

## **IGNITION AND EXTINGUISHMENT OF SODIUM FIRES IN AIR DILUTED BY NITROGEN**

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### **ABSTRACT**

Ignition and extinguishment of sodium fires was investigated in air diluted by nitrogen using a coaxial burner. Oxygen concentration and temperature were changed from 0.5% to 21% and from 110°C to 700°C, respectively. In undiluted air, ignition occurred near the crust of sodium oxides at temperatures below 600°C. At temperatures higher than 625°C, ignition was observed in a vapour layer and a conical diffusion flame appeared on a sodium pool at 700°C. The flame was observed for only one second after the ignition before a dense cloud from burning sodium obscured vision. In this study, the lowest ignition temperature of sodium was 115°C under an air flow rate of 5 L/min. There were extinguishing limits of oxygen concentrations for burning sodium. The limits decreased linearly with increasing sodium temperature up to a temperature of 700°C.

Anomalous ignition was found in a region of oxygen concentrations lower than the limits. One example was an observed ignition occurring in the region of oxygen concentrations below 3% and temperatures above 400°C. The ignition was observed on the crust of sodium oxides after relatively long induction periods, but no stable combustion followed. Another anomaly was re-ignition of a cooled combustion residue exposed to fresh air. Such ignition was even observed below 50°C. The oxidized sodium prepared in a low oxygen atmosphere also ignited at the same temperature. Both types of anomalous ignition were attributed to production of sodium peroxide. Thus, the extinguishment of sodium fires by nitrogen requires consideration of methods to block the production of sodium peroxides.

### **INTRODUCTION**

Sodium is an important metal for chemical engineering and fast breeder reactors (FBR). Since liquid sodium exists in a wide temperature range from the melting point 98°C to the boiling point 880°C, large amounts of sodium are used as coolants of FBR. It is well known, however, that liquid sodium is very reactive and burns in air with an incandescent yellow light and produces dense smoke. The smoke is composed mainly of toxic and corrosive sodium oxides and obstructs view. These facts describe why fire fighting is difficult against sodium fires.

There are many studies on sodium fires aimed at reducing the severity of accidents in FBR<sup>1-6</sup>. Fire extinguishing agents used against sodium fires have also been studied<sup>7-12</sup>. The main interests of these studies were the ignition phenomena of sodium droplets and sodium pools, properties of the fires, effective extinguishing agents, and how to best fight sodium fires. However, there are few studies on the fundamentals of sodium combustion<sup>13-16</sup>.

In 1995, a fire erupted when hot sodium leaked from a coolant pipe in the FBR "Monju" in Japan. Monju has not restarted operations since the accident. The introduction of a nitrogen fire extinguishing system is discussed in this paper as one of the measures proposed for use against sodium fires. Gracie et al.<sup>1</sup> reported "Sodium at 1000 °F (538 °C) did not undergo rapid combustion as characterised by incandescence at oxygen concentrations of 4 % and below." However, there is scarce data on extinguishing sodium pool fires by inert gases over a wide temperature range. Therefore, it is the purpose of this study to examine the ignition and the extinguishment of sodium pool fires by nitrogen under a range temperatures.

This paper is a study on ignition phenomena and extinguishable oxygen concentrations of sodium combustion. Measurements were carried out in a temperature range of 110°C to 700°C and oxygen concentration range of 0.5% to 21 %. The spread of sodium combustion will be reported elsewhere.

## **Previous studies on sodium ignition and extinguishment**

Gracie et al.<sup>1</sup> summarised the existing studies on the ignition temperatures of sodium, and they concluded that there is no precise ignition temperature value. This conclusion appears reasonable as it is known that a sodium oxide film on a sodium pool affects the ignition temperature<sup>13,16</sup>. However, the ignition temperature has been the focus of many studies, to aid understanding of the spontaneous ignition mechanism.

