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Study of the Aging Impact on the Extinction Efficiency of an Extinguishing Powder for Sodium Fire

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The French Atomic and alternatives Energy Commission (CEA) developed an effective powder capable of extinguishing sodium fire. However, ever since the dismantling of several old sodium installations facilities, CEA has at its disposal an important stock of unused powder batches, some of which have not been kept in suitable conditions. The idea of reutilizing these powders initiates the question about their efficiency to extinguish a sodium fire after long term storage. The various physicochemical analyses that have been carried out to characterize these stocked powder batches highlight the presence of lithium sodium carbonate ($LiNaCO_3$), which is not a product of aging, and trôna that, contrarily, formed because of aging during storage. This study presents the first experimental results of small sodium pool fire extinction using the powder samples previously characterized. The presence of trôna did not affect significantly the extinction. Moreover, it did not affect the fusion temperature of the powders due to its decomposition at low temperature. On the contrary, the powder having high percentage of $LiNaCO_3$ encountered a difficulty in extinguishing the fire. This happened because of their difficulty to flow, which enhanced by the external condition of the tests. These first results show that this facility allows us to test the extinguishing powders on sodium fires, with temperature monitoring at different positions and video recording. Improvements suggested from these preliminary tests should permit to discriminate the extinguishing efficiency of the powders as a function of their chemical composition.

1. Introduction

As part of the new sodium test platforms and the development of Sodium Fast Reactors (SFR), a sufficient stock of effective extinguishing powders is mandatory to contribute to the safety of installations in case of sodium leakage provoking a sodium fire. An adequate extinguishing powder, based on a mixture of lithium carbonate and low-hydrated sodium carbonate in a near eutectic proportion (melting temperature is around 500 °C) associated with graphite, was developed by the CEA (Reuillon et al., 1979). The mass ratio (R) of the powder employed over the sodium to obtain extinction is 0.5 as opposed to 2.3 for chloride based extinguishant (which is corrosive). A similar ratio is obtained for sulphuric acid exfoliated graphite powder (Graphex), but the latter is only effective at high temperature (> 620°C). Moreover, it can also be used for extinguishing other metal and hydrocarbon fires. This powder was produced from the early 1980s to the late 1990s by CACI, a company that ceased its production nowadays. Following the shutdown of several old facilities (consequently, no more risk of sodium fire), the CEA has at its disposal an important stock of unused powder batches, some of which have not been kept in suitable conditions. Hence, the reutilization of these powders raises the question about their efficiency to extinguish a sodium fire, notably due to the long term storage that could possibly deteriorate their composition.

According to Reuillon, the hydrated water present in the sodium carbonate helps to form the sodium hydroxide as the first barrier layer. However, Reuillon observed that water content in the sodium carbonate slightly lower than the corresponding water quantity of carbonate monohydrate (14.5%) is favourable to extinction. Indeed, for mixtures with water content of 10-12% hydrated water, none or only small re-ignition of sodium fire was observed after powder spreading. On the contrary, with 14.5% and 15% of hydrated water, the re-ignition

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appeared to be more frequent. At higher temperatures, the carbonates' eutectic composition allows the powder to reach its total or partial melting, thus creating a second protective barrier layer against the oxygen (Reuillon, 1976).

Various physicochemical analyses have been carried out to characterize samples of unused powder batches currently in stock (Kusumanindyah et al., 2015). The results highlight, in certain samples, the presence of a mix sodium/lithium carbonate compound defined as lithium sodium carbonate ($LiNaCO_3$), which is not a product of aging, as well as trôna ($Na_2CO_3.NaHCO_3.2H_2O$) that, contrarily, formed because of aging during storage. The role of ambient moisture and carbon dioxide has been studied through some single or multi-compound aging experiments. $LiNaCO_3$ is sensitive to the presence of moisture, which is able to transform it into lithium carbonate (Li_2CO_3) and sodium carbonate monohydrate ($Na_2CO_3.H_2O$), meanwhile the latter reacts with water and carbon dioxide to form trôna (Kusumanindyah et al., 2015).

