Evaluation on thermal explosion induced by slightly exothermic interface reaction

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Abstract

An asphalt–salt mixture (ASM), which once caused a fire and explosion in a reprocessing plant, was prepared by imitating the real bituminization process of waste on a lab scale to evaluate its actual thermal hazards. Heat flux reaction calorimeters were used to measure the release of heat for the simulated ASM at a constant heating rate and at a constant temperature, respectively. Experimental results show that the reaction in the ASM below about 250 °C is a slightly exothermic interface reaction between the asphalt and the salt particles contained in the asphalt, and that the heat release rate increases sharply above about 250 °C due to melting of the salt particles. The reaction rates were formulated on the basis of an assumed reaction model, and the kinetic parameters were determined. Using the model with the kinetic parameters, temperature changes with time and drum-radius axes for the ASM-filled drum were numerically simulated assuming a one-dimensional infinite cylinder system, where the drum was being cooled at an ambient temperature of 50 °C. The minimum filling temperature, at which the runaway reaction (MFTRR) can occur for the simulated ASM in the drum is about 194 °C. Furthermore, a very good linear correlation exists between this MFTRR and the initial radius of salt particles formed in the bituminization product. The critical filling temperature to the runaway reaction is about 162 °C for the asphalt–salt mixture, containing zero-size salt particles, filled in the same drum at an ambient temperature of 50 °C. Thus, the runaway reaction will never occur in the drum filled with the asphalt–salt mixture under the conditions of the filling temperature below 162 °C and a constant ambient temperature of 50 °C. As a consequence, the ASM explosion occurred in the reprocessing plant likely was due to a slightly exothermically reaction and self heating.
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Keywords: Thermal hazard; Asphalt–salt mixture; Interface reaction; Thermal analysis; Numerical simulation

1. Introduction

In a nuclear waste processing plant in Japan, pre-treated low-level radioactive liquid waste, including the salts $NaNO_3$, $NaNO_2$, Na_2CO_3 as well as other salts was generally mixed with hot asphalt in an extruder in a batch treatment, while the water in the mixture was evaporated. The obtained asphalt–salt mixture (ASM) was then poured into 220-L drums at about 180 °C and naturally cooled at an ambient temperature of about 50 °C in the filling room. However,

on 11 March 1997, a fire and violent explosion occurred in the drums about 25 h after the ASM was filled [1]. Analysis of the accident showed that there were three differences from standard operating procedures that had prevented any accidents since the plant started up in 1982 [1]. These differences include (1) a lowering of the feeding rate of the waste into the extruder from 200 to 160 L/h, (2) an occasional addition of phosphate ($H_2PO_4^-$) into the waste, and (3) shorter agitation time of the waste. Furthermore, it was discovered that the existence of sodium hydrogen-carbonate in the salt particles (dehydration product of liquid wastes) contained in the ASM is a major contributing factor to this accident. Each of the above three irregularities with respect

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Nomenclature

List of symbols

A	pre-exponential factor (s^{-1} or m/s)
A	surface area of a salt particle (m^2)
Area	reaction interfacial area per unit mass of salt (m^2/kg)
C_P	specific heat (J/K/kg)
D	diameter of a sphere (m)
D_s	interfacial thickness (m)
dH/dt	overall heat flow (J/s)
E	activation energy (J/mol)
g	gravity acceleration (m/s^2)
ΔH_R	heat of reaction per unit mass of initial reactant (J/kg)
h	heat transfer coefficient from N_u (J/m^2/K/s)
K	rate constant (s^{-1} or m/s)
L	height of drum (m)
m_0	initial salt mass per unit surface area of reaction interface
M_0	mass of the asphalt–salt mixture
N_u	Nusselt number
P_r	Prandtl number
$\dot{q}$	rate of heat generation per unit volume (J/m^3/s)
R	gas constant (J/K/mol)
R	radius of a spherical salt particle (m)
r	radius of a sphere or radius axis of a drum (m)
T	temperature (K)
t	time (s)
V	volume (m^3)
x	conversion ratio
Y	rearranged expression

Greek letters

α	temperature conductivity (m^2/s)
β	$1/T$ (K^{-1})
κ	thermal conductivity (J/m/s/K)
ν	kinetic viscosity (m^2/s)
θ	ratio of salt concentration at time t to initial one in the reaction interface
ρ	density (kg/m^3)
δ	thickness of the diffusion layer (m)

Subscripts

D	diffusion
E	experimental
I	initial
L	liquid
R	reaction
S	solid
w	wall
0	initiation or surroundings
∞	surroundings

to the standard operation conditions contributes to a build up of sodium hydrogen-carbonate in the salt particles and much of the observed evidence is consistent with the existence of sodium hydrogen-carbonate in the salt particles [1,2]. The ASM samples used in our previous work [1], however, were obtained by mixing asphalt at about 100 °C directly with pre-simulated mixed salt particles.

In order to assess its actual thermal hazards, the ASM evaluated in this study was prepared by imitating the real bituminization process for waste on a lab scale. Heat flux reaction calorimeters, C80D and MS80II, with high detection sensitivity were used to measure the release of heat for the simulated ASM. Based on an understanding of interface reaction mechanisms, the reaction rates for the entire reaction processes of the simulated ASM were formulated. By the use of the observed heat flows, the kinetic parameters were then determined by a self-consistent method. Therefore, the temperature changes with time and drum-radius axes for the ASM-filled drum can be numerically simulated under the conditions of presumed filling temperature and constant ambient temperature of 50 °C. The minimum filling temperature to runaway reaction finally was determined for the drum filled with the simulated ASM at an ambient temperature of 50 °C.

