Influence of Iron Ion on Thermal Behavior of Ammonium Nitrate and Emulsion Explosives

Zhixiang XU, Dabin LIU, Yiting HU*, Zhiwen YE and Yanan WEI

School of Chemical Engineering,
Nanjing University of Science and Technology,
200 Xiaolingwei St., Nanjing 210094, Jiangsu Province, China
E-mail: huyiting@hotmail.com

Abstract: The influence of ferric nitrate on the thermal stability of ammonium nitrate and emulsion matrix were used to study with Accelerating Rate Calorimeter (ARC) and constant temperature thermal decomposition experiment in this paper. It is shown that ferric nitrate has significant catalytic property to the ammonium nitrate and emulsion matrix, which decrease the initial decomposition temperature of ammonium nitrate by 60.16 °C and emulsion matrix by 30.33 °C. The results of the influence of ferric nitrate on catalysis of ammonium nitrate using ARC and constant temperature thermal decomposition experiment are the same. The most probable mechanism function, activation energy and the pre-exponential factor of ammonium nitrate with ferric nitrate were determined to be $f(\alpha) = 1-\alpha$, E = 195.41 kJ/mol, $A = 2.08 \times 1019$ s^{-1}. The kinetics of ammonium nitrate decomposition can be used to calculate the critical temperatures for ammonium nitrate decomposition with and without the presence of ferric nitrate, based on the Frank-Kamenetskii model of thermal explosion. Furthermore, as the iron-plate experiment shows, ferric nitrate can significantly reduce the critical temperature of emulsion matrix decomposition. Once the ferric nitrate interfuses in the ammonium nitrate and emulsion matrix, the thermal stability of ammonium nitrate and emulsion matrix is decreasing.

Keywords: Accelerating Rate Calorimeter (ARC), ammonium nitrate, critical temperature, emulsion explosives, thermal stability

Introduction

A great attention was paid to emulsion explosives for its superior characteristic and lower price. Recently, many accidents happened during its

production process, that more focused people's attention on the safety of emulsion explosives production [1-3]. The water phase material used in the production of emulsion explosive is the oxidizer which is mainly composed of ammonium nitrate (AN). It can erode an equipment during production of emulsion explosives. So the presence of the ferric nitrate in the ammonium nitrate solution is inevitable. In our previous study, we found that ferrous ion was oxidized to iron ion, for the strong oxidation of ammonium nitrate. The study about the effect of equipment corrosion on the thermal stability of emulsion explosives is important for the safety of production.

Numerous studies about the thermal stability of emulsion explosives [4] and ammonium nitrate [5] have been reported. Chromium ion [6], chloride ion [7-9], pyrite [10] and soot [11] can promote the decomposition of ammonium nitrate, but alkali metal salt and sulfate cannot [6, 12-14]. The influence of oil phase, water content, pressure [15-19] on emulsion explosives thermal stability has also been studied.

The decomposition mechanism of ammonium nitrate and emulsion explosives has been a subject of several studies in the literature. Several mechanisms have been proposed, since the observed thermolysis of ammonium nitrate and emulsion explosives is greatly dependent on the experimental conditions, including pressure, temperature, state of confinement, heating rate, and the presence of trace amounts of impurities or additives. On the other hand, the kinetics of the thermal decomposition of ammonium nitrate and emulsion explosives has also been extensively studied, using a variety of techniques under different experimental conditions. However, the results reported in the literature are inconsistent and inconclusive. For example, the reported activation energy for ammonium nitrate decomposition varies from 86.2 to 206.9 kJ·mol^{-1}, emulsion explosives also has many different calculated values.

One of the most important parameters for the thermal stability of explosives is the critical temperature under a given set of conditions. The critical temperature is defined as the lowest constant surface temperature of thermal explosion, at which a specific material with a given size and shape will self-heat auto-thermally. However, the critical temperature for ammonium nitrate and emulsion explosives decomposition has not been determined and reported before.

The present study aims to verify influence of ferric nitrate on ammonium nitrate and emulsion explosives thermal stability, and to obtain the critical temperature of ammonium nitrate and emulsion explosives decomposition, as an indication of the thermal stability of ammonium nitrate and emulsion explosives that can be used to evaluate the risk of spontaneous explosion. In order to determine the critical temperature of ammonium nitrate decomposition with

the presence of ferric nitrate, it is necessary to obtain the kinetics of ammonium nitrate decomposition. The similar results can be obtained by the same method for the emulsion explosives.

Experimental

Materials

Pure ammonium nitrate and other inorganic salt were used to prepare the samples, which are analytical reagent. Paraffin and SP-80 were used to prepare the emulsion matrix, which are of industrial grade in the present investigation.

The preparation of emulsion matrix

The procedure consisted in preparing the oxidizer solution (oxidizer 83%, water 10%, mass percent) by dissolving the ingredients in a large stainless steel beaker immersed into a water bath maintained at 90 to 100 °C. The oil phase (consisting of oil, wax and surfactant) (7%, mass percent) was then introduced in the mixer bowl and heated until all the wax was melted and maintained at about 90 °C. At this point, the mixer was stirred at medium speed (approximately 200 rpm) and the hot oxidizer solution was slowly poured into the bowl as the mixture was constantly agitated. After pouring was completed, medium speed mixing was continued for a few minutes. This was followed by remote high-speed mixing (600 rpm) for an additional few minutes to achieve the final refinement.