The purpose of this study is to compare the powders' efficiency with regards to their chemical composition and to understand the mechanism of extinction. Therefore experiments of small sodium pool fire's extinction using the powder samples previously characterized (Kusumanindyah et al., 2015) have been conducted. Three different powder samples have been chosen based on the presence or absence of $LiNaCO_3$ and trôna. Scanning Electron Microscope (SEM) analyses were conducted to compare their microstructure. As a fusible powder, its thermal decomposition properties play an important role when it comes to extinguish a fire. Therefore, Differential Thermal Analysis (DTA) was also realized. Finally, an experimental facility dedicated to this study named Chris(X)ti-Na (eXtinction Na), has been developed. The first experiment results are reported in this paper.

2. Experiments

2.1 Fire extinguishants

Three powders have been chosen for the small sodium pool fire experiments. Powder A is rich in $LiNaCO_3$ and contains no trôna, powder B is a trôna rich powder and no longer contains $LiNaCO_3$, while powder C is rich in trôna but still has a moderate quantity of $LiNaCO_3$ (Kusumanindyah et al., 2015). The average of their physicochemical characteristics are listed in Table 1 based on X-Ray Diffraction (XRD), Thermo Gravimetry (TG), micro Gas Chromatography (µ-GC), and Atomic Absorption Spectroscopy (AAS), LASER particle size, and FT4 powder rheometry analysis. Besides affecting the chemical composition, the aging also change their physical properties, notably for their particle size. Apparently it makes the particle becomes bigger especially for powder B. This fact indicated a different mechanism of aging between these powders (Kusumanindyah et al., 2015). Two experiments for each powder have been conducted to ensure their reproducibility.

Table 1: The physicochemical characteristics of powder A, B, and C

Powder	$Na_2CO_3.H_2O$ (% mass)	Li_2CO_3 (%mass)	$LiNaCO_3$ (%mass)	Trôna (%mass)	Graphite (%mass)	Free water (%mass)	Particle size, D_v50 (µm)	Flowing type (FT4 powder rheometry)
Powder A	31	33	26	1	9	0	5.6	Cohesive
Powder B	30	38	0	20	8	4	30.2	Easy flow
Powder C	16	35	18	26	5	0	7.5	Cohesive

2.2 Experimental set-up

Chris(X)ti-Na is a facility used to study the extinction of sodium pool fires. Basically, it consists of a metallic table equipped with a powder spreader device, which is placed above a small insulated crucible (as a sodium container heated with a hot plate) and the measurements devices. It is located in an installation supplied with air ventilation in order to aspirate the caustic smokes produced during the combustion. Figure 1 shows a general view of the facility.

The powder spreader is equipped with a series of vibrating sieves-diffuser to ensure the continuous distribution of the powder on the sodium container. The spreading can be interrupted so that the quantity of the powder needed to extinguish the sodium fire could be measured. The sodium is conserved in a sealed insulated stainless steel container. The sodium temperature can be raised up to 500°C with the hotplate.

Fire extinction was observed by the temperature measurements and by video recording of the experiment. Four thermocouples were installed inside the sodium container at different important locations: inside the sodium, at the sodium pool surface, in the flame and the powder.