Akita et al.<sup>13</sup> investigated the ignition of sodium pieces on a glass stage in a cylindrical glass furnace. They reported that ignition takes place above 290°C, but if the oxide film over the surface is broken artificially, it decreases to around 140°C. Richard et al.<sup>14</sup> studied the combustion of liquid sodium droplets in a furnace, and they found that the ignition temperature does not vary appreciably with the oxygen concentration in the gas phase. Yuasa<sup>16</sup> studied the behavior of spontaneous ignition in the stagnation region of impinging air streams at various humidity conditions. He defined that *T<sub>cr</sub>* is the lowest initial sample temperature where the sample ignites spontaneously, and *T<sub>ig</sub>* is the sample temperature at the instant of ignition. In his results, *T<sub>cr</sub>* increased with humidity, but *T<sub>ig</sub>* was almost insensitive to humidity. He concluded that the effect of humidity on *T<sub>cr</sub>* is attribute to the formation of a "protective" sodium hydroxide film on the sodium surface. In these works, "usual" sodium ignition was discussed, as sodium ignition was only observed in atmospheres containing oxygen levels over 10 % at moderate temperatures.

In spite of the lack of a precise ignition temperature and precise extinguishing data, the ignition temperature is now a good guide to fire safety with sodium. Gracie et al.<sup>1</sup> introduce the lowest ignition temperature of 121°C (250°F) reported by Cowen and Vickers for liquid sodium forced through a small

hole into air.

## **EXPERIMENTAL**

In order to reduce obstruction caused by dense smoke, a small coaxial diffusion-flame burner was employed to observe the pool burning process of sodium as illustrated in Figure 1. The burner was similar to the apparatus of Reuillon et al.<sup>17</sup>, however the heating method and dimensions differed. The burner was equipped with a glass chimney and an SUS 316 cell held on a heater block in the center of the chimney. The dimensions of the chimney were 85 mm inner diameter and 400 mm height, and the dimensions of the cell were 17 mm outer diameter, 15 mm inner diameter, and 10 mm depth.

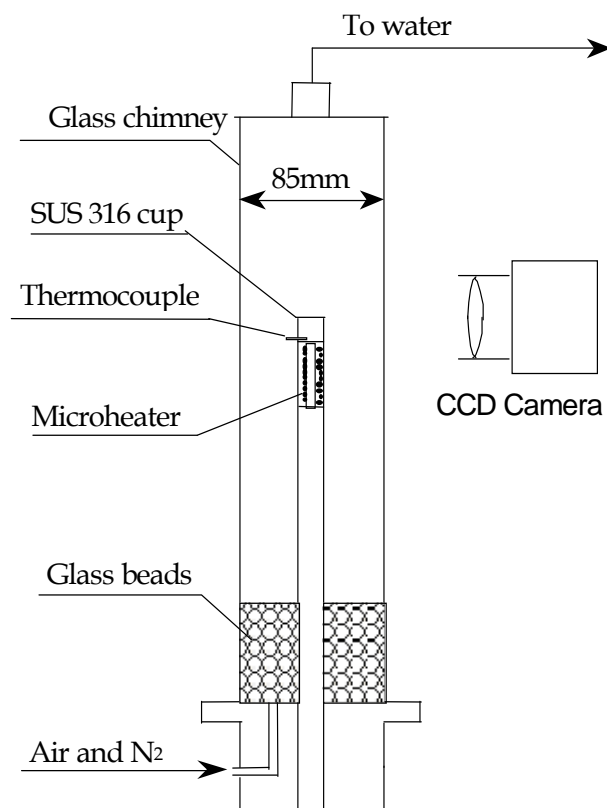
Total flow rates of gaseous agents through the coaxial burner were usually fixed at 20 L/min, but 5 L/min and 40 L/min were also employed to measure their effect on the lowest ignition temperature. The gaseous agents were dry air from an oil-free compressor equipped with a dryer, and commercial nitrogen in a gas cylinder. The dry air contained moisture at a level less than 1000 ppm. Calibrated mass flow controllers were employed to control the flow rates of the agents. The errors in the measurements of flow rate were within 1 % of a set value. The sodium used in the study was a commercial agent shaped in a block with a cross section of 25 mm x 25 mm and length of 150 mm.

