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## Suppression of sodium fires with liquid nitrogen

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### ABSTRACT

Sodium has unusual fire hazards, including autoignition when heated in air or exposed to liquid water. Owing to limitations of existing suppression agents for sodium pool fires, suppression using liquid nitrogen (LN<sub>2</sub>) is examined here. Sodium pools of 5–80 g were heated in stainless steel beakers. At about 290 °C, pool surface autoignition occurred and caused a rapid pool temperature increase. Vapor phase combustion occurred when the pools reached 320–450 °C, ultimately leading to pool temperatures up to 700 °C. For suppression tests, LN<sub>2</sub> delivery (at 2.7 g/s) began when the fires became fully-developed, near a pool temperature of 600 °C. Liquid nitrogen was found to be an effective suppression agent. The minimum amount of LN<sub>2</sub> required to suppress a fully-developed sodium pool fire was found to be about three times the initial sodium pool mass.

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### 1. Introduction

Elemental sodium is highly reducing. This contributes both to its extensive use as a reducing agent and to its unusual fire hazards. Nearly all fast nuclear reactors use liquid sodium for cooling, owing to its high thermal conductivity, radiation stability, and large margin between melting (98 °C) and boiling (883 °C) points [1]. Elemental sodium is also used as a reagent in chemical industries, in alloying and refining metals, in vapor lamps, and in sodium sulfur batteries. Sodium's high electrical conductivity makes it attractive for hydro-magnetic experiments [2].

Sodium has several unusual fire hazards [3–8]. Its autoignition temperature in air (i.e., the temperature of the onset of self-sustaining reactions on the surface) varies between 120 and 470 °C [1,3–5,8–10], leaving little safety margin above its melting point. Sodium is frequently used in molten form (which can introduce leaks associated with thermal expansion), whereby any leak is likely to autoignite. Like other alkali metals (e.g., lithium and potassium), sodium reacts vigorously with water at room temperature. The resulting release of hydrogen and heat can lead to explosions [1,3,8] and the violent ejection of burning sodium droplets. The adiabatic flame temperature for sodium combustion in air is 1920–2044 K [5,11,12]. The heats of combustion for  $\text{Na} + 0.25\text{O}_2 \rightarrow 0.5\text{Na}_2\text{O}$  and  $\text{Na} + 0.5\text{O}_2 \rightarrow 0.5\text{Na}_2\text{O}_2$  are 9.48 and 11.3 kJ/g [13], respectively, these being similar to that of wood. Sodium's main combustion products in dry air are sodium oxide (Na<sub>2</sub>O), which largely remains on the pool surface, and sodium

peroxide (Na<sub>2</sub>O<sub>2</sub>), which largely escapes as caustic smoke [5,14]. These fire hazards have contributed to an extensive history of serious sodium fires in sodium-cooled nuclear reactors [13,15].

Sodium fires cannot be suppressed with water. Dry powder agents (e.g., NaCl, Na<sub>2</sub>CO<sub>3</sub>, CaCO<sub>3</sub>, graphite, soda ash, and sand) are effective, but can be difficult to apply and clean up [5,16,17]. Total flooding by inert gases, such as Ar or N<sub>2</sub>, is effective but requires prior evacuation of personnel [3,18]. Catch pans that smother burning sodium are in wide use and are effective when leak size and location can be anticipated.

Liquid nitrogen (LN<sub>2</sub>) holds promise as a sodium fire suppressant. Its low boiling point (77 K) makes it effective in both cooling exposed sodium below its autoignition temperature and in cooling leaking sodium such that it solidifies and plugs the leak. Upon gasification, the nitrogen displaces oxygen, water vapor, and hot gases. Nitrogen is an effective inerting agent for metal fires [3,18] and does not react with sodium [19]. LN<sub>2</sub> is a clean agent and can be applied very rapidly. LN<sub>2</sub> has been used to suppress building and pool fires [20–22]. It was proposed for sodium fire suppression as early as 1972 [23]. Two past studies delivered LN<sub>2</sub> to burning sodium pools [19,24], but neither measured the amount of LN<sub>2</sub> required for suppression. Owing to limited past work in this area, the objective of this work is to quantify the effectiveness of LN<sub>2</sub> for sodium fire suppression.

