asbestos withstand contact with splashes of burning metal for about 15 to 20 seconds before penetration occurs. Figure 5 shows one form of clothing. It will be seen that additional protection to the face shield is given by a stainless steel mesh and some shielding to the breathing apparatus connections is afforded by the cape. There are no pockets in which liquid metal can collect. Chrome leather, which is heavy, is the main material used. The design of the clothing has a disadvantage, in that it cannot be removed quickly. Figure 6 shows protective clothing manufactured from aluminised asbestos and Figs 7 to 9 show the effect produced by a splash of burning sodium. A feature of this design is that when breathing apparatus is not being worn, the clothing can be removed rapidly.

Whatever form of external protection is favoured, loose fitting flame-proofed cotton overalls should be worn beneath. Stainless steel wire of SWG 0.0032 in twill woven into 150 mesh will withstand penetration of high temperature sodium for a significantly longer time than materials in current use. It is reasonably light in weight and it appears to be sufficiently flexible for a helmet skirt, apron and gaiters to be fashioned from it.

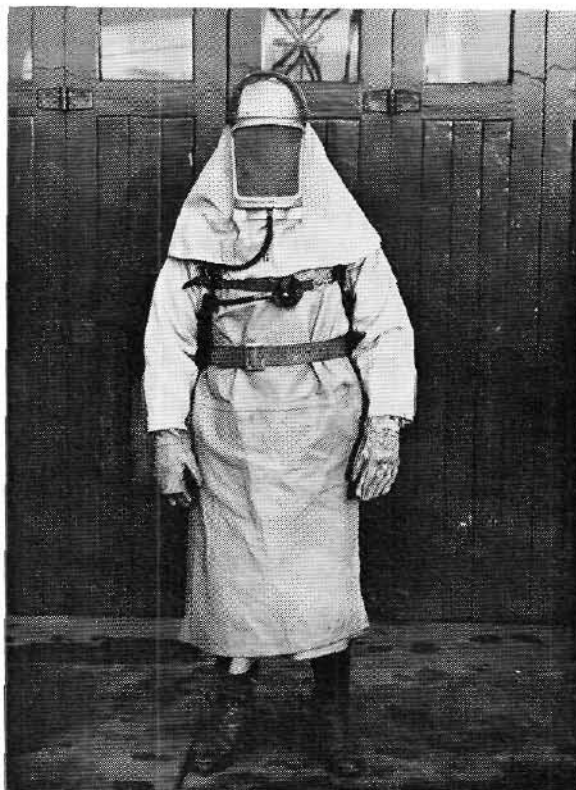


Fig. 5.—Protective clothing—chrome leather



Fig. 6.—Protective clothing—aluminised asbestos



Fig. 7.—Coat damaged by splash of burning sodium

Application of extinguishants. Powders are supplied in sealed double-skinned plastic bags. These may be used for forming a bund wall or as a convenient manner in which to transport material for the control of small spills of metals. Extinguishant may be stored in bins and applied manually by means of long handled scoops. Extinguishants may also be made available near potential trouble spots in fire extinguishers located strategically. The size of this equipment varies from fully portable 10 kg capacity models, to wheeled

ones of up to around 150 kg capacity. The extinguishers may be connected to distribution pipework for applying material remotely, for example, within a metal screen containment. Each extinguisher allocated for use on sodium fires should be fitted with a low velocity applicator. Plant operatives should be trained regularly in the use of the fire protection equipment. A few kilograms of extinguishant applied immediately following an outbreak of fire whilst visibility is comparatively good, is far more effective than a large amount used later when the plant is fume-logged. Large capacity powder storage vessels may be employed to supply extinguishant to powder hose reels for manual use, or to an installed piping system working on automatic discharge. In locations where fires involving large quantities of metal are possible, an automatically operating installation of high reliability, which fluidises and conveys extinguishant automatically at rates of tonnes/min is essential. For complex plant, the pattern of extinguishant discharge can be on a zone basis linked to cable-type heat sensing elements or to spark-plug type detectors.

Fire-fighting Aids

Aids to fire-fighting which may prove helpful are:

Locating the fire and determining its geometry. A portable, battery-operated instrument which will detect a radiant heat source is of value in a fume-logged building for determining the location, and to a limited extent, the geometry of a fire.

Fume control. To assist an overloaded ventilation system to cope with the large volume of fume produced by burning sodium, building air may be extracted via a high expansion foam generating unit and encapsulated in the foam produced. On no account should high expansion foam be used in an attempt to control the burning metal, as a hydrogen/air explosion is certain to result (see Fig. 10). Smoke extraction fans may also be employed for helping control fume emission from a building. Water sprays should be used to remove some of the sodium compounds from the extracted air. The efficiency of this type of improvised scrubbing operation is not high, but reasonable results can be obtained where the spray and fume are in contact for as long as is practicable.