Accelerating Rate Calorimeter (ARC)

AN (0.5 g) and AN-based emulsion explosive (0.2 g) were placed in spherical vessels which were closed in order to maintain any pressure resulting from vaporization or decomposition of the sample. The sample was heated quickly to a pre-selected initial temperature, equilibrated at that temperature for a period of time and subsequently subjected to the standard ARC procedure of "heat- wait-search", the temperature of the system was raised to 5 °C and the system was maintained adiabatic both during periods of dissipation of thermal transients and of "search" for an exotherm, defined as a self-heating rate S, exceeding 0.02 °C min^{-1}. The temperature at this rate is a measure of the onset temperature (T_0), T_0 for decomposition, although exotherms are not detected during the "heat'" or "wait" modes. Whenever $S \geq 0.02$ °C min^{-1} (detected during the "search" mode), the "heat-wait-search" procedure is automatically interrupted, but collection of time, temperature and pressure data continues. Data collection was programmed to stop in the event that some other pre-selected condition was exceeded.

Results and Discussion

The influence of ferric nitrate on the thermal decomposition on ammonium nitrate by ARC

In order to investigate the influence of ferric nitrate on the thermal decomposition of ammonium nitrate, the comparative experiments in the presence of ammonium chloride or ferric nitrate were conducted. Experiment without the addition of chloride ion or ferric nitrate was used as blank.

Table 1.   The measured initial decomposition temperature of ammonium nitrate samples by ARC

| Number	Sample	Ratio	Mass (g)	$T_0/°C$
1	Ammonium nitrate (AN)	—	0.497	241.066
2	AN+ ferric nitrate	9 : 1	0.496	180.911
3	AN+ ammonium chloride	9.5 : 0.5	0.501	181.033

When attempting to quantify the hazards associated with manufacture and use of ammonium nitrate and AN-based emulsion explosives, a key parameter is the temperature at which these energetic materials begin to self-heat through runaway exothermic decomposition: the "onset" temperature (T_0). The onset temperature of ferric nitrate and ammonium nitrate mixture are shown in Table 1. The thermal decomposition curves are shown in Figures 1-3.
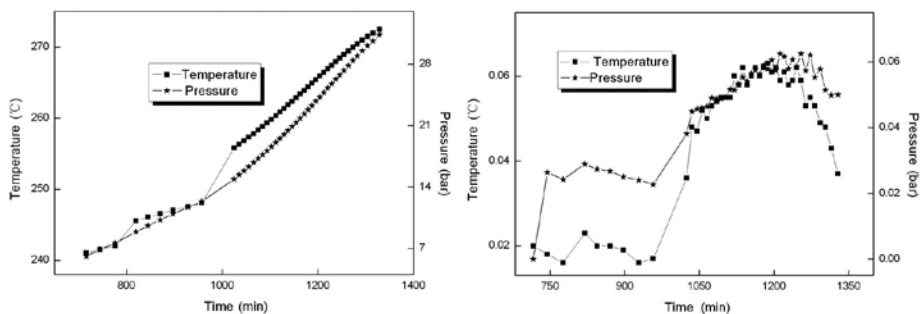
Figure 1.   Temperature and pressure vs. time and rate vs. time plots for ammonium nitrate.
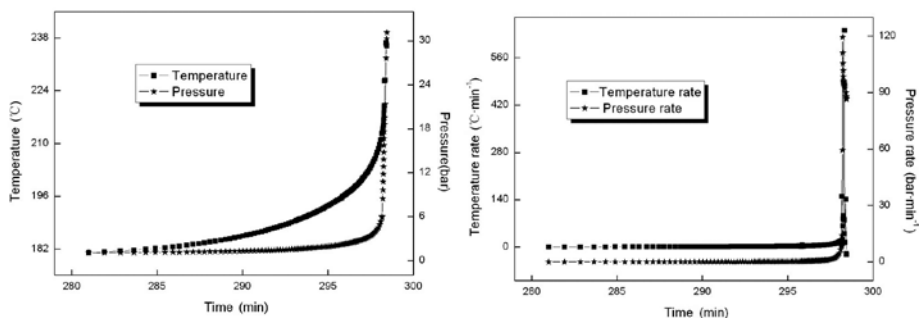
Figure 2. Temperature and pressure vs. time and rate vs. time plots for ammonium nitrate with ammonium chloride.
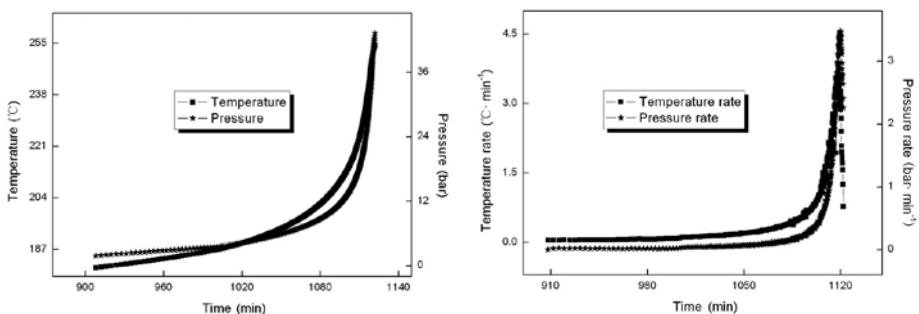
Figure 3. Temperature and pressure vs. time and rate vs. time plots for ammonium nitrate with ferric nitrate.

