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IMPACT OF IMPURITIES AND pH ON AMMONIUM NITRATE STABILITY (a)

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1. Abstract

Thermal decomposition of ammonium nitrate is characterized by a complex reaction network. The presence of impurities as well as low pH conditions enhances significantly the reaction. This may lead to an uncontrolled decomposition, or even to an explosion. In the present work, the thermal stability of ammonium nitrate has been characterized by using different calorimetric methods both at low pH, and in the presence of probable process related impurities. Special attention has been given to the onset (initial) temperature, and to the time for reaching maximum rate of the decomposition. According to the results, pH seems to be the major parameter in decreasing the thermal stability of ammonium nitrate while the effect of impurities seems in most cases to be only secondary. A violent decomposition of ammonium nitrate may be possible even at ambient temperature due to the self heating behaviour started by low pH.

2. Introduction

Ammonium nitrate is a compound known to be thermally unstable. Thermal decomposition of pure ammonium nitrate starts when it is heated beyond its melting point (169 °C). The first reaction usually observed is the endothermic dissociation back to ammonia and nitric acid. This reaction is reversible. However, in an open system the ammonia gas tends to leave the solution. The following decrease in pH as well as a higher temperature will enhance the other decomposition reactions being both exothermic and irreversible [1]. More generally, from mechanistic point of view the decomposition of ammonium nitrate is largely effected by the confinement of the system. The main reaction characterizing a violent high temperature exothermic decomposition of ammonium nitrate is thought to be (1) although it is clear that the decomposition always is a combination of several simultaneous reactions [1, 2]:

$$NH4NO3 \rightarrow\ N2 + 2H2O + \tfrac{1}{2}O2 \qquad [\Delta H = -1460 \text{ kJ/kg}] \qquad (1)$$

In this connection, it is also important to notice that the heat released by the decomposition of a mixture of ammonium nitrate and other fertilizer components may be a lot greater than that of ammonium nitrate alone [2]. In addition, several materials are known to have a strong catalytic effect on the thermal decomposition of ammonium nitrate [1, 3]. These include inter alia, components like acids, chlorine, copper, iron, and chromium.

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3. Experimental Methods

Thermal stability of ammonium nitrate has in the present work been studied both at low pH conditions by using HNO_3 for acidification, and in the presence of Cl^-, Cu^{2+}, Fe^{3+}, and Cr^{3+} salts. Also, the effect of different acids in the pH adjustment has been included into the experimental set. The experiments have been carried out by using several calorimetric methods. The main experimental equipment is the standard screening instrument DSC (Differential Scanning Calorimeter), and the advanced adiabatic instrument ARC (Accelerating Rate Calorimeter). The basics of the methodology have largely been described already earlier [4].

The key parameters measured are the onset temperature (T_{onset}), and the time to maximum rate under adiabatic conditions (TMR_{ad}). T_{onset} is defined to be the lowest temperature at which exothermic activity is detected in a small scale DSC or ARC test. It is dependent on both the sample size and system sensitivity which means that the result may vary with the instrument used. TMR_{ad} measured by ARC (on the basis of the self-heating behaviour) is defined to be the time taken for the reaction system to reach its maximum self-heating rate under completely adiabatic conditions. It gives the indication of the time available, at different temperatures, to take corrective action in the event of a failure [5].

All the experiments reported in this paper have been made by using samples containing 90 wt-% ammonium nitrate. The pH values given are always corresponding to 1:10 dilution. All the concentration data of impurities is on the weight basis. The experiments both by DSC and ARC have been made by using a closed sample cup corresponding to a confined reaction system.

4. Results and Discussion

4.1 Effect of pH

The pH of pure ammonium nitrate is around 4.7 the compound having practically no buffer capacity. As can be seen in Figure 1, even a minor decrease in pH (adjusted by nitric acid) to 2.5 has a significant effect on the thermal stability of ammonium nitrate measured as Tonset. A further decrease in pH down to 1.0 will strenghten this effect but only slightly.