2. Experiments

2.1. Preparation of ASM

The liquid waste was prepared by dissolving inorganic salts like $NaNO_3$, $NaNO_2$, Na_2CO_3 and NaH_2PO_4 in distilled water, precipitating the mixed solution by $Ba(OH)_2$, adjusting pH value to 9.0 with HNO_3, and then adding the other two extra salts ($K_4Fe(CN)_6$ and $NiSO_4$). The bituminization process of the waste was carried out in a self-designed lab system [2] by mixing hot asphalt at about 180 °C with the above mixed waste solution at a feeding rate of 50 mL/h. All the chemical reagents used in the processing were from the Kanto chemical limited company, Japan. The ingredients of the waste solution and the simulated ASM, listed in Table 1, are almost identical to those of the accident. In addition, the salt particles contained in the simulated ASM were extracted from the mixture in toluene solvent and the diameter distributions of the extracted salt particles were measured as listed in Table 2.

2.2. Measurement of heat flows

A heat flux reaction calorimeter, C80D, with high detection sensitivity of 10 μW was used to measure heat flows of sample at a constant heating rate. In order to decrease the error in measurement due to exerting thermal inertia on the sample [3], the heating rate should be as low as possible, in particular for the low thermal conductivity sample so as to obtain more exact information. In order to investigate faint heat release phenomena, the other heat flux reaction calorimeter MS80II

Table 1
Ingredients and preparation of ASM

Operation	Component	Concentration (g/L)
Mixed aqueous wastes	$NaNO_3$	80
	$NaNO_2$	50
	Na_2CO_3	80
	NaH_2PO_4	20
Precipitation step	$Ba(OH)_2 \cdot 8H_2O$	18.93
	pH adjustment with HNO_3	9.0
	$K_4Fe(CN)_6 \cdot 3H_2O$	9.72
	$NiSO_4 \cdot 6H_2O$	12.09
Bituminization step	Salt content (wt.%)	45.00
	Method: prepared by adding mixed aqueous wastes at the rate of 50 mL/h to asphalt at about 180 °C while stirring and then cooling naturally	

with high detection sensitivity of 1 μW was used to measure the heat release for the simulated ASM at the initial reaction stage under the condition of a constant temperature below 200 °C. All measurements on a sample were undertaken in nitrogen atmosphere and equivalent-amount alumina was used as reference material. Both C80D and MS80II devices are manufactured by SETARAM Co. in France.

Table 2
Observed diameter distributions of salt particles contained in ASM

Diameter (μm)	f_i	D_i (μm)	$D_i * f_i$ (μm)	$\sum f_i$
0–5	0.088	2.5	0.220	0.0880
5–10	0.132	7.5	0.990	0.2200
10–15	0.171	12.5	2.138	0.3910
15–20	0.132	17.5	2.310	0.5230
20–25	0.096	22.5	2.160	0.6190
25–30	0.088	27.5	2.420	0.7070
30–35	0.075	32.5	2.438	0.7820
35–40	0.044	37.5	1.650	0.8260
40–45	0.044	42.5	1.870	0.870
45–50	0.026	47.5	1.235	0.8960
50–55	0.022	52.5	1.155	0.9180
55–60	0.013	57.5	0.748	0.9310
60–65	0.0188	62.5	1.175	0.9498
65–70	0.0088	67.5	0.594	0.9586
70–75	0.0044	72.5	0.319	0.9630
75–80	0.0088	77.5	0.682	0.9718
80–85	0.0144	82.5	1.188	0.9862
85–90	0.0088	87.5	0.77	0.9950
90–95	0.0088	92.5	0.814	1.0038
95–100	0.0000	97.5	0.000	1.0038
100–105	0.0044	102.5	0.451	1.0082
105–110	0.0000	107.5	0.000	1.0082
110–115	0.0000	112.5	0.000	1.0082
115–120	0.0044	117.5	0.517	1.0126
120–125	0.0044	122.5	0.539	1.0170
125–130	0.0000	127.5	0.000	1.0170
130–135	0.0044	132.5	0.583	1.0214
135–140	0.0000	137.5	0.000	1.0214
Total	1.0214	–	26.9645	
Average	26.9645 μm/1.0214 = 26.4 μm			
	(50% D 16.4 μm)			

Note: f_i is mass percentage.

3. Results and discussions

3.1. Heat flows at a constant heating rate

Heat flows for the simulated ASM were measured at a constant heating rate of 0.01 °C/min in the C80D. Fig. 1 shows the measured heat flows for the simulated ASM, corrected from the base line, as well as those for the extracted salt particles at 0.1 °C/min. As seen from Fig. 1, as the temperature increases, the heat flow for the simulated ASM increases slowly and gradually with temperature increase in the range 155–200 °C, keeps almost constant from about 200 to about 250 °C, and then increases very sharply from about 250 °C to the peak point. All stages are exothermic as a whole. The reactions between the asphalt and the salts (such as $NaNO_3$ and $NaNO_2$) in the bituminized product are very complicated and meanwhile obey neither Arrhenius nor n-order rules. The heat of reaction for the mixture was calculated as 1352.0 J/g for the entire reaction processes.