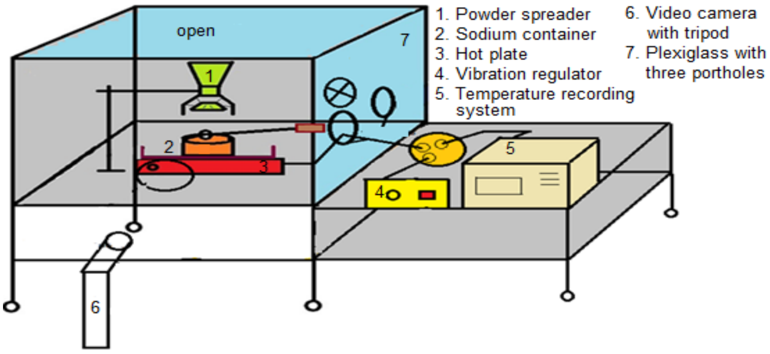

Figure 1: The schema of Chris(X)ti-Na experimental facility

2.3 Experimental procedure

The sodium was initially put in a stainless steel container wrapped by the heat insulator in order to prevent the heat losses. The container was connected to a stainless steel cone, through which an inert gas was introduced in order to prevent sodium oxidation. Furthermore, a container lid was placed onto the ensemble preventing the direct contact with oxygen during heating by a hotplate. As soon as the sodium temperature attained 450°C, the aspiration system was started and the inert gas circulation was stopped. The container lid was then removed, allowing a direct contact of liquid sodium with the oxygen. Even if there was a sodium oxide layer observed on the surface of liquid sodium, the fire took place in a few seconds. After the sodium fire has established (sodium temperature around 540°C), the powder in the reservoir located above the sodium container was spread. A vibration regulator allowed us to control the spreading rate. The hotplate was unplugged to prevent the renewal of heat source. The vibration was stopped when no more flames were observed. The combustion residue was then cooled down to room temperature for sampling. The mass of the powder loss (that either fell outside of the container or remained in the sieves) was noted. The difference between the initial mass of powders stored on the reservoir with the one loss during the experiment indicated the mass of the powder used to extinguish the sodium fire. The sequence of the experiments was recorded by a video camera. Test personnel were protected by nomex gowns, fire-resistant gloves, and full face shields. The aerosols produced as the product of combustion were aspired by the high flow rate of the ventilation system available on the installation.

2.4 Scanning Electron Microscopy (SEM)

The structures of the three powders were studied using Environmental Scanning Electron Microscope (SEM). Figure 2 displays the difference microstructures of these powders at similar magnifications. Powder A is constituted of regularly shaped needle-like particles (5µm length), which coexist with larger particles of 20µm length. On the other hand, powder B has much bigger irregular shaped particles (with agglomerated needle shape particles). Powder C looks more like powder A, although most of its needle shape particles appeared to be broken when compared to powder A.

The results of particle size analysis using a Malvern mastersizer LASER particle size analyzer showed that powder A has the smallest particle size of 5.62 µm diameter, close to powder C: 7.62µm, whereas powder B particles are 6 times bigger with 30.20 µm. These results fit with the SEM observations. It appears that the aging affects the physical properties by comparison with their change in particle size. The flowability test using FT4 powder rheometry was also conducted to compare their flow behaviors. The plot of flow function showed that they exhibit different flow index. Powder A and C have the same flow index (i<4) that corresponds to cohesive powders, meanwhile powder B (i<10) conforms as easy flow powders. However, these three types of powders could still be considered as cohesive according to Geldart's (1972) powder classification based on their fluidization behavior.

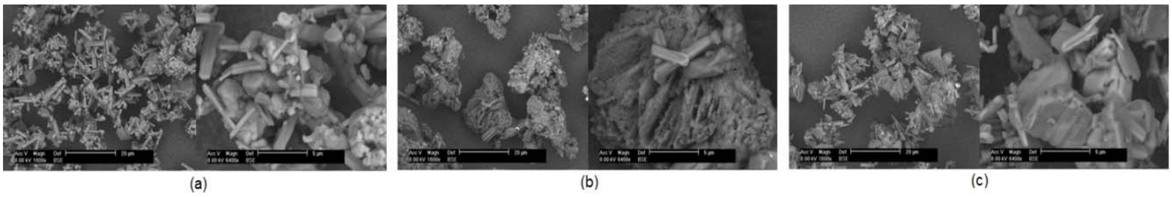
(a) (b) (c)

Figure 2: (a) Powder A (b) Powder B (c) Powder C with 1600x (left) and 6400x (right) magnification

2.5 Differential Thermal Analysis (DTA)

The analyses were conducted using a DTA Mettler Toledo calorimetry. The powders were heated from 25 to 600°C with 2°C/s heating rate, and then cooled at the same rate. Figure 3 presents the comparison chart of the thermal decomposition for these three powders. During heating, large endothermic peaks were observed at 80-90°C and 497±1°C, which are attributed, respectively, to the decomposition of $Na_2CO_3.H_2O$ and/or trôna and the melting of the powder. Reaction 1 and 2 represent the thermal decomposition of $Na_2CO_3.H_2O$ and trôna respectively. It corresponds to an endothermic gas release (including hydrated water). The powders having more quantity of trôna decompose at a slightly higher temperature (around 90°C) for powder B and C than powder A (at 80°C), and absorb about twice more energy. Due to its decomposition at low temperature, the presence of trôna did not affect the melting temperature of carbonates at eutectic composition (as it decomposes to Na_2CO_3, the initial composition in carbonates remains unchanged).

