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PREDICTION OF DECOMPOSITION BEHAVIOUR OF FERTILIZERS CONTAINING AMMONIUM NITRATE[1]

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SUMMARY

A simple general methodology has been developed for estimating and predicting the decomposition risk of process slurries as well as final fertilizers. The methodology is based on experimental methods and classifications practised widely in other areas of chemical industry.

The major equipment used is Differential Scanning Calorimeter (DSC) together with a well equipped high pressure laboratory reactor like RC-1 Reaction Calorimeter. In the present paper, experimental results from the thermal as well as catalysed decomposition of both model and process originating fertilizer samples will be described. The interpretation of the results and their use in modelling and simulating the decomposition behaviour at large scale processes will also be discussed.

RESUME

Une méthodologie générale simple a été mise au point pour estimer et prévoit le risque de décomposition de mélanges de procédé ainsi que d'engrais finis. La méthodologie repose sur des méthodes expérimentales et des classifications largement utilisées dans d'autres secteurs de l'industrie chimique.

L'équipement principal est un calorimètre de sélection différentielle (DSC) ainsi qu'un réacteur de laboratoire bien équipé à haute pression comme le calorimètre de réaction RC-1. Dans l'exposé, les résultats expérimentaux de décomposition thermique et catalytique d'échantillons modèles et industriels sont décrits. L'interprétation des résultats et leur emploi dans la modélisation et la simulation de la décomposition dans le cas de procédés industriels sera également présentée.

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INTRODUCTION

Manufacturing in the chemical industry involves often the processing of highly reactive chemicals. Hence, a strategy is required to ensure that these manufacturing activities are carried out safely. Many chemical reactions that are operated on the industrial scale release heat, *i.e.* they are exothermic. In addition, even larger amounts of heat can be released when decomposition reactions are initiated through wrong operating conditions. A runaway reaction describes the situation when for any reason an exothermic reaction system becomes uncontrollable. Although this is often linked with cooling failure on a reaction vessel, runaway reaction can take place due to self-heating at any stage of a process, *e.g.* during the storage or transport.

The consequences of a violent exothermic runaway reaction often including strong gas formation can be severe. It is important that any exothermic reaction which could arise is identified at an early stage and that possible chemical reaction hazards are considered [1-4]. This requires the knowledge and ability to evaluate and test safety aspects of chemicals, chemical reactions, and processes.

Fertilizers containing ammonium nitrate represent a typical example of chemical products which are thermally unstable. The chemical environment may also during processing have a significant effect on their stability through catalytic and often synergistic mechanisms that are only partly understood. Hence, although the methodology for defining the safety properties of final fertilizer products is well developed there is an obvious need for a simple methodology for estimating the thermal safety properties of various process streams inside the fertilizer plant. The present paper describes some of the most common screening methods used in the chemical industry for studying thermal safety, and evaluates their applicability for fertilizer industry through some related case examples.

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[1] *Prédiction du comportement au point de vue décomposition d'engrais contenant du nitrate d'ammonium*

THE BASIC METHODOLOGY FOR THERMAL SAFETY EVALUATION

The approach taken for characterising the reactive nature of chemical processes focuses primarily on gaining an understanding of both undesired and desired chemistry. The thermal risk potential of different chemical processes or operations (*e.g.* evaporations) can according to Rogers [5] be evaluated by determining the **severity** and **probability** of a potential incident that may occur. In the case of chemical reaction hazards, the energy release potential of the reaction or decomposition and the following adiabatic temperature rise (ΔT_{ad}) can be used as a measure of the severity while the initial temperature of a decomposition reaction (onset temperature, T_{onset}), time required for the decomposition rate maximum (Time to Maximum Rate under adiabatic conditions, TMR_{ad}), and initiations, or accumulation problems can be used to indicate the probability of the event occurring. Correspondingly, the evaluation of thermal risk potential may be based on the simple three level criteria as given in Table 1.

Table 1 - Criteria for Thermal Risk Assessment according to Rogers [5]

Risk Criteria	Severity	Probability
High	ΔTad > 200K or Tmax-Tp > 200K or bp surpassed	Tonset-Tp < 50K or TMRad < 8h or initiation/accumulation
Medium	50K < ΔTad < 200K or 50K < Tmax-Tp < 200K or gas evolution	100K > Tonset-Tp >50 K or 8h < TMRad < 24h
Low	ΔTad < 50K or Tmax-Tp < 50K	Tonset-Tp > 100K or TMRad > 24h

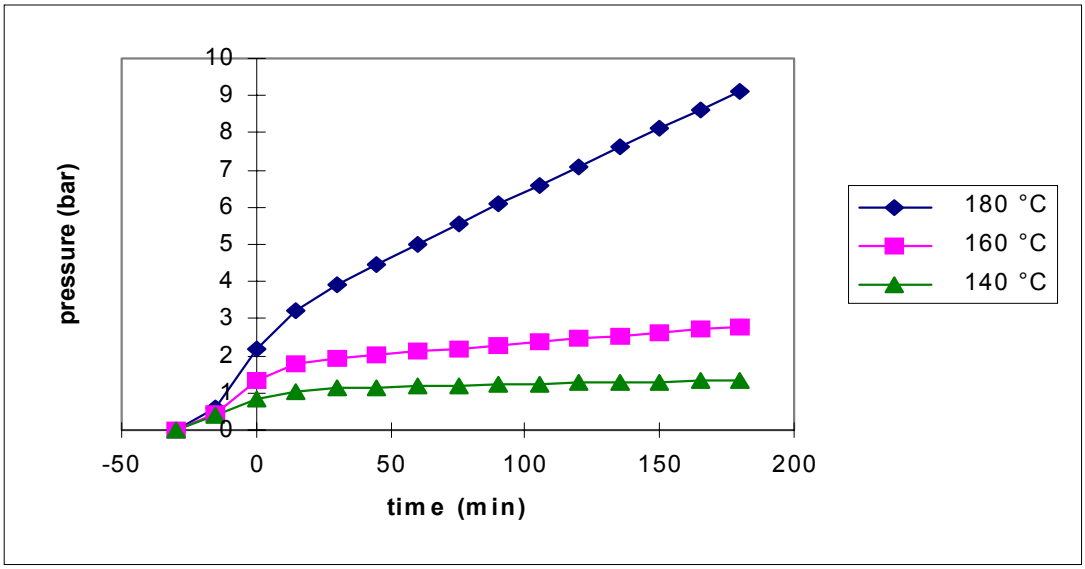
As a preliminary screening tool, the measurements by a Differential Scanning Calorimeter (DSC) may be used for evaluating both the severity and probability of the potential hazards arising from the desired as well as from the possible decomposition reactions. DSC being the most popular technique in thermal analysis allows the determination of any heat of reaction occurring while the temperature is either increased linearly or held isothermally. The covered temperature range is usually from room temperature up to about 500°C. In cases where a more thorough evaluation is needed these measurements may be completed by other calorimetric methods, like *e.g.* reaction calorimetry, and adiabatic calorimetry [6].