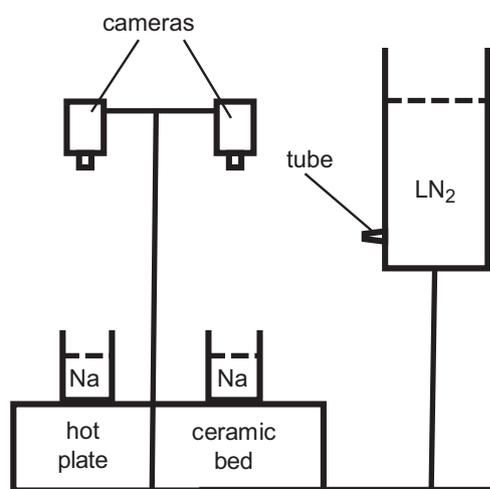
### 2. Experimental

The experimental schematic is shown in Fig. 1. Tests were performed indoors surrounded by quiescent air at 25 °C, 1.0 bar, and 50% relative humidity. Sodium discs, stored in kerosene, were

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cut to the desired mass, placed in stainless steel beakers (grade 304, i.e., 18/8), and covered with kerosene. The beaker capacities were 125 ml (diameter 50 mm, height 67 mm, and mass 70 g) and 250 ml (diameter 60 mm, height 89 mm, and mass 100 g), with the smaller beaker generally used for the smaller pools. The sodium was flattened into the beaker bottom using a steel hammer. Two K-type thermocouples, with 304 stainless steel sheaths and diameters of 3 mm, were placed 5 mm below the pool surface and were averaged in the results that follow. The kerosene was then poured from the beakers.

Between 600 and 700 g of LN<sub>2</sub> was maintained in an insulated polypropylene Dewar (diameter 120 mm and height 190 mm) with an open top. A polypropylene tube (inside diameter 2 mm and length 15 mm) with a cap that allowed manual activation released LN<sub>2</sub> from the bottom of the supply Dewar. Tests using a receptacle Dewar on a load cell found the LN<sub>2</sub> delivery rate to be  $2.7 \pm 0.3$  g/s depending on the fill level. Owing to LN<sub>2</sub> boiling, this is slightly lower than the rate of mass loss from the supply Dewar.



**Fig. 1.** Experimental setup showing the sodium beaker in both of its positions and the LN<sub>2</sub> Dewar.

During suppression tests, the LN<sub>2</sub> stream was directed into the center of the pool. The amount of LN<sub>2</sub> delivered to the pool was determined from the delivery duration and the previously measured delivery rate.

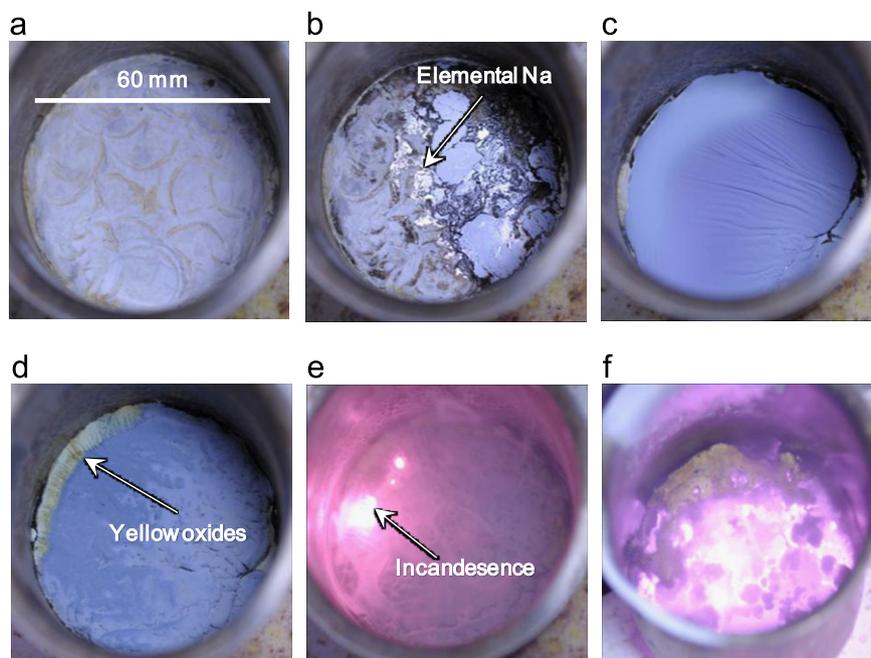
An electric hot plate operating at 620 W heated a beaker containing sodium until vapor phase ignition. This arrangement yielded quick ignition and a slow increase in pool temperature following beaker removal from the hot plate. Upon vapor phase ignition, which was recognized from the onset of luminous emissions [4], the beaker was moved onto a ceramic bed. Images were recorded by still and video cameras to allow post-test observations of the fire and suppression dynamics and, when used, the amount of LN<sub>2</sub> delivered.