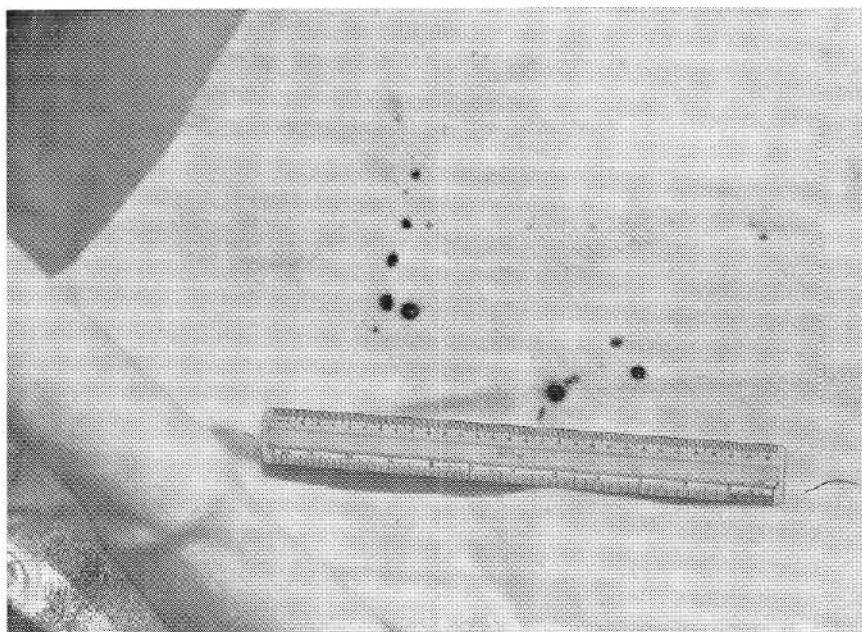


Fig. 8.—Rear of material showing points of penetration



Fig. 9.—Close up of damaged fabric

Leak control. Sodium leaking from a circuit tends to produce a large volume of fume and a troublesome fire, as it is difficult to apply extinguishant to surfaces which are not horizontal. Multi-layers of stainless steel knitted mesh (180 needle, 33 gauge) arranged in layers to form a pad is sufficiently flexible to permit its use as a sleeve. When secured, it arrests the flow of sodium to some degree and the mesh helps retain powdered extinguishant to control combustion. Alternatively, vermiculite granules in plastic bags may be packed around the trouble spot to contain leaking metal.

Support Facilities

Large scale usage of sodium requires support facilities and these require planning and safety control if incidents involving injury to personnel, fire and explosion, are to be avoided. Typical requirements are for:

An equipment cleaning facility. Plant repair, alterations and maintenance operations usually require that a cleansing facility be provided. The method employed is usually that of reacting metal and its residues chemically, for example, with steam plus nitrogen or argon, steam alone, and alcohols. The hydrogen which is generated in the majority of cleaning operations can produce dangerous pressures within equipment, causing metal to be ejected violently. Strict control of cleansing work is therefore necessary and some detailed guidance can be found in References 28 and 29.

The facility provided for cleansing equipment should be of adequate size and located conveniently to the main plant and to the area set aside for the disposal of sodium residues. A high extract ventilation rate linked to an air scrubbing system is essential.

Waste disposal. There may be a need to dispose of sodium metal or of metal contaminated waste. A burning hearth or

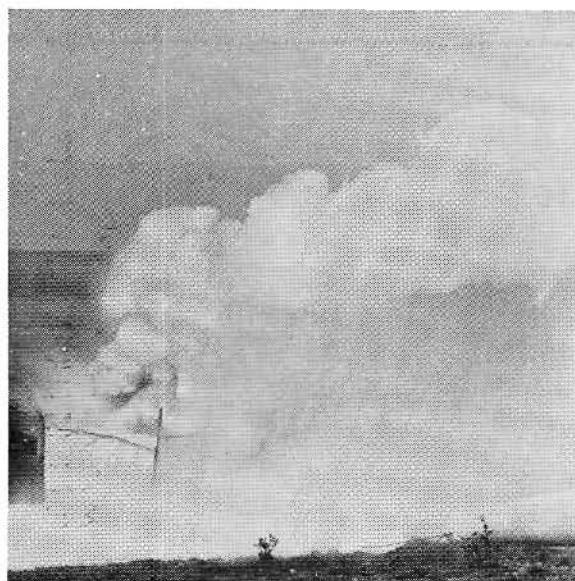


Fig. 10.—High expansion foam being applied to burning sodium

an incinerator is sometimes used for this purpose. Where, for convenience, such a facility adjoins that provided for cleansing, it is necessary that combustion products be passed through a water spray before they encounter air extracted from the cleansing facility. This is to avoid spark ignition of any hydrogen or other flammable vapours which may be present.

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The manuscript of this paper was received on 19 March, 1971.