In a fertilizer plant the major **severity risk** is connected with the decomposition reactions of the processed material. The energy potential of any decomposition reaction is easily measured by DSC. In many cases, the measurement is not even needed as the decomposition enthalpies may be found directly from the literature. The descriptive parameters, adiabatic temperature rise (ΔT_{ad}) for decomposition or maximum temperature (T_{max}) for the desired reaction, may then be calculated from the reaction enthalpy value divided by the specific heat (c_p) value. If the c_p value of the process stream is not known it can easily be measured by DSC which is one of the best instruments for measuring c_p values especially for solids and slurries.

The best screening parameter to measure the **probability** of a potential thermal hazard incident in a fertilizer process is the onset temperature (T_{onset}) which is the temperature at which exothermic activity is first detected in a small scale DSC screening test.

The decomposition kinetics (TMR_{ad}) as a risk **probability** parameter may also be determined on the basis of a standard DSC measurement [7] but for fertilizer process slurries we have found it more suitable to measure the decomposition kinetics through gas formation by using a pressure reactor under isothermal conditions. Due to the accuracy requirement and also due to the thermal risks incorporated in the processing of ammonium nitrate containing slurries we have here used a RC-1 Reaction Calorimeter. Also, no experiment with the pressure reactor is allowed before the T_{onset} has been measured. As shown in Figure 1 this simple method gives after the heating period a constant rate of pressure increase which may be described as a zero order initial decomposition reaction (reaction rate is independent of the concentration of starting materials).

Figure 1 - The decomposition of a FINN CAN slurry at pH 1.25 as a function of time and temperature



By knowing the free gas volume in the reactor one may quite easily calculate the reaction rate coefficient (k) based *e.g.* on the thermal decomposition reaction of ammonium nitrate (1).

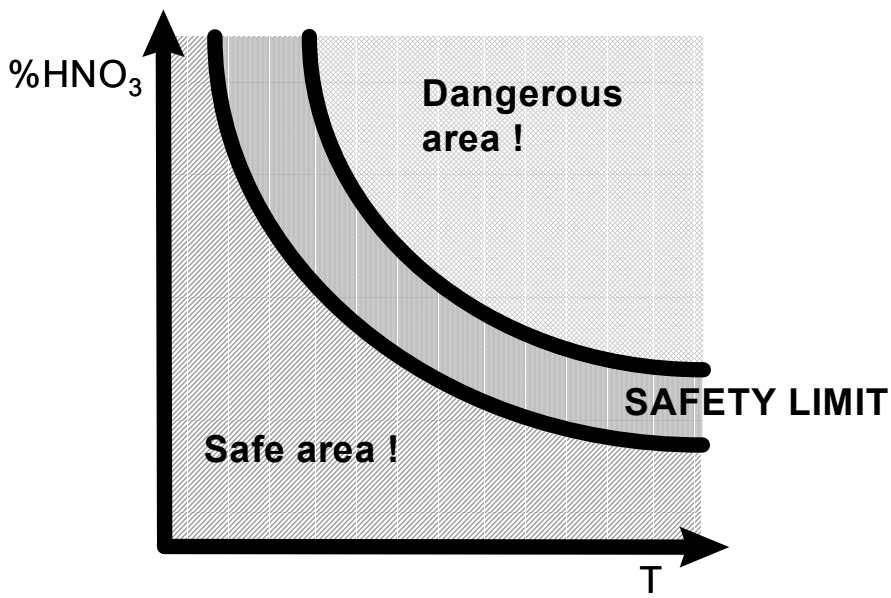
$$NH_4NO_3 \rightarrow N_2 + 2H_2O(g) + ½O_2 \quad [\Delta H = -1460 \text{ kJ/kg}] \qquad (1)$$

Further, by repeating this measurement at several temperatures one may calculate the temperature dependency of the reaction rate coefficient according to the Arrhenius equation (2). This will enable the modelling and simulation of the decomposition reaction as a function of temperature.

$$k = A \cdot EXP[-E_a/(R \cdot T)] \qquad (2)$$

Based on one hand on the measured T_{onset} value and on the other hand on the measured and/or simulated gas and heat production values one has a good basis for defining the safe operation conditions for the plant scale process. This is schematically demonstrated in Figure 2 for a fertilizer process system where the decomposition reaction is affected by the temperature and free nitric acid content (pH effect).

Figure 2 - The effect of temperature and free nitric acid content (pH) on the thermal safety of a typical fertilizer process



In the following, the applicability of DSC and pressure reactor measurements in the thermal safety screening of fertilizer processes is demonstrated through some related case experiments.