Figure 1. The effect of pH (HNO_3) on ammonium nitrate stability measured by DSC.
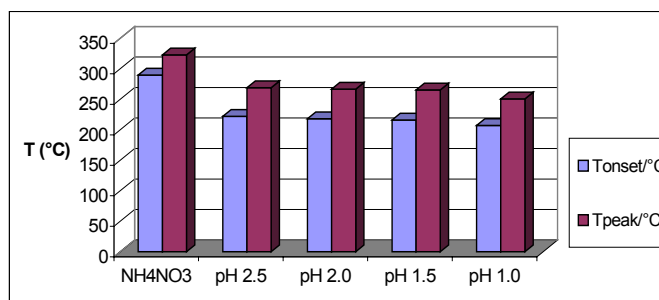
When phosphoric or sulphuric acid instead of nitric acid is used in the pH adjustment of ammonium nitrate an interesting effect shown in Figure 2 is found. The T_{onset} values are practically the same at corresponding pH values when either nitric or sulphuric acid is used but significantly lower Tonset values are measured in the presence of phosphoric acid. A corresponding effect caused by phosphoric acid is also seen in ammonium nitrate decomposition rate (Figure 3) measured at pH 1.5 by the confined space decomposition method [4].

Figure 2. The effect of acid on ammonium nitrate stability measured by DSC as a function of pH.
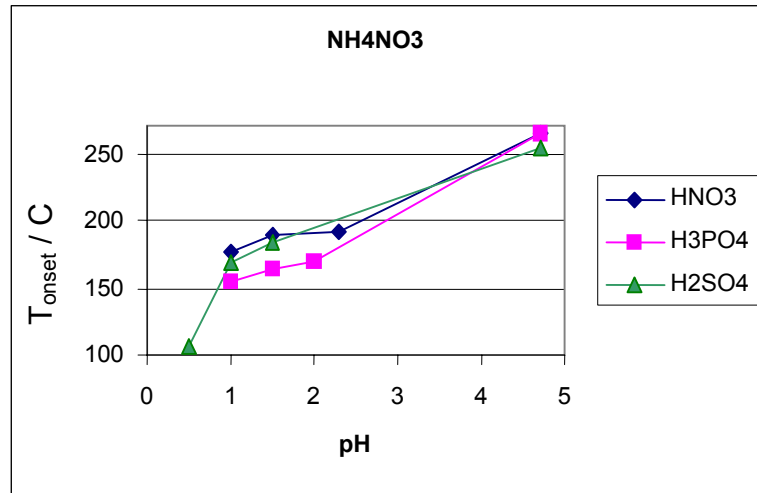

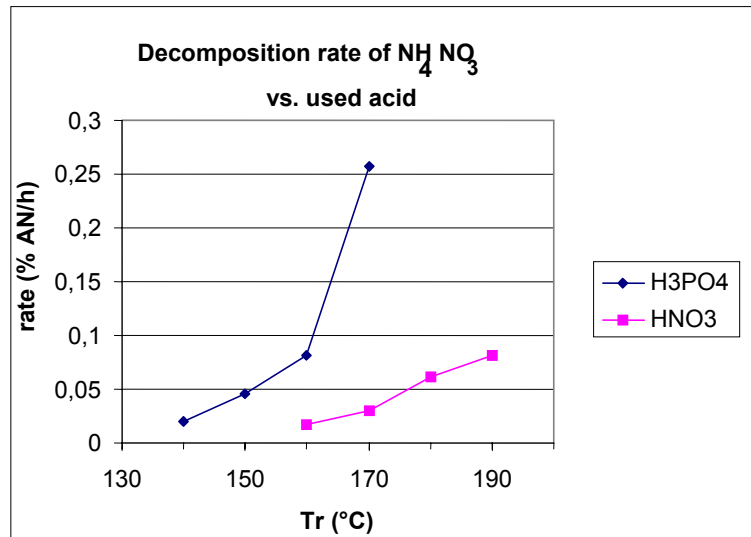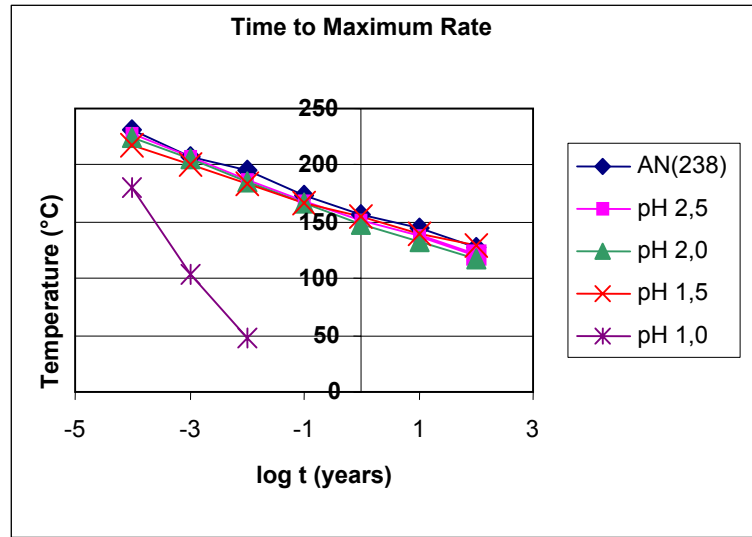Figure 3. Ammonium nitrate decomposition rate at pH 1.5 as a function of temperature and acid.