$$Na_2CO_3.H_2O \rightarrow Na_2CO_3 + H_2O \qquad (1)$$

$$Na_2CO_3.NaHCO_3.2H_2O \rightarrow \frac{3}{2}Na_2CO_3 + \frac{1}{2}CO_2 + \frac{5}{2}H_2O \qquad (2)$$

Initially, the powders were composed of carbonates with a proportion close to the eutectic composition, the eutectic temperature being reported at 499.7°C (Cairns and MacDonald, 1962). This temperature also corresponds to the incongruent melting temperature of $LiNaCO_3$ (500.5°C) which is absent in powder B. Thus, it seems that at least of the experiment in DTA, $LiNaCO_3$ is not requested to allow the melting at around 500°C. However, it should be verified if the melting at eutectic temperature can be obtained for a more or less mixed lithium and sodium carbonate powder or if the presence of $LiNaCO_3$ helps in its low temperature melting. Therefore the comparison of the extinction tests using these powders is essential to understand the role of each composition to obtain extinction.

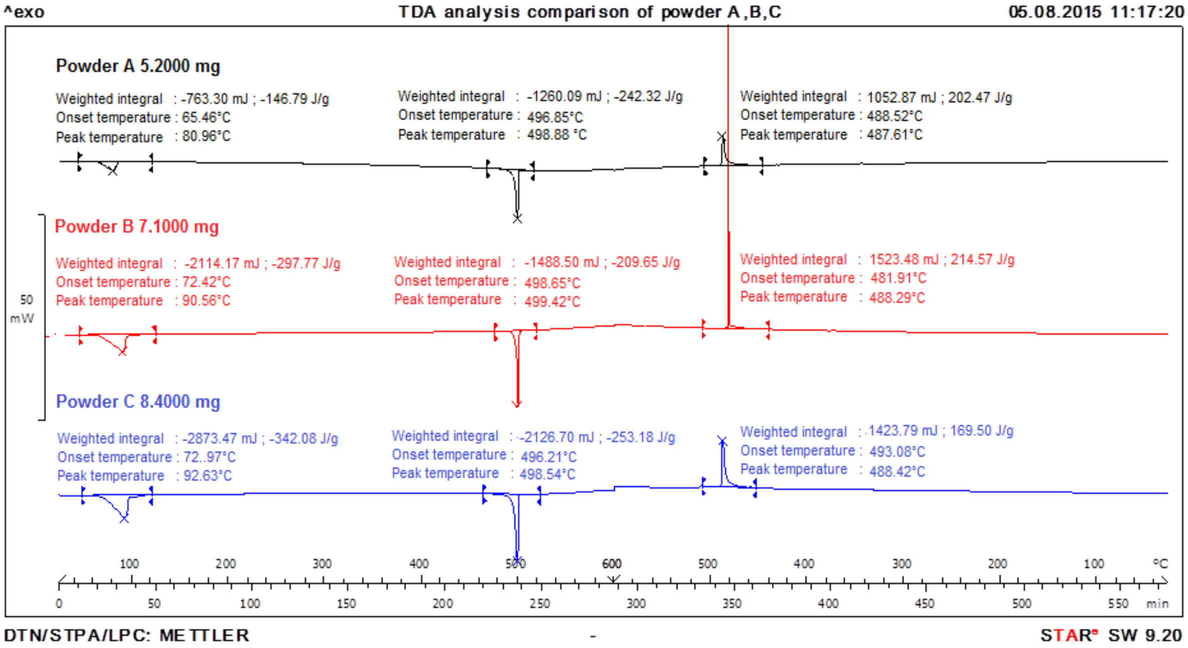

Figure 3: DTA analysis comparison chart of powder A, B, and C

3. Results and discussion

The progress of the experiment from the inflammation until the extinction phase is illustrated by shots from the video recording in figure 4. At the moment when the sodium container lid was opened, we observed a white crust of sodium monoxide (Na_2O). The yellow crust that corresponds to the sodium peroxide (Na_2O_2) didn't appeared as what was observed in the experiments conducted by An et al., 2013 where the sodium was heated in contact of atmosphere since the beginning. The inflammation starts at some privileged sites named nodules, which represent the beginning of vapor phase reactions. These nodules were extended as there were larger areas of contact with oxygen. The combustion phase was established after the yellow flame propagates. Once the temperature of the surface of the sodium attains 540°C, the powder began to spread.

The powders covering the sodium surface prevent direct contact with oxygen allowing the decrease of the flame temperature. These powders melt then formed the protective layer against the oxygen.

