

Abstract

Title of Document: Sodium fire suppression using liquid nitrogen

Deukkwang An, Master of Science, 2011

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Sodium has unusual fire hazards, notably a violent reaction with water. Experiments were conducted by heating stainless steel beakers (125 ml for 5 and 10 g sodium, and 250 ml for 20,40 and 80 g) to examine the effectiveness of liquid nitrogen against sodium fire. At 285 °C, vigorous surface reaction arises, resulting in a rapid temperature increase; ignition temperatures vary from 320-450 °C. At 600 °C, LN2 was added at a flow rate of 3 g/s. Applying LN2 to the sodium fire was effective as a sodium fire extinguisher. The linear correlation of the mass of sodium versus the mass of LN2 is approximately 1:2.9, whereas the analytical calculation of this ratio gives 1:3.0.

Sodium fire suppression using liquid nitrogen

By

Deukkwang An

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Dedication

To my parents, my brother and God.

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Chapter 1: Introduction

1.1 Sodium properties

Sodium is a reactive alkali metal. Its color is silvery white, but it has a faint pink color when freshly cut. As a metal, sodium is soft and ductile. It melts at 97.81 °C and boils at 881 °C. It has 11 atoms and an atomic weight of 23. Sodium is the sixth most abundant element, making up of 2-6% of the earth's crust, and it is the most abundant alkali metal. Sodium can be a good fluid for transferring heat because it has a high thermal conductivity, a high boiling point, and a high thermal stability. Even though sodium has these excellent physical properties, its violent chemical reactivity with water and air is a strong disadvantage to its use in the commercial industry. Some properties of sodium are shown in Table 1.

Na properties	Values
Atomic mass	22.99
Melting point ^a	97.8 °C
Boiling point ^a	882.9 °C
Density ^b	828.6 kg/m ³
Specific heat ^b	1262 J/kg-K
Thermal conductivity ^b	68.7 W/m-K
Viscosity ^b	0.2358x10 ⁻³ Pa-s
Latent heat of fusion	0.113 kJ/g
Electrical resistivity ^c	13.5 μΩcm
Vapour pressure ^c	2 Pa

Table 1-1. Sodium properties (Fast Reactor Nuclear Power Plant Safety, A Review of Sodium Release Fire Scenarios, 2010 and Developments in sodium technology, 2004)

^aEvaluated at p= 101.325 kPa

^bEvaluated at p= 101.325 kPa, T= 500 °C

^cEvaluated at T= 300 °C

1.2 Sodium usage

Sodium has been widely used as a reducing agent in chemical industries, pharmaceutical companies, and perfumeries. One example of its use as a reducing agent is the indigo dye in jeans. It is also used in storing energy in sodium sulfur batteries, in alloying metals, in refining metallic lead and zinc, and in smelting as scavenging agent. One well-known usage of sodium is sodium vapor lamps as streetlights due to their high efficiency. The high thermal conductivity and thermal stability of sodium allow its use as a medium for heat transfer. In this section, several applications of sodium will be discussed briefly.

The International Energy Agency built a Small Solar Power System plant in 1981. To transfer the heat generated by sunlight, liquid sodium was used instead of water. Seventy tons of sodium was used to store and transport this heat. This sodium was heated on the top of a

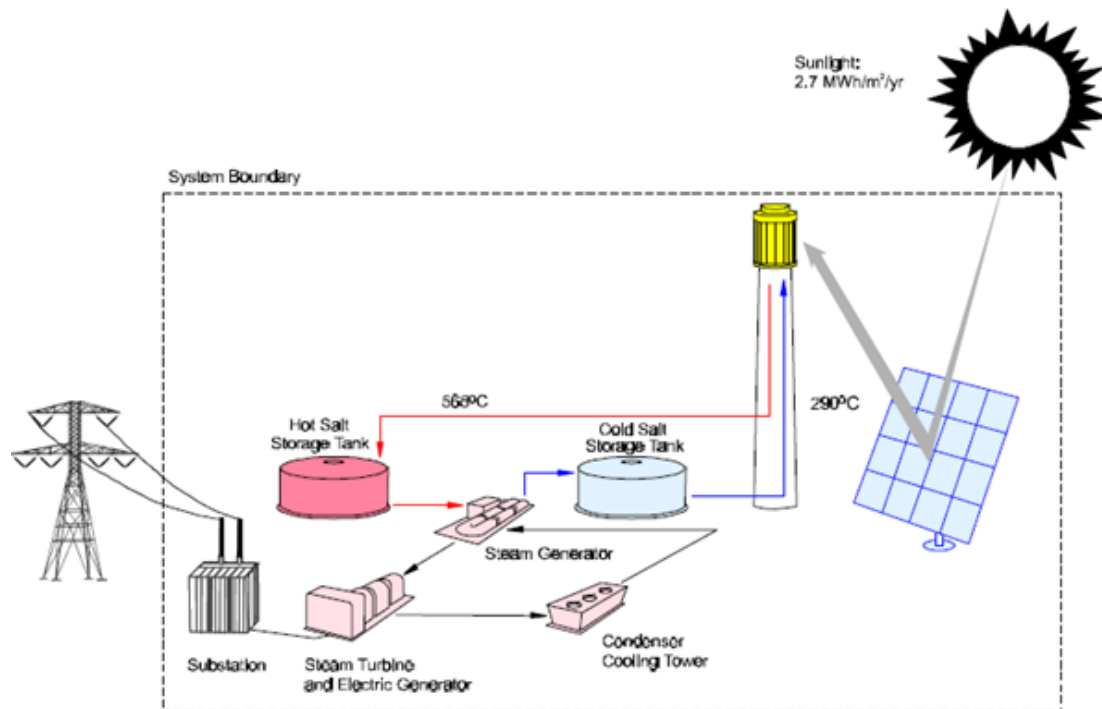


Figure 1-1. Solar energy system (<http://www.solarpaces.org>)

44m tower, and then pumped to a heat exchanger, where steam was generated. Then the

steam entered a tubogenerator for electricity. Figure 1-1 shows how sodium is used as a heat transfer medium. After a sodium fire accident in 1986, air was favored over sodium as a heat transfer medium in Europe. However, once the violent reaction of sodium with water and air is overcome, thus preventing sodium fires, sodium can become one of the best mediums for heat transfer.

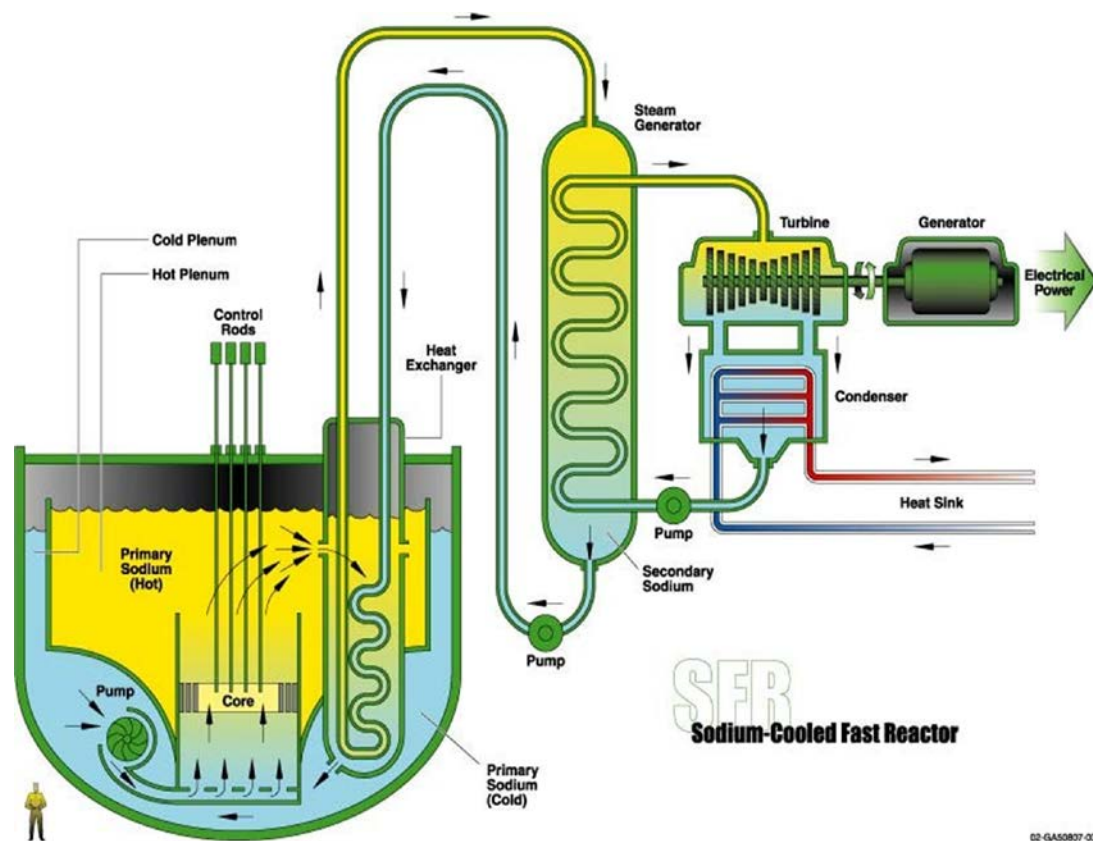


Figure 1-2. Sodium-cooled Fast Reactor (A Technology Roadmap for Generation IV Nuclear Energy Systems, 2002)

The first sodium reactor experiment in the United States began in 1957. Since then, Sodium-cooled fast reactors have been studied extensively in regards to their safety issues. Following fifty plus years of familiarity, sodium-cooled fast reactors still retain interest for nuclear industries. Ten experimental and six prototype and commercial-sized sodium-cooled

fast reactors have been constructed and more than US \$50 billion has been invested in this technology globally. The China Experimental Fast Reactor was constructed in July 2011 while the prototype PFBR of India and the commercial BN-800 of the Russian Federation are still under construction. Figure 2 shows the schematic of a sodium-cooled fast reactor. As shown in Fig. 1-2, the reactor has two sodium loops, the primary loop and the secondary loop. If the primary loop begins to leak sodium, the sodium will be contaminated by nuclear radioactivity. In this case, any sodium fire must be quickly suppressed so that any harmful effects on the facility or public will be minimized.