The cell was heated to a set temperature on a heater block. The cell temperature was measured by a sheathed K-type thermocouple of 1.6 mm in outer diameter. About 2 g of sodium was used in each experiment. Before the start of each experiment, sodium in the cell was heated up to 600°C and the nitrogen flow was set at 20 L/min. This process improved reproducibility of experiments. A temperature controller was used to heat sodium in the cell at the set temperature. Ignition behaviors were recorded by a CCD camera system and an 8 mm video system.

## **RESULTS**

### **Usual ignition and extinguishing limits of oxygen concentration**

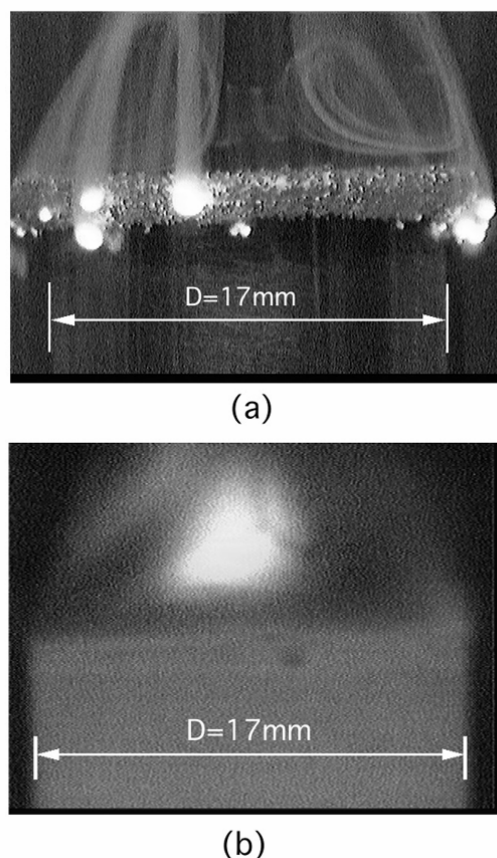
While changing the initial temperature of sodium from 110°C to 700°C, ignition phenomena were observed in air. There were two types of usual ignition. The boundary between both types of ignition was close to 600°C. In the case of ignition below 600°C, the metallic surface of sodium changed to a gray colour just after supplying air into the burner, and reaction products grew on the surface and often overflowed from the cell. Then, red hot spots appeared at tips of nodular products. A typical photograph of the ignition at 500°C is shown in Figure 2(a). At 700°C, another type of ignition occurred in a vapour layer on the sodium pool as shown in Figure 2(b)<sup>18</sup>.



**Figure 1:** Illustration of sodium coaxial burner.

These ignition behaviors interchanged gradually with increasing temperature from 600°C to 700°C. The ignition in the sodium vapour layer appeared above 625°C, and the position of the ignition was gradually higher from the top of the surface with increasing temperature. At 700°C, the flame with yellow and green emissions propagated after the ignition in the vapour layer, then a conical diffusion flame was formed on the cell for about one second<sup>18</sup>. However, dense smoke and the strong emissions obscured the flame preventing further observations.

The lowest ignition temperature was measured by the burner system. In the experiments, the sodium temperature decreased gradually from 200°C. Flow rates of air of 5 L/min, 20 L/min, and 40 L/min were employed to examine the effect of flow rate on the ignition. The results are summarized in Table 1. The lowest ignition temperature was 115°C. The temperature was affected by the flow rate of air.