On the other hand, for the extracted mixed salts from the mixture, an endothermic effect from about 230 to about 280 °C is shown in Fig. 1. As the temperature increases, the heat flow decreases slowly in the range from about 230 to about 250 °C and then sharply until the peak point. The ASM has about 50° melting point range from about 230 °C, which is due to the mixed salts' melting gradually. Therefore, a sharp increase of heat flow for the simulated ASM, over about 250 °C likely, is caused by melting of the salts contained in the mixture and its rapid reaction with asphalt, because the molecules or micelles of salt in liquid diffuse easier through the reaction product layer (as discussed in Section 4.1) than those of salt in solid or those of asphalt in liquid. The heat of melting for the extracted mixed salts from the mixture is −85.2 J/g.
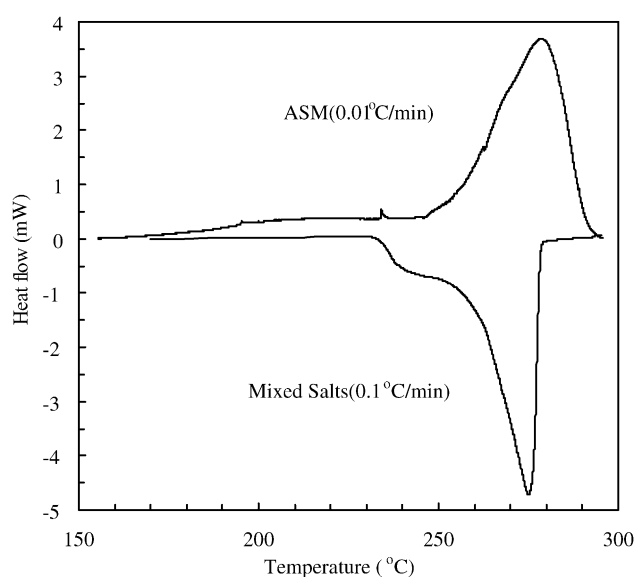

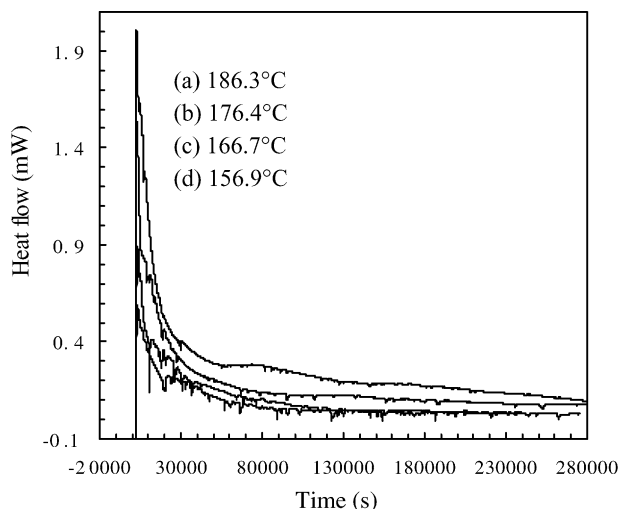Fig. 1. C80D heat flows vs. temperature at a constant heating rate (0.5000 g sample).

Fig. 2. MS80II heat flows vs. time at constant temperatures of 186.3, 176.4, 166.7, and 156.9 °C, respectively (1.0000 g ASM).

3.2. Heat flows at a constant temperature

In order to investigate the heat-generation phenomena at the initial reaction stage of the simulated ASM, isothermal analysis has been performed by the MS80II calorimeter, as shown in Figs. 2 and 3. The heat flow decreases very sharply at the initial stage until about 30000 s at a constant temperature of 186.3 °C (Fig. 2). The heat flow then continues to decrease very slowly and still slightly exothermally. The same situation occurs somewhat at the other temperatures (176.4, 166.7, or 156.9 °C). Total exothermic amount and a reaction conversion ratio of salt were obtained within 300,000 s and are listed in Table 3. A low conversion ratio shows that the reaction in the simulated ASM is blocked. Fig. 3 shows the heat flow for the mixture versus time at low temperatures (152.0, 147.1, or 142.2 °C). As a whole, the heat flow at each temperature is almost constant and still shows slightly exothermic effect. In fact, the exothermic amount is too faint to be detected by some reaction calorimeters such as ARC.

From these observations, authors could understand that the chemical reaction takes place directly on the contact surface between solid salt particles and liquid asphalts at first as shown in Fig. 4a and is gradually blocked by the layer of reaction products as shown in the enlarge section (in the right of Fig. 4a), and then changes into the very slow reaction stage because of slow diffusion of reactants' molecules through the diffusion layer. In addition, since the salts such as
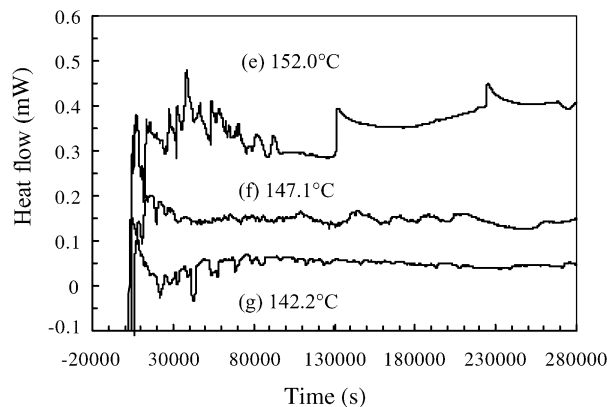
Table 3
Isothermal results by MS80II

Temperature (°C)	Maximum heat flow (mW)	Total exothermic amount (J)	Conversion ratio (%)
156.9	0.586	17.565	1.3
166.7	0.880	20.684	1.5
176.4	1.536	31.422	2.3
186.3	2.005	52.308	3.9

Fig. 3. MS80II heat flows vs. time at constant temperatures of 152.0, 147.1, and 142.2 °C, respectively (1.0000 g ASM).