A sodium-sulfur battery uses liquid sodium. The battery has been studied for over 20 years by research and development companies. It consists of liquid sodium at the positive

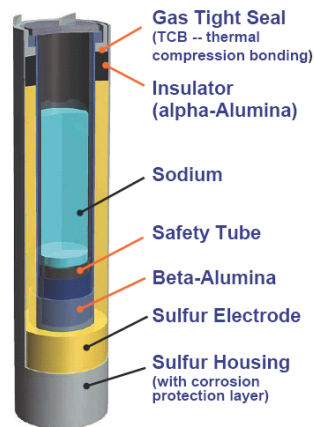


Figure 1-3. Sodium sulfur battery

(http://thefraserdomain.typepad.com/energy/2006/01/sodiumsulfur_na.html)

electrode and liquid sulfur at the negative electrode. This battery has about an 89% efficiency, and has a long life cycle with high pulse power capability. Also, the sodium sulfur battery has a high energy density, making it three times more compact than a lead acid battery. The largest sodium sulfur (NAS) battery has been recently built in Texas to serve as a back-up source of power. The NAS battery can be used for storing energy generated by renewable

energy facilities such as wave, solar, and wind power plant. Figure 1-3 shows one cell of a NAS battery while Figure 1-4 displays multiple batteries installed in a single module.

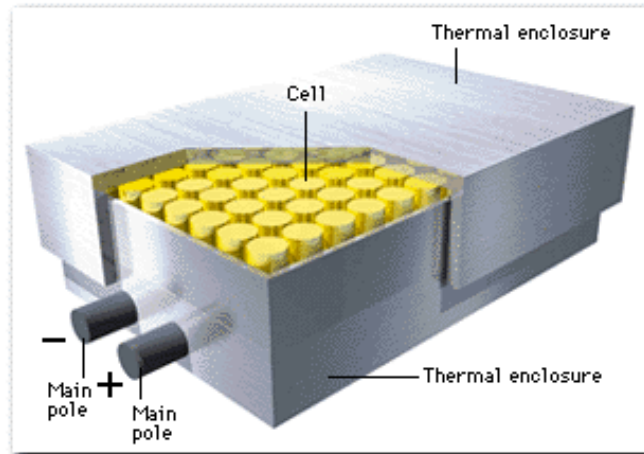


Figure 1-4. Sodium sulfur battery multiple cells

(http://thefraserdomain.typepad.com/energy/2006/01/sodiumsulfur_na.html)

Sodium is also used in laboratories for small-scale experiments. The dynamo lab team from the University of Maryland is one team that performs these small-scale experiments.

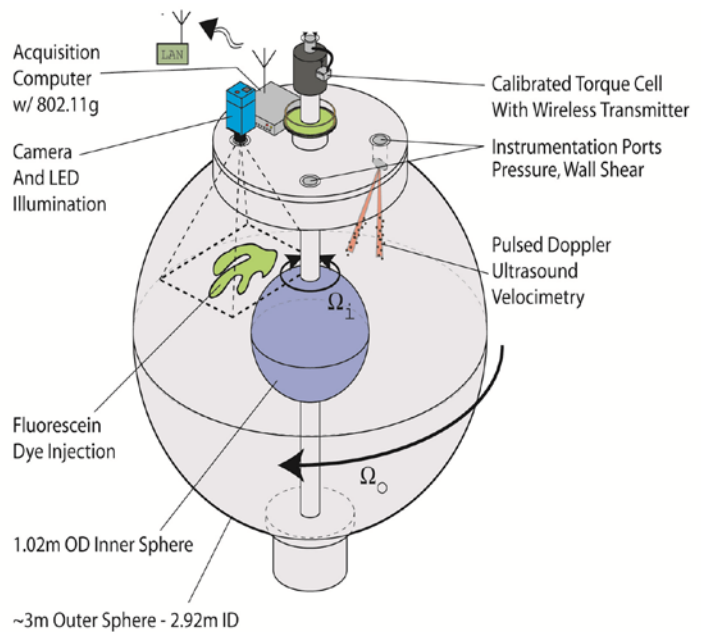


Figure 1-5. Sodium use in dynamo experiments)

(http://complex.umd.edu/3m_nonlinear_lab.html.html)

The dynamo effect has been experimentally studied to understand various phenomena that

arise in turbulent flows of magnetized fluids. Liquid sodium was chosen as a magnetized fluid due to its excellent electrical conductivity, which is advantageous to studying hydro-magnetic effects.

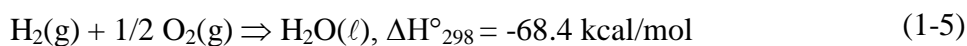
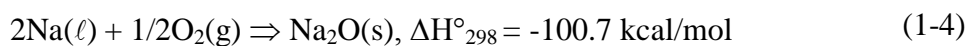
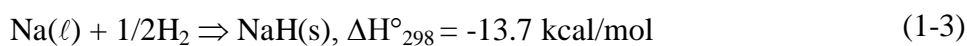
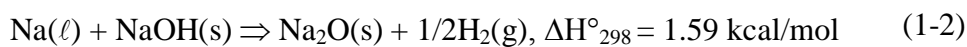
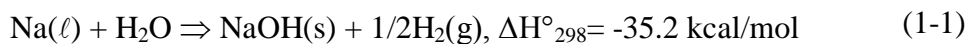
Sodium reacts with oxygen to form various oxides such as sodium monoxide (Na_2O), sodium peroxide (Na_2O_2), sodium hydroxide (NaOH), sodium superoxide (NaO_2), and sodium carbonate (Na_2CO_3) on the surface. Among them, sodium monoxide and sodium peroxide are dominant during sodium-air reaction. Sodium monoxide is a white powder in pure concentrations, but it is usually red or gray due to traces of impurities and excess sodium metal. Its melting point is 1132°C while its boiling point is 1950°C . Sodium peroxide is a pale yellow powder which darkens as the temperature rises. The melting point is 675°C . After it melts, sodium peroxide starts to evolve oxygen. Sodium hydroxide is made up of white, waxy, opaque crystals. As a solid, it is a white substance that can be in the form of lumps, sticks, pellets and chips. The melting point of sodium hydroxide is 320°C , and it has a boiling point of 1388°C . As sodium reacts with the air, sodium hydroxide may melt at 320°C and sink into the sodium metal itself, due to its high density. It may melt as the surface reaction occurs and sink below sodium due to its higher density (density of sodium: 0.968 g/cm^3 , density of sodium hydroxide: 2.13 g/cm^3).

1.3 Sodium reactions

If sodium reacts with water vapor or liquid water, the resulting formation of hydrogen can lead to violent explosions. When water reacts with sodium, it usually reacts with the surface of sodium. The heat generated by this reaction raises the temperature of the sodium so that it releases both burning and non-burning sodium droplets into the air with the explosion. The burning sodium projects outward and is the primary burn injury hazard to personnel engaged

in combating sodium fires, causing third degree burn injuries. Sodium's reactivity with air and water can pose a serious threat to people or facilities through its fire and fumes. In excess of water or in the absence of air, the reactions of sodium are not violent but relatively smooth. Oxygen mole fractions of less than 3% will prevent explosions from the interaction of hydrogen and oxygen. Absent water, sodium burns non-explosively in the air to produce irritating caustic sodium oxide smoke. Newman and Smith (1974) conducted experiments to analyze the reaction of sodium with water. They heated 10 g of sodium in an atmosphere of water vapour. The temperature of sodium rose rapidly, and ignition occurred at 98 °C. There was no smoke production and no accumulation of sodium products on the sodium surface. Within 2 minutes, the sodium temperature rose to the boiling point of sodium. It was also reported that small pyrophoric droplets of sodium were projected from the pool and burned in the atmosphere of water vapour with the occurrence of bright lights and smoke production.

The major Sodium-water reaction equations (Gracie and Droher, 1960) are

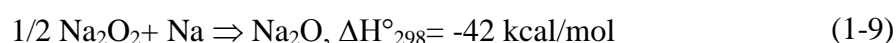
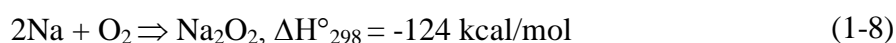
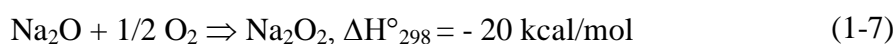
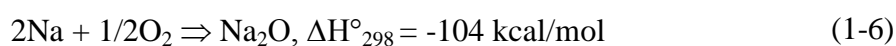


Reaction 1-1 is the dominant reaction in excess water and produces sodium hydroxide and hydrogen. The heat released from this reaction is of primary concern. In the presence of excess sodium, the hydrogen from Reactions 1-1 and 1-2 may react with sodium to generate hydride as shown in Reaction 1-3. Reaction 1-2 is the dominant reaction at high temperatures

only.

Reactions 1-4 and 1-5 show that the reactions between sodium and oxygen as well as those between hydrogen and oxygen have high exothermal reaction energies. The energy from reaction 1-5 is responsible for the resulting violent reaction and explosion; in just milliseconds, detonation occurs and a shock wave is produced.

Newman (1983) reported that the combustion of a liquid metal and the combustion of a liquid hydrocarbon have major differences. Liquid hydrocarbon fires start with the external ignition of a mixture of hydrocarbon vapour and oxygen above the surface while liquid metal reacts with oxygen as long as the reactants can mix freely. The ignition source of liquid hydrocarbon produces initial quantities of free radicals which start the branching of free radical chain reactions while the ignition of liquid metal occurs with rapid oxidation and temperature increase. Malet (1981) reported that ignition can even take place at room temperature if the sodium is a small particle. That is because the surface to volume ratio of the small particle is high enough that it allows for rapid temperature increase with ignition. Gracie and Droher (1960) discussed the following reactions when sodium combustion occurs.



The initial reaction may be represented by Reaction 1-6. The sodium monoxide reacts with oxygen to generate sodium peroxide in excess oxygen at 230 - 400 °C as shown in Reaction 1-7. Reactions 1-6 and 1-7 sometimes combine, as expressed in Reaction 1-8. Reaction 1-9

shows that sodium peroxide can react with sodium and revert to sodium monoxide. The formation of sodium hydroxide is caused by water vapour present in the air as shown in Reaction 1-10.

