

## Experimental determination of the minimum onset temperature of runaway reaction from a radioactive salt disposal in asphalt<sup>☆</sup>

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### Abstract

In order to clarify the reason for the most hazardous explosion in the history of the Japanese nuclear power development by a radioactive salt disposal in asphalt, an adiabatic process was developed using a Dewar vessel to minimize the temperature difference between the reactants and the surroundings. By this means, the heat evolution from a reaction which is readily lost can be detected at a lower temperature imitating the accidental condition. A series of ambient temperature-tracking Dewar experiments on asphalt salt mixtures were conducted under different initial ambient temperatures, such as 230, 210, 190, and 170 °C, respectively. As a result, it was observed that from 190 °C the sample's temperature rose until a runaway reaction occurred. The minimum onset temperature for the runaway reaction of the asphalt salt mixture was determined to be 190 °C, which is close to the initial temperature of approximately 180 °C, the same temperature as the real accident. This implies that at near this operational temperature, initial faint chemical reactions may occur and lead to further rapid reactions if heat is accumulated at this stage.

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### 1. Introduction

On 11 March 1997, a fire and explosion occurred in a bituminization demonstration facility (BDF) when low-level radioactive liquid wastes coming from a reprocessing plant were disposed at the Tokai Works of the Power Reaction and Nuclear Fuel Development Corporation, Japan. The disposal process involved mixing the waste solution including salts of  $\text{NaNO}_3$ ,  $\text{NaNO}_2$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{NaH}_2\text{PO}_4$  with asphalt in an extruder at 180 °C, pouring the mixture into ten 220 l drums, and then storing them at the ambient temperature of 50 °C to allow cooling. A fire and violent explosion of the stored drums caused total damage to BDF and was considered the most hazardous accident in the history of the Japanese nu-

clear power development [1,2]. On the whole, there were three operational changes before the accident which violated the standard of safe operation. They were: a decrease of the feeding rate of wastes into the extruder from 200 to 160 l/h; an occasional addition of phosphate into the waste; a shorter agitation time for the waste mixing.

It was assumed that all these changes might contribute to certain undesirable reactions in the extruder. However, whether such reactions could result in a final severe explosion is still under investigation. One theory is that the major runaway reaction started at an onset temperature at least above 230 °C and that the cause of the temperature rising to this point was physical factors such as the heat of friction between the extruder and salt particles [2,3]. Contrarily, Hasegawa and coworkers put forth the viewpoint that the major oxidizing reaction occurring in the asphalt and  $\text{NaNO}_2$  were facilitated by some molecules containing intramolecular hydrogen, such as  $\text{NaH}_2\text{PO}_4$  and  $\text{NaHCO}_3$ . Moreover,  $\text{NaHCO}_3$  decomposition which produces gases created many micro

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bubbles in the interior of the salt particles. These supplemental reactive areas in turn promoted the oxidizing reactions that were controlled by diffusion of the reactants throughout the product layer. The reason that a runaway reaction started at about 180 °C or lower is believed to be a consequence of both the chemical effect of intramolecular hydrogen and the physical effect of the NaHCO<sub>3</sub> decomposition gases [4–7].

However, it is difficult to verify on a laboratory scale that the runaway reaction happened at an initial temperature lower than 230 °C [2,3], for the oxidation–reduction reaction of asphalt and NaNO<sub>2</sub> in the mixture is very complicated, undergoing solid–liquid interface-controlled reaction to homogeneous liquid reaction. In the early stage, heat generation from the mixture is weakly dependent on temperature and its amount is too small to be detected in conventional experiments.

For a thorough study, a Dewar experiment, one of the most useful techniques in the assessment of chemical reaction hazards, was herein developed to carry out such a strictly adiabatic self-heating test with a lesser amount of sample. The Dewar calorimeter, which uses a vacuum-jacketed flask, enables an accurate estimation of data on the rate and quantity of heat evolved in a large-scale process. Experimental results have shown that the cooling rates of 250 and 500 ml Dewar flasks are equivalent to those of 0.5 and 2.5 m<sup>3</sup> plant vessels, respectively [8].

It is also necessary to consider the faint heat generated by the mixture, so heat loss from a Dewar vessel must be eliminated further by reducing the temperature difference between the sample and the ambient atmosphere. In this study we let the ambient temperature follow the sample's temperature when it rose during the experiment.