NaNO$_3$ and NaNO$_2$ are strong oxidizers and the asphalt is an organic material, the chemical reaction among them should be an oxidation–reduction reaction.
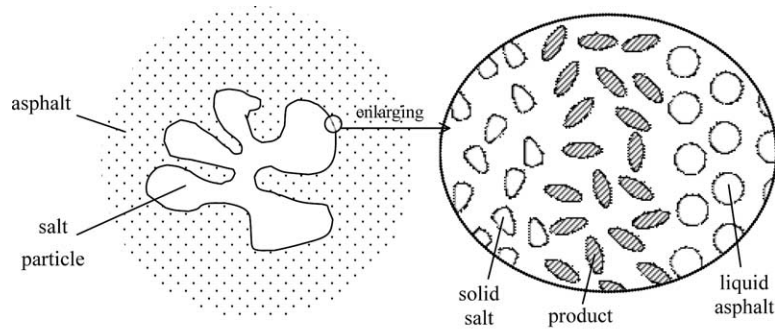
4. Reaction model and reaction rate
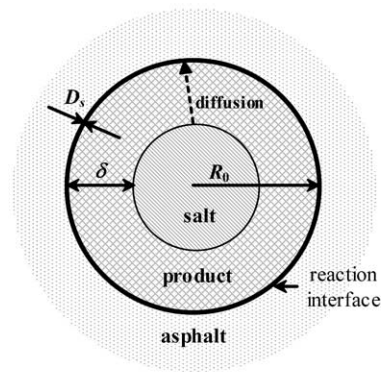
4.1. Reaction mechanism and model

As discussed above, the entire reaction for the simulated ASM as shown in Fig. 1 can be divided in general into the two processes, the reaction between solid salt and liquid asphalt and the reaction between liquid salt and liquid asphalt while accompanying solid salt's melting simultaneously. At the temperature before salt's melting, the reaction between liquid asphalt and solid salt particles in the mixture should take place directly on their contact surface at first, since they are not mutually soluble. At the initial stage, due to direct contact with each other on a molecular or micelle scale, the reaction rate should be chemical reaction-controlled in the range 155–200 °C. After that stage, a reaction product layer, i.e. a diffusion layer (Fig. 4a), exists between the asphalt and the salt particle. Both the molecules of liquid asphalt and that of solid salt must diffuse through the layer to react together with each other. In fact, it is not easy for either large molecules of asphalt in liquid or small ones of salt in solid to diffuse, which can be illustrated by the above isothermal experiments (Section 3.2). So, the reaction is almost blocked by the reaction product layer and the reaction rate should be diffusion-controlled in the range 200–250 °C. However, as the temperature approaches about 250 °C, the salt particles contained in the mixture begin to melt gradually. Because the diffusion of molecules or micelles of liquid salt is much easier than that of liquid asphalt or solid salt, it makes the heat-releasing rate quicker. In a word, the reaction between asphalt and salt in the mixture is an interface reaction, and the reactants firstly diffuse into the reaction interface and then react with each other.

(*a*) Schematic drawing of a real salt particle contained in liquid asphalt

Three Assumptions:

(1)   One-way diffusion for salt

(2)   A spherical salt particle

(3)   Neglecting volume variation

(*b*) Schematic drawing of a simplified reaction and diffusion Model

Fig. 4. Reaction mechanism and model.

At the diffusion-controlled stage, there might be binary diffusion of molecules or micelles of asphalt and salt. It seems easily acceptable that the diffusion for liquid asphalt is easier than that for solid salt. In fact, however, the diffusion for liquid asphalt might be more difficult than that for solid salt through the product layer for the following reasons. First, some gases such as CO_2 and H_2O produced by the reaction exit the reaction zone, which prevent liquid asphalt from diffusing from outside to inside of solid salt particles. On the contrary, diffusion of molecules or micelles of salts is more favorable. Second, it is easier for small salt molecules or micelles to diffuse than large organic ones of asphalt. Third, asphalt molecules cohere together with each other, which makes the diffusion of asphalt molecules difficult, despite the fact that asphalt is liquid above 83 °C. Finally, heat generated by the reaction diffuses outward, which also promotes the diffusion of salt molecules. Based on these reasons, a simplified one-way diffusion model of salt components is reasonable as shown in Fig. 4b. As the temperature increases, the salts contained in the mixture gradually melt above about 250 °C. Because of much easier diffusion of molecules or micelles of liquid salt than those of solid salt or liquid asphalt through the reaction product layer, the above model is more reasonable to the reaction in the range of high temperature above about 250 °C.

4.2. Reaction rate and heat flow

4.2.1. Solid salt–liquid asphalt reaction stage

Since the interface reaction mechanism between the asphalt and the mixed salts are too complicated to be formulated, the chemical reaction rate in the interface could be defined simply as:

$$\left(-\frac{d\theta}{dt}\right)_R = K_R \cdot \theta \tag{1}$$

where θ is defined as the ratio of salt concentration at time t to initial one in the reaction interface, K_R is the salts' chemical reaction rate constant obeying the Arrhenius equation, and the subscript "R" indicate the reaction-controlled stage. The diffusion rate of solid salt molecules can be expressed according to Fick's Law as:

$$\left(\frac{d\theta}{dt}\right)_D = K_D \cdot \frac{(1-\theta)}{\delta} \tag{2}$$

where K_D is the diffusion rate constant expressed by the Arrhenius equation, the subscript "D" indicates the diffusion-controlled stage, and δ is thickness of diffusion layer (that is, thickness of the reaction product layer) evaluated by the following equation under the assumption of a spherical particle

(Fig. 4b) neglecting in volume variation:

$$\delta = R_{salts,\,0}\,(1 - \sqrt[3]{1 - x_{salt}}) \tag{3}$$

where $R_{salts,0}$ and x_{salt} are the initial radius of salt particles and a mass conversion ratio of salts, respectively.