Test personnel were protected by nomex gowns, fire-resistant gloves, and full face shields. Smoke from the tests was treated in an exhaust system with a scrubber. After each test, the beaker was heated above 98 °C and unburned sodium was poured out. Any remaining solids were then removed at room temperature using a chisel followed by a methanol wash.

Experimental uncertainties are estimated at  $\pm 1$  g for the initial sodium mass,  $\pm 10\%$  for the mass of added LN<sub>2</sub>, and  $\pm 20$  °C for the mean pool temperature.

### 3. Results

Sodium oxidation in air was apparent even at room temperature, where the surface changed from shiny to dull within about 10 s of kerosene removal from the pool surface. When the sodium was heated to about 70 °C, it began to generate smoke without any luminous emissions. Upon sodium melting, an oxide layer appeared on the surface (Fig. 2a). This layer consisted of Na<sub>2</sub>O, Na<sub>2</sub>O<sub>2</sub>, and sodium hydroxide, NaOH (produced by reactions with water vapor in the air). This layer was a barrier to sodium oxidation [3–5,10], thus delaying pool surface autoignition [10,11]. Autoignition occurred when the pool reached about 290 °C (Fig. 2b), and was associated with an increased pool heating rate, the approach to the 318 °C melting point of NaOH, and the brief appearance of unreacted sodium at the surface [3,4]. Wrinkles



**Fig. 2.** Color images of a 40 g sodium burn test in the 250 ml beaker without LN<sub>2</sub> delivery. Time zero is the start of heating. (a) 100 °C, 6 min, (b) 285 °C, 17 min, (c) 292 °C, 17.2 min, (d) 346 °C, 17.8 min, (e) 385 °C, 17.8 min and (f) 443 °C, 29 min

appeared when the oxide layer covered the entire surface (Fig. 2c). The oxide layer near the beaker wall then began to turn yellow (Fig. 2d), indicating the presence of  $\text{Na}_2\text{O}_2$ . For this test, vapor phase reactions – as revealed from luminous emissions [4] – began at a pool temperature of  $385^\circ\text{C}$  (Fig. 2e). Fig. 2(f) shows the entire pool surface burning. Also evident are white and yellow oxide pillars, with diameters and heights of about 5 and 30 mm. These consist mainly of  $\text{Na}_2\text{O}$  and  $\text{Na}_2\text{O}_2$  and they modify the fire behavior by serving as sodium wicks [3–5,11].

Fig. 3 shows the pool temperature versus time for representative burn tests without  $\text{LN}_2$  delivery. The temperature profiles exhibit two notable features in the approach to the peak temperature. Near its melting point of  $98^\circ\text{C}$ , sodium's latent heat of fusion results in a brief temperature plateau. Later, at about  $290^\circ\text{C}$ , pool surface autoignition is evident from the rapidly increasing temperature. The onset of luminous emissions, which coincides with vapor phase combustion [4], was observed to occur for pool temperatures of  $320$ – $450^\circ\text{C}$ . Fully-developed fire conditions are defined here to commence when the pool temperature reaches either  $600^\circ\text{C}$  or a plateau above  $500^\circ\text{C}$ . The peak temperature generally decreased and occurred later for increasing pool depths, in agreement with past observations [11], which is attributed to increased heating rates for shallow pools. The measured temperatures of Newman [4] for a 10 g sodium pool are included in Fig. 3. These reveal a shorter burning time, a higher autoignition temperature, and a higher peak temperature. These effects are attributed to Newman's use of shallower pools, a nickel beaker, and insulation around the heater and beaker.