CASE EXPERIMENTS

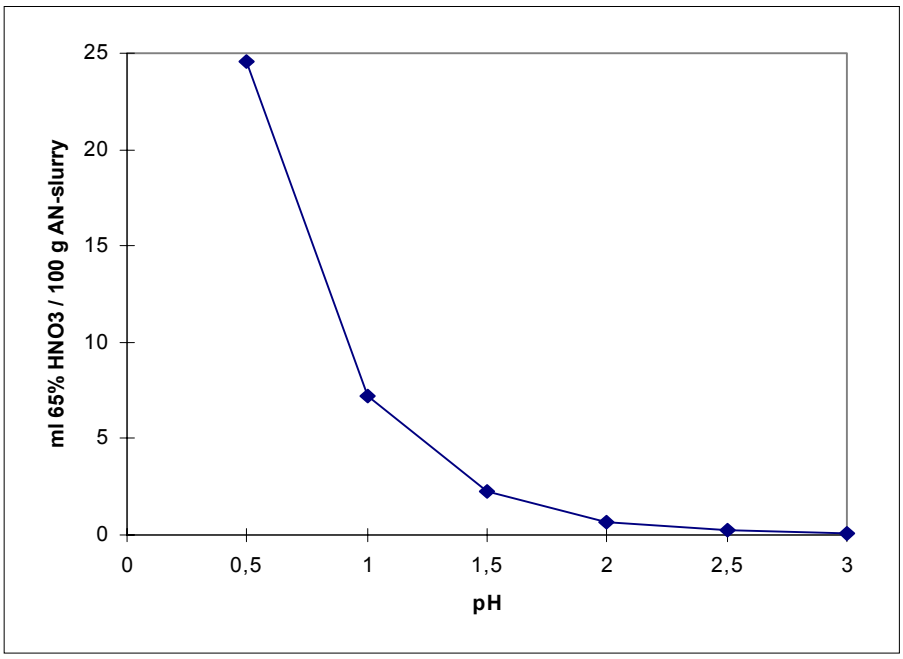
1. Thermal decomposition of ammonium nitrate

Ammonium nitrate (NH_4NO_3) is a fertilizer component known to have explosive properties. In addition, other fertilizer components may even increase the heat released from detonation of ammonium nitrate containing mixtures [8]. In the present case the sensitising effect of pH and chlorine on the thermal stability of ammonium nitrate was studied both by DSC and the pressure reactor method in order to understand better the relative effects.

In order to make the handling (mixing) of the starting material easier especially in the pressure reactor tests 10 wt-% water was always added to the sample before the measurement. In the DSC measurements carried out this water addition has not been found to have any significant effect on the thermal stability parameters of ammonium nitrate (*e.g.* T_{onset}, or the temperature at DSC peak maximum, T_{peak}). A similar procedure has also been applied to the other case experiments reported in the present paper.

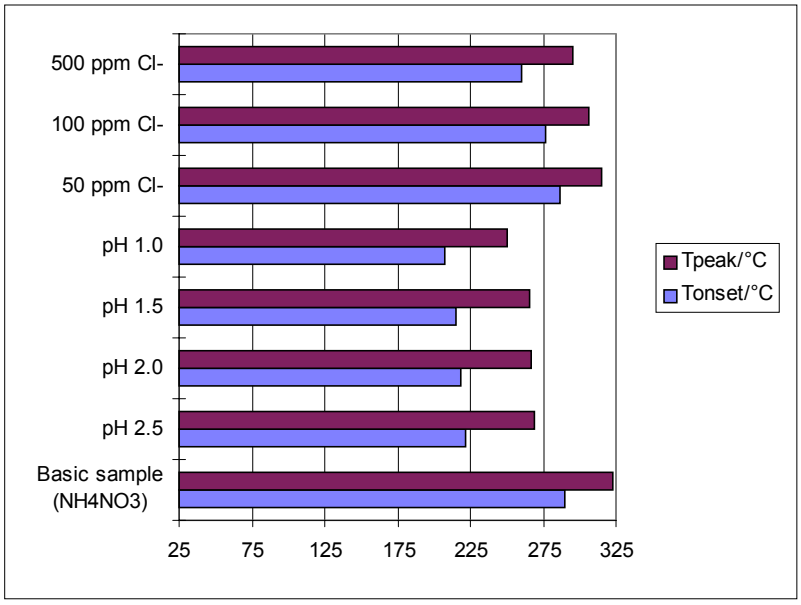
Before the effect of pH on the thermal stability of ammonium nitrate can be studied by DSC the effect of nitric acid addition on its pH has to be determined. Following the usual procedure the pH measurements were carried out from a 10 wt-% water solution. The results are shown in Figure 3 calculated as ml 65% HNO_3 per 100 g of ammonium nitrate slurry (including 10 wt-% water). As can be seen from the Figure the amount of nitric acid required increases strongly at pH values below 2.