Figure 4: The progress of Chris(X)ti-Na experiment (a) sodium oxide crust with some apparent nodules, (b) the propagation of the nodules, (c) sodium combustion established, and (d) the beginning of sodium fire's extinction with the extinguishing powder.

Six experiments of sodium fire extinction were conducted with three powders of different chemical proportions to compare their extinction capacity. The extinction using powder A encountered some difficulty in terms of homogeneity during spreading, thus provoking re-ignition notably for uncovered sodium surface. Its small particle size makes it more difficult to flow and more sensitive to the influence of the external experimental condition (i.e. high aspiration flow rate in the installation and the air circulation pass through the porthole). On the contrary, having the bigger particles, powder B experienced no difficulty during spreading, thus facilitating a faster extinction contrarily to powder A that needs manual intervention at the end of experiment in order to obtain a total extinction.

The temperature during the experiments were observed using thermocouples. Figure 5 shows the comparison of the evolution of sodium surface temperature among these three powders. The rapid decrease of temperature was found directly after the powders were spread although the re-ignition appeared during the extinction using powder A and B. Re-ignition happened after 400 s of powder A's spreading allowing fast temperature decrease from 680 to 350°C. The re-ignition increased the temperature to 380°C in a quick 100 s. In the case of powder B, a brief re-ignition appeared to increase the temperature from 380 to 460°C in 18 s. However, the continuous powder B distribution has succeeded to attain an immediate total extinction afterwards.

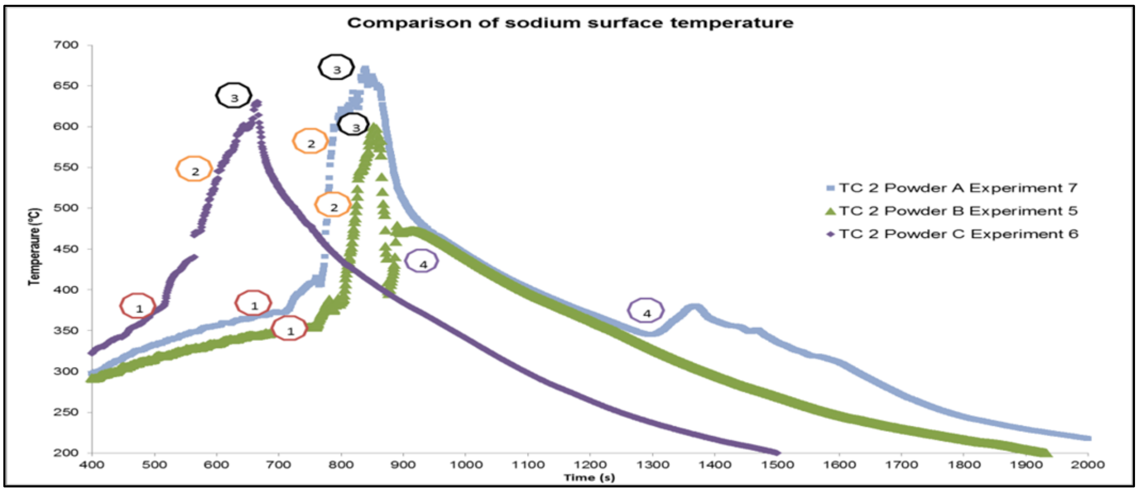

Figure 5 : The comparison of sodium surface temperature during the extinction experiment using powder A, B, and C [1 : Ignition, 2 : Combustion, 3 : Extinction, 4 : Re-ignition].