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Figure 4. TMR$_{ad}$ of ammonium nitrate as a function of pH (HNO$_3$).

The pH effect on ammonium nitrate decomposition rate measured as TMR$_{ad}$ shows a clearly different pattern. As can be seen in Figure 4 the acidification by nitric acid has a significant effect on the rate only when pH is down to 1.0 at which value the calculated TMR$_{ad}$ is only about 4 days even at such a low temperature as 50 °C. The acid itself has also in this connection a clear effect on the results. The TMR$_{ad}$ at pH 1.0 is significantly higher when sulphuric acid is used instead of nitric acid (Figure 5) which again does not directly correspond to the T$_{onset}$ results (Figure 2).

Figure 5. The effect of acid on ammonium nitrate TMR$_{ad}$.
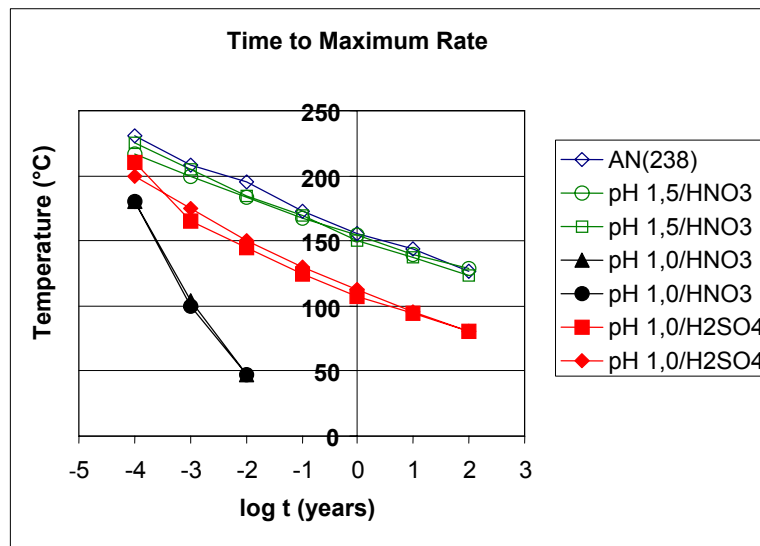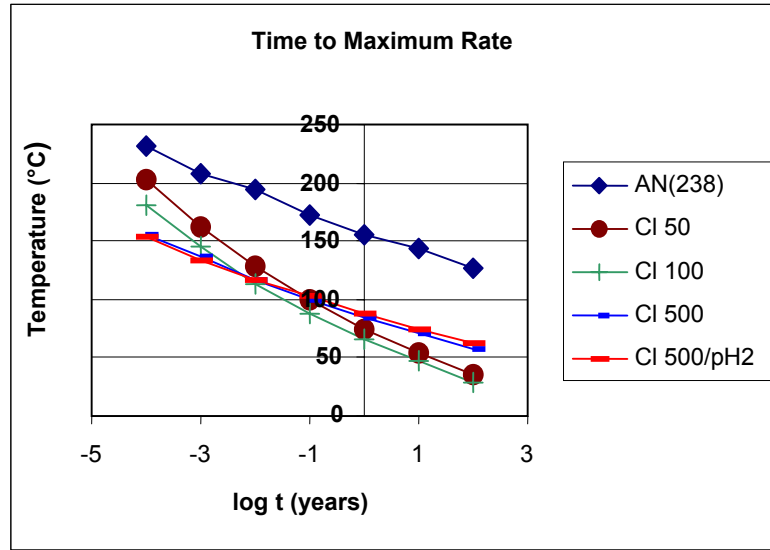
4.2 Effect of Cl-

The effect of Cl- has been measured by adding NH4Cl to ammonium nitrate either as such or at a decreased pH. As can be seen in Figure 6 the thermal stability of ammonium nitrate measured as Tonset decreases with increasing Cl- content up to about 1000 ppm. The effect of Cl- is, however, clearly less than the effect of low pH (Figure 1).