Tests were also performed with  $\text{LN}_2$  delivery. Delivery started when pool temperature reached either  $600^\circ\text{C}$  or a plateau above  $500^\circ\text{C}$ . This was slightly after the onset of full-blown vapor phase combustion over the entire pool surface. During these tests the  $\text{LN}_2$  boiled in the beakers but did not spill over the beaker walls. A color image of a test with  $\text{LN}_2$  is available in Ref. [25], but as is typical of such tests the pool surface is obscured by smoke and condensed water droplets.

Fig. 4 shows the pool temperatures for representative tests in which the minimum amount of  $\text{LN}_2$  delivery successfully suppressed all reactions in a fully-developed pool fire. In other words, performing these tests with slightly less  $\text{LN}_2$  resulted in the resumption of self-sustaining heat release. Fig. 4 shows that sodium melting and autoignition occurred, respectively, near  $98$  and  $290^\circ\text{C}$ , and that deeper pools heated more slowly. The pools cooled quickly upon  $\text{LN}_2$  delivery and did not subsequently approach

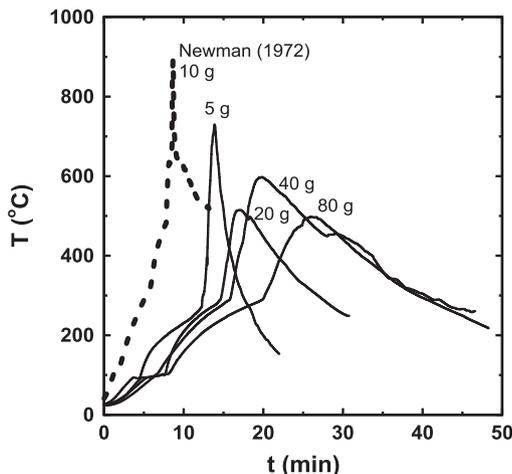


Fig. 3. Pool temperature versus time for representative sodium burn tests without  $\text{LN}_2$  delivery. The initial masses of sodium are shown. Beaker size was 125 ml for initial masses of 5 and 20 g, and 250 ml otherwise.

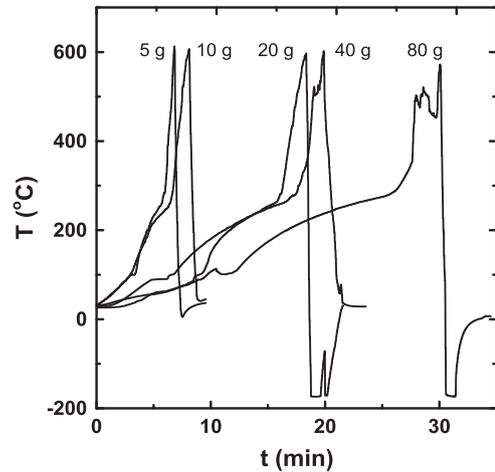


Fig. 4. Pool temperature versus time for representative sodium burn tests for which the minimum amount  $\text{LN}_2$  required for suppression was delivered (namely 30, 48, 78, 159, and 245 g of  $\text{LN}_2$  for initial sodium masses of 5, 10, 20, 40, and 80 g, respectively). Beaker size was 125 ml for initial masses of 5 and 10 g, and 250 ml otherwise.