## 2. Reaction characteristics of an asphalt salt mixture

The samples were prepared by simulating the different processes known to have taken place prior to the accident and illustrated in Table 1. As mentioned in the accidental

scene [2,3,6], several kinds of salts, such as NaNO<sub>3</sub>, NaNO<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> and NaH<sub>2</sub>PO<sub>4</sub> were dissolved in distilled water and precipitated by Ba(OH)<sub>2</sub>·8H<sub>2</sub>O. The pH value of the solution was adjusted to 9.0 using 1.3 N HNO<sub>3</sub>. NaHCO<sub>3</sub> was produced at this pH value. Afterward another two salts, K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O and NiSO<sub>4</sub>·6H<sub>2</sub>O were added to the solution. After being stirred, the aqueous salts, whose components simulated the waste from the nuclear power plant in industry, were dried at 45 °C for 10–15 days until most of the water was evaporated. This was done to avoid the decomposition of NaHCO<sub>3</sub> before it was mixed with the asphalt and to easily crush and sift the waste salts in a milling machine. Only particles under 40 μm were mixed with the asphalt at a weight ratio of 45–55 under the test temperatures.

The reaction of the mixture is so intricate that a common heat calorimeter could not obtain the full information, especially for the early stage of the reaction. Therefore, a highly sensitive thermal analyzing apparatus, C80D, manufactured by Setaram Co. in France, was employed as a screening test to measure the heat flux  $dH/dt$  versus the temperature of the asphalt salts mixture at a very slow scanning rate of 0.01 K/min. As shown in Fig. 1, the whole reaction could be depicted into three stages assuming the following simplified reaction scheme: an initially chemical reaction-controlled stage on an interface (166–186 °C), a diffusion-controlled stage in a product layer (205–245 °C), and a homogeneous reaction-controlled stage in liquid phase (255–270 °C). The reaction characteristic is exactly the same as what was prepared by Sun et al. [5], in which the waste solution was directly stirred into the asphalt at 180 °C. This implies that both methods are representative of the real process in the accident, provided that intramolecular hydrogen remained in the mixture as micro bubbles due to NaHCO<sub>3</sub> decomposition occurring in the asphalt mixture.

Subsequently, the kinetic parameters listed in Table 2 are derived from the different stages in Fig. 1. These are obtained from the slope of logarithmic values of  $(dH/dt/M_0/\Delta H_R)$  plotted against the reciprocal of the corresponding absolute temperature (correlations are linear in the typical stages). The reaction starts at about 166 °C and undergoes a short ini-

Table 1  
Preparation of asphalt salt mixture

Ingredients	Concentration (g/l)
Solution <sup>a</sup>	
NaNO <sub>3</sub>	250
NaNO <sub>2</sub>	50
Na <sub>2</sub> CO <sub>3</sub>	80
NaH <sub>2</sub> PO <sub>3</sub>	20
Precipitated by Ba(OH) <sub>2</sub> ·8H <sub>2</sub> O	18.93
Extra salts added	
K <sub>4</sub> Fe(CN) <sub>6</sub> ·3H <sub>2</sub> O	9.72
NiSO <sub>4</sub> ·6H <sub>2</sub> O	12.09

After the aqueous salts being dried at 45 °C, crushed and sifted, the salt particles under 40 μm were mixed with asphalt (45:55) at the initial temperature of each test.

<sup>a</sup> pH modified by HNO<sub>3</sub>: 9.0.

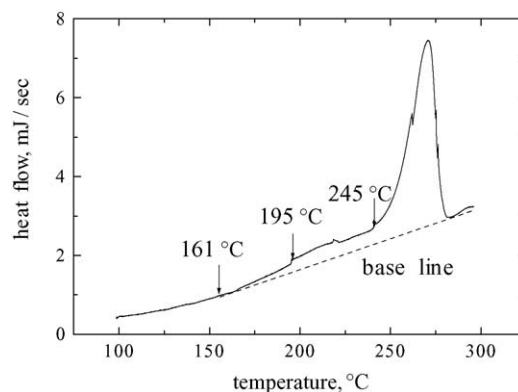


Fig. 1. Heat flux curve of asphalt salt mixture measured by C80D (sample mass: 500 mg, program temperature rising rate: 0.01 K/min).

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