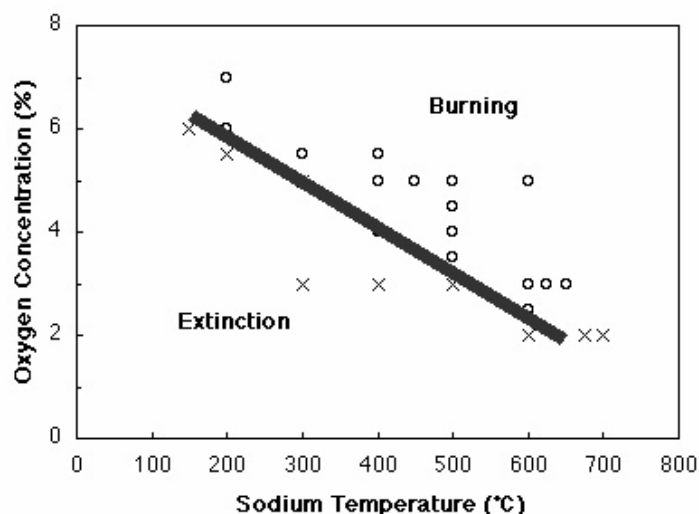
**Figure 2:** Photographs of usual ignition (a) ignition near sodium surface below 600°C (b) ignition in vapour layer at 700°C.

**Table 1:** Lowest ignition temperatures and air flow rates.

Sodium Temp.(°C)	Air Flow Rate (L/min)		
	5	20	40
120	-	ignition	no ignition
115	ignition	no ignition	-
110	no ignition	-	-

- : not observed

Tests of extinguishing sodium combustion were carried out through decreasing oxygen concentrations by adding nitrogen in the temperature range 150°C to 700°C. In the study, extinction of sodium combustion was defined by disappearance of red hot spots on a sample according to Gracie et al.<sup>1</sup>. The results are showed in Figure 3 where marks of circles and crosses refer to not extinguishing and extinguishing, respectively.

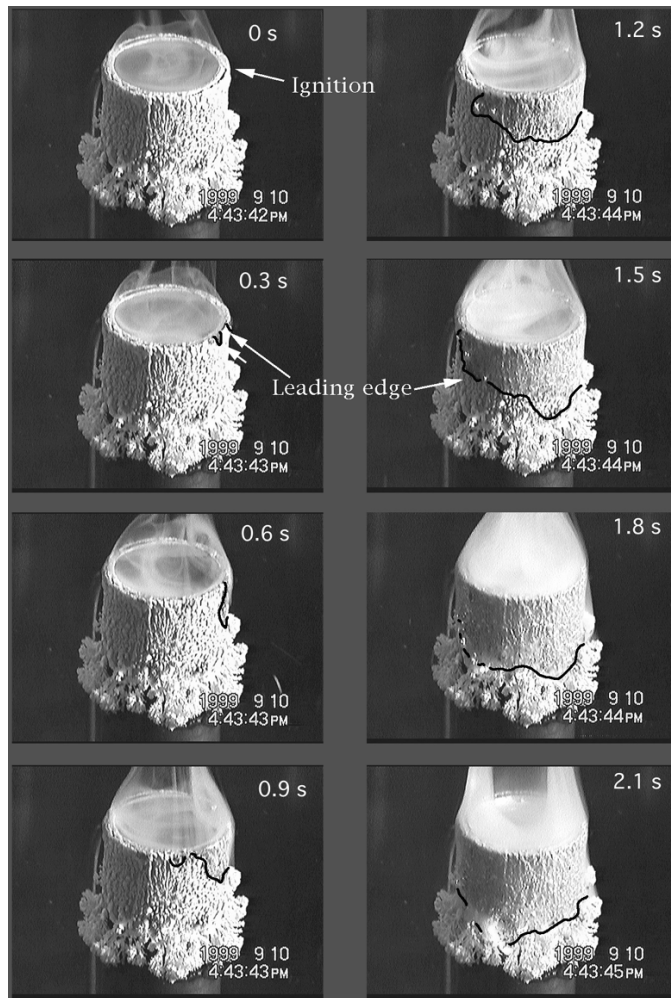


**Figure 3:** Extinguishable limit (solid line) of oxygen concentration for sodium combustion and its temperature dependence.