Therefore, the rate of net accumulation of salt concentration at the interface is expressed as:

$$\left(\frac{d\theta}{dt}\right)_{Net} = K_D \cdot \frac{(1 - \theta)}{\delta} - K_R \cdot \theta \tag{4}$$

The solution of Eq. (4) is:

$$\theta = \frac{K_D/\delta + K_R \cdot \exp\left[-(K_R + K_D/\delta) \cdot t\right]}{K_D/\delta + K_R} \tag{5}$$

Thus, the overall heat flow through the entire reaction process between solid salt and liquid asphalt can be expressed as:

$$\left(\frac{dH}{dt}\right)_S = A_R \cdot \theta \cdot m_0 \cdot \text{Area} \cdot M_0 \cdot \Delta H_R \cdot e^{-E_R/RT} \tag{6}$$

where M_0 and ΔH_R are the mass of ASM and the heat of reaction per unit mass of ASM, respectively, A_R and E_R are pre-exponential factor and activation energy, respectively for the chemical reaction, and m_0 is defined as the initial salt mass per unit surface area of reaction interface and can be estimated by the mass within the very thin layer (D_s, thickness of the layer) on the surface of a salt particle as the following:

$$m_0 \equiv \frac{W}{A} = D_s\frac{W}{V} = D_s \cdot \rho_{salts} \tag{7}$$

where A is the surface area of a salt particle, and ρ_{salts} is the mixed-salt density.

"Area" is the reaction interfacial area per unit mass of salts and can be calculated on the basis of an assumed sphere particle model by:

$$\begin{aligned}\text{Area} &= \frac{4\pi R_{salts,\,0}^2}{\rho_{salts} \cdot 4\pi R_{salts,\,0}^3/3} \\ &= \frac{3}{\rho_{salts} \cdot R_{salts,\,0}} \cdot \left(\sqrt[3]{1 - x_{salt}}\right)^2 \end{aligned} \tag{8}$$

Therefore, Eq. (6) is then rewritten as:

$$\left(\frac{dH}{dt}\right)_S = A_R \cdot \theta \cdot \frac{3D_s}{R_{salts,\,0}} \cdot \left(\sqrt[3]{1 - x_{salt}}\right)^2 \cdot M_0 \cdot \\ \Delta H_R \cdot e^{-E_R/RT} \tag{9}$$

In addition, the heat flow equation for the diffusion-controlled stage can be also expressed as the following equation:

$$\left(\frac{dH}{dt}\right)_S = A_D \cdot \frac{(1 - \theta)}{\delta} \cdot \frac{3D_s}{R_{salts,\,0}} \cdot \left(\sqrt[3]{1 - x_{salt}}\right)^2 \cdot M_0 \cdot \\ \Delta H_R \cdot e^{-E_D/RT} \tag{10}$$

where A_D and E_D are pre-exponential factor and activation energy, respectively for the diffusion process.

4.2.2. Liquid salt–liquid asphalt reaction stage

As the temperature increases, the solid salt particles contained in the mixture starts to melt. Since the diffusion of molecules or micelles of liquid salt is very fast through the reaction product layer, the heat flow in the high temperature range over about 250 °C in Fig. 1 might be determined mainly by the melting rate, $(d\theta/dt)_M$, of the mixed salts contained in the bituminization product. Therefore, the following approximate expression can be considered:

$$\left(-\frac{d\theta}{dt}\right)_R \approx \left(\frac{d\theta}{dt}\right)_D \approx \left(\frac{d\theta}{dt}\right)_M \tag{11}$$

and the above Eq. (10) can then be applied to the liquid–liquid reaction stage. Thus, the synthetical heat flow in the reaction process between liquid salt and liquid asphalt, including solid salt's melting simultaneously can be expressed by:

$$\left(\frac{dH}{dt}\right)_L = A_L \cdot \frac{(1 - \theta)}{\delta} \cdot \frac{3D_s}{R_{salts,\,0}} \cdot \left(\sqrt[3]{1 - x_{salt}}\right)^2 \cdot M_0 \cdot \\ \Delta H_R \cdot e^{(-E_L/RT)} \tag{12}$$

where A_L and E_L are apparent pre-exponential factor and apparent activation energy, respectively for the liquid–liquid reaction process accompanying the phase transfer process

4.3. Self-consistent solutions of kinetic parameters

By substitution of the observed heat flow $(dH/dt)_E$ for $(dH/dt)_S$ in Eqs. (9) and (10), they can be rearranged as the following equations, respectively:

$$\begin{aligned}&\text{Ln}\left[\left(\frac{dH}{dt}\right)_E /\theta/ \frac{3}{R_{salts,0}} /\left(\sqrt[3]{1 - x_{salt}}\right)^2 /M_0/\Delta H_R\right] \\ &= \text{Ln}(A_R \cdot D_s) - \frac{E_R}{RT}\end{aligned} \tag{13}$$

$$\begin{aligned}&Ln\left[\left(\frac{dH}{dt}\right)_E / \frac{1 - \theta}{\delta} / \frac{3}{R_{salts,0}} /\left(\sqrt[3]{1 - x_{salt}}\right)^2 /M_0/\Delta H_R\right] \\ &= \text{Ln}(A_D \cdot D_s) - \frac{E_D}{RT}\end{aligned} \tag{14}$$

