

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

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Received 24 December 2003; received in revised form 14 January 2005; accepted 24 January 2005

## 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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**Keywords:** Radioactive salt disposal; Asphalt salt mixture; Dewar adiabatic test; Onset temperature; Faint heat generation; Runaway reaction

## 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 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> 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 NaNO<sub>2</sub> were facilitated by some molecules containing intramolecular hydrogen, such as NaH<sub>2</sub>PO<sub>4</sub> and NaHCO<sub>3</sub>. Moreover, NaHCO<sub>3</sub> decomposition which produces gases created many micro

<sup>☆</sup> This paper was originally presented at the Third International Conference on Loss Prevention, held in Singapore, December 2000.

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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.

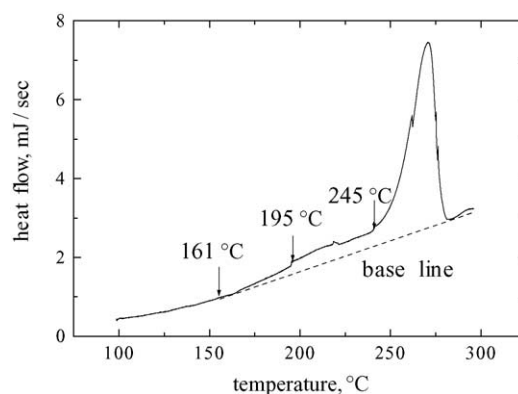


Fig. 1. Heat flux curve of asphalt salt mixture measured by C80D (sample mass: 500 mg, program temperature rising rate: 0.01 K/min).

Table 2  
Reaction kinetic parameters for different reaction stages of asphalt salt mixture

Temperature range (°C)	Activation energy, $E$ (kJ/mol)	Pre-exponential, $A$ ( $s^{-1}$ )
166–186	137.28	$3.88 \times 10^9$
205–245	49.42	$1.80 \times 10^{-1}$
255–270	191.35	$2.37 \times 10^{13}$

Heat of reaction  $\Delta H_R$ : 1297.8 J/g integration area between heat flow curve and base line, regression of base line:  $Y = 0.01578T - 0.7971$ .

tial active stage whose activation energy is 137 kJ/mol because in the fresh sample as the reaction starts the salt particles can directly contact the asphalt. Afterwards, a product layer emerges between the reactants, and the reaction will change to a comparably slow stage whose activation energy decreases to less than half of that of the previous stage. This second stage is sustained by the diffusion of the reactants throughout the product layer up to 250 °C. Then when all the salts melt and the asphalt becomes fluid above this point, the reaction will follow a homogeneous one in which the reaction rate is sufficiently quick to lead to a final runaway reaction.

It seems that the first two stages are induction periods which give rise to the runaway reaction if the heat generated by the reaction is accumulated to such a degree that its rate exceeds the rate over which heat is removed by the system. The accident can be possibly reproduced under a lower temperature than the 230 °C that had been expected. However, such weak reactions produce such small amounts of heat that they cannot be observed using conventional techniques. Some adiabatic technique must be used to meet the special measurement requirement.

### 3. Sensitivity of the technique

The test results obtained during an investigation of chemical reaction hazards are dependent on a number of experimental parameters, such as:

- the sample—its physical and chemical properties and size,
- the adiabaticity (or heat loss) of the test system,
- the thermal inertia or phi factor of the calorimeter, and
- the detection limit for self-heating rate.

Because of these variables, test data has to be obtained using methods whose characteristics can be quantified and related to the plant situation, as discussed below.

#### 3.1. Adiabaticity

In an experimental system it is not possible to achieve complete adiabatic conditions, and a control system requires a certain temperature difference, however small, between the desired set point and the actual temperature in order to func-

tion. Therefore, the sensitivity of any experimental apparatus for measuring self-heating is given by

$$\text{sensitivity (W/l)} = U(W/(1\text{K})) \times \Delta T(\text{K}) \quad (1)$$

where  $U$  is the overall heat transfer coefficient which characterize the rate of heat loss from the sample inside a vessel to the surrounding and can be readily measured by the test cell using a hot non-reactive liquid and measuring its rate of cooling; e.g., silicon oil above 100 °C used in this study.  $\Delta T$  is the temperature difference between the sample and the surrounding and is a function of the accuracy and response of the measurement and control system.