1.4 Sodium combustion

The release of aerosol is crucial in terms of nuclear and environmental safety. In a sodium fast-cooled reactor, an accidental sodium fire may be caused by leakage. Sodium leakage can cause sodium fire and eventually lead to sodium pool combustion. As sodium burns, sodium aerosol is released due to the reaction of sodium with oxygen and evaporation. The radioactive sodium aerosol itself may be harmful to the environment and extremely harmful to people. Cherdron and Jordan (1978) have experimentally studied the release of aerosol from sodium fires. This experiment was motivated by the fact that the radioactivity released during a pipe leakage can be attached to the sodium particles in a fast breeder reactor. They found that 10-30% of the burned sodium produced aerosols during sodium pool fires whereas 30-60% of the burned sodium during sodium spray fires generated aerosols. The particle size of sodium has been studied by Murata and Yusa (1977). In their experiments, the particle sizes of the aerosol followed a log normal distribution and the mass median diameter ranged from 0.6 to 2.0 μm .

Newman and Payne (1978) found that the flame temperature was 1200 – 1300 K at most and that the flame region extended only 1 mm from the surface. The temperature was measured by a thermocouple, and the flame region was examined visually. Yamaguchi (2009) reported that the flame temperature and the flame region agree well in computations.

Atomic International has developed an analytical model for the surface combustion of sodium, assuming that sodium burns at the pool surface. This model has large errors when it is compared with the experimental results of the combustion rate and of sodium temperature.

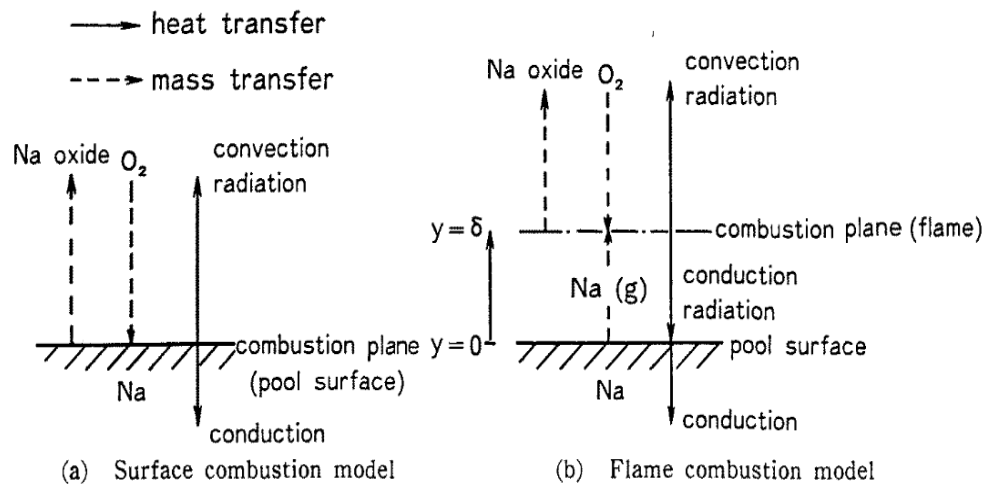


Figure 1-6. Combustion model (Sagae and Suzuoki, 1985)

However, this model for combustion has been often used because it is simple. Another analytical model is the flame combustion model. In the flame combustion model, it was assumed that sodium burns at the flame, which is separate from the pool surface. Sagae and Suzuoki (1985) have developed an analytical model of sodium pool combustion and compared it with their experimental results. The calculated combustion rates agree within 15% of the experimental results.

After sodium combustion, most of the residue consists of sodium oxides and unburned sodium. Humphreys found that the residue of sodium peroxide is dominant in excess oxygen whereas the sodium monoxide is dominant in excess sodium, while in the intermediate zone, both oxides are present. Subramani (2010) conducted experiments on a shallow sodium pool with a depth of 12 and 16 mm. In his report, it was found that the average burning rate of a shallow pool is higher by a factor of two than the steady burning rate value of 40 kg/hr-m^2

commonly used in most of the sodium fire safety computer codes. In his experiments, all of the sodium was consumed. He insisted that this may be characteristic of shallow pool sodium.

1.5 Sodium accidents

Sodium fire accidents have erupted in many places. A sodium fire hazard can be present anywhere and can come from false maintenance, manufacturing defects, design defects, and external events such as earthquakes. Sodium fire is extremely hazardous in, around, or near nuclear reactor due to the radioactivity. The radioactive sodium fume can seriously damage people's health. To establish the safety and reliability of sodium-cooled fast breeder nuclear reactors, extensive researches on sodium combustion have been conducted both experimentally and theoretically. In this section, several sodium incidents of sodium fire are reviewed to understand its causes and effects.

In 1968, more than 100 liters of sodium were spilled in United States. The incident occurred during the replacement of a valve in the secondary sodium system of the EBR-II Boiler plant building. The 300 liters of sodium were initially under a pressure of 13.5 psig at a temperature of 265 °C. The sodium ignited immediately when it leaked into the air. The fire alarm sounded and within 2 minutes, firefighters came and discharged 13.5 kg of portable, 160 kg of wheeled, and 90 kg of hosed Met-L-X powder onto the sodium fire. (No casualties were reported, but most of the equipment in the room were damaged.) The plant was able to restart operation after 13 days of the incident

In August of 1986, another sodium fire accident occurred in the Central Receiver System of the Small Solar Power Systems test facility near Almeria, Spain. The facility used 70 tons of sodium as a medium to transfer the solar energy in a generator. A solid sodium plug was cut, causing pressurized sodium to spew out as violent sodium spray fire. Unfortunately, only

several personnel were slightly injured, and there were no fatalities. A total of 14 tons (14 kg/s) of sodium were leaked, but the fire was suppressed within two hours. The temperature reached an estimated 1200 °C for 15 minutes during that time. It was also reported that the propagation of the fire was limited to natural convection and resulted in the destruction of the roof as well as damage to a neighboring room.

H.C. Starck, Inc. experienced a sodium fire explosion in 1993. Eleven firefighters were splashed by the sodium explosion and injured severely. The failure to extinguish the sodium fire was not from a lack of knowledge of dealing with sodium fire, for the firefighters were trained in metal fires in coordinating with the company of H.C. Starck, Inc. However, the moment they tried to extinguish the fire with a shovel of sodium chloride, the firefighters were splashed with sodium. The report does not specify the exact cause of the explosion; rather it only mentions that the explosion was most likely from the moisture transported to the sodium chloride.

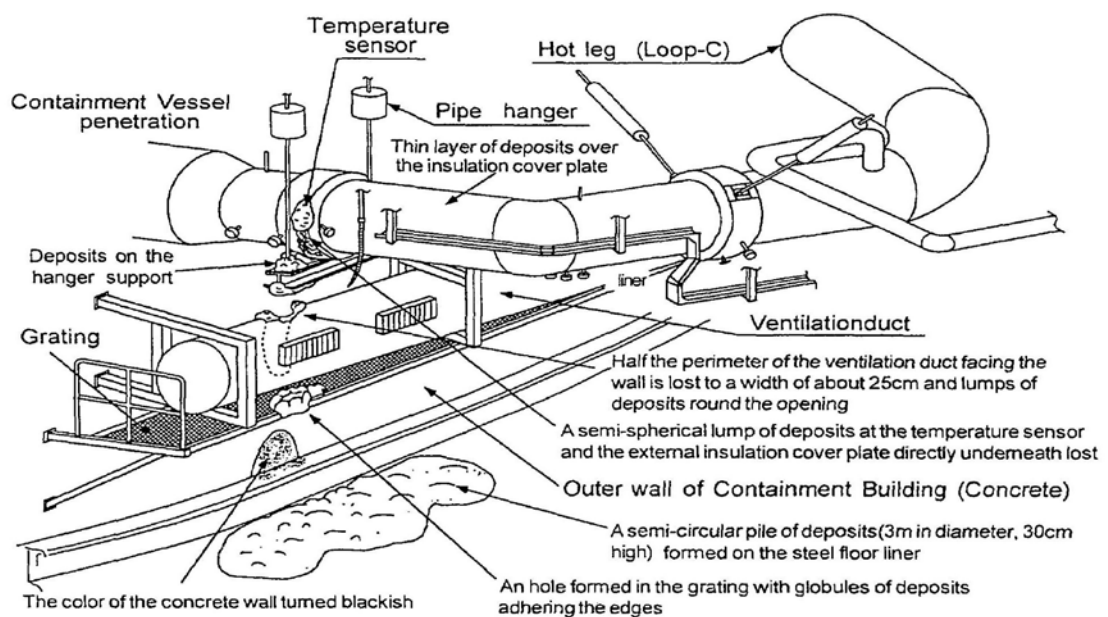


Figure 1-7. The Monju Prototype Fast Breeder Reactor (FBR) incident in japan (Fast Reactor Nuclear Power Plant Safety A Review of Sodium Release Fire Scenarios, 2010)

In December 1995, operators in the Monju Prototype Fast Breeder Reactor heard an alarm from the secondary side of the intermediate heat exchanger. Smoke detectors were also simultaneously functional. Operators closed the plant 1.5 hours after the alarm sounded. Fortunately, the sodium did not leak from the first coolant loop, so there was no emission of radioactive material. The leakage was due to an instrument port failure in the intermediate heat exchanger. The amount of sodium leaked was 640 kg (0.05 kg/s). The design has been re-evaluated and the facility shut down, but the plant is undergoing tests run now.

1.6 Sodium fire extinguishing agents

Gracie and Droher (1960) tested solid and liquid material over sodium fire and also determined desirable characteristics of sodium-fire extinguishing agents based on those of magnesium-fire extinguishing agents. The followings are the list of those characteristic.

1. The extinguishing agent should be compatible with sodium (no violent chemical reaction should occur).
2. It should not support the combustion of sodium; rather, it should prevent or inhibit further combustion.
3. It should have a high heat absorbing capacity.
4. It should be nonflammable.
5. It should be compatible with other chemical agents used in fighting different fires which may happen simultaneously.
6. It should be stable under storage condition; it should not be hygroscopic.
7. It should not be corrosive to the materials normally used in the construction of fire-extinguishing equipment.