As it is shown in Figure 1, the pure ammonium nitrate reacts relatively slow and onset temperature is relatively high. After slow temperature-rising, ammonium nitrate is rapidly decomposed at about 180 °C with the addition of ammonium chloride (Figure 2) and ferric nitrate (Figure 3). The temperature, pressure, temperature rate and pressure rate are steep rising. The initial decomposition temperature of ammonium nitrate with presence of ferric nitrate is as low as that of ammonium nitrate with ammonium chloride. With the addition of ferric nitrate and ammonium chloride, the initial decomposition temperature of ammonium nitrate decreases by about 60 °C. The initial composition pressure of neat ammonium nitrate is 6.105×10^5 Pa, but the onset pressure of ammonium nitrate with presence of ferric nitrate and ammonium chloride is about 1.8×10^5 Pa. The temperature, at which reaction rate reached maximum, is 263.39 °C, for purity ammonium nitrate, but for the experiment with the addition of ammonium

chloride and ferric nitrate is 212.65 °C and 244.76 °C, respectively. The maximum reaction rate for the ammonium nitrate with addition of ferric nitrate and ammonium chloride is faster than purity ammonium nitrate (Figures 2 and 3). So it can be deduced that ferric nitrate has the catalysis to ammonium nitrate. From Figures 1-3, can be also found that at the beginning stage of autocatalytic reaction ammonium nitrate with ferric nitrate and ammonium chloride reacts is mitigating relatively. After a period of energy accumulation, temperature rate and pressure rate are dramatically raise, however purity ammonium nitrate reaction process is different. It can be also found that ammonium nitrate with ferric nitrate and ammonium chloride begins to violent reaction near 190 °C. The catalysis activity of ferric nitrate toward thermal decomposition of ammonium nitrate is identical with that of ammonium chloride.

Constant temperature thermal decomposition experiment

In order to characterize the impact of the ferric nitrate on ammonium nitrate thermal stability more precisely, a thermal decomposition of ammonium nitrate in the presence of ammonium chloride and ferric nitrate was conducted under constant temperature condition. Experiment without addition of ammonium chloride and ferric nitrate was used as blank. The method of experiment was according to literature [20]. The instrument was used by self-made, with the temperature error ±5 °C. All samples were analyzed after re-crystallization and drying for 48 h. The mass of the samples was 10 mg.

Table 2.   The measured conversion level of several ammonium nitrate samples

No.	Sample	Percent of conversion for 30 min at 220 °C, (%)	Percent of conversion for 10 min at 220 °C, (%)	Percent of conversion for 3 min at 220 °C, (%)	Percent of conversion for 1 min at 220 °C, (%)
1	AN	27.40	45.05	76.89	84.65
2	AN+ferric nitrate	73.32	86.36	94.62	99.04
3	AN+ ammonium chloride	70.68	84.72	95.04	99.59

Table 2 shows that conversion ratio of ammonium nitrate with and without ammonium chloride and ferric nitrate show the same trends compared with the ARC experiment. At temperature of 280 °C, neat ammonium nitrate mass loss is about 45.05%, but ammonium nitrate with ferric nitrate and ammonium chloride conversion ratio increase to about 85%. At 280 °C, purity ammonium nitrate

conversion ratio is lower than that in the literature [21], in which ammonium nitrate almost decompose completely at 290 °C. At 360 °C, the ammonium nitrate almost decomposed completely with the addition of ferric nitrate and ammonium chloride, but purity ammonium nitrate do not. From the results of constant temperature thermal decomposition experimentation, can be seen that both the ferric nitrate and ammonium chloride can accelerate the decomposition of ammonium nitrate. The catalysis activity of ferric nitrate toward thermal decomposition of ammonium nitrate is identical with that of ammonium chloride.

Influence of ferric nitrate on emulsion matrix thermal stability

In order to further analyses of ferric nitrate on the influence of emulsion explosives, emulsion matrix thermal stability with the addition of ferric nitrate was studied. Comparative experiments in the presence of chloride ion and ferric nitrate were conducted. Experiment without the addition of chloride ion or ferric nitrate was used as blank. The initial decomposition temperature of emulsion matrix with and without ferric nitrate is detailed in Table 3.

Table 3.   The measured initial decomposition temperature of emulsion matrix samples by ARC

| Sample	Percent (%)	Mass (g)	T_0/°C
emulsion matrix	—	0.20	241.18
emulsion matrix+ ferric nitrate	1	0.20	210.85
emulsion matrix+ ammonium chloride	1	0.21	230.75