Figure 6. The effect of Cl⁻ addition on ammonium nitrate stability measured by DSC.
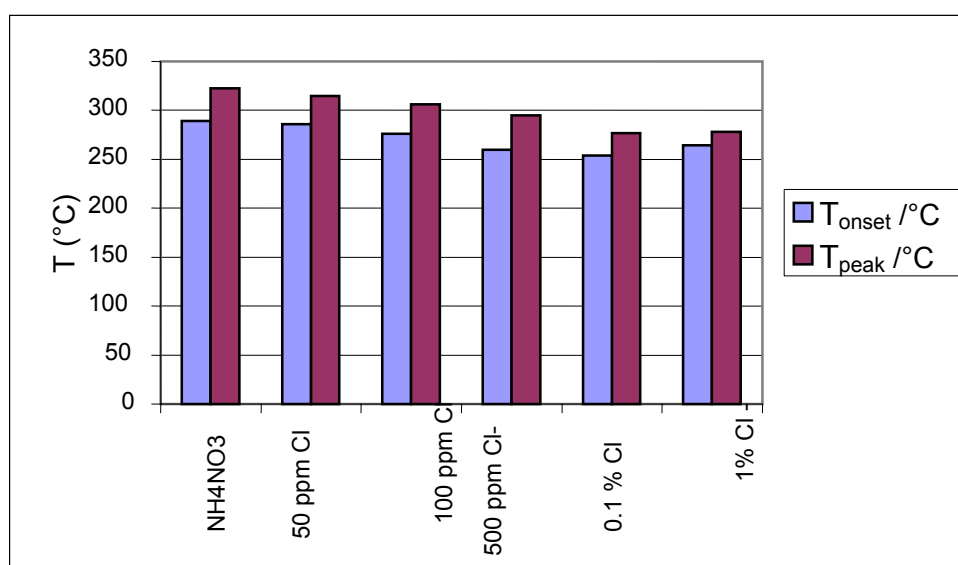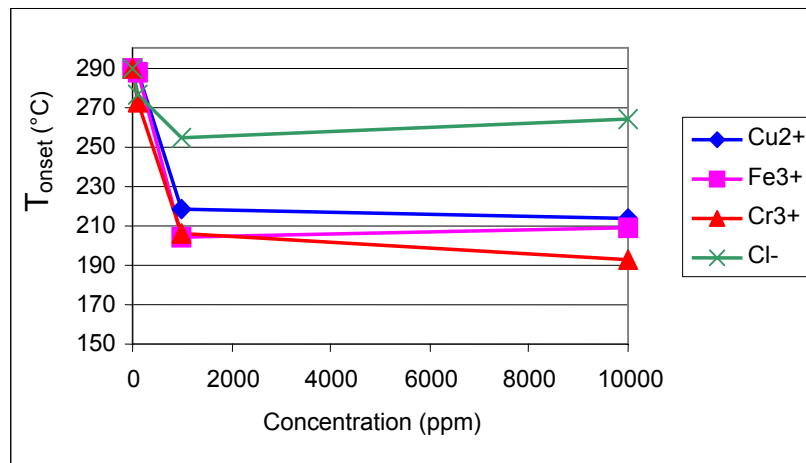

The effect of Cl- addition on the decomposition rate measured as TMRad is clearly different. As can be seen in Figure 7, the presence of Cl- significantly increases the decomposition rate of ammonium nitrate but the concentration seems to have no clear role. A similar catalyzing effect of Cl- on the decomposition of ammonium nitrate has earlier been reported in the confined space decomposition test [4].

 As can also be seen in Figure 7, the decomposition rate of ammonium nitrate with 500 ppm Cl- at pH 2 does not significantly differ from the decomposition rate of the corresponding sample without pH adjustment. Earlier, some synergetic effect of Cl- addition and low pH conditions on the Tonset value of ammonium nitrate has been reported [4].

Figure 7. TMR$_{ad}$ of ammonium nitrate as a function of Cl$^-$ content.

4.3 Effect of Cu2+, Fe3+, and Cr3+ salts

The effect of Cu^{2+}, Fe^{3+}, and Cr^{3+} salts on ammonium nitrate stability has been studied by adding the corresponding nitrates into the samples. As can be seen in Figure 8, all these components have a clearly higher decreasing effect on the T_{onset} of ammonium nitrate than Cl$^-$ has. The effect is comparable with that of low pH (Figure 2), and it is mainly due to concentrations up to 1000 ppm.