Figure 3 - The effect of HNO_3 addition on the pH of ammonium nitrate slurry



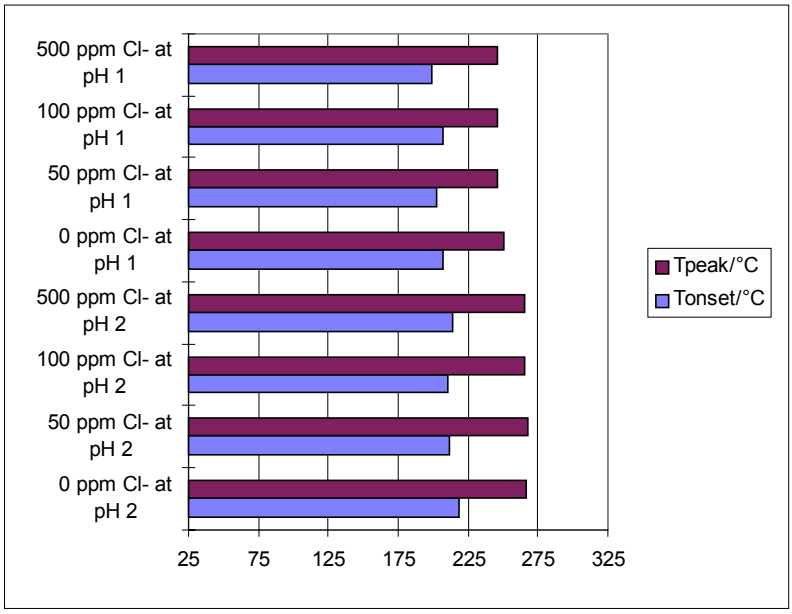
The DSC measurements (T_{onset} and T_{peak}) were carried out at pH values 1.0, 1.5, 2.0, 2.5, and without HNO_3 addition. The additions of chlorine as NH_4Cl were 0, 50, 100, or 500 ppm calculated as Cl^-. As can be seen from Figure 4 the initial effect of pH at 2.5 on both T_{onset} and T_{peak} is quite dramatic while the further decrease of pH value has only a minor effect. On the other hand, the effect of Cl^- on the thermal stability of the basic sample increases with increasing Cl^- content although it with the used Cl^- concentrations is clearly less than the effect of low pH.

Figure 4 - The effect of pH and Cl^- on the thermal stability of ammonium nitrate slurry



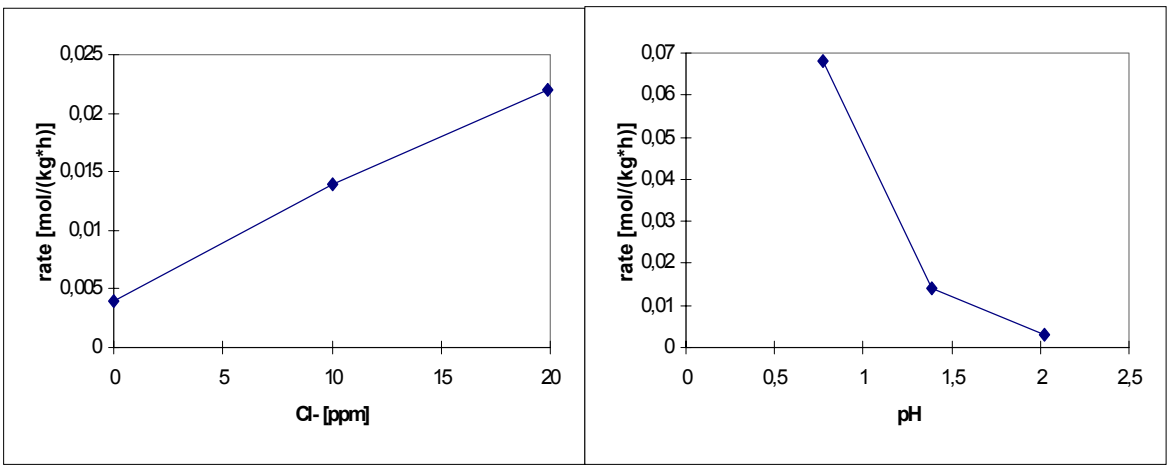
The effect of Cl^- addition under low pH conditions is different. As can be seen from Figure 5 the Cl^- containing samples at pH 2.0 and 1.0 seem to give a slightly lower T_{onset} than the samples without added Cl^- (the Cl^- content of the ammonium nitrate was <5 ppm) but the increase of the Cl^- content does not have any significant effect. This might be interpreted to indicate a synergistic effect caused already by relative low amounts of Cl^- under low pH conditions.

Figure 5 - The effect of Cl^- on the thermal stability of ammonium nitrate slurry at low pH



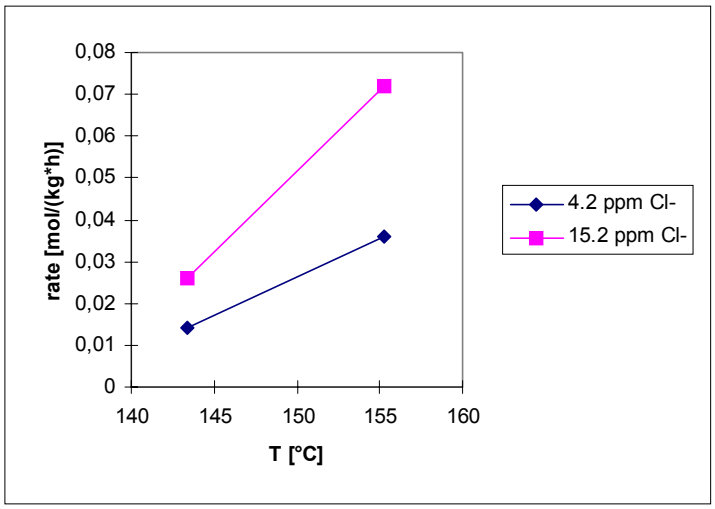
The pressure reactor experiments were used to get more information about the synergistic effect of pH and Cl^- concentration on the decomposition rate of ammonium nitrate. As can be seen from Figure 6 the decomposition rate (measured as gas formation) at a constant temperature and pH increases almost linearly with increasing Cl^- concentration (0..20 ppm) while the decrease in pH at a constant temperature and Cl^- content leads to an exponential increase in the decomposition rate.

Figure 6 - The effect of Cl^- concentration (at pH 1.4) and pH (with 10 ppm Cl^-) on the thermal decomposition rate (measured as gas formation) of ammonium nitrate at 149.5°C



The effect of Cl^- concentration at a constant pH on the thermal decomposition rate of ammonium nitrate as a function of temperature is shown in Figure 7. As can be seen from the Figure even small changes in the Cl^- content have a significant effect on the decomposition rate. This means that the pressure reactor results are needed in order to evaluate the actual consequences of the decomposition of ammonium nitrate under process conditions even though the T_{onset} values measured by the DSC as such are enough to indicate the thermal risk probability.