In order to attain a high degree of sensitivity, the experimental technique must accurately control with temperature to minimize the temperature difference and/or a low overall heat transfer coefficient.

The overall heat transfer coefficient of a sample in a 500 ml aluminum container is given as 0.58 W/(1 K). Thus, to attain the sensitivity required to detect slow self-heating on the plant scale, a temperature measurement/control of better than 0.1 K is required. Dewar flasks reduce the overall heat transfer coefficient of the vessel, so the sensitivity required to simulate full-scale plant can be obtained with less accurate temperature measurements. For example, a typical 500 ml glass Dewar has an overall heat transfer coefficient of 0.03 W/(1 K), hence the desired sensitivity can be easily obtained with a temperature control of 1 K.

#### 3.2. Thermal inertia

The second important factor that affects the sensitivity of the apparatus is the phi factor, i.e., the ratio of the heat capacity of the sample and the container to the heat capacity of the sample, which indicates heat absorption by the vessel. Both the net self-heating and the rate of temperature rise from the reaction will be abated by this factor. The phi factor for a 500 ml Dewar filled with 400 g asphalt salt mixture is 1.89, considering that the mass of the Dewar is 502 g and the specific heats ( $C_p$ ) of the Dewar and the sample are 0.84 and 1.18 J/(K g) [4], respectively. The value of the phi factor is even smaller than 1.57 if only the mass of the inner wall of Dewar (of 320 g) is considered, since the outer wall can hardly influence the heat transfer due to the vacuum layer between the walls. Comparably the phi factor is 5.98 for an ARC with a 1.00 g sample (the mass and  $C_p$  are 11.3 g and 0.52 J/(K g) of a titanium bomb).

#### 3.3. Detection limit for self-heating rate

After the modification, the Dewar test had a higher sensitivity and the detection limit of temperature change dropped to 0.003–0.006 K/min, whilst the prescribed minimum scanning rate are 0.01 K/min for C80D and 0.02 K/min for ARC, respectively. This ensured that the Dewar could detect very weak heat generation even below what the C80D could do

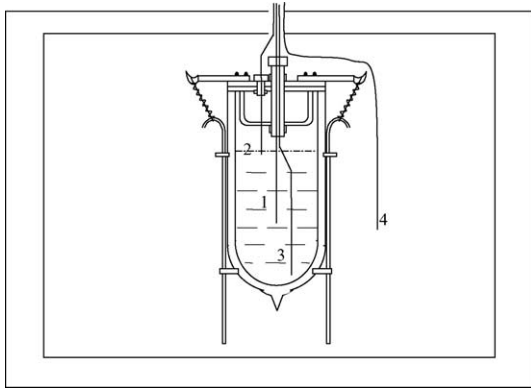


Fig. 2. A temperature measuring system of asphalt salt mixture inside a Dewar flask (1, 2, 3 and 4: positions of thermocouples).

and whether this generation could cause the runaway reaction at the plant conditions.

#### 4. Experimental apparatus

In each experiment, the sample was electrically heated at first quickly to reach the desired initial temperature, such as 230, 210, 190 and 170 °C, in a stainless steel vessel. Four hundred grams hot sample was then added to a 500 ml cylinder-shaped Dewar, whose construction is shown schematically in Fig. 2. The Dewar was equipped with three thermocouples of 1 mm diameter in a type of sheath, to monitor the temperatures at the center (no. 1), upper surface (no. 2) and bottom (no. 3) of the sample. When the Dewar equipped with thermocouples was placed in a chamber, the temperature of the sample attained the preset initial temperature again due to the conduction from the surrounding oven. And when self-heating due to the reaction of the sample occurred, an ambient temperature controlled experiment was conducted. The feedback was judged by the readings of the thermocouples of the temperature differences between the center of the Dewar and the oven (no. 4). Whenever a 1 K increase of the sample from the preset temperature was observed, the oven's temperature was manually increased by the same increment. All the thermocouples were connected to a recorder and a computer to collect raw data.