Emulsion matrix, after slow temperature-rising, was rapidly decomposed with ferric nitrate (Figure 4) and ammonium chloride (Figure 6). The pure emulsion matrix reacts relatively slow and onset temperature is relatively high (Figure 5). The onset temperature of emulsion matrix, which contains ferric nitrate and ammonium chloride, is not significantly different as compared with purity emulsion matrix. The temperature, pressure, temperature rate and pressure rate of emulsion matrix in presence of ferric nitrate are anomalous (Figure 4). The initial decomposition temperature of emulsion matrix with ferric nitrate, which makes the initial decomposition temperature decrease by 30.33 °C, is different with ammonium chloride. The initial composition pressure of emulsion matrix with and without ammonium chloride is separately 1.74×10^5 Pa and 1.91×10^5 Pa, however the initial pressure of emulsion matrix with ferric nitrate is 2.79×10^5 Pa. The maximum reaction rate for emulsion matrix with ferric nitrate and ammonium chloride is faster than purity emulsion matrix (Figures 4 and 6).
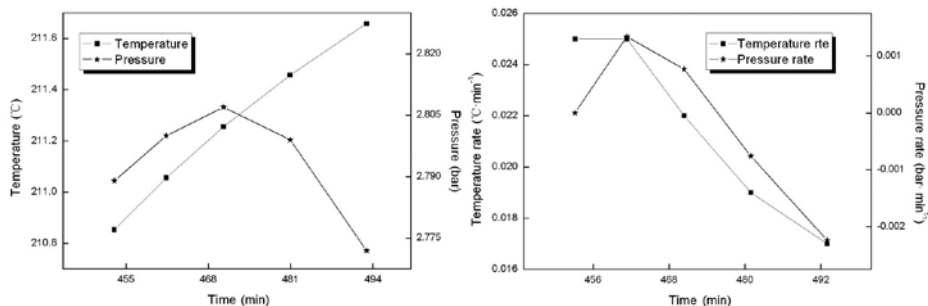
Figure 4. Temperature and pressure vs. time and rate vs. time plots for emulsion matrix with ferric nitrate.
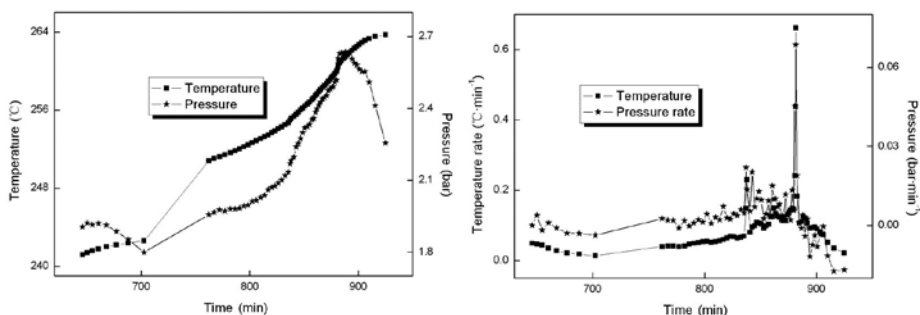
Figure 5. Temperature and pressure vs. time and rate vs. time plots for emulsion matrix.
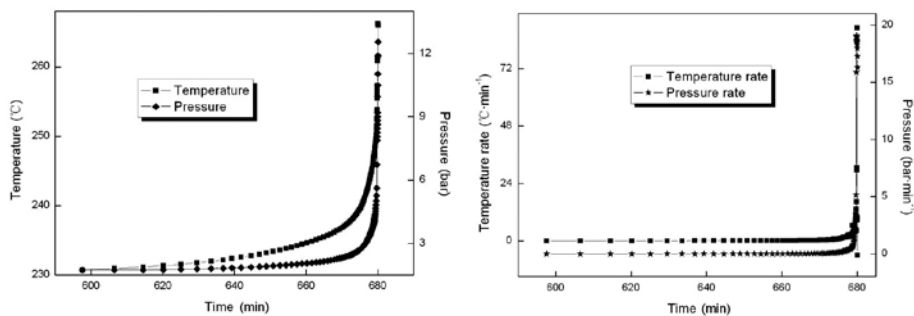
Figure 6. Temperature and pressure vs. time and rate vs. time plots for emulsion matrix with ammonium chloride.

The results show that the impact of chloride ion (1%) toward the thermal stability of emulsion matrix is insignificant. The initial decomposition temperature was decreased by 10.43 °C, compared with the blank experiment. Maybe the initial decomposition temperature varied with the concentration of ammonium chloride. However, the decomposition curve is different as compared to emulsion explosives without ammonium chloride. After a period of energy accumulation temperature rate and pressure rate dramatically raise. The influence of the same concentration of the ferric nitrate on the thermal stability of emulsion matrix is much greater than that of ammonium chloride, and the initial decomposition temperature of emulsion matrix decreases by about 30.33 °C. It proves that the influence of ferric nitrate on emulsion matrix thermal stability is quite obvious. Based on the former test results, ferric nitrate plays an important role of catalysis to the thermal stability of ammonium nitrate and emulsion matrix. It is incredible that a few data was detected by ARC, as shown in Figure 4.The temperature of emulsion matrix with addition of ferric nitrate was shifted only 1 °C. Reaction rate of emulsion matrix with ferric nitrate was reduced. In the process of the experiments, we also found that much pore was existed in emulsion matrix in the presence of ferric nitrate. With the addition of ferric nitrate, the samples are easy to get harden, causing emulsion breaking.

