

## **INFLUENCE OF DOPING OF NaNO<sub>3</sub> ON THE SOLID PHASE THERMAL DECOMPOSITION OF BITUMEN AND CEMENT**

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### **Abstract**

The thermal stability of solidified NaNO<sub>3</sub> salts in bitumen and cement has been investigated for safety considerations in the field of solidification of radioactive waste. The thermal decomposition of bitumen and cement in presence of NaNO<sub>3</sub> in a temperature range 22–650°C has been studied. The fraction decomposed of the pure samples and mixtures showed slow linear reactions followed by acceleratory and decay stages. Data are analyzed according to both Freeman–Carroll and Coats–Redfern kinetics to evaluate the activation energy and the order of reactions of all mixtures. It is found that the activation energies of bitumen and cement were 594 and 203 kJ mol<sup>-1</sup>, respectively. The order of reactions of bitumen and cement was 2 and 4, respectively. The addition of NaNO<sub>3</sub> shortens the duration of the induction period in all mixtures. It was concluded that solidification of radioactive waste containing NaNO<sub>3</sub> in bitumen and cement should be applied in the temperature range 22–300°C. At temperature higher than 300°C solidification should be in cement.

**Keywords:** bitumen, portland cement, safety considerations, solidification, thermal stability

### **Introduction**

The effect of temperature on physical and mechanical properties of concrete containing silica fume has been studied [1]. The distribution and composition of organic matter in oil and bitumen containing rocks in deposits of different ages had been investigated [2]. Several authors [3–7] studied the thermal decomposition of the solidified salts in bitumen and cement by using thermogravimetric method. The influence of additives on the thermal decomposition of solidified salts in bitumen and cement was found to be more active in bitumen than in cement [8]. Many studies on NaNO<sub>3</sub> and NaNO<sub>2</sub> incorporated in bitumen had been investigated [9, 10]. Exothermic reactions from bitumen–salts mixtures containing low masses of NaNO<sub>3</sub> were safe. The aim of the present work is to study the thermal decomposition of bitumen and cement in presence of different percentage of NaNO<sub>3</sub>. The role of NaNO<sub>3</sub> as a catalyst has been studied. Calculations of the kinetic parameters of the thermal decomposition of dop-

ing of  $\text{NaNO}_3$  in either bitumen or cement were evaluated by using two different kinetic methods.

## Experimental

The bitumen– $\text{NaNO}_3$  mixture has been prepared according to the thin film evaporator [11]. The cement– $\text{NaNO}_3$  mixture has been prepared in the extruder using a simple grout batch mixer [12]. The mixer is electrically driven and mobile to facilitate the mixing process. The sodium nitrate used was of pure analytical grade. The percent doping of  $\text{NaNO}_3$  in either bitumen or cement was in the range of (5–40)% by mass. The physico-chemical properties of bitumen are given in Table 1. The chemical analysis of cement as certified by National Portland Cement Company, Helwan, Cairo, Egypt was as follows:  $\text{CaO}$ =61.01,  $\text{SiO}_2$ =19.84,  $\text{Al}_2\text{O}_3$ =4.47,  $\text{Fe}_2\text{O}_3$ =4.0,  $\text{MgO}$ =2.5,  $\text{K}_2\text{O}$ =0.60 and  $\text{SO}_2$ =2.37. The thermogravimetric analysis measurements were carried out using Shimadzu TG-50 type connected with a high temperature detector. The measurements were carried out in a temperature range from room temperature up to  $650^\circ\text{C}$  with heating rate  $10^\circ\text{C min}^{-1}$  in nitrogen atmosphere.

**Table 1** Physical and chemical properties of bitumen (A-80)

Property	Values
Salt content in product/mass%	40
Softening point/ $^\circ\text{C}$	51–55
Flash point/ $^\circ\text{C}$	238–247
Leach rate of Cs-137 after 63 days/ $\text{g cm}^{-1} \text{d}^{-1}$	$3.9\text{--}5.3 \cdot 10^{-5}$
Leach rate of salts after 63 days/ $\text{g cm}^{-1} \text{d}^{-1}$	$3.9\text{--}7.8 \cdot 10^{-5}$
Viscosity at $100^\circ\text{C}$	40–5.3 P
Viscosity at $160^\circ\text{C}$	1–16 P
Water content in product/mass%	<1

## Results and discussion

The effect of  $\text{NaNO}_3$  on the thermal stability of bitumen and cement in the solid phase reactions can be considered by the following reactions:

### *Solid–solid reactions*

These reactions take place through surface migration of one or both reactants, diffusion of one reactant into the grains and channels of the other reactants or the penetration of one reactant into the other [13].

*Solid-state reactions of single reactants*

These reactions can be controlled by nucleation, diffusion or by partial liquid action [14].