Figure 7 - The effect of Cl^- concentration and temperature on the thermal decomposition rate (measured as gas formation) of ammonium nitrate at pH 1.04



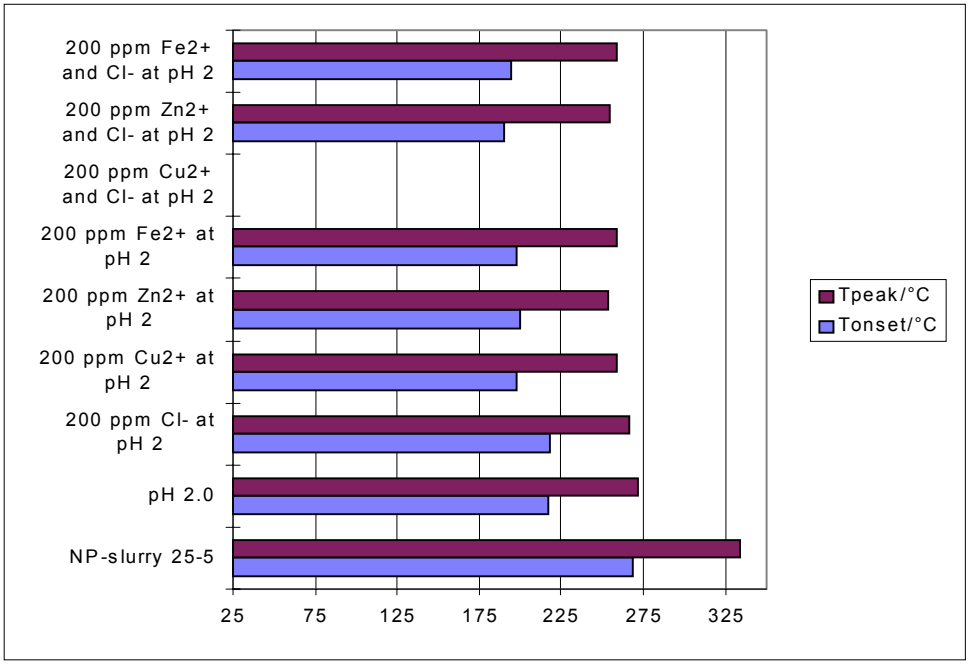
2. Thermal decomposition of a NP slurry

In this case the starting material was a bench scale batch of a NP model slurry corresponding the composition of the first ammoniation stage of a plant formulation (25-5-5). The sensitising effects of pH and some trace elements on the thermal stability of the slurry were studied by using mainly DSC. The main target was to find out the major synergistic effects.

The DSC measurements (T_{onset} and T_{peak}) were carried out as such and at pH 2.0. Without HNO_3 addition the pH of the sample was about 3.2. The additions of chlorine as well as copper, zinc, or iron were either 0 or 200 ppm calculated on element basis. The initial content of these elements was <5 ppm excluding iron (150 ppm). The addition of Cl^- was as KCl while the metallic trace elements were added as M(II) sulphates.

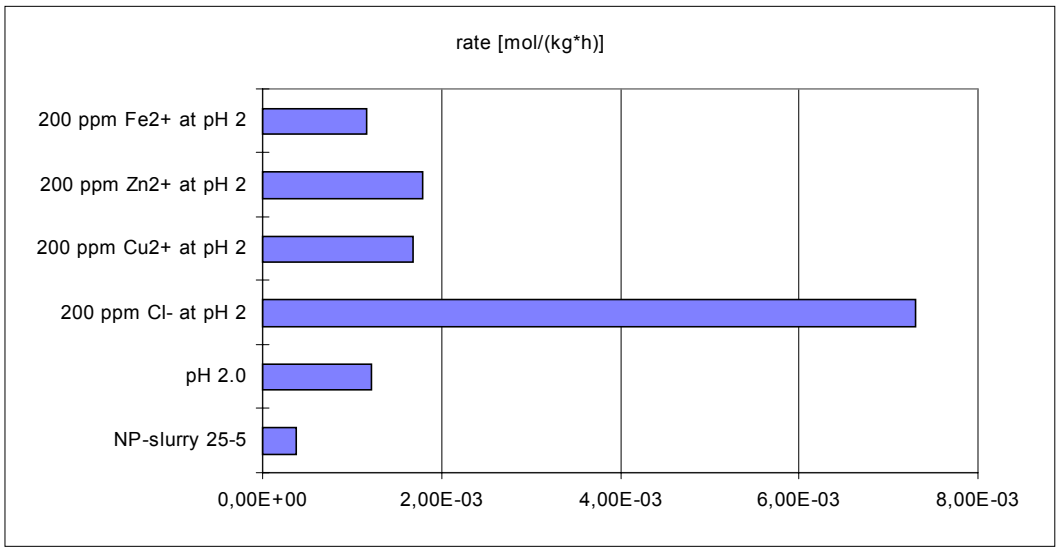
As can be seen from Figure 8 the decrease of the pH has also in this case the major effect on both T_{onset} and T_{peak} values. Correspondingly, the addition of Cl^- at pH 2 does not have any significant additional effect while the addition of the metallic trace elements at pH 2 clearly decreases both the T_{peak} and especially the T_{onset} values. A synergistic effect of Cl^- with Zn^{2+} or Fe^{2+} at pH 2 is also seen in the Figure, and again especially in the T_{onset} value. The corresponding Cl^-/Cu^{2+} results are not included due to repeatability problems. The initial results, however, indicate that the synergistic effect of Cl^- with Cu^{2+} is similar to that of Cl^- with Zn^{2+} or Fe^{2+}. As a conclusion, the DSC results of the present case indicate that all the three metallic trace impurities studied have at low pH and especially in the presence of Cl^- a sensitising (lowering) effect on the initial temperature of thermal decomposition (T_{onset}).