Dynamic calculation

The results of ammonium nitrate with and without ferric nitrate and ammonium chloride experiments conducted with ARC are shown in Figures 1-3. Emulsion matrix with and without ferric nitrate and ammonium chloride ARC experiments are shown in Figures 4-6. Especially, the data from the figures indicate a more complex decomposition mechanism. It was found that the mass of samples affect the experiment results, for example – the initial decomposition temperature maybe different, so the sample mass was kept the same as much as possible. In fact, it is much different in process of emulsion matrix experiments. Choice of data also influence the activation energy and mechanism function of samples because of temperature range as the key factor.

Complications regarding the determination of reaction order are encountered during the standard data analysis with convergence to linearity occurring at an infinite order. This is due to the non-ideal behavior of the system. In order to eliminate the discrepancies between the model and the data, an analytical approach using a simpler model was developed. At the present, the difference of calculated results were caused by different people select different dynamic reaction mechanism function [22~24]. So the most probable mechanism function method to calculate was used. First, estimation of the mechanism function, then

finding out a kinetic parameter.

Dynamical equation of this approach is:

$$\ln\frac{m_T}{f(\alpha)} = \ln(A\Delta T_{ad}) - \frac{E}{RT}$$

(1)

m_T – reaction rate; $f(\alpha)$ – reaction mechanism function; $\alpha = \dfrac{T - T_0}{\Delta T_{ad}}$; T – sample temperature; T_0 – initial decomposition temperature; ΔT_{ad} – the adiabatic temperature rise of sample.

If the selective mechanism is suitable, then $\ln\dfrac{m_T}{f(\alpha)} \sim \dfrac{1}{T}$ is linear. Based on this way, data were one by one calculated by literature [25], got a series of $\ln\dfrac{m_T}{f(\alpha)} \sim \dfrac{1}{T}$ curve. It was namely the most probable mechanism function of samples when the correlation coefficient was the maximum. The data of ammonium nitrate in the presence of ferric nitrate were calculated. The results are shown in Table 4.

Table 4.   The calculated results of different mechanism function

Number	$f(\alpha)$	R^2	S	$A(S^{-1})$	E(kJ/mol)
1	$1-\alpha$	0.9906	0.2029	2.08×10^{19}	195.41
2	$(1-\alpha)^{-2}$	0.8527	1.2443	7.94×10^{26}	278.62
3	$2(1-\alpha)^{\frac{3}{2}}$	0.9642	0.4802	1.67×10^{23}	232.76
4	$\frac{1}{4}(1-\alpha)^{-3}$	0.3455	1.7604	4.80×10^{11}	119.44
5	$\frac{1}{2}\alpha^{-1}$	0.8830	0.7694	7.99×10^{18}	196.81
6	$[-\ln(1-\alpha)^{-1}]$	0.9278	0.6824	1.45×10^{22}	228.40
7	$\frac{3}{2}(1-\alpha)\left[-\ln(1-\alpha)\right]^{-\frac{1}{3}}$	0.8938	0.2599	5.31×10^{5}	70.42
8	$\frac{1}{4}(1-\alpha)\left[-\ln(1-\alpha)\right]^{-3}$	0.9448	1.3821	1.89×10^{55}	533.72

9	$4(1-\alpha)^{\frac{1}{2}}\left[1-(1-\alpha)^{\frac{1}{2}}\right]^{\frac{1}{2}}$	0.9676	0.2082	2.05×10^9	106.22
10	$\frac{3}{2}(1+\alpha)^{\frac{2}{3}}\left[(1+\alpha)^{\frac{1}{3}}-1\right]^{-1}$	0.8455	0.8109	4.14×10^{15}	176.53
11	$\frac{3}{2}(1-\alpha)^{\frac{4}{3}}\left[(1-\alpha)^{-\frac{1}{3}}-1\right]^{-1}$	0.9632	0.7253	5.71×10^{34}	346.41

From the results is known that the most probable mechanism function, activation energy and pre-exponential factor of ammonium nitrate with ferric nitrate are determined to be $f(\alpha) = (1-\alpha)$, E = 195.41 kJ·mol^{-1}, A = 2.08×10^{19} s^{-1}, respectively. By the same method, the most probable mechanism function and activation energy of ammonium nitrate with ammonium chloride are determined to be $f(\alpha) = \frac{3}{2}(1-\alpha)^{\frac{3}{2}}\left[1-(1-\alpha)^{\frac{1}{3}}\right]^{-1}$, E = 136.93 kJ/mol, respectively. Compared with the study described by Li J.S. et al. [26], ammonium chloride and ferric nitrate can change the ammonium nitrate reaction mechanism.

For data anomaly in emulsion matrix with ferric nitrate, the reaction mechanism function and kinetic parameters were not calculated.

Theory and analysis

Based on theory of thermal explosion, once explosion and violent reaction were happened on energy materials in heating process, it can be validated that hot-spot temperature and size exceed critical temperature and size.

According to Luo et al. [27], the critical temperature, Tc, may be calculated from Eq. (2) for an infinite cylinder, which is derived from the Frank-Kamenetskii theory of thermal explosion.

$$\frac{E}{RT_C} = 4.72918 + \frac{1.04565 \ln RQAr_0^{\ 2}}{E\lambda} \tag{2}$$

where r_0 is the radius of the cylinder (m), R is the universal gas constant (8.314 J·mol^{-1} ·K^{-1}), λ is the thermal conductivity of the material (W·m^{-1}·K^{-1}), Q is the heat of reaction (J·m^{-3}), E and A are the activation energy (J·mol^{-1}) and pre-exponential factor (s^{-1}) of the reaction, respectively. It is clear that the critical temperature is a function of E, A, and r_0.