These two equations are linear and can be used to determine the kinetic parameters by use of the experimental data of heat flows at a constant heating rate. At the first step, for a solid salt particle contained in asphalt, the rate-determined step is chemical reaction-controlled in the initial stage of the reaction. During this stage, the concentration of oxidizing salts on the asphalt-salt interface may be considered to be approximately equal to that inside the salt particle, i.e. $\theta \approx 1$. But during the diffusion-controlled stage, the concentration

on the interface is nearly equal to zero, i.e. $\theta \approx 0$. By applying the observed individual heat flows (as shown in Fig. 1) in the range 155–200 °C and in the range 200–250 °C into Eq. (13) at $\theta \approx 1$ and Eq. (14) at $\theta \approx 0$, respectively, initial approximate values of the kinetic parameters, $A_R D_s$, E_R, $A_D D_s$ and E_D, for the ASM can be determined by linear regression. Then, by applying the observed heat flows in the range from 250 to 290 °C into Eq. (15) at $\theta \approx 0$, initial approximate values of $A_L D_s$ and E_L can also be determined by linear regression. By use of these approximate data and Eq. (5), the re-calculations above can then yield new values of these kinetic parameters. The calculations will be repeated in circles until these parameters converge to the coincidence, i.e. a self-consistent method (SCM). Finally, the results by means of SCM are shown in Fig. 5 and the obtained kinetic
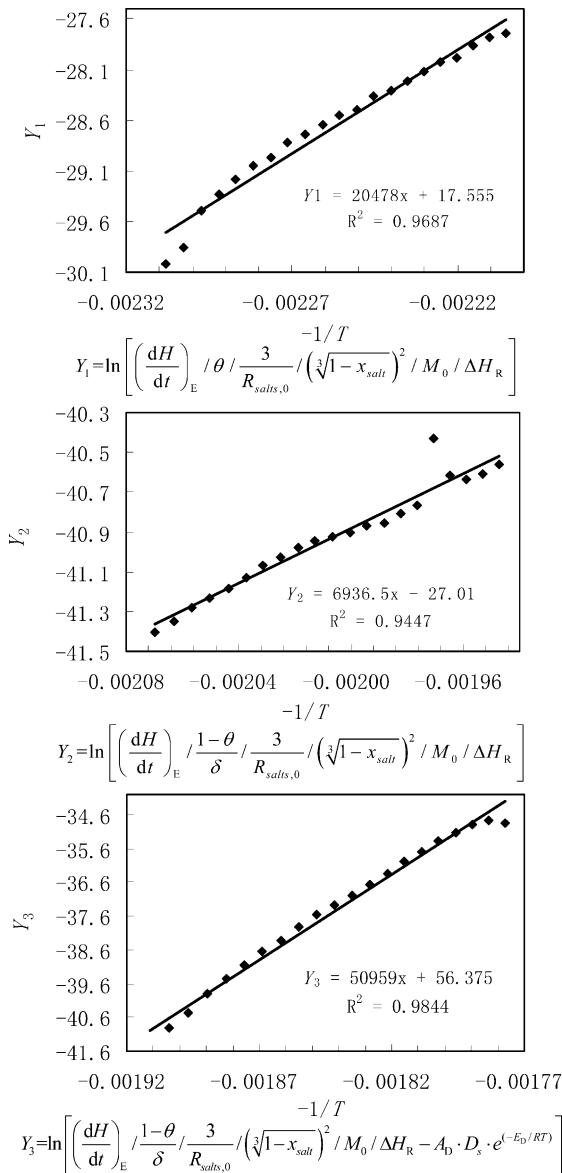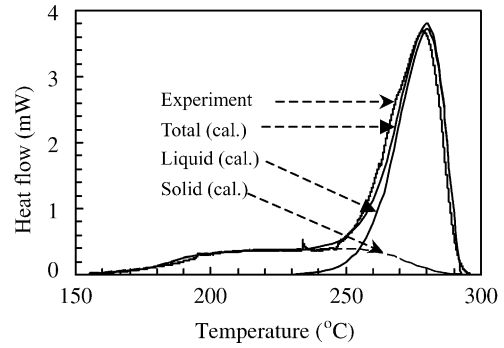
Fig. 6. Observed and calculated heat flows vs. temperature at a constant heating rate of 0.01 °C/min (0.5000 g ASM).

parameters are listed in Table 3.

$$\ln\left[\left(\frac{dH}{dt}\right)_E / \frac{1-\theta}{\delta} / \frac{3}{R_{salts,0}} /(\sqrt[3]{1-x_{salt}})^2 / M_0 / \Delta H_R\right.$$

$$\left. - A_D \cdot D_s \cdot e^{-E_D/RT}\right] = \mathrm{Ln}\,(A_L \cdot D_s) - \frac{E_L}{RT} \qquad (15)$$

$$x_{salt} = \int_0^t \left(\frac{(dH/dt)_E}{\Delta H_R \cdot M_0}\right) dt = \int_0^t \frac{(dH/dt)_E dt}{\Delta H_R \cdot M_0} \qquad (16)$$

By use of these obtained parameters and Eqs. (9) and (12), the numerically simulated heat flows can be obtained as illustrated in Fig. 6. Resulting from the close agreement between the observed and calculated overall heat flows as shown in Fig. 6, the above reaction model is reasonable and feasible and the obtained kinetic data are usable.

5. Simulation of runaway reaction

The ASM-filled drum has a cylindrical shape (Table 4). Based on the very low thermal conductivity of the mixture and on the fact that the drum radius is much less than its height, a one-dimensional infinite cylinder coordinate system can be assumed [1]. In fact, as the drum diameter is little less than its height, the other one-dimensional equivalent-amount sphere coordinate system was also adopted for contrast in this work. Under a one-dimensional infinite-cylindrical or equivalent-spherical coordinate system, the equation of heat balance can be expressed as:

$$\frac{\partial^2 T}{\partial r^2} + \frac{n}{r}\frac{\partial T}{\partial r} + \frac{\dot{q}}{\kappa} = \frac{1}{\alpha}\frac{\partial T}{\partial t}\ (n=1\ or\ n=2) \qquad (17)$$

where $\dot{q}$ is the rate of heat generation per unit volume and $\alpha = \kappa/\rho/C_P$. In addition, κ is the thermal conductivity of the reacting material or steel drum material depending on the location for which the calculation has been done.