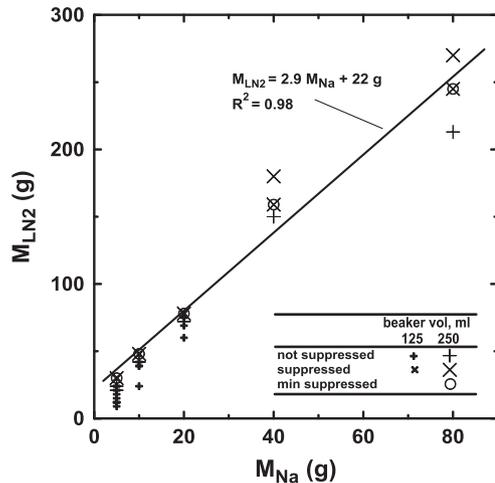


Fig. 5. Mass of  $\text{LN}_2$  delivered versus initial mass of sodium, with suppression result and beaker volume indicated by symbol type.

autoignition temperatures. It is estimated that approximately 10% of the initial sodium mass burned in these tests, based on post-test inspections of the pool and the  $20\text{ g/m}^2\text{ s}$  burning rate reported by Ref. [4]. Fig. 4 indicates that  $\text{LN}_2$  suppresses these fires by cooling the entire pool below its autoignition temperature.

Additional tests were performed with  $\text{LN}_2$  delivery amounts that were both above and below those of Fig. 4. The results are summarized in Fig. 5, which shows the initial mass of the sodium pool,  $M_{\text{Na}}$ , versus the mass of added  $\text{LN}_2$ ,  $M_{\text{LN}_2}$ . This figure includes tests for which the fire was suppressed (crosses and circles) and tests for which self-sustained heating resumed (plusses). Circles denote the minimum mass of  $\text{LN}_2$  that suppressed a pool fire of the indicated mass in the 250 ml beaker. A linear fit to the circles yields:

$$M_{\text{LN}_2} = 2.9M_{\text{Na}} + 22\text{ g}. \quad (1)$$

The high regression coefficient of this fit, 0.98, indicates that reasonable repeatability was obtained despite the inherently stochastic nature of sodium pool ignition and combustion. The mass of  $\text{LN}_2$  required for suppression is approximately 3 times the initial mass of the sodium.

It is hypothesized that when the minimum amount of LN<sub>2</sub> required for suppression is delivered, the enthalpy removed by LN<sub>2</sub> vaporization equals the enthalpy change in cooling the pool and beaker from their initial temperature to just below the autoignition temperature. This can be approximated as

$$M_{\text{LN}_2} L_{\text{LN}_2} = (M_{\text{Na}} c_{p, \text{Na}} + M_{\text{beaker}} c_{p, \text{beaker}})(T_{\text{Na}} - T_{\text{ig}}), \quad (2)$$

where  $c_p$  is the specific heat (1.23 J/g K for Na and 0.5 J/g K for the beaker);  $L$  is the latent heat of vaporization (200 J/g for LN<sub>2</sub> at 77 K);  $M_{\text{beaker}}$  is the mass of the beaker (100 g);  $T_{\text{Na}}$  is the temperature at the onset of LN<sub>2</sub> delivery (600 °C); and  $T_{\text{ig}}$  is the sodium autoignition temperature (290 °C). Inserting these values into Eq. (2) yields

$$M_{\text{LN}_2} = 1.9M_{\text{Na}} + 78 \text{ g}. \quad (3)$$

Considering the assumptions made, Eq. (3) is in reasonable agreement with the empirical finding of Eq. (1). This supports the hypothesis that LN<sub>2</sub> vaporization suppresses these fires primarily by cooling the pool and beaker below the sodium autoignition temperature. LN<sub>2</sub> can be expected to be similarly effective in suppressing pool fires of other metals.

#### 4. Conclusions

Sodium pool fires and their suppression by LN<sub>2</sub> were observed for pools between 5 and 80 g. The sodium was contained in stainless steel beakers and heated to autoignition with a hot plate. Pool temperatures were measured with thermocouples. The pools were found to autoignite upon heating to 290 °C and to commence vapor phase combustion at 320–450 °C. For some tests a stream of LN<sub>2</sub> was applied at 2.7 g/s when the fires became fully-developed. Still and video cameras recorded the tests.

LN<sub>2</sub> was found to suppress fully-developed sodium pool fires when delivered in sufficient quantity. For a burning pool at 600 °C, the mass of LN<sub>2</sub> required for suppression is about three times the initial mass of the sodium. Less LN<sub>2</sub> would be required if applied before the fire became fully-developed. A simple analytical model indicates that the suppression mechanism is the cooling (via LN<sub>2</sub> vaporization) of the pool and its surroundings below the sodium autoignition temperature.

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