#### 5. Discussion of the result

The adiabatic Dewar experiment allowed the direct simulation of the plant conditions. Figs. 3–5 show temperatures versus time traces for the asphalt salt mixtures inside the 500 ml Dewar at initial temperatures of 230, 210, and 190 °C, respectively. In the figures, temperatures at the center, the upper surface, and the bottom of the sample in the Dewar, as well as one for the ambient oven, were recorded. Generally, the overall tendencies of temperature change were

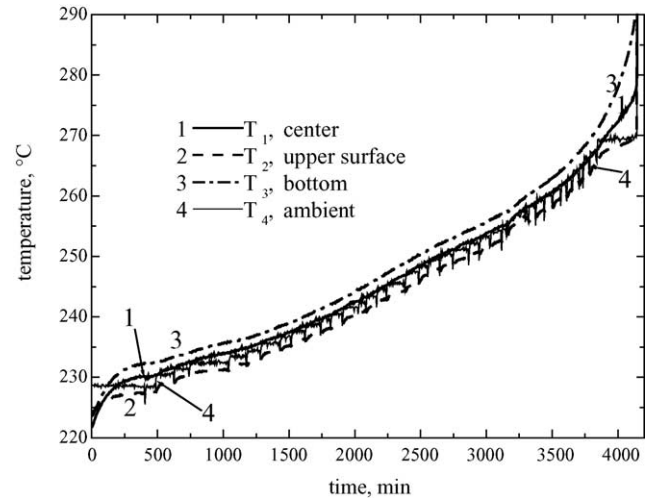


Fig. 3. Temperature of mixture in a 500 ml Dewar flask (initial 230 °C).

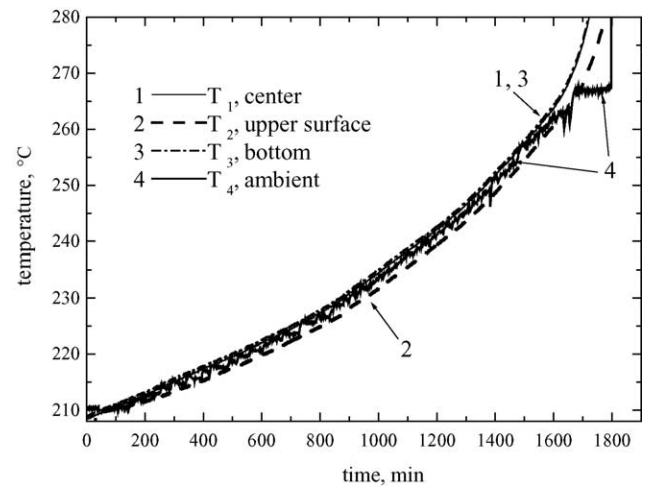


Fig. 4. Temperature of mixture in a 500 ml Dewar flask (initial 210 °C).

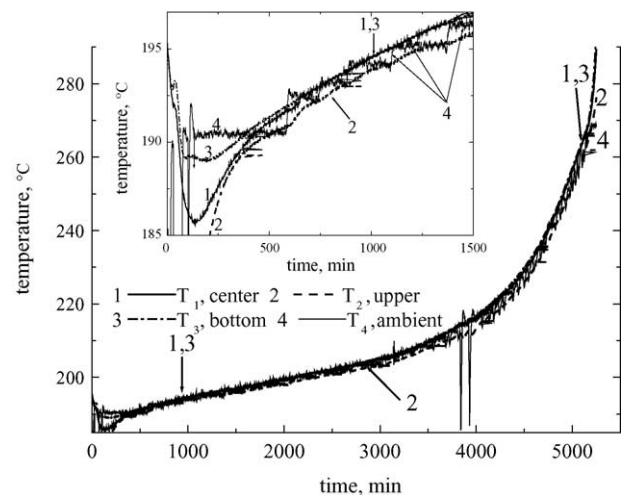


Fig. 5. Temperature of mixture in a 500 ml Dewar flask (initial 190 °C).