8. It should have a low toxicity hazard. This also applies to the decomposition products formed on contact with a fire as well as the extinguishing agent.
9. It should have a lower density than sodium so that the extinguishing material will float on top of a pool of burning sodium.
10. It should be available in sufficient quantity and at a reasonable cost.
11. It should not contain any high-capture-cross-section materials if there is a nuclear reactor nearby.

Class D fire suppression agents such as sodium chloride have proven to be effective against combustible metal fire. Gracie and Droher (1960) tested various dry powder materials on 2.3 kg of sodium fire. They measured the time it took to extinguish the fire, the amount of extinguishing agents necessary to suppress the fire, and the difference in temperature, and also observed the sodium pool during and following the application of the extinguishing agents. A shovel was used to apply the extinguishing agents. From the experiments, it was concluded that Met-L-X was the outstanding powder extinguishing agent tested and that the powder would be even more effective if applied on a hotter fire. The Met-L-X consists of 85-90% of sodium chloride and 10-15% of polyacetate, magnesium stearate and attapulugus clay. Sodium carbonate was also reported as a good powder extinguishing agent, but it required relatively large quantities to be effective, so it was not practical. However, there are limitations associated with a dry powder based agent. The reports of Sodium Combustion and its Extinguishment state that the application of a powder system is being seriously questioned by most sodium fire protection experts in the United States. The followings are the disadvantages of dry powder agents suggested by the report:

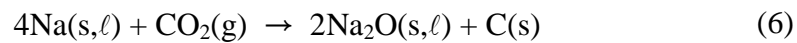
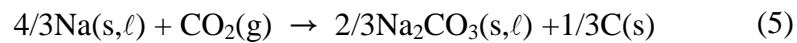
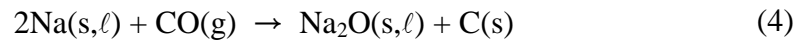
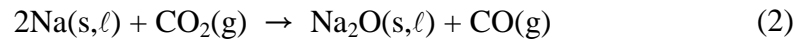
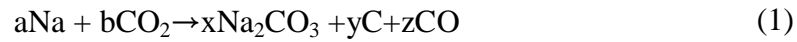
1. possible corrosive effects of powder on system components.

2. possible plugging of delivery pipe or nozzles.
3. operation is limited to one-time use, if the fire is not extinguished.
4. when the fire reignites, no further control is available.
5. all existing powder systems use an agent with a density greater than that of liquid sodium. Rapid or uneven discharge may permit the powder to sink.
6. possible incomplete coverage of burning surface due to "shadows" by cell structures.
7. possible non-uniform coverage due to thermal convection currents.
8. possible non-uniform coverage due to jet action of compressed gas.
9. possible caking or packing in the storage tank with attendant incomplete discharge.

Due to these disadvantages, Gracie and Droher (1960) tested oil based liquid agents to observe their effectiveness and behavior toward sodium fires. Liquid agents have a relatively low density and high flash point, as well as high auto ignition temperatures. The results of their experiment showed that oil-based liquid suppression agents alone are not effective on sodium fires because of the secondary fires. The secondary fires were then suppressed with sodium bicarbonate.

Carbon dioxide was tried as a sodium fire extinguishing agent at Atomics International despite the common belief that CO₂ explodes on contact with sodium fire. The results of that experiment show that the CO₂ did not suppress the sodium fire, but there was no violent reaction either. When liquid CO₂ was rapidly applied onto sodium fire, droplets of liquid CO₂ sputtered and crackled. Newman also conducted small scale experiments of sodium pool fires (10 and 30 cm diameter and up to 15 cm in depth) by varying CO₂ levels to examine their effectiveness in extinguishing sodium fires and concluded that extinction is possible with the proper level of CO₂. Miyahara et al (2011) have experimentally studied reaction behavior between carbon dioxide and liquid sodium. They found that the reaction between carbon

dioxide and liquid pool sodium is exothermic and that the continuous reaction starts with a threshold temperature, 250 -300 °C. The following reaction equations are from Miyahara et al (2011). It was assumed that overall possible sodium-carbon dioxide reactions might progress by equation 1. Reactions (2) and (3) are equivalent to reaction (7) when they occur at the same time. The relationship between reactions (5), (6), and (3) is like the relationship among reactions (2), (3), and (7). Figure 1-8 shows the calculated results for the changes of enthalpy, H, between 300 and 1500 K and the numbering in the plot was from chemical reaction equation. All of the reactions are exothermic, except for reaction (8). The properties of carbon dioxide are tabulated in Table 1-2 with the properties of nitrogen for comparison.



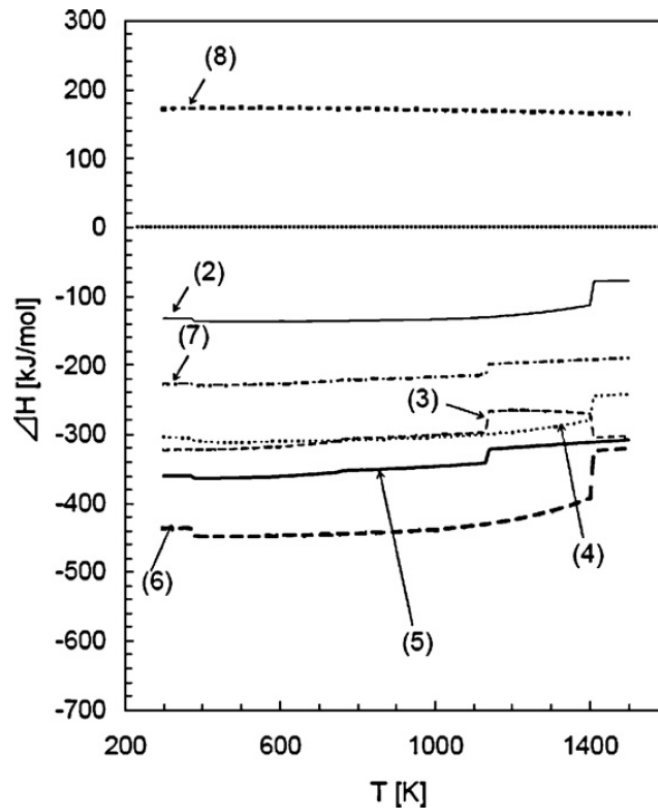


Figure 1-8. ΔH of Na/CO₂ reactions. $2\text{Na}(s,\ell) + \text{CO}_2(g) \rightarrow \text{Na}_2\text{O}(s,\ell) + \text{CO}(g)$ (2);
 $\text{Na}_2\text{O}(s,\ell) + \text{CO}_2(g) \rightarrow \text{Na}_2\text{CO}_3(s,\ell)$ (3); $2\text{Na}(s,\ell) + \text{CO}(g) \rightarrow \text{Na}_2\text{O}(s,\ell) + \text{C}(s)$ (4);
 $4/3\text{Na}(s,\ell) + \text{CO}_2(g) \rightarrow 2/3\text{Na}_2\text{CO}_3(s,\ell) + 1/3\text{C}(s)$ (5); $4\text{Na}(s,\ell) + \text{CO}_2(g) \rightarrow 2\text{Na}_2\text{O}(s,\ell) + \text{C}(s)$ (6);
 $\text{Na}(s,\ell) + \text{CO}_2(g) \rightarrow 1/2\text{Na}_2\text{CO}_3(s,\ell) + 1/2\text{CO}(g)$ (7); $\text{C}(s) + \text{O}_2(g) \rightarrow 2\text{CO}(g)$ (8).
 (Experimental investigation of reaction behavior between carbon dioxide and liquid sodium, 2011)

State	Nitrogen			Carbon dioxide		
	Solid	Liquid	Gas	Solid	Liquid	Gas
Specific heat ^a [J/g-K]	-	-	1.04	-	-	0.846
Latent heat of vaporization [J/g]	-	200 ^c	-	-	574 ^d	-
Latent heat fusion ^b [J/g]	25.7	-	-	184	-	-
Melting point ^b [°C]	-210	-	-	-78	-	-
Boiling point ^b [°C]	-	-196	-	-	-57	-
Liquid to Gas Expansion ratio	-	-	1:691 ^c	-	-	1:845 ^d

Table 1-2. Properties of carbon dioxide and nitrogen.

^a Evaluated at p= 1 atm, T= 300 K

^b Evaluated at p= 1 atm

^c Evaluated at p= 1 atm, T= 77 K

^d Evaluated at p= 5.11 atm, T= 216.4 K

(www.wikipedia.org, <http://www.engineeringtoolbox.com>, and Emergency characterization of unknown materials, 2007)

1.7 Liquid nitrogen

Liquid nitrogen (LN2) is inexpensive, easily available, and environmentally friendly. It has the following major advantages as a sodium fire extinguisher:

1. Very low boiling temperature, which allows for surface cooling.
2. Rapid extinguishment of fire through high expansion and heat absorption.
3. Depletion of oxygen and water through its atmosphere.

Application of LN2 on pool fire (ethanol, isopropanol and diesel oil) rapidly extinguishes the fires. LN2 on sodium fire may quickly extinguish the flame as well. The rapid extinction of sodium pool fire is desirable as it will minimize the thermal damage done to a plant as well as the emission of fumes. Furthermore, LN2 does not react with sodium and the evaporation of LN2 can reduce cleanup problems. Therefore, LN2 is one of the most effective candidates among all extinguishing agents.

Sodium fires are extremely hazardous and hard to suppress. Despite the expected advantages of liquid nitrogen (LN2) for extinguishing sodium fires, the research on this subject is limited. LN2 was discussed as a sodium fire extinguishing agent in lieu of dry powder in the UK. An experiment using LN2 over the large quantities of burning sodium was conducted, but the amount of LN2 applied to the burning sodium was not enough to suppress the sodium fire. Thus, this experiment was started to find out how LN2 is effective in suppressing sodium pool fires. The objectives are the followings:

1. Observe sodium fires for masses of 5-80 g.

2. Measure pool temperatures of sodium, LN2 mass versus time, and the amount of LN2 to extinguish sodium fires.
3. Evaluate the effectiveness of liquid nitrogen as a liquid extinguishing agent for sodium fire by quantifying the mass of sodium over the mass of liquid nitrogen.
4. Compare analytical calculation and experimental results.