Figure 8 - The effect of pH, Cl^-, and some trace elements on the thermal stability of a NP slurry



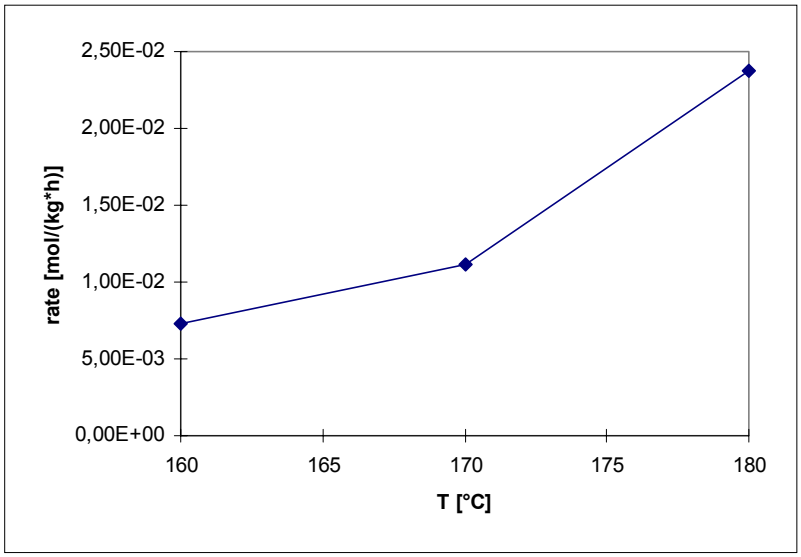
The screening experiments carried out by the pressure reactor method complicate somehow the situation. As can be seen from Figure 9 the addition of 200 ppm Cl^- at 160°C and pH 2.0 increases the thermal decomposition rate of the NP slurry significantly more than the addition of 200 ppm Cu^{2+}, Zn^{2+}, or Fe^{2+} under the same reaction conditions. In this connection it is, however, important to remember that the measured decomposition rates are still very small and they should only be used to indicate the relative differences.

Figure 9 - The effect of pH, Cl^-, and some trace elements on the thermal decomposition rate (measured as gas formation) of a NP slurry at 160°C



The effect of temperature increase on the decomposition rate of the NP slurry in the presence of 200 ppm Cl^- is also significant as shown in Figure 10. As all the experimental temperatures in Figure 10 are lower than the measured T_{onset} value for the corresponding sample this case experiment demonstrates also the well known fact that a decomposition reaction takes place in practice at temperatures significantly under the threshold values measured by the conventional thermoanalytic methods. This fact is also one of the basis for the risk criteria given in Table 1.

Figure 10 - The effect of temperature on the thermal decomposition rate (measured as gas formation) of a NP slurry in the presence of 200 ppm Cl^- at pH 2



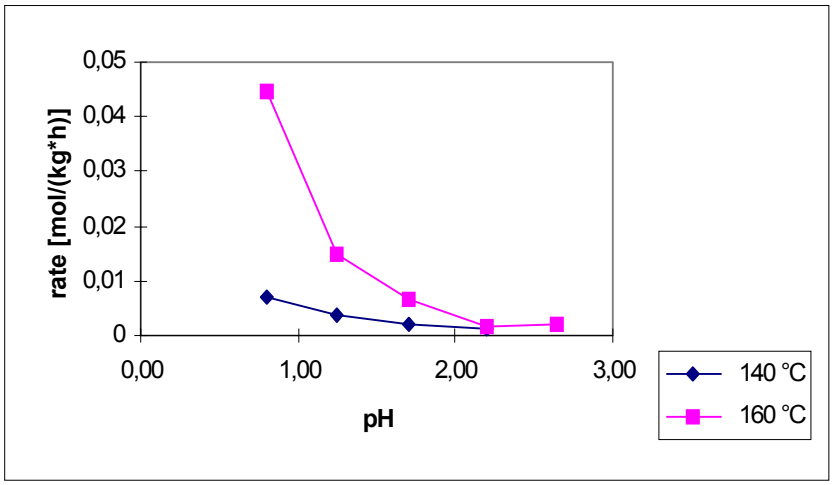
3. Thermal decomposition of a FINN CAN slurry

FINN CAN is a N fertilizer (26-0-1) containing some potassium which originates from an included mineral component. In this case the thermal stability of FINN CAN slurry samples taken from the first ammoniation reactor was studied by the pressure reactor method against several parameters suspected to decrease the stability of the slurry under process conditions. The target was to develop a model for the thermal decomposition which would cover at least the effect of temperature and pH. In addition to these, the chlorine content was also used as an experimental variable. The results given in the present case are a combination of experiments carried out with samples from two separate plants. This means that in principle also the sample origin is a variable having an effect on the results.

The DSC measurements carried out gave the T_{onset} values of 270, 197, and 193°C for the FINN CAN slurry as such, at pH 1.0, and 0.5, correspondingly. The normal process temperature is about 140°C the maximum being about 150°C. According to Table 1 this means a low risk level under normal process conditions and a high risk level under low pH conditions.

An example of the pressure reactor measurements has already been given in Figure 1 describing the decomposition rate as a function of temperature. Correspondingly, the effect of pH and temperature on the decomposition rate (measured as gas formation) of the FINN CAN slurry is given in Figure 11. The measured decomposition rate at 180°C and pH 1.25 not shown in the Figure was remarkably higher [8.84E-02 mol gas/(kg·h)] as those at lower temperatures and at the same pH.