**Table 2** Effect of NaNO<sub>3</sub> concentration on thermal stability of solidified NaNO<sub>3</sub> with bitumen (A-80) by using thermogravimetric analysis (TG)

T/°C	NaNO <sub>3</sub> concentration/%					
	0	5	10	20	30	40
Mass loss/%						
22	0	0	0	0	0	0
200	0.80	0.70	0.52	0.44	0.38	0.29
250	0.95	0.78	0.61	0.54	0.42	0.34
300	1.00	0.87	0.70	0.60	0.50	0.41
320	1.20	1.00	0.95	0.84	0.80	0.60
340	1.40	1.20	1.10	0.90	0.85	0.70
360	4.00	3.80	1.50	3.00	2.80	2.30
380	10.00	9.30	8.00	7.70	7.10	6.10
400	16.10	15.30	13.00	13.00	12.70	12.30
420	23.20	21.50	21.50	18.50	16.50	14.00
440	36.00	34.50	32.10	30.00	29.50	28.40
460	49.00	46.60	45.30	45.00	33.20	32.00
480	57.00	51.90	52.80	51.50	38.00	34.50
500	59.40	55.50	54.80	52.80	40.20	35.70
520	60.50	56.40	55.80	53.50	41.40	36.60
540	61.50	57.40	56.30	54.00	42.80	37.20
560	62.30	56.00	54.00	54.80	44.20	3.60
580	64.00	59.00	58.00	56.00	46.00	37.60
600	65.50	60.40	59.50	57.30	48.50	38.20

In these systems different concentrations of NaNO<sub>3</sub> are solidified in bitumen and the degradation decrease as the mass percent of NaNO<sub>3</sub> increase (Table 2). The last elementary diffusion of the resulting mixture was found to show that the diffusion may occur in the solid matrix only as the diffused element is forced in a solid solution with the salt matrix. The principle reason for diffusion in the solid solution and in particular chemical heat treatment is the tendency to homogenize the concentration through the matrix. The rate of diffusion of the atoms entering the solidified matrix will vary according to the type of the solid solution that is forced. When bitumen is doped by NaNO<sub>3</sub> to form interstitial solid solutions, diffusion will proceed more easily. In interstitial solid solutions, NaNO<sub>3</sub> moves between interstitial positions [15].

The atoms can jump by this mechanism from one interatomic position to another. The variation of the diffusion coefficient ( $D$ ) with temperature is expressed by:

$$D = D_0 e^{-Q/RT} \quad (1)$$

where  $D_0$  is the diffusion coefficient which is temperature independent in  $\text{cm}^2$ ,  $Q$  is the heat of diffusion,  $R$  is the gas constant and  $T$  is the absolute temperature in degree Kelvin. The greater the value of  $Q$  is, the smaller the value of  $D$  is at the given temperature and the rate of diffusion was slow. The higher the temperature is, the longer the time of chemical heat treatment needed to obtain a given depth of the diffusion layer. The mass loss vs. temperature for different doping  $\text{NaNO}_3$  percents in bitumen and cement are given in Figs 1 and 2. From Fig. 1 the decomposition of pure bitumen started at about  $280^\circ\text{C}$  and the mass decreases sharply to 64% mass loss at  $500^\circ\text{C}$ . The effect of doping  $\text{NaNO}_3$  in bitumen is clear since the decomposition started at  $330^\circ\text{C}$  and a mass loss level reached a

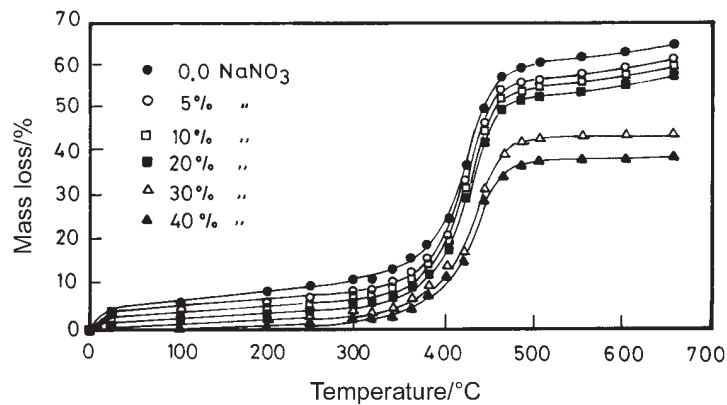


Fig. 1 Effect of mass percent of  $\text{NaNO}_3$  on the thermal stability of bitumen, TG