These experiments focus on minimizing the sodium hazard by validating the effectiveness of liquid nitrogen as a suppression agent. Clarifying the effectiveness of LN2 over sodium fire will contribute to overall sodium science.

Chapter 2: Experimental

2.1 Experimental hazard

Sodium is corrosive, and can cause serious burns due to an almost immediate reaction with water, including on moist skin. If the metal ignites on the skin, very deep burns and tissue destruction can occur. Sodium is particularly and extremely dangerous and corrosive to the eyes or mouth. The sodium will react immediately with saliva to cause serious burns and possible local combustion even explosion of hydrogen in the mouth or esophagus. The metal's low melting point can cause further complications. Sodium splashes on a flammable material may cause a fire due to its high temperature and extreme water reaction.

If sodium splashes on the skin, the following steps must be taken.

1. Take off the splashed clothing, and uncover the splash area.
2. Remove all of the sodium immediately. Never use water. (If a large amount of sodium has been splashed on the protective clothing, make sure that the cloth is not burning. If it is on fire, promptly cover it with soda ash.)
3. Make sure that there is no more sodium left on the skin.
4. Wipe off any excess material from the skin. Then, immediately flush the skin with plenty of water for at least 15 minutes.
5. Get medical attention.

The sodium fumes evolve from a sodium fire of comparatively small size quickly reduce visibility to a yard or less. Inhalation of the fumes damages the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing, with possible occurrence of lung edema. Furthermore, sodium oxides are highly

corrosive and can cause severe burns. It is extremely destructive to mucous membranes and very damaging to the eyes. Table 2-1 shows the effects of sodium fume.

Concentration of sodium fumes	Effect
2 mg/m ³	Continuous exposure is acceptable
50 mg/m ³	Tolerable for 2-5 minutes. Visibility reduced to under 15 m
100 mg/m ³	Eye and lung discomfort. Serious loss of visibility, conditions intolerable
200 mg/m ³	Zero visibility

Table 2-1. The effect of sodium fume (Liquid metals fire control engineering handbook, 1979)

If fumes are inhaled, loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek medical attention. If sodium fumes make contact with the skin, the affected area should be washed immediately with plenty of water. The contaminated skin should be gently but thoroughly washed with running water and non-abrasive soap. It is recommended that folds, crevices, creases and the groin are particularly and carefully cleaned. Cold water may be used here. If skin infection occurs, wash the skin with disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Medical attention must be sought and received.

A splash of liquid nitrogen on skin may freeze skin tissue and cause severe cryogenic burns. Depending on the volume, suffocation may occur. If liquid nitrogen is inhaled, then the persons suffering from a lack of oxygen should be moved to where fresh air is abundant. If the victim is not breathing, administer artificial respiration. If breathing is difficult, administer oxygen. Prompt medical attention must be obtained. Any clothing should be removed that may restrict the circulation of blood to the frozen area. Do not rub any frozen tissue as tissue damage may result. As soon as is practical, place the affected area in a warm water bath not exceeding 40 °C. Never use dry heat to treat injury. Contact a physician as

soon as possible. Frozen tissue is painless and appears waxy with a possible yellow color. The tissue will become swollen, painful, and prone to infection when thawed. If the frozen part of the body has been thawed, cover the area with dry sterile dressing that has a large bulky protective covering, pending medical care. In case of massive exposure, remove clothing while showering the affected areas with warm water. Call a physician. If liquid nitrogen makes contact with the eye, the frostbitten area should be immediately placed in warm water not exceeding 40 °C.

2.2 Experiment condition

A schematic of the experiment is shown in Fig.2-1. Sodium samples with the

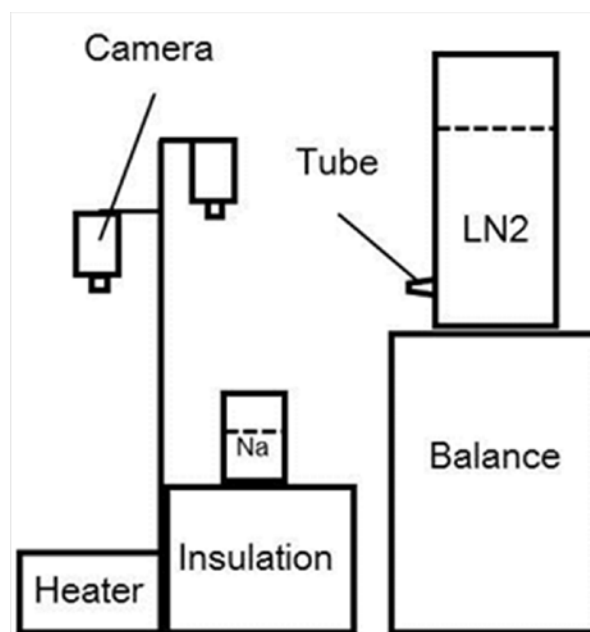


Figure 2-1. Experimental set-up. Objects shown are not to scale except the Na and LN2 containers.

masses of 5, 10, 20, 40 and 80 g were placed in 304 stainless steel beakers. The beaker size was 125 ml (diameter 500 mm, height 670 mm) for the 5 and 10 g of sodium while the 250 ml beaker (diameter 600 mm, height 890 mm) was used for the others. The sodium was

pounded flat under kerosene until the bottom of the beaker was covered with the metal. The kerosene was then removed. This pounding was done to prevent the sodium from oxidizing before the experiments had begun. Two K-type thermocouples were placed 5 mm below the sodium surface to measure the sodium pool temperature. The thermocouples were fixed by a clamp, and temperatures were recorded through a data acquisition system. Beside the two thermocouples, one more thermocouple was placed on the heater. This thermocouple was used for the purpose of observation. A web camera was placed to record the ignition of sodium as well as the extinguishment on its surface. Humidity and ambient temperature were measured with an electric hygrometer as well as a thermometer. A ventilator was turned on to remove the fumes created by the burning sodium as shown in Figure 2-2.



Figure 2-2. Ventilator for sodium fumes

An insulated plastic dewar (diameter 12 cm, height 19 cm) was used as a liquid nitrogen discharger. The tube of the LN2 dewar has an inside diameter of 2 mm and the length of

120 mm as shown in Figure 2-3. To measure the flow rate of liquid nitrogen (LN2), a LN2 cryogenic dewar was loaded onto a balance. LN2 was poured from an insulated plastic dewar into the LN2 cryogenic dewar. The LN2 lost to evaporation during the pouring process is negligible. This is because the balance recorded the mass of LN2 that was poured into the LN2 cryogenic dewar and because the cryogenic dewar is thermally well insulated. After the LN2 mass over time was recorded, the flow rate of LN2 was plotted as shown in Figure 2-4.



Figure 2-3. An insulated plastic dewar that has the tube (2 mm inside diameter and 120 mm of length)

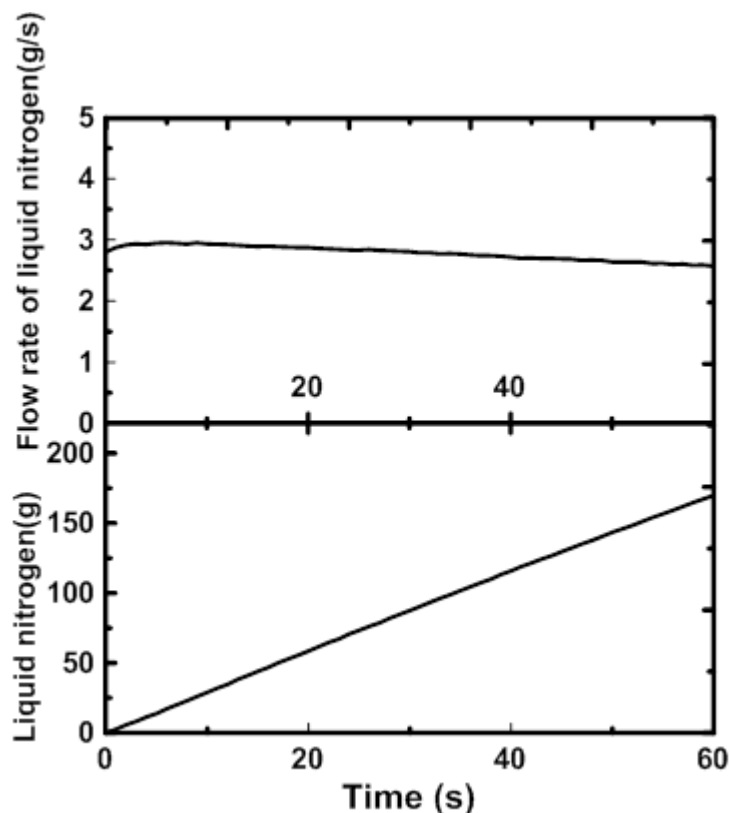


Figure 2-4. Flow rate of liquid nitrogen versus time and the mass of liquid nitrogen versus time during 60 seconds.

Liquid nitrogen (LN2) was kept in an insulated plastic dewar, which was then placed on a balance. The LN2 dewar and the balance were positioned so that LN2 could fall into the center of the beaker. Figure 2-5 shows the position of the stainless steel beaker and the plastic dewar. The distance between the beaker and the LN2 dewar was 200 mm, and the distance from the bottom of the beaker to the spout was 160 mm. Once the sodium is ignited, a cap is removed from the tube. The LN2 in the dewar can maintain a flow rate of 3 g/s (with an initial mass of 715 g of LN2), but decreases to 2.5 g/s after 60 s. When the mass of LN2 decreases to 600 g, additional LN2 (115 g) is poured into the dewar so that the flow rate is maintained even after 60 s.

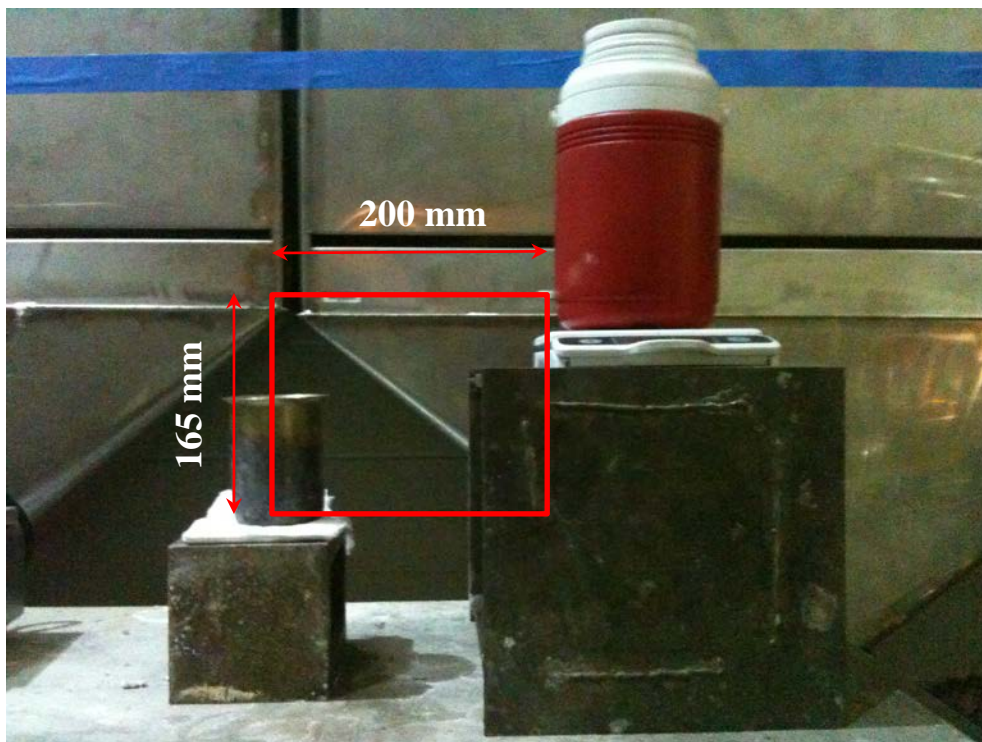


Figure 2-5. The distance from the stainless steel beaker to the insulated plastic dewar

The stainless steel beaker containing sodium was placed on an 890 W hot plate heater. After the heater was turned on, a mirror was then positioned over the heater to detect the ignition of sodium. After ignition, the sodium became incandescent and started to produce smoke. Then, the beaker was moved onto the insulating material. When the sodium pool temperature reached 600 °C, the tube cap was removed and liquid nitrogen was poured onto the sodium surface. The amount of LN2 that was poured into the beaker was estimated. If the amount of LN2 applied did not extinguish the sodium fire, then the experiments were repeated until the critical mass of LN2 needed to extinguish sodium fire was found. The experiments were recorded by a web cam, and the top view of the beaker is shown in Figure 2-6. A camera was used to capture the surface of sodium looking down into the beaker.



Figure 2-6. A capture image of a web cam recording file.

Nomex gowns, gloves, and face shield were worn during the experiment and were not taken off until after the experiments were over. Dry soda ash was on hand for emergency suppression of sodium fire while water was prohibited in the experimental area. Before the experiments, failure mode effect analysis was conducted to cope with any possible hazards of sodium fire and liquid nitrogen. Due to a misjudgment of how much sodium was left in the beaker during one of the experiments, sodium accidentally splashed out. At that time, a small amount of water was poured into the beaker. As soon as the water made contact with the sodium, some of the sodium burst out and penetrated the Nomex gown, causing skin burns. Therefore, water should be prohibited during this experiment. If water must be used with sodium during an experiment, extreme care should be taken and better protective clothing must be considered.

After each liquid pool sodium experiment, the sodium was cleaned up from the stainless steel beakers. The sodium residues were stuck to the beaker and made it hard to remove the sodium residues. The sodium residues mainly consisted of unreacted sodium and oxides. The small mass of sodium (5-10 g) was relatively easy to clean. The sodium was heated up until most of the sodium was burned. Once it was observed that the sodium was gone, the residues were scooped with chisels and scrapers, and they were disposed in a container with kerosene inside. After the sodium residue was removed, the beaker was cleaned with methanol. Methanol reacts more slowly than water does with sodium. Therefore, a violent reaction can be avoided in the case of any remaining sodium in the beakers. The same methods at the beginning of the experiments were used to remove the 20-80 g of sodium. However, the attempt to try to remove the sodium residues was time consuming and delayed the experiment significantly. Therefore, the sodium was heated to the point where it became liquid, and it was then poured onto a stainless steel panel to cool down. The rest of the residue in the beaker was removed in the same way the small mass of sodium was applied. Uncertainties in the experiments are estimated at $\pm 5\%$ for the flow rate of LN2, ± 30 °C for the temperature of sodium, and ± 1 g for the initial mass of sodium, $\pm 10\%$ for the minimum LN2 required for extinction, $\pm 30\%$ for the ratio of the mass of burning sodium to the minimum mass of LN2 required for extinction.

Chapter 3: Result and discussions

The behavior of sodium combustion and the relationship between the mass of sodium and the mass of liquid nitrogen were carefully observed and characterized through several experiments. The effectiveness of liquid nitrogen over sodium fires was focused on. In this section, the experimental results will be presented and discussed in detail.

3.1 Description of sodium pool burning

Removing kerosene from the beaker changed the silver surface of sodium to a dull grey

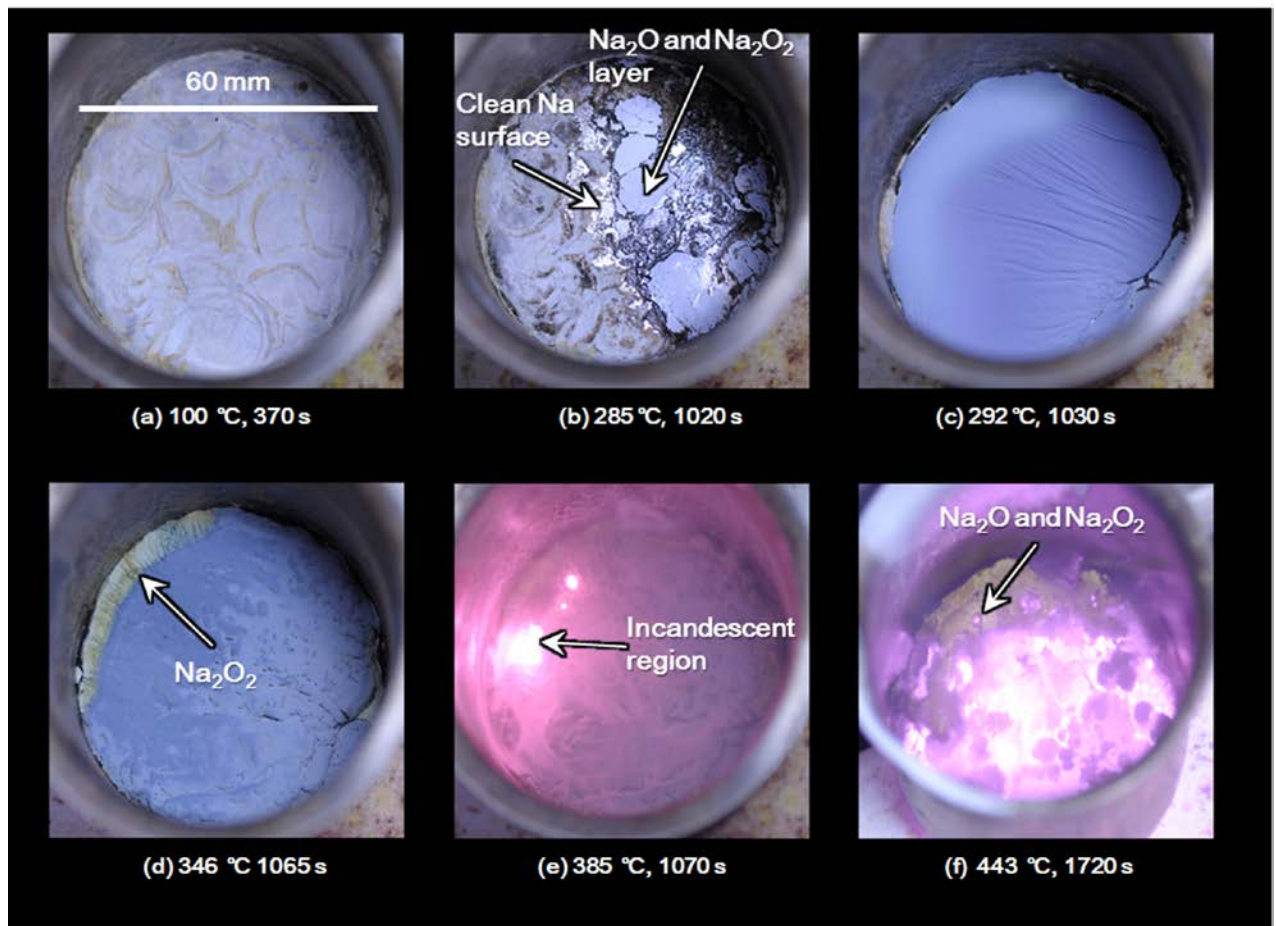


Figure 3-1. Color images of the top view of a 40 g sodium burn test prior to LN₂ addition. Beaker size was 250 ml. Times and temperatures 5 mm below sodium surface shown are approximate. The colors are indicative of the various oxidation states.

color within about 10 s as it made contact with the air. Sodium started to generate smoke as it

reached 70°C. The temperature increased gradually and there was no visible change in the beaker while it was forming oxides on the surface. The oxide layer prevents sodium from reacting with the air at low temperatures, so ignition of the sodium does not start immediately. When the temperature reached 97.81 °C, the sodium melted, leaving crust in some places on the surface, see Fig. 3-1 (a).

As soon as the pool temperature reached 285 °C, the surface of sodium started to melt away as shown in Fig. 3-1 (b). The molten hydroxide layer commences a vigorous surface oxidation process. During this process, the clean surface of sodium shown in Fig. 3-1 (b) was briefly observed. After the grey surface layer covered the entire surface, it started to crease the surface with wrinkles. Figure 3-1 (c) shows the initial stages of wrinkling. The oxide surface layer at the brim of the beaker partly changed from grey to the yellow area as shown in Fig. 3-1 (d). Further oxidation of the surface produced incandescent regions as well as smoke as shown in Fig. 3-1 (e). The incandescent region was generated between the sodium peroxide and the oxide layer. Figure 3-1 (f) shows sodium burning in the shape of a pillar.

Figure 3-2 shows the pool temperature versus time for representative sodium burn tests without the addition of LN2. Different mass samples of sodium showed similar trends of temperature profiles. The sodium had a phase change at 97.81 °C and rose in temperature gradually. As the temperature reached 285 °C, a vigorous reaction at the surface started along with a rapid rise in temperature, and the surface layer melted away from the side of the beaker to form the grey oxide layer on the surface. The dotted line shows the temperature profile from Newman (1972) as shown in Fig. 3-2. The Newman's result shows behavior that is similar to the results of this paper. However, the temperature profile has a shorter burning time and a higher temperature, with a 320 °C surface layer melting temperature compared to

the 285 °C here. One of the reasons for this disparity may be the use of different beakers and the area of contact with the heater. A nickel beaker was used in Newman's experiment and the exterior surface area of the beaker was completely surrounded by the heater. Other reasons may include different heating rates and a low depth of sodium. The heating rate was slowed (60-70% of rated heater power) to control the timing of when to apply LN2 during this experiment.

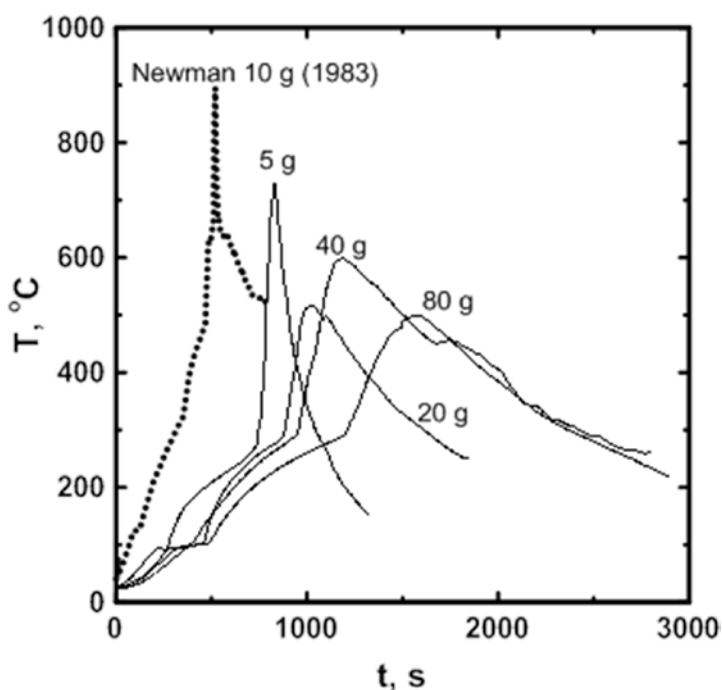


Figure 3-2. Pool temperature versus time for representative sodium burn tests without LN2 addition. The initial masses of sodium are shown. Beaker size was 125 ml for initial masses of 5 and 20 g, and 250 ml otherwise. The time datum is the start of heating. Data of Newman is shown for a beaker size of approximately 10 ml.

Unlike ordinary fires, the sodium fire is close to the surface and generates dense clouds of white smoke, but the heat generated by the sodium fire has about the same amount of heat as an equivalent weight of burning wood. As the sodium burns, sodium rises upward in the shape of pillar about 5-8 cm. These oxides showing yellow and white colors are sodium oxide

and peroxide. After the sodium burning, all of the mass samples of sodium except the 5 g had a large portion of unburned sodium left in the beaker. The temperature of the 5 g of sodium rapidly decreased because no sodium was left in the beaker.

3.2 Ignition of sodium

Newman (1983) reported that liquid metal reacts with oxygen in the air, that the point of ignition is the temperature at which the oxidation is rapid enough to cause a bulk rise in temperature, and that the reaction can occur in the gas phase or on the surface of the metal fuel. He mentioned that combustion can be a surface process, which precedes a vapour phase reaction or that the surface reaction may be the major process. He also defined the ignition temperature of sodium as a surface reaction temperature, which marks a self-heating and rapid surface oxidation at the surface. Malet (1981) as well reported that sodium burns in either the vapor phase reaction or on the surface. For this paper, ignition will be termed as surface reaction while the incidence of incandescence with smoke will be called the vapour phase ignition. Newman (1972) concluded that the ignition temperature is related to the melting point of sodium hydroxide (318 °C) as it prohibits sodium from reacting with the air. Therefore, breaking this surface layer will lead to low ignition temperature. Gracie and Droher (1960) found that liquid pool sodium exposed to the air did not ignite until after 204 °C. If the pool of sodium was agitated up to the point where the surface oxide residue was removed, then it was ignited at 287 °C. For this experiment, sodium ignited at 285 °C whereas Newman's ignition temperature was 320 °C. Casselman stated that the ignition temperatures in literatures ranged from 120 to 470 °C and that these temperatures depend on the sample size, static or turbulent states of metal, the degree of sodium purity and oxidation. (The meaning of ignition temperature from Casselman seems to be vapour phase ignition

temperature, and the ignition temperatures in the literature may include both surface ignition temperature and vapour phase ignition temperature.) In addition, Polykhalov mentioned that the heating rate is also an ignition parameter, and that the slow heating of sodium in air affects ignition temperature substantially.

Glassman (1960) has established criteria to determine whether metals have undergone a vapour phase reaction or a surface reaction. If the boiling point of metal oxides is higher than the metal, it is be classified as being in vapour phase combustion. In all other cases, the metal is undergoing surface reaction combustion. Sodium oxides have a high boiling temperature, which occurs at 1950 °C while the sodium only boils at 883 °C. According to Glassman’s criteria, sodium is in vapour phase reaction combustion.

The ignition temperature of the vapor phase combustion varied from 335 to 455 °C in this experiment as shown in the Table 3-1. The vapour phase ignition temperatures shown in the table are average values for each mass samples of sodium, and the ignition temperature for vapour phase combustion was hard to reproduce due to various conditions. However, a temperature for the rapid surface reaction was easily reproduced in most of the experiments.

Mass (g)	Ignition temperature (°C)	
	125 ml	250 ml
5	377	402
10	395	455
20	386	422
40	-	339
80	-	335

Table 3-1. Average ignition temperature of different sodium mass samples

3.3 Sodium pool temperature

Tables 3-2 and 3-3 show the maximum temperatures depending on a ratio of height over surface area. The peak temperature of 600 °C was reached when the sodium pool depth over surface area ratio was smaller than 0.054 cm⁻¹. Otherwise, the maximum pool temperature reached 510 °C to 550 °C (125 ml for 10 g and 250 ml for 80 g). In Newman's experiments, the maximum sodium pool temperature was 727 °C for an unconfined burning pool. This may be due to the small amount of sodium (10 g) and the high thermal conductivity of sodium beaker. In this experiment, the maximum temperature of the pool was never reached except the 5 g of sodium.

125 ml			
Mass (g)	Temperature (°C)	Height (cm)	Height/Surface area (cm ⁻¹)
5	700	0.275	0.014
10	600	0.549	0.028
20	500-510	1.099	0.056
40	-	-	-
80	-	-	-

Table 3-2. Sodium mass with maximum pool temperature corresponding to height over surface area for 125 ml of beaker

250 ml			
Mass (g)	Temperature (°C)	Height (cm)	Height/Surface area (cm ⁻¹)
5	700	0.191	0.007
10	600	0.382	0.014
20	600	0.763	0.027
40	600	1.526	0.054
80	500-510	3.052	0.108

Table 3-3. Sodium mass with maximum pool temperature corresponding to height over surface area for 250 ml of beaker

3.4 The mass of LN2 over the mass of sodium

As soon as the sodium pool temperature reached 600 °C, LN2 was poured onto the sodium surface. The sodium pool generated large quantities of black smoke as the liquid nitrogen made contact with the sodium as shown in Figure 3-3. The pool temperature dropped rapidly upon LN2 addition. The sodium fire was suppressed soon after the LN2 reached the surface of sodium, and the LN2 that was poured onto sodium evaporated rapidly.



Figure 3-3. A capture image of a web cam recording file when the LN2 contacts the sodium fire

However, after all the LN2 evaporated, the sodium, having a less than critical amount of LN2 for sodium fire extinguishment, re-ignited sporadically. When the critical mass of LN2 was applied over the sodium fire, the fire was suppressed. Figure 3-4 shows the temperature

profile of the sodium pool when the LN2 successfully extinguished the sodium fire. The suppression time increased as the mass of sodium increased. Greater LN2 flow rate may reduce suppression time.

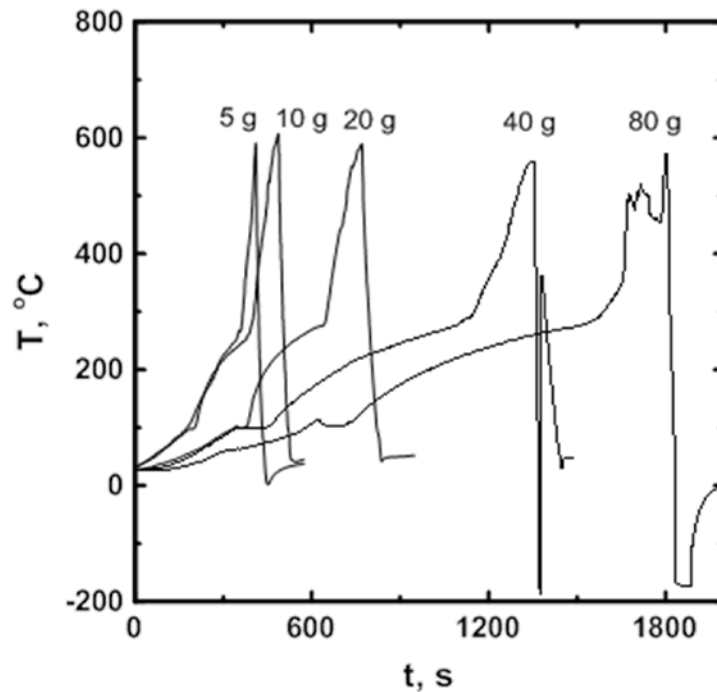


Figure 3-4. Pool temperature versus time for representative sodium burn tests with LN2 addition that led to extinction. The initial masses of sodium are shown. Beaker size was 125 ml for initial masses of 5, 10 and 20 g , and 250 ml otherwise. The time datum is the start of heating. Addition of LN2 commenced when the pool temperature reached 600 °C.