Under the initial conditions of the presumed temperature, T_i, of the ASM-filled drum, an ambient temperature

$$Y_1 = \ln\left[\left(\frac{dH}{dt}\right)_E / \theta / \frac{3}{R_{salts,0}} /\left(\sqrt[3]{1-x_{salt}}\right)^2 / M_0 / \Delta H_R\right]$$

$$Y_2 = \ln\left[\left(\frac{dH}{dt}\right)_E / \frac{1-\theta}{\delta} / \frac{3}{R_{salts,0}} /\left(\sqrt[3]{1-x_{salt}}\right)^2 / M_0 / \Delta H_R\right]$$

$$Y_3 = \ln\left[\left(\frac{dH}{dt}\right)_E / \frac{1-\theta}{\delta} / \frac{3}{R_{salts,0}} /\left(\sqrt[3]{1-x_{salt}}\right)^2 / M_0 / \Delta H_R - A_D \cdot D_s \cdot e^{(-E_D/RT)}\right]$$

Fig. 5. Arrhenius plot of the kinetic parameters for the simulated ASM determined at the last step by means of SCM.

Table 4
Simulation conditions and physicochemical property constants

Sample: ASM	
Initial temperature, T_i (°C)	
Density (g/cm^3)	1.30
Specific heat (J/K/g)	$1.18 + 0.002092 \times (T/K)$
Thermal conductivity, κ_{ASM} (J/cm/K/s)	0.002[a]
Heat of reaction (J/g-sample)	1352.0
Radius of salt particle, R_0 (μm)	13.2 (average)
Drum: Fe	
Thermal conductivity	$1.0336 - 0.0008 \times (T/K)$
Radius, R_W (cm)	28.0
Thickness (cm)	0.16
Height (cm)	71.5
Equivalent sphere diameter (cm)	69.5
Kinetic parameters	
$A_R D_s = 4.206 \times 10^7$ m/s	$E_R = 170.258$ kJ/mol
$A_D D_s = 1.862 \times 10^{-12}$ m^2/s	$E_D = 57.670$ kJ/mol
$A_L D_s = 3.044 \times 10^{24}$ m^2/s	$E_L = 423.677$ kJ/mol
Boundary conditions	
Nusselt number	Natural-convection heat transfer model across vertical flat [1] and sphere [4], respectively[b]
Prandtl number	0.70
Thermal conductivity of air (J/cm/K/s)	0.000383
Kinetic viscosity of air (cm^2/s)	0.239
Ambient temperature, T_0 (°C)	50.0
Mesh number on radius axis	100

[a] Measured within the temperature range from 100 to 120 °C using the thermal conductivity meter (Model THP-202) by Dr. X. Li in Hasegawa's group.

[b] $Nu = \frac{h \cdot L}{\kappa} = 0.795 \left(\frac{Pr}{1 + 2Pr^{1/2} + 2Pr} \right)^{1/4} \cdot \left(\frac{L^3 \cdot \beta \cdot g \cdot (T_W - T_\infty)}{\nu^2} \cdot Pr \right)^{1/4}$ (cylinder [1]). $Nu = \frac{h \cdot D}{\kappa} = 0.558 \cdot \left(\frac{D^3 \cdot \beta \cdot g \cdot (T_W - T_\infty)}{\nu^2} \cdot Pr \right)^{1/4}$ (sphere [4]).

$T_0 = 50$ °C, and the given boundary conditions, the Eq. (17) simultaneous equations are numerically and successively solved, using the physicochemical properties constant shown in Table 4. These equations are solved as functions of the elapsed time, t, and radial distance, r.

5.1. Minimum filling temperature to runaway reaction

The minimum temperature, T_i, at which the calculated temperature in the center of self-heating body can run away steeply from an upward trending temperature is taken as the minimum filling temperature to runaway reaction (MFTRR). Of course, the MFTRR varies according to the package size and material, and the ambient temperature. Typical examples of simulation results are shown in Figs. 7–10. These examples illustrate how the temperature of the bituminized product behaves as a function of time and drum radius.

Figs. 7 and 8 show the simulated temperature change with time and drum-radius axes under the conditions of filling temperatures of 195 and 194 °C, respectively, and an ambient temperature of 50 °C on the basis of the one-dimensional
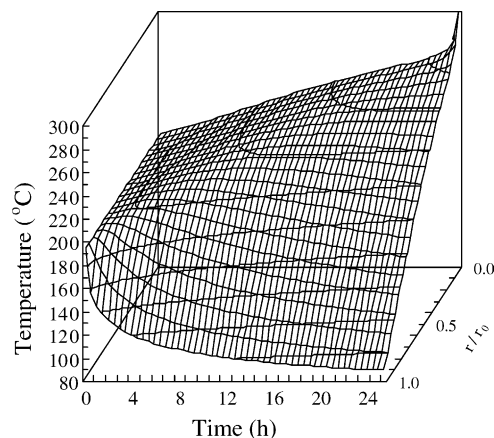

Fig. 7. Simulated temperature changes on time and drum-radius axes (T_i=195 °C, T_0=50 °C, Infinite Cylinder Model).
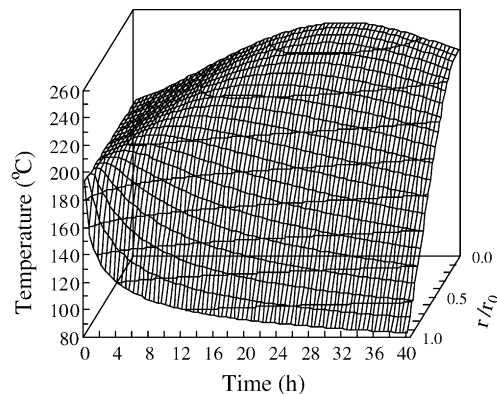