o: Non extinguishing      x: Extinguishing

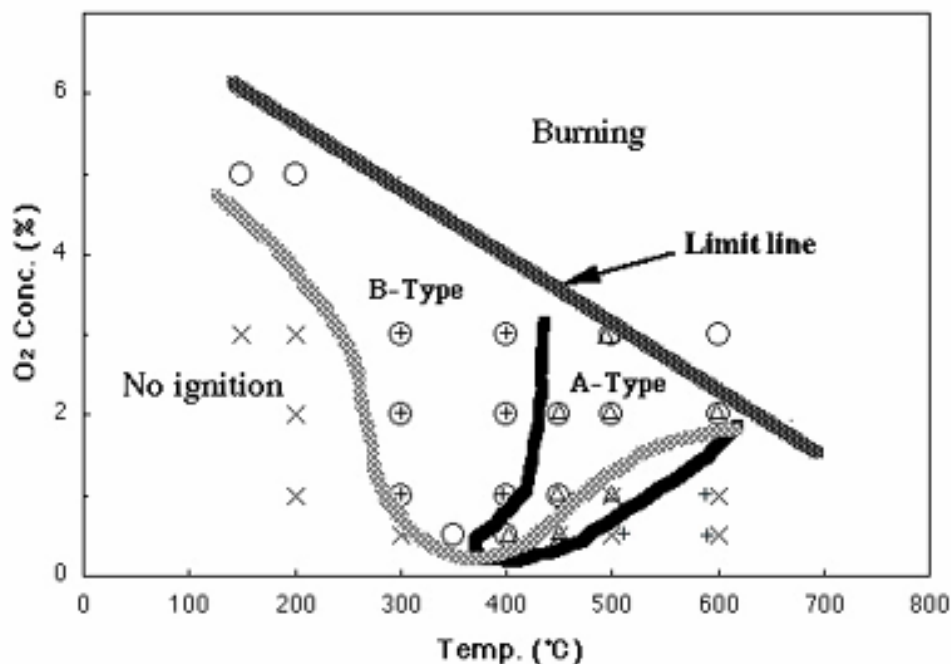
### Anomalous ignition

Two types of anomalous ignition were found in the study. One was ignition in a low oxygen atmosphere above 400°C. Figure 4 shows successive snapshots of such ignition and subsequent fire spread in 1% oxygen at 500°C. Fire spread after the ignition appeared like combustion of explosives. This ignition was characterised by a long induction time from a few minutes to ten minutes or more and by intermittent repetition on the crust of sodium oxides. The ignition occur even in atmospheres containing only 0.5 % oxygen near 450°C. Above 600°C, the ignition was limited by lack of an oxidized sodium layer on an outer surface of the cell, that is, the oxide layer was not sufficiently formed on the surface. The region of ignition is shown in Figure 5 by the solid line and marked "A-type" anomalous ignition. In Figure 5, the symbol "Δ" refers to the occurrence of A-type ignition, and the symbol "+" denotes no ignition.



**Figure 4:** Snapshots of A-type anomalous ignition and subsequent fire spread.

The second “B-type” anomalous ignition appeared as re-ignition of combustion residues of sodium at low temperatures. Such ignition was discovered in a process of cleaning up the combustion residues after extinguishing tests. In each test, sodium was burned freely for 10 s in air, and then the burning sodium was extinguished by applying deficient air diluted by nitrogen. Then, the extinguished residue was cooled down in nitrogen flow to below 50°C. The cold residue ignited again when the fresh air was introduced into the burner. Such an ignition region are shown in Figure 5, distinguished by a mesh line and marked as “B-type.” The same ignitable residue was produced at the deficient air conditions marked by “o”, but not at the conditions shown by “x”.



**Figure 5:** Ignition regions of both A-type (solid line) and B-type (meshed line) of anomalous ignition on oxygen concentration vs. temperature diagram.