The mass of LN2 over the mass of sodium for sodium fire suppression is shown in Fig. 3-5. In each case, the sodium pool fire was considered to be extinguished if no re-ignition occurred after ignition flameout. The Figure 3-5 shows that no differences are discernible between the big beaker and the small beaker for the mass of liquid nitrogen over the masses of sodium. The intercept depicted in the figure is from the stainless steel beakers and it was assumed that there was a negligible difference between the big beaker and the small beaker for the intercept. The linear correlation was found for all the mass of sodium

conducted. The line shown is a least-squares fit through the five round symbols. The fit

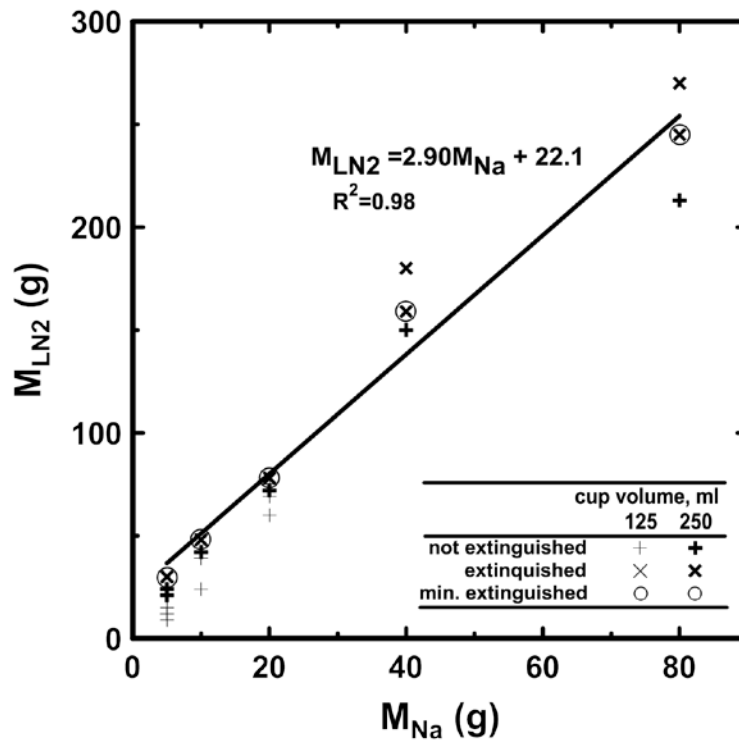


Figure 3-5. Mass of LN2 applied (M_{LN2}) versus initial mass of sodium (M_{Na}) along with fire suppression effects by symbol. In each case the sodium pool fire was only considered to be extinguished if no re-ignition occurred after LN2 application.

line equation is $(M_{LN2} - 22.1 \text{ g}) / M_{Na} = 2.90$ with $R^2=0.98$. Therefore, a unit mass of sodium may require 2.9 times a unit mass of LN2 for the suppression of a sodium fire. The intercept from the beaker should be considered when the equation is applied. Tables 3-2 and 3-3 show the mass of LN2 applied over the initial mass of sodium for the 125 ml and 250 ml beaker respectively. The experiments to find out the minimum LN2 required for sodium fire suppression were repeated by adding more LN2.

125ml cup		
Mass of sodium	Mass of LN2	Extinguishment
5	9	N
	12	N
	15	N
	18	N
	21	N
	24	N
	30	Y
10	24	N
	39	N
	42	N
	48	Y
20	60	N
	69	N
	75	N
	78	Y

Table 3-4. Mass of LN2 applied versus initial mass of sodium along with fire suppression effects for 125 ml beaker

250ml		
Mass of sodium	Mass of LN2	Extinguishment
5	21	N
	24	N
	30	Y
10	42	N
	48	Y
20	72	N
	78	Y
40	150	N
	159	Y
	180	Y
80	213	N
	245	Y
	270	Y

Table 3-5. Mass of LN2 applied versus initial mass of sodium along with fire suppression effects for 250 ml beaker

The mass ratio of sodium to liquid nitrogen was calculated with the equation below.

$$M_{LN2} = M_{Na} C_{pNa} (T_{pool} - T_a) / L + M_{beaker} C_{pSteel} (T_{beaker} - T_a) / L \quad (3-1)$$

where T_{pool} is the pool temperature of sodium (600 °C)

T_a is ignition temperature (120 °C)

L is latent heat of evaporation for LN2 (200 J/g at -196 °C).

C_{pNa} is specific heat of sodium (1.23 J/g-K)

C_{pSteel} is specific heat of beaker (0.5 J/g-K)

The heat transfer from nitrogen ($m_{N_2} C_{pLN2} \Delta T$) to the air was assumed to be negligible and the lowest ignition temperature (120 °C) was selected for the calculation. T_{beaker} was assumed to be 230 °C. The average value between the small beaker (70 g) and the big beaker (100 g) was used for the mass of the beaker in the calculation. The equation from analytic calculations is $(M_{LN2} - 24 \text{ g}) / M_{Na} = 2.95$. The experimental and analytical results for sodium agree to within 10%.

3.5 Mass loss

The Figure 3-5 shows the change in mass over time as the sodium was heated. The small masses of sodium (5-20 g) showed no remarkable change in their overall mass, but, as the sodium burned, the mass of sodium increased with time. The large mass samples of sodium (40-80 g) increased their mass by more than 10 g. This unusual behavior may come from a reaction of sodium with water vapor in the air. As the sodium oxides rise in the shape of a pillar during the burning of sodium, their surface area increases. This also may increase the mass of sodium as more water vapor in the air is able to bond with the exposed surface of

sodium oxides. After the sodium combustion, it was also observed that the sodium oxides remained in a dried condition. However, as time progressed, the dried sodium oxides became moist, at least on the surface. Further research is needed to understand this behavior more clearly.

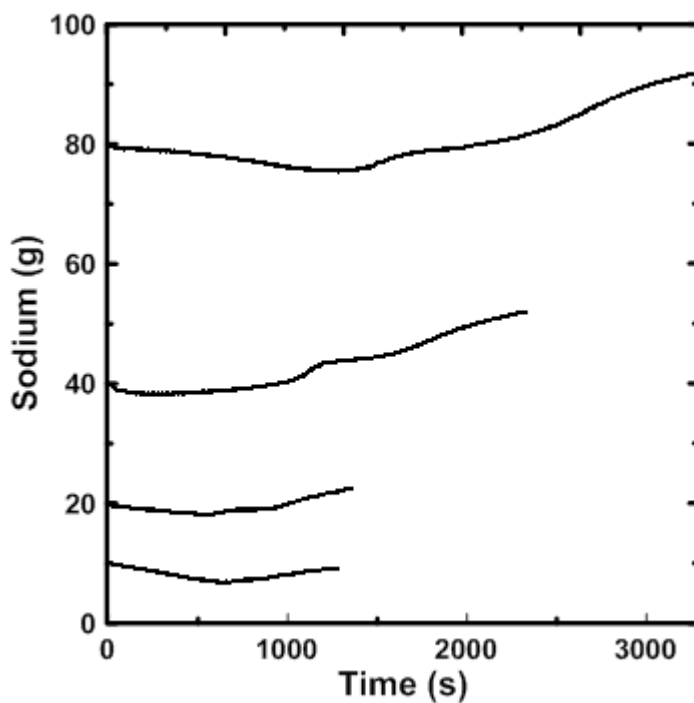


Figure 3-6. The initial mass of the sodium is 5-80 g. Mass of sodium versus time for representative sodium burning without liquid nitrogen. The initial masses of sodium are shown. Beaker size was 125 ml for initial masses of 5 and 10 g, and 250 ml otherwise. The time datum is the start of heating.

Chapter 4: Conclusions

Through these experiments, the behaviors of sodium combustion were observed, and the critical mass ratio of LN2 to sodium mass were evaluated and compared with analytical calculations. No reaction occurred between sodium and LN2 while the LN2 cooled the sodium pool temperature and depleted oxygen around the sodium. LN2 also satisfies all of the desirable conditions of an optimal sodium fire extinguishing agent. LN2 as a sodium fire extinguishing agent was effective against sodium fire in the mass range of 5-80 g. If a greater flow rate of LN2 is applied to the sodium fire, the time required to suppress the sodium fire may be reduced. Therefore, a large scale experiment will be conducted in the future. The major conclusions are as follows.

1. LN2 was effective for suppressing sodium fires. Pouring the minimum mass of LN2 over the sodium fire extinguished the fire and cooled the pool temperature rapidly to below 60 °C.
2. The minimum mass of LN2 that is required to extinguish a sodium pool fire is about 2.9 times the mass of sodium.
3. The deviation of equation between analytic calculation and experiments is within 10%.
4. Heating the sodium raised the temperature gradually without any visible reactions, but the sodium surface initiated a vigorous reaction at 285 °C as the surface layer melted. The temperature was reproducible, but the temperature of the vapour phase ignition varied from 320 to 450 °C and was therefore not reproducible.
5. Surface combustion preceded vapour phase combustion. Prior to vapour phase combustion, the yellow color of sodium peroxide was present at the wall brim in the beaker.

6. The maximum pool temperature depended on the geometry of the container. For samples in which the ratio of sodium depth to sodium surface area was less than 0.054 cm^{-1} , the sodium reached $600 \text{ }^\circ\text{C}$. Otherwise, it reached $510 - 550 \text{ }^\circ\text{C}$.
7. No reaction occurred between sodium and LN2.
8. Sodium increased in mass as it burned. This may be attributed to the bonding of the sodium oxides to the water vapor in the air.

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