A modification of the experimental set up was brought during the experiment using powder C. A higher vibration rate was opted in order to facilitate powder spreading. Figure 6 shows the details of the temperature evolution for each thermocouple installed in the sodium container during the experiment. The change indeed improved the spreading performance. Rapid extinction with no re-ignition was achieved after powder spreading. The powder's temperature was observed to be constant at around 500-550°C, which corresponds to be the fusion of powder. The fact that powder C, which has a moderate quantity of $LiNaCO_3$ and has the high amount of trôna, is still able to extinct the fire, demonstrates that the re-ignition in powder A only happened due to the difficulty to flow. Overall, based on only these experiments, it is still difficult to conclude on which powders have the best efficiency to extinguish a sodium fire according to their composition.

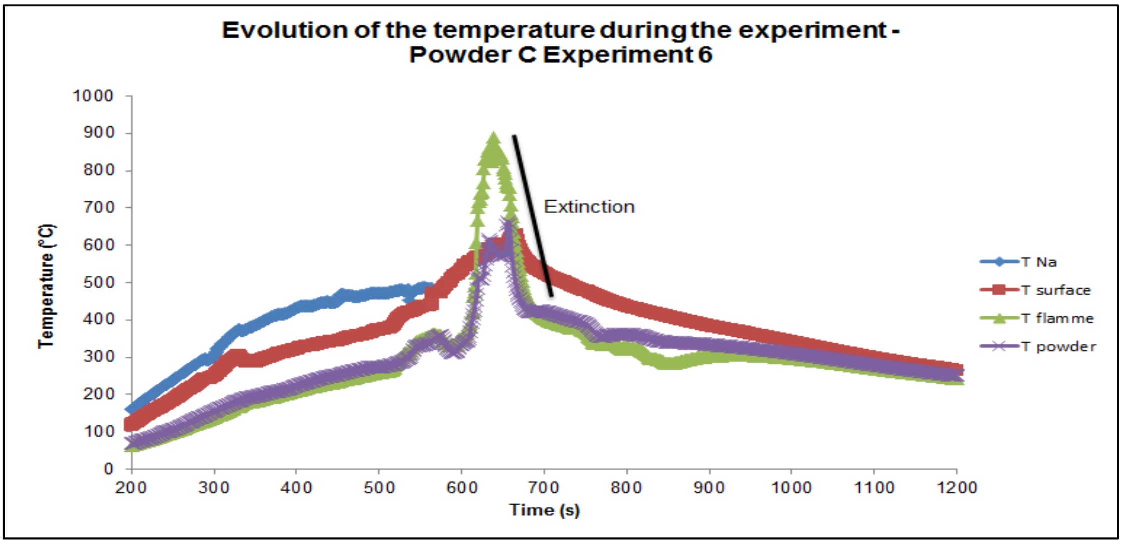

Figure 6 : The evolution of temperature during the extinction experiment using powder C.

4. Conclusion and Perspectives

The Chris(X)ti-Na experimental device has been developed to study the impact of aging towards the extinction efficiency of an extinguishing powder for sodium fire. Three powders of different compositions were used, which each represents compositions of different aging states, containing more or less trôna and $LiNaCO_3$. The presence of trôna apparently did not affect the quality of extinction. A rapid extinction and only a slight re-ignition were observed. Moreover, the presence of trôna did not affect the melting temperature of the powders due to its decomposition at low temperatures. On the contrary, the powder having a high percentage of $LiNaCO_3$ encounters a difficulty in extinguishing the fire. This happened because of its flowing difficulty that could be related to its small particle size. The high flow rate of air ventilation and also the air circulation through the porthole of the table affects the powder spreading. Thus far, it is still difficult to compare the efficiency of these powders based on their chemical composition due to their physical properties and the conditions of experimentations that influence the spreading performance. Therefore other experiments will be conducted in order to be able to study solely the influence of the chemical composition, by using synthetic powders of similar flowing behavior, with no effect of external condition during the extinguishing test.

Acknowledgments

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