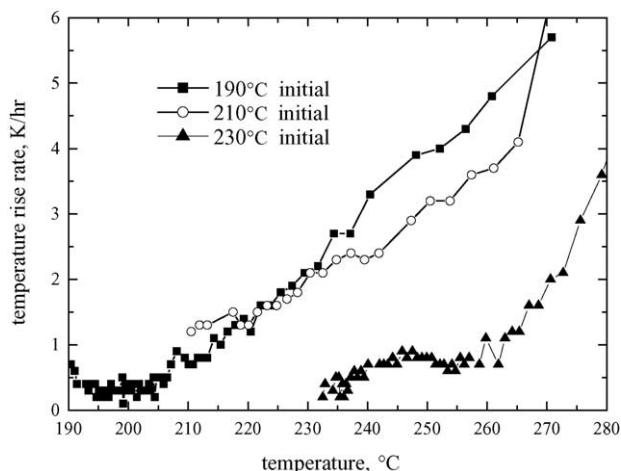


Fig. 6. Temperature rise rate of mixture.

similar in these three cases. The sample was preheated to each onset test temperature and during the process of filling the Dewar with the sample and putting it in the oven, the sample's temperature decreased somewhat. The oven's temperature was controlled and the no. 4 thermocouple remained apart in the oven to read the temperature of the surrounding, which fluctuated due to fluid air convection especially whenever the oven's temperature needed to change. The other three thermocouples were put in the sample inside the Dewar, so they gradually increased by the self-heating after the temperatures reached the onset test temperature. The temperature rise rates are represented in Fig. 6. When the sample's temperature in the Dewar center (no. 1) increased 1 K above the ambient because of the self-heating, the oven temperature was incremented stepwise by the same amount. This could be done up to about 265 °C, at which point the sample temperature started rising too quickly to be tracked by this feedback procedure. The manually controlled ambient temperature no longer followed the runaway reaction which developed thereafter. When the sample's temperature went beyond 290 °C, the sample burned violently.

As mentioned above, it is necessary to set up the experiment as close to adiabatic conditions as possible in order to reproduce real processes. The Dewar's own structure can prevent the heat generated by such a weak reaction from losing to the container and the ambient within a sufficient time. In addition, the temperature of the sample was taken as the set point for the ambient temperature control, in order to maintain a near-adiabatic condition for the Dewar and its sample. As the two temperature readings (center of sample and ambient) were maintained within 1 K, heat input to the controller indicated that there was heat produced from the sample. Only those whose temperature difference less than 0.4 K were selected. From the enlarged early stage shown in Fig. 5, it took 50 h for the reaction to go through the early stage of induction time from 190 to 210 °C, and after that it took another 30 h to

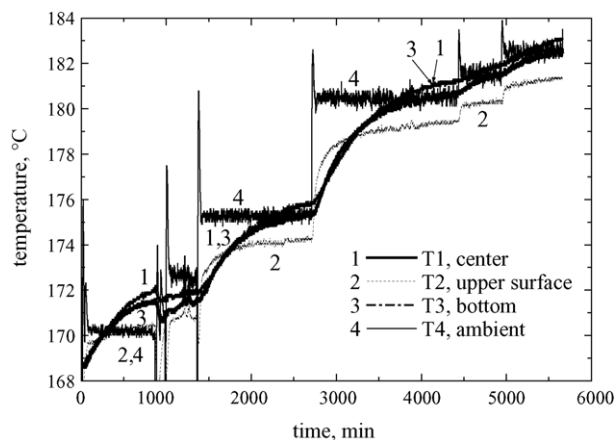


Fig. 7. Temperature of mixture in a 500 ml Dewar flask (initial 170 °C).

attain a runaway reaction and fire. It can also be observed in Fig. 6 that below 210 °C, the temperature rise rate of the self-heating was less than 1 K/h, while after 210 °C. It increased and eventually attained about 5 K/h immediately before the fire occurred.

In the 230 °C experiment, the temperature difference between the sample and ambient was as high as 2.7 K due to a thermocouple's unexpected failure during the experiment. The sensitivity of the experiment worsened and it took longer than 70 h for a runaway occurrence. In Fig. 6, the temperature rise rate in this experiment is much lower than for the other two cases. This lack of control demonstrates the importance of maintaining the temperature difference between the sample and its surroundings as small as possible. This is a key in achieving the sensitivity required for such experiments. It can also be seen in Fig. 3 that the temperatures inside the sample were heterogeneous with the temperature difference between the bottom and the center attaining almost 2 K. On the other hand, the temperatures of the bottom (no. 3) and the center (no. 1) in Figs. 4 and 5 were nearly the same curves, indicating that the temperature distribution is reduced under a modified adiabatic condition.

With an initial temperature as low as 170 °C, it was difficult for the sample's temperature to increase beyond the ambient, and it took a much longer time for the simulated asphalt salt's temperature to reach a balanced temperature, as shown in Fig. 7. Thus in this case, a larger temperature increment was taken. Even when the ambient temperatures were increased up to 183 °C, the sample's temperature did not go 1 K higher than the ambient for a long time.

Other studies, using an ARC and a beaker heat accumulation test [1–3], showed no indication that there is a hazardous reaction below 230 °C. But we found the minimum onset temperature for a runaway reaction was 190 °C. Thus, the initial temperature for industrial waste disposal, 180 °C, is not within a safety margin.

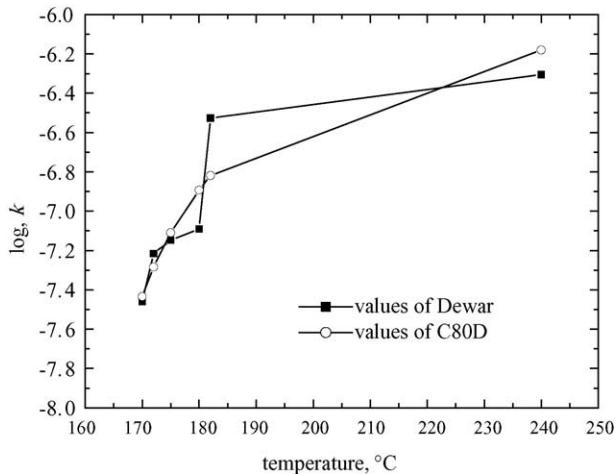


Fig. 8. Comparison of reaction rate constant in Dewar and C80D.

## 6. Evaluation of the reaction rate constant

In this study, the temperature time data from the adiabatic Dewar experiment can also be readily analyzed to yield overall heats of reaction and kinetic data. From a series of isothermal Dewar experiments, the reaction rate constant  $k$  can be determined according to Eq. (2):

$$M_0 \Delta H_R k = US(T - T_a) \quad (2)$$

where  $k$  is the reaction rate constant,  $M_0$  the asphalt solid's mass added to the Dewar,  $\Delta H_R$  the heat of reaction,  $U$  the overall heat transfer coefficient of the Dewar,  $S$  the surface area of heat transfer,  $T$  the sample's temperature when a heat balance is reached, and  $T_a$  is the ambient temperature.

On the other hand, kinetic parameters can also be obtained from data from the C80D calculated by the following equation:

$$k = A \exp(-E/RT)/M/\Delta H_R \quad (3)$$

where  $A$  is the pre-exponential factor,  $E$  the activation energy,  $R$  the gas constant,  $M$  the mass,  $\Delta H_R$  is the reaction heat and  $T$  is the reaction temperature.

Fig. 8 compares two sets of  $k$  values at different temperatures, indicating that both values obtained by Eqs. (2) and (3) are reasonably consistent. It implies that a Dewar vessel can be a practical assessment method, and its sensitivity is consistent with the other thermal analysis calorimeter, C80D. The results will be reliable when applied to the scale of an industrial process.

## 7. Conclusions

In summary:

- (1) To settle a long-standing puzzle of whether or not a runaway reaction can arise from a faint chemical reaction starting at a low feed temperature around 180 °C, it is important to examine whether there is heat generation and to protect it from loss through the container.
- (2) The main advantage of our Dewar technique is the ability to directly simulate the process conditions which occurred in the plant. No extrapolation of experimental data is required and therefore any assumptions about the reaction mechanism, which may not be completely understood, are eliminated. The adiabatic Dewar calorimetry has a potential sensitivity more than sufficient to identify any self-heating that occurred on the largest plant scale. As a result, a runaway reaction can follow from a reaction starting from an onset temperature of 190 °C and above. So the experimentally determined minimum onset temperature for a runaway reaction of a simulated mixture can be considered to be 190 °C.
- (3) This study supports the point suggested by Hasegawa and coworkers [6,7] that a reaction starting near 180 °C cannot be negligible and runaway reaction was the possible cause of the explosion of an asphalt salt mixture in the accident.
- (4) The reaction rate constant value of an asphalt salt mixture was assessed and applied by direct scale to the industrial process. It provides a feasible approach to measure the minimum onset temperature for all other similar reactions whose heat generation is very weak.

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