Table 5. Thermophysical parameters required for the calculation of the critical temperature

Sample	Density $(g \cdot cm^{-3})$	Thermal conductivity $(W \cdot m^{-1} \cdot K^{-1})$	Heat of reaction $(J \cdot g^{-1})$	Activation energy $(kJ \cdot mol^{-1})$	Pre-exponential factor (s^{-1})
AN	1.72	0.142	4425	169.50	6.3×10^{13}
AN+ ferric nitrate	1.725	0.143	4028	195.41	2.08×10^{19}
Emulsion matrix	1.39	0.39	2275.64	206.28	8.84×10^{15}
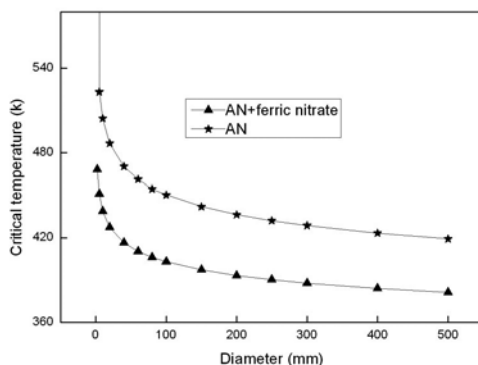
Figure 7. The critical temperature as a function of diameter for ammonium nitrate decomposition with and without ferric nitrate.

The activation energy and pre-exponential factor for ammonium nitrate decomposition with and without ferric nitrate are listed in Table 5. The critical temperatures were calculated for different diameters and the results are given in Figure 7. It can be seen from Figure 7 that the critical temperature decreases with the increase of the diameter. More importantly, Figure 7 also demonstrates that the presence of ferric nitrate significantly reduces the critical temperature of ammonium nitrate. For the diameter of a typical diameter of 300 mm, the critical temperature is drastically decreased from 428.64 to 387.79 K, so it is very dangerous for process of emulsion explosives production if the water phase is in presence of the ferric nitrate. In the process of production of emulsion explosion, ammonium nitrate solution was heated to about 100 °C, even to about 130 °C for the powder emulsion explosives production. For water phase dissolving tank size far exceeds the 500 mm in China and presence of large amount of ammonium

nitrate solution, it can potentially cause undesired premature explosion with the presence of ferric nitrate.

Emulsion matrix iron-plate experiment

As the ARC experiment is abnormal, it was impssible to obtain more information from ARC experiments about emulsion matrix with ferric nitrate. In order to further understand emulsion matrix with ferric nitrate, the iron-plate experiment of emulsion matrix with and without ferric nitrate was conducted, according to GB18095-2000 experiments method (China). From the results of GB18095-2000 it could be obtained critical temperature at which emulsion explosives or emulsion matrix happened deflagration or explosion. The results are shown in Table 6.

Table 6.   Critical temperature and size of hot spots

Sample	Calculated value (cylinder hot)		Test value (°C)	Cell diameter (mm)
	Temperature (°C)	Size(mm)		
Emulsion matrix	239.27	4.64	246.3	15
Emulsion matrix with ferric nitrate	—	—	223.7	15

According to thermal explosion theory, when violent reaction or explosion in the process of explosives heated, it can be assured that the temperature and size of samples exceed the critical condition. Then the critical temperature by time to ignition can be calculated. Time to ignition can be calculated by Eq. (3) [28]:

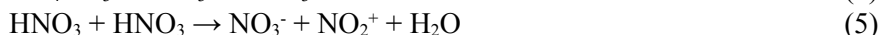$$t_{ad} = \frac{C_v R T^2}{QEA} \exp\left(\frac{E}{RT}\right) \tag{3}$$

t_{ad} is the time to ignition (s); C_V is the specific heat (J·kg^{-1} K^{-1}); R is the universal gas constant 8.314 J·mol^{-1} K^{-1}; Q is the heat of reaction (J·kg^{-1}); E and A are the activation energy (J·mol^{-1}) and pre-exponential factor (s^{-1}) of the reaction, respectively.

On the basis of GB18095-2000 (China), emulsion explosives also can be analyzed thermal stability at 200 ±5 °C for about 20 minutes. Assuming the time to ignition is 20 minutes, the critical temperature can be calculated by Eq. (3). Then critical size according to the Frank-Kamenetskii theory of thermal explosion can be calculated. The critical temperature and critical size were calculated for emulsion matrix without ferric nitrate (Table 6).

It can be seen from Table 6 that the critical temperature of emulsion matrix with ferric nitrate decreases by 22.6 °C. For anomaly in data of emulsion explosives with ferric nitrate, critical size and critical temperature were not calculated.

Mechanism analysis

The above-mentioned results show that ferric nitrate can catalyze the ammonium nitrate and emulsion matrix decomposition reaction. Based on the above discussion, in principle, the initial step of ammonium nitrate decomposition involves the endothermic dissociation of gasification reaction zone into ammonia and nitric acid. Ammonium nitrate at 169 °C begins to decompose as soon as it melts, the first step being dissociation into ammonia and nitric acid (Eq. (4)). Study has shown that the decomposition of ammonium nitrate operates by an ionic mechanism in the temperature range 200~300 °C and formation of nitronium ion is rate-determining. It is well-known that the thermal decomposition of ammonium nitrate is acid-catalyzed [5]. C. Oommen [29] and J.H. Suna [30] assumed the following known equilibrium reaction for HNO_3 that leads to the oxidizing species NO_2^+ (Eq. (5)). It is easy to form complex $Fe[(NO_3)_4]^-$ by ferric nitrate and nitrate, due to ferric nitrate is Lewis acid. It can also continues to form $Fe[(NO_3)_6]^{3-}$, but the reaction rate is relatively slow (Eq. (8)) [31]. The reaction of equation (6) is relatively fast and much NH_4^+ was oxidized to NO_2^+ by HNO_3. Finally gas product is formed, which results in reaction acceleration and affects the thermal stability of ammonium nitrate (Eq. (9)).

$$NH_4NO_3 \rightarrow NH_3 + HNO_3 \tag{4}$$
$$HNO_3 + HNO_3 \rightarrow NO_3^- + NO_2^+ + H_2O \tag{5}$$
$$Fe(NO_3)_3 + NO_3^- \rightarrow Fe[(NO_3)_4]^- \tag{6}$$
$$Fe[(NO_3)_4]^- + NO_3^- \rightarrow Fe[(NO_3)_5]^{2-} \tag{7}$$
$$Fe[(NO_3)_5]^{2-} + NO_3^- \rightarrow Fe[(NO_3)_6]^{3-} \tag{8}$$
$$NH_3 + NO_2^+ \rightarrow N_2O + H_3O^+ \tag{9}$$

In fact reactions of ammonia and nitric acid are complex and ultimately generate heat through the formation of thermodynamically favoured products such as nitrogen and water. On the whole, the gas generation is a gentle process. In the process of reaction, formulation $Fe[(NO_3)_4]^-$ is the key step, for it can promote NO_2^+ generation, thus increasing the generation rate of mediate product $[NH_3NO_2^+]$ at lower temperature. Therefore, once mixed with ferric nitrate in the process of production and storage, the thermal stability of ammonium nitrate and emulsion explosives will deteriorate.

Conclusions

The paper describes the thermal stability of ammonium nitrate and emulsion matrix with the presence of ferric nitrate. The following conclusions were extracted from the study.

1. Ammonium nitrate, with and without the presence of ferric nitrate, has been studied. And the activation energy, the pre-exponential factor and mechanism function of ammonium nitrate decomposition of ammonium nitrate were determined to be E = 195.41 kJ/mol, A = 2.08×10^{19} s^{-1} and $f(\alpha) = (1-\alpha)$ with the presence of ferric nitrate by ARC experiment. It was dramatically decreased by 60.16 °C of initial decomposition temperature with presence of ferric nitrate. Initial decomposition temperature of emulsion matrix with the presence of ferric nitrate has decreased by 30.33 °C.

2. The critical temperatures for ammonium nitrate decomposition, with and without the presence of ferric nitrate, were calculated using the kinetic parameters thus determined and were shown to decrease with increasing the diameter. It has been further shown that ferric nitrate can significantly decrease the critical temperature of ammonium nitrate decomposition, potentially causing undesired premature detonation of the explosives in the process of emulsion explosives production, especially in process of dissolving, emulsifying and pumping. Emulsion matrix with and without the presence of ferric nitrate, has been studied by iron-plate experiment. The critical temperature of emulsion matrix with ferric nitrate decreases by 22.6 °C.

3. Formulation $Fe[(NO_3)_4]^-$ is the key step, in the process of reaction, for it can promote NO_2^+ generation, thus increasing the generation rate of with mediate product $[NH_3NO_2^+]$ at lower temperature.

Reference

[1] Perlid H., Pump Safety Tests Regarding Emulsion Explosive, *Proc. 22nd Annual Conference in Explosives and Blasting Technique*, **1996**, 101-107.
[2] Olson D., Presented at the fall 1997 research center for energetic materials open safety seminar, Socorro NM, **1997**.
[3] Jones D.E.G., Feng H.T., Mintz K.J. et al., Parameters Affecting the Thermal Behaviour of Emulsion Explosives, *Thermochim. Acta*, **1999**, *331*, 37-44.
[4] Wang X.H., Li X.J., Research of Thermal Decomposition Kinetic Characteristic of Emulsion Explosives Base Containing Fe And Mn Elements, *J. Therm. Anal. Calor.*, **2008**, *91*, 545-550.
[5] Turcotte R., Lightfoot P.D., Fouchard R. et al., Thermal Hazard Assessment of AN

and AN-Based Explosives, *J. Hazard. Mater*., **2003**, *101*, 1-27.

[6] Oxiey J.C., Kaushik S.M., Gilson N.S., Thermal Stability and Compatibility of Ammonium Nitrate Explosives on a Small and Large Scale, *Thermochim. Acta*, **1992**, *212*, 77-85.

[7] Oxley J.C., Smith J.L., Rogers E. et al., Ammonium Nitrate: Thermal Stability and Explosivity Modifiers, *ibid.*, **2002**, *384*, 23-45.