For A-type ignition: “Δ”: ignition, “+”: no ignition

For B-type ignition: “o”: ignition, “x”: no ignition

## DISCUSSION

### Usual ignition phenomena of sodium

According to Gracie et al.<sup>1</sup> and Yuasa<sup>16</sup>, the ignition temperature of sodium in air depends on purity, absolute humidity, heat loss, etc. However, the minimum ignition temperature of sodium is essential information to treat sodium safely. In the present study, the minimum ignition temperature was 115°C at a gas flow rate of 5 L/min, and increased with increasing gas flow rate. Akita et al.<sup>13</sup> reported a value of 140°C for the ignition temperature of scratched sodium, and Gracie et al.<sup>1</sup> reported 121°C for sodium with a fresh surface. Yuasa<sup>16</sup> observed higher ignition temperatures than other researchers, and he reported that a sodium hydroxide film on the surface of sodium increased the ignition temperature. These facts show that the ignition of sodium is affected by conditions of the surface and the flow, so an ignition temperature may be achievable below the 115°C reported here.

Sodium was shown to display two types of ignition and combustion in the normal ignition region. One is ignition and combustion on the crust of oxidized sodium below 600°C, and the other is ignition and combustion in a vapour layer typically at 700°C, where a conical diffusion flame is observed. This fact



points out that sodium fires are not always characterised by “very low flames”<sup>1</sup>. If a fire heats up a sodium pool near the boiling point, the sodium pool will burn with higher flames.

### **Anomalous ignition phenomena**

A-type anomalous ignition occurs above 400°C and a spreading fire like gunpowder combustion follows. The B-type anomalous ignition appears like spontaneous ignition of unstable materials in air. Both types of anomalous ignition produced difficulties in extinguishing sodium fires by inert gases. That is, if sodium fires are controlled through decreasing the oxygen concentration by inert gases, sodium above 400°C has a potential for intermittent ignition. On the other hand, even if a combustion residue cools down to room temperature, the combustion residue ignites and burns again by introducing fresh air into a fire room. These situations make certainty in extinguishing sodium fires difficult.

There is a report on the ignition between sodium and sodium peroxide mixtures by Newman et al.<sup>19</sup>. They made samples of sodium cut into discs and used a commercial agent of sodium peroxide. Ignition of the samples was observed through heating in both atmospheres of air and argon close to the melting point of sodium. They demonstrated the ignition of a substitute for a combustion residue of sodium, but not for a real residue. In their study, the anomalous ignition was observed on the real combustion residues and on the surface of oxidized sodium. The detection of anomalous ignition suggests the production of sodium peroxide in the sodium combustion process. Indeed, the present authors found concentrated sodium peroxide in the chemical analysis of the residues. The results will be reported in the near future. Moreover, the ignition of the cool combustion residues below 50°C suggests the existence of more active products than sodium peroxide, or a particular state of sodium oxides. Further investigation is required to better understand the anomalous ignition.

### **CONCLUSIONS**

Sodium shows two types of the usual ignition in air in the temperature range 115°C to 700°C. The combustion after the usual ignition has extinguishing limits of oxygen concentration. The limits decrease linearly with increasing sodium temperature. One type of usual ignition is ignition near to the oxide crust below 600°C, and the other type is ignition in the vapour layer above 625°C. Sodium burns with a conical diffusion flame at 700°C. Therefore, very low flames do not always characterize sodium pool fires.

Two types of anomalous ignition were found in the region of oxygen concentration lower than the extinguishing limits of oxygen concentrations. Both types of anomalous ignition were attributed to the production of sodium peroxide. It is necessary to prevent the production of sodium peroxide for successful extinguishment of sodium fires by inert gases like nitrogen. The ignition of the cool combustion residues below 50°C suggests the existence of more active products than sodium peroxide, or a particular state of sodium oxides. Further investigation is necessary to understand anomalous ignition.

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