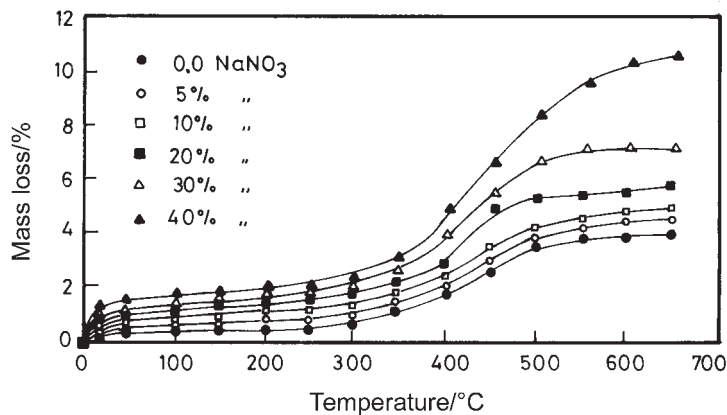


Fig. 2 Effect of mass percent of  $\text{NaNO}_3$  on the thermal stability of cement, TG

steady value in the range 500–650°C corresponding to the formation of blown bitumen. A nearly horizontal level was observed in the range 22–330°C while the nucleation of the decomposition is rapid in the range 330–500°C. Figure 1 shows that doping of NaNO<sub>3</sub> increases the stability of bitumen. As the mass percent of the doped NaNO<sub>3</sub> increases the total mass loss percent of the matrix decreases.

Figure 2 shows the same general behaviour for cement except that the decomposition started at 350°C. The steady state value in the range 500–650°C corresponds approximately to the decomposition of the total oxides in the chemical composition of cement [16]. The effect of doping NaNO<sub>3</sub> on cement on the mass loss percent was found to be in range 4–11%. Hence, one can say that doping of NaNO<sub>3</sub> in cement decreases the thermal stability of the solidified matrix.

**Table 3** Effect of NaNO<sub>3</sub> concentration on thermal stability of solidified NaNO<sub>3</sub> with ordinary portland cement by using thermogravimetric analysis (TG)

T/°C	NaNO <sub>3</sub> concentration/%					
	0	5	10	20	30	40
	Mass loss/%					
22	0	0	0	0	0	0
25	0.10	0.20	0.30	0.70	0.90	1.20
50	0.20	0.30	0.50	0.80	1.10	1.50
100	0.30	0.40	0.60	0.95	1.30	1.60
150	0.31	0.55	0.70	1.20	1.50	1.80
200	0.32	0.72	0.80	1.30	1.60	1.90
250	0.35	0.78	0.93	1.40	1.80	2.00
300	0.40	0.86	1.00	1.80	1.90	2.30
350	1.10	1.95	1.10	2.30	2.80	3.00
400	1.70	1.87	1.69	2.50	4.00	4.80
450	2.50	2.97	2.40	5.20	5.50	6.50
500	3.80	3.97	3.40	5.30	6.80	5.80
550	3.90	4.20	4.30	5.40	7.00	9.80
600	4.00	4.50	4.50	5.50	7.10	10.60
650	4.10	4.60	4.80	5.80	7.20	10.70
700	4.10	4.65	4.90	5.90	7.30	10.80

We can see from the last two figures, the mass loss of the solidified bitumen is higher than that in cement, Table 3. The solid-state reactions take place in four steps:

1. Molecular loss at which the reactant molecules gain enough motion to react.
2. Molecular change in which the chemical reaction occurs and new chemical bonds are formed.
3. Solid solution formation product.
4. Separation of phases [13].

Steps 1 and 2 are the rate determining steps for most solid-state reactions.

The concentration of the diffused element on the surface depends upon the potential of the surrounding medium that ensures the sample supply of atoms to the surface of the matrix. The concentration gradient is one of the main factors that determines the rate of diffusion. The higher the concentration of the diffused  $\text{NaNO}_3$  on bitumen is, the deeper the diffused layer obtained in a given interval of time is.

The fractions decomposed with time ( $\alpha-t$ ) plots for the isothermal decomposition of the solidified bitumen and cement are shown in Figs 1 and 2, respectively. The decomposition proceeds through: 1 – Initial gas evolution, 2 – Slow linear reaction and 3 – Accelerator stage and decay.

The initial gas evolution,  $\alpha \sim 0.006$  is the same in all cases and is possibly due to the release of the occluded air. The length of sigmoid regime for bitumen follows the order of the percent degradation in range  $300-500^\circ\text{C}$   $40 < 30 < 20 < 10 < 5\%$  pure bitumen. The length of sigmoid regime in case of portland cement follows the order of the percent degradation in range  $300-500^\circ\text{C}$ : pure portland cement  $10 < 20 < 30 < 40\%$ . During the induction period in the range  $22-300^\circ\text{C}$ , the reaction nucleates at energetically favourable sites. The nuclei are relatively small initially and grow to a larger size during the accelerating stage. The shortening of the induction period indicates that the nucleation of the decomposition process is rapid in the presence of additives. The linear stage followed the induction period may be attributed to the surface decomposition, caused by the growth of the nuclei formed during the induction. The enhancement in the rate may be as a result of the favourable growth of nuclei.