[8] Chen W.H., Chen L.P., Wu Y. et al., Influence of Nitrate Acid and Chlorine Ion on the Decomposition of Ammonium Nitrate in Aqueous Solution with High Temperature, *China Safety Science Journal*, **2007**, *7*, 101-105.

[9] Zhang W.P., Decomposition of Ammonium Nitrate Catalyzed by Chlorine Ion in Acid Solution, *Chinese Journal of Explosive & Propellants*, **2004**, *27*, 33-35.

[10] Gunawn R., Zhang D.K., Thermal Stability and Kinetics of Decomposition of Ammonium Nitrate in the Presence of Pyrite, *J. Hazard. Mater.*, **2009**, *165*, 751-758.

[11] Lure B.A., Chzhan L., Effect of Soot on the Kinetics and Mechanism of the Thermal Decomposition of Powdered Ammonium Nitrate, *Fizika Goreniya Vzryva*, **2000**, *36*, 63-73.

[12] Li X.-R., Koseki H., Study on the Contamination of Chlorides, *Process Saf. Environ.,* **2005**, *83*, 31-37.

[13] Tang S.L., Liu Z.L., Zhou X.L. et al., Studies on the Detonation Safety of Modified Ammonium Nitrate. The Influence of Inorganic Chemical Fertilizer, *Chinese Journal of Applied Chemica*, **2004**, *121*, 400-404.

[14] Kaljuvee T., Edro E., Kuusik R., Influence of Lime Containing Additives on the Thermal Behaviour of Ammonium Nitrate, *J. Therm. Anal. Calorim.*, **2008**, *92*, 215-221.

[15] Rubtsov Y.I., Kazakov A.I., Lempert D.B. et al., Kinetic Regularities of the Heat Release for the Interaction of Some Organic Compounds with Ammonium Nitrate, *Propellants, Explos., Pyrotech.*, **2006**, *31*, 421-434.

[16] Sosnin V.A, Cabdullin R.Kh., Study of the Thermal Stability of a Poremit Emulsion, *Combust. Explo. Shock*, **1994**, *30*, 810-816.

[17] Ma Zh.G., Zhou Y.K., Wang J., Influence of Water Content in Emulsion Explosives Basic Substance on Their Thermal Decomposition and Calculation of Kinetic Parameters, *Chinese Journal of Explosive & Propellants,* **2009**, *32*, 44-47.

[18] Yin L., Guo Z.R., Thermal Decomposition Kinetics of Class 2 Coal Mine Permissible Emulsion Explosive, *Chinese Journal of Energetic Materials*, **2007**, *15*, 175-177.

[19] Zhou X.L., Liu Z.L., Lu C.X., Analysis on Adiabatic Decomposition Safety of Rock Emulsion Explosive Using Accelerating Rate Calorimeter, *Chinese Journal of Explosive & Propellants*, **2003**, *62*, 62-65.

[20] Tang S.L., Liu Z.L., Zhou X.L. et al., Detonation Safety of Modified Ammonium Nitrate. The Influences of Calcium Carbonate and Magnesium Sulfate, *Chinese Journal of Applied Chemical*, **2004**, *21*, 64-69.

[21] Humienik M.O., On the Thermal Stability of Some Ammonium Salts, *Thermochim. Acta*, **2001**, *378*, 107-112.

[22] Qian X.M., Liu L., Feng C.G., Calculating Apparent Activation Energy of Adiabatic Decomposition Process Using Pressure Data, *Acta Phys-Chim. Sin.*, **2005**, *21*, 134-138.

[23] Townsend D.I., Tou J.C., Thermal Hazard Evaluation by an Acceleration Rate Calorimeter, *Thermochim. Acta*, **1980**, *37*, 1-30.

[24] Sempere J., Nomen R., Serra R., Gallice F., Determination of Activation Energics by Using Different Factors Ø in Adiabatic Calorimeter, *J. Therm. Anal. Calorim.*, **1999**, *58*, 215-223.

[25] Hu R.Z., Shi Q.Z., *Thermal Analysis Kinetics*, Beijing: Science Press, China, **2001**.

[26] Li J.S., Wang X.G., Thermal Stability Assessment of Anti-Explosive Ammonium Nitrate, *Journal of University of Science and Technology Beijin*, **2005**, *12*, 12-15.

[27] Luo K.M., Hu K.H., Lu K.T., The Calculation of Critical Temperatures of Thermal Explosion for Energetic Materials, *Journal of the Chinese Institute of Chemical Engineers*, **1997**, *48*, 21-28.

[28] Manasev G.T., Bobolev V.K., Initiation of Solid Explosives by Impact, (Translated from Russian, Israel Program for Scientific Translation), Jerusalem **1971**.

[29] Oommen C., Jain S.R., Ammonium Nitrate: a Promising Rocket Propellant Oxidizer, *J. Hazard. Mater.*, **1999**, *67*, 253-281

[30] Suna J.H, Suna Z.H., Wang Q.S. et al., Catalytic Effects of Inorganic Acids on the Decomposition of Ammonium Nitrate, *ibid.*, **2005**, *127*, 204-210.

[31] Li Y.X., Nitration and Nitrosation Reactions of Methyl Salicylate with Rare Earth or Transition Metal Nitrates, Ph.D. dissertation, Nanjing University, China, **2003**.