Figure 8. T_{onset} of ammonium nitrate as a function of Cu^{2+}, Fe^{3+}, and Cr^{3+} salt, and Cl$^-$ concentration.

The effect of Cu2+ or Cr3+ on the decomposition rate of ammonium nitrate is significantly less. As can be seen in Figure 9, only the contents on the level of 1 wt-% (10000 ppm) show any clear decrease in the TMRad.

Figure 9. The effect of Cu^{2+} and Cr^{3+} salts (in ppm) on ammonium nitrate TMR_{ad}.
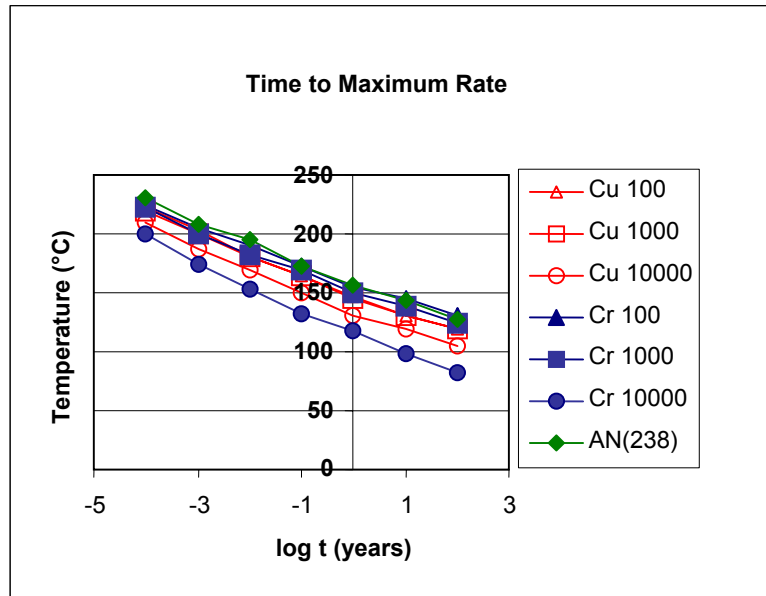
The catalytic effect of different metal salts on the decomposition of ammonium nitrate has earlier been reported e.g. by Rosser et al [6] and Kümmel and Pieschel [7] but the experiments have mostly been made by using clearly higher contents than in the present work. The same applies to the experiments with halides reported e.g. by Maycock et al. [8]. Also, thepH conditions have earlier been reported to have a probable indirect effect on the catalyzing effect of iron on the decomposition of ammonium nitrate containing fertilizers as the concentration of water soluble iron increases significantly at low pH conditions (below 2) [4].

5. Conclusions

The measurements of the present work were made in a closed system which, in general, can be seen to represent the worst case scenario of ammonium nitrate decomposition. It is clear that the pH conditions have the largest effect on ammonium nitrate stability when concluded on the basis of the initial temperature (Tonset) of the exothermic behaviour. Already at pH 2.5 the stability is significantly decreased. Also, the acid used in the pH adjustment (HNO3/H2SO4/H3PO4) has a clear effect. This is probably connected with the reaction chemistry [2]. The effect of impurities on the Tonset of ammonium nitrate varies, e.g. for Cl- (ppm level) it seems to be only secondary while the effect of Cu2+, Fe3+, and Cr3+ seems to be more significant.

The situation changes when the stability of ammonium nitrate is considered on the basis of the decomposition rate (TMRad). The effect of Cl- is much higher than could be concluded on the basis of the corresponding Tonset value while the effect of both the low pH conditions and Cu2+, Fe3+, and Cr3+ remains mainly less significant. However, at pH 1.0 (HNO3) a clear increase of the decomposition rate is seen. The interpretation of the low pH result remains still open for discussion. It is not at all clear if the calculated result based on the extrapolation of the experiments at significantly higher temperature is valid, especially when the measurements are from the liquid phase, the system at lower temperature being a salt slurry containing

mainly solids. In any case, it is important to remember that thermal decomposition reactions take place in practice at temperatures significantly under the threshold values measured by any conventional thermoanalytic method (see also [9]).

It is also important to notice that the results of the present work cannot be used to evaluate the behaviour of ammonium nitrate in an open system. However, in any large tank or reactor the question of the degree of confinement in the case of normal as well as abnormal operation should carefully be considered.

6. <u>Literature</u>

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