It is obvious that  $\text{NaNO}_3$  has a good advantage on solidification of bitumen i.e. it causes inhibition for the degradation process and increases the thermal stability of the solidified matrix. The thermogravimetric analysis of the solidified bitumen and cement has often been studied but the nature and stability of the solidified products are in dispute. No systematic investigations on their dissociation behaviour in an inert atmosphere, such as nitrogen have been reported.

## Calculations of rate parameters

Freeman–Carroll [17] showed that the kinetic parameters of any decomposition process could be calculated from the thermoanalytical curve using the relation:

$$\frac{-\frac{E}{2.3R}\Delta(T^{-1})}{\Delta\log W_r} = n + \frac{\Delta\log\left(\frac{dW}{dt}\right)}{\Delta\log W_r} \quad (2)$$

where  $E$  is the energy of activation,  $T$  is the absolute temperature,  $R$  is the gas constant,  $W_r$  is the mass loss at completion of reaction minus mass loss upon time,  $n$  is the order of reaction and  $dW/dt$  is the rate of mass loss with time.

The plot of  $[\Delta\log(dW/dt)]/\Delta\log W_r$  vs.  $\Delta(T^{-1})/\Delta\log W_r$  gives a straight line with intercept  $-n$  and slope  $\pm(E/2.3R)$ . The values of the activation energy and the order of reaction are given in Tables 4 and 5. The activation energies and order of reactions were also calculated by Coats–Redfern [18] according to:

$$\log \left[ \frac{1-(1-\alpha)^{1-n}}{T^2(1-n)} \right] = \log \frac{AR}{aE} \left[ 1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \quad (3)$$

for all values of  $n$  except  $n=1$ , where  $n$  is the order of reaction,  $\alpha$  is the fraction decomposed,  $T$  is the temperature in K,  $A$  is a frequency factor,  $R$  is the gas constant,  $a$  is the heating rate in degree per minute and  $E$  is the energy of activation.

The plot of  $\log \{ [1-(1-\alpha)^{1-n}] / [T^2(1-n)] \}$  vs.  $1/T$  give a straight line of slope  $-E/2.3R$  for the correct values of  $n$ . For most values of  $E$  and for the temperature range of any reaction the expression  $[AR/(aE)](1-2RT/E)$  is sensibly constant. The variations in the calculated activation energies are given in Tables 4 and 5. Coats and Redfern calculations can be used to investigate one series of samples and detect any variation in the activation energy. The values of  $n$  from either Freeman–Carroll calculations or Coats–Redfern calculations given in Tables 4 and 5 seemed to be reasonable. The calculated order of reaction of doping  $\text{NaNO}_3$  in bitumen was 2 due to its organic constituents and  $\text{NaNO}_3$  that thermally decompose. While the calculated order of reaction of cement was 4 due to the thermal decomposition of the four constituents of portland cement (tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite) [16].

**Table 4** Rate parameters calculated from thermodynamic data for bitumen using thermogravimetric analysis (TG)

NaNO <sub>3</sub> /%	Freeman–Carroll		Coats–Redfern	
	$n$	$E/\text{kJ mol}^{-1}$	$n$	$E/\text{kJ mol}^{-1}$
0.0	1	585	1.0	576
5.0	2.1	590	2.1	577
10	2.2	594	2.1	581
20	2.1	594	1.8	582
30	2.2	594	2.2	581
40	2.2	594	2.2	582

**Table 5** Rate parameters calculated from thermodynamic data for portland cement using thermogravimetric analysis (TG)

NaNO <sub>3</sub> /%	Freeman–Carroll		Coats–Redfern	
	$n$	$E/\text{kJ mol}^{-1}$	$n$	$E/\text{kJ mol}^{-1}$
0.0	4	209	3.5	207
5.0	4.1	209	3.4	204
10	4.2	210	3.7	207
20	4.1	210	3.8	202
30	4.2	210	3.9	209
40	4.1	214	4.0	207

## Conclusions

Based on the data, it may be concluded that the solidification of radioactive waste containing  $\text{NaNO}_3$  take place in either cement or bitumen in a temperature range 22–300°C. At temperature higher than 300°C cement is recommended. Doping of  $\text{NaNO}_3$  in bitumen increases the stability of bitumen. As the concentration of doped  $\text{NaNO}_3$  increases the total mass loss of the matrix decreases. Doping of  $\text{NaNO}_3$  in cement decreases the thermal stability of the solidified matrix. According to the kinetics of Freeman–Carroll and Coats–Redfern the calculated order of reaction of bitumen and cement are 2 and 4, respectively. The calculated activation energy of both matrices are 591 and 207  $\text{kJ mol}^{-1}$  respectively.

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