Fig. 8. Simulated temperature changes on time and drum radius axes (T_i=194 °C, T_0=50 °C, Infinite Cylinder Model).

infinite cylinder model. As indicated in these figures, about 26 h later, a runaway reaction will occur in the center of the drum filled with the simulated ASM at 195 °C or above, when the drum is being cooled at an ambient temperature of 50 °C. So, the minimum filling temperature to runaway reaction (MFTRR) for the sample is 195 °C. Either the min-
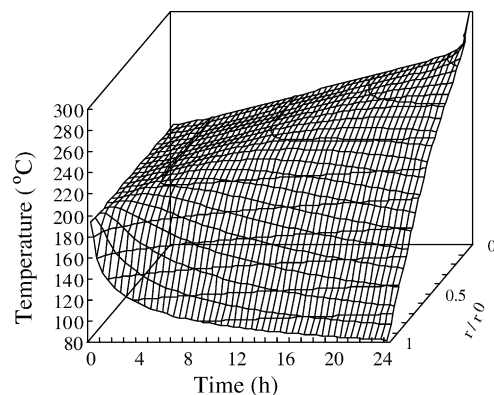

Fig. 9. Simulated temperature changes on time and sphere radius axes (T_i=193 °C, T_0=50 °C, Equivalent Sphere Model).
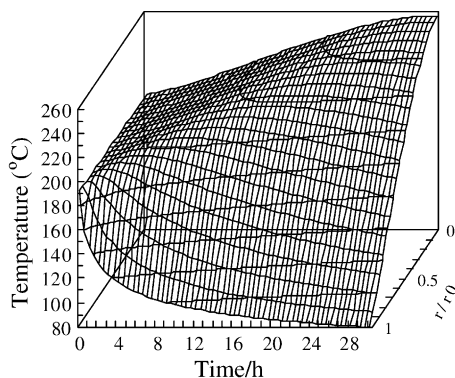
Fig. 10. Simulated temperature changes on time and sphere radius axes (T_i=192 °C, T_0=50 °C, Equivalent Sphere Model).

Fig. 11. Linear correlation between the MFTRR and initial radius of the salt particle (Infinite Cylinder Model, T_0=50 °C).

imum filling temperature or the minimum time to runaway reaction is close to that for the accident [1].

On the other hand, the onset temperature to the runaway reaction is around 250 °C. Therefore, the salt's melting and reaction with asphalt contribute mainly to the runaway reaction. In the meanwhile, a slight heat release below 250 °C, which may usually be ignored by some calorimeters, contributes to a temperature increase of self-heating material, especially in the center of large mass material.

In addition, the simulated results based on the equivalent-amount sphere model as shown in Fig. 9 and Fig. 10 are almost identical to those above in that there is only 2 K difference in the MFTRR between both models. This agreement implies that the equivalent-amount sphere model can be considered for any shape of self-heating body.

5.2. Critical filling temperature to runaway

There are many factors, which affect the size of salt particles formed in the mixture, such as the liquid waste-feeding rate, the concentration of phosphate, etc. Nonetheless, the size of salt particles contained in the bituminization product has distinct effect on the onset temperature of heat release [1]. However, provided the salts' ingredients in the asphalt–salt mixture are the same as those in the simulated sample, the kinetic parameters for the mixture can be used to calculate the change in the MFTRR as the radius of the salt particles contained in the bituminization product changes. The calculated results are shown in Fig. 11, and a very good linear correlation exists between the MFTRR and the salt-particle size. Thus, the MFTRR is about 162 °C when the diameter of the salt particles contained in the asphalt–salt mixture is extrapolated to zero, at which point they admix with each other on a molecular or micelle scale. Therefore, the drum filled with the asphalt–salt mixture containing zero-size salt particles under the filling temperature below 162 °C is expected to be safe when the drum is being cooled at an ambient temperature of 50 °C. That is to say, the critical filling temperature to a runaway reaction is about 162 °C for the asphalt–salt mixture. On the contrary, while the filling temperature is more
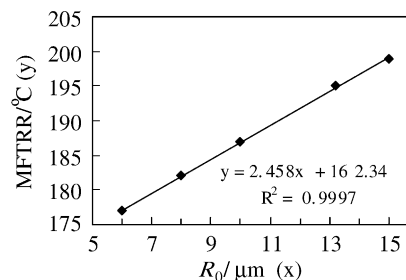
than 162 °C, a runaway reaction induced by the very slightly exothermic interface reaction and self heating may initially occur in the center of the ASM-filled drum at an ambient temperature of 50 °C.

6. Conclusions

The following conclusions are derived from this study:

(1) The reaction between asphalt and salt particles in the bituminization product is an interface reaction that includes two different rate-controlled stages, viz., a chemical reaction-controlled stage for a short time followed by a diffusion-controlled stage for a long time. Over about 250 °C, melting of the salt highly accelerates the heat release rate. The reaction rates were formulated under the assumption of an interfacial reaction model, and the kinetic parameters were determined.
(2) The minimum filling temperature to runaway reaction (MFTRR) is about 194 °C for the experimentally simulated asphalt–salt mixture filled in the 220-L drum, which was cooled at a constant ambient temperature of 50 °C.
(3) As the salts admix with the asphalt on a molecular or micelle scale, the MFTRR is about 162 °C for the asphalt–salt mixture filled in the same drum at a constant ambient temperature of 50 °C.
(4) The asphalt-salt explosion that occurred in the reprocessing plant likely was caused by a slightly exothermic interface reaction and self heating.

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