Figure 11 - The effect of pH and temperature on the thermal decomposition rate (measured as gas formation) of a FINN CAN slurry



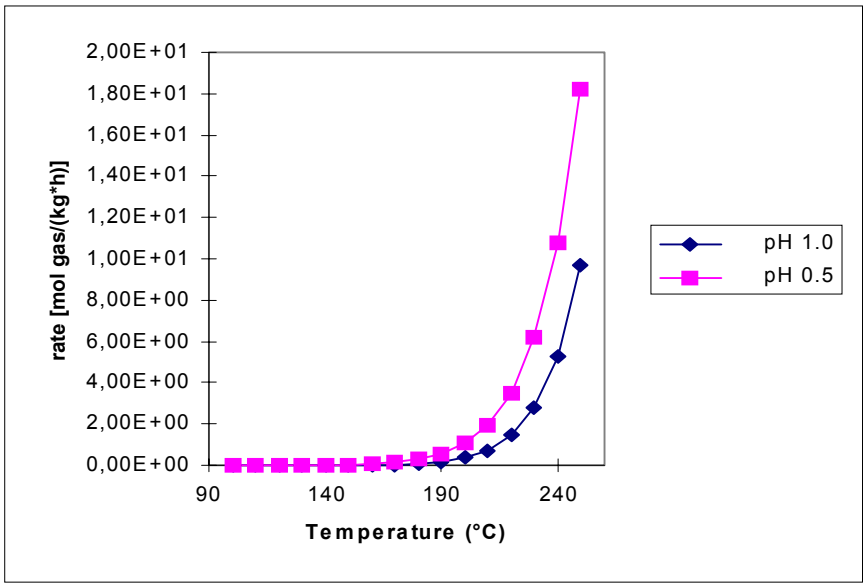
As a conclusion, the studied FINN CAN slurry from the first ammoniation reactor can as such be regarded in practice as thermally stable under normal process conditions (T_{onset} is over 250°C). Under low pH conditions there is, however, a clear decomposition reaction which produces gaseous compounds. By assuming zero order decomposition kinetics this could be modelled for the gas production (moles gas / kg FINN CAN slurry in 1 hour) according to equation (1) as follows:

pH 1.0 $$\text{rate[mol gas/(kg·h)]} = 3.637 \cdot 10^{14} \cdot \text{EXP}[-16349/T(K)] \quad (3)$$

pH 0.5 $$\text{rate[mol gas/(kg·h)]} = 9.857 \cdot 10^{12} \cdot \text{EXP}[-14129/T(K)] \quad (4)$$

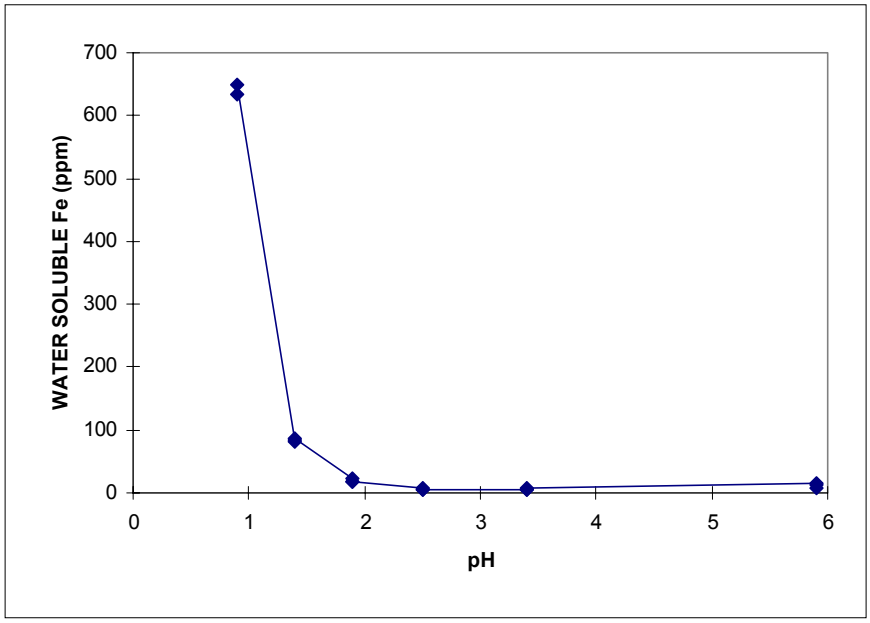
The gas production rate as a function of temperature based on these equations is given in Figure 12. It shows that at pH 0.5 the gas production begins to be noticeable [>0.1 mol/(kg·h)] at temperatures above about 170°C and at pH 1.0 at about 190°C. When compared to the process temperature range (about 140..150°C) these temperatures are clearly higher.

Figure 12 - The gas production rate from a FINN CAN slurry as a function of pH and temperature



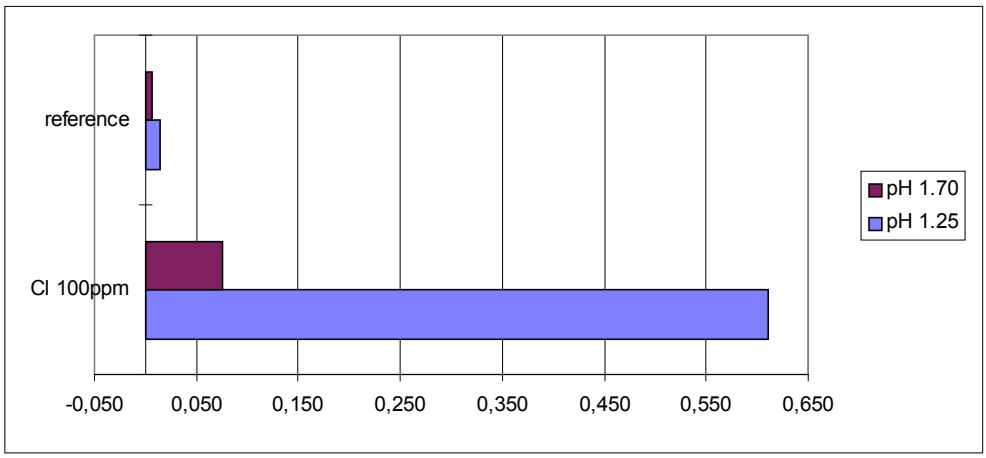
An interesting pH effect was found from the chemical analyses which may have an additional effect on the observed increase in the decomposition rate at low pH values. As shown in Figure 13 the amount of the water soluble iron in the FINN CAN slurry increases significantly below pH 2.

Figure 13 - The effect of pH on the concentration of water soluble iron in a FINN CAN slurry at room temperature



The effect of chlorine was studied at 160°C by adding 100 ppm Cl^- as NH_4Cl at two pH levels. The results compared with decomposition rates without Cl^- addition under the same reaction conditions are shown in Figure 14. The significant effect of Cl^- especially at the lower pH level is clearly seen.

Figure 14 - The effect of Cl^- addition on the thermal decomposition rate [mol gas/(kg·h)] of a FINN CAN slurry at 160°C



The experimental data was further used for a regression model to correlate the decomposition rate of the FINN CAN slurry with pH and T. The data from the Cl^- experiments could not be included into the model. The semi-empirical model describing the experimental data (gas production) satisfactorily was as follows:

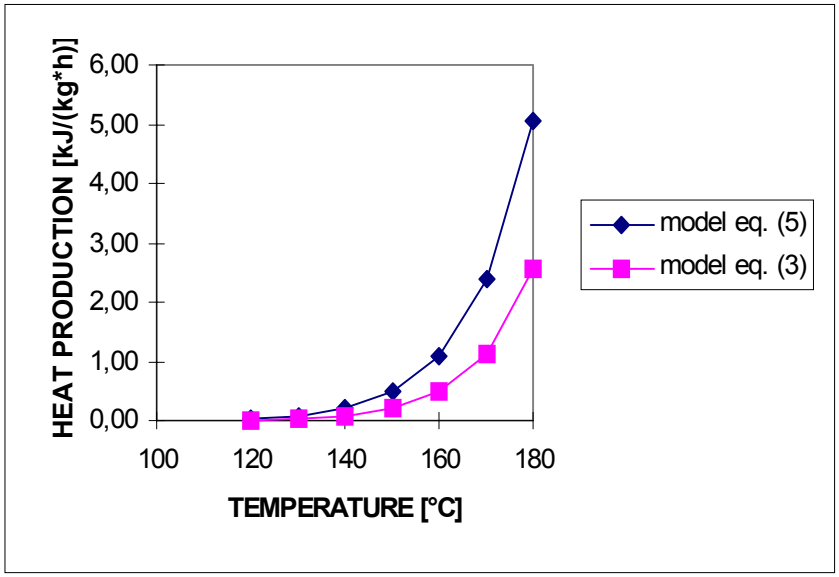
$$\ln(\text{rate}[\text{mol gas}/(\text{kg}\cdot\text{h})]) = b_0 + b_1\cdot pH + b_2/T[K] + b_3\cdot pH/T[K] \qquad (5)$$

where $b_0 = 44$
$b_1 = -13$
$b_2 = -19700$
$b_3 = 4800$

The fit (R^2) of the model is 0.99, the prediction capability (Q^2) is 0.95 and the standard error is about ±12 %. As the model is an empirical regression model one should, however, remember that it should not be extrapolated outside the experimental area (pH ≈ 0.5..3.0, T ≈ 120..180°C). For example, a combination of high temperature and low pH calculated by the model tends to give a lower decomposition rate than the experimental one is. This may at least partly be due to the remarkable increase in the concentration of the water soluble Fe at low pH values (Figure 13). In general, this also means that for a proper mechanistic model of the thermal decomposition of the FINN CAN slurry a lot more parameters than only pH and T are needed.

In order to demonstrate the applicability of the model equation (5) it was used to calculate the heat production of the thermal decomposition of the FINN CAN slurry as a function of temperature at pH 1.0 on the basis of the reaction enthalpy given in equation (1). The results are shown in Figure 15 together with corresponding results calculated by the pH 1.0 model equation (3). The difference between the results based on these two model equations can at least partly be explained by the sample origin.

Figure 15 - Heat produced by the thermal decomposition of a FINN CAN slurry as a function of temperature at pH 1.0 calculated on the basis of the rate model equations (3) and (5)



The heat production shown in Figure 15 is still quite moderate even at 180°C, about 1.4 W/kg slurry based on equation (5). It is, however, important to remember that the presence of extra Cl^- may dramatically increase the thermal decomposition rate as shown in Figure 14.

CONCLUSIONS

There are, of course, some practical problems when the above described DSC and pressure reactor measurements are used in the thermal safety screening of fertilizer products and processes. First of all, the small sample size used in DSC measurements (1 to 10 mg) may have an effect on the reliability of the results especially when the samples are not totally homogeneous. With repeated measurements by using separate samples we have, however, found that the repeatability can easily be kept within ±3°C which for screening purposes may be regarded as acceptable. The differences between DSC instruments (especially the principle of measurement and temperature calibration) may also have an effect on the results which means that the comparison of results from different sources may be misleading.

The DSC crucible material is an important topic. A stainless steel crucible would be the best one to represent the actual reactor material. Due to the small sample amounts used the wall effects are, however, especially under low pH conditions (steel reacting with nitric acid!) so significant that all the other effects are masked. Hence, we highly recommend the use of gold plated crucibles which also have the benefit that they may be used at higher temperatures (>250°C) without any leakage problems.

In the interpretation of the simulation results based on pressure reactor measurements an important topic is the characteristic performance of the actual process. In setting the safety limits one has to have a realistic understanding about how much gas and/or heat formation can be tolerated under normal operation. This also defines how the measured T_{onset} values are rated in regard to the process safety limits. In addition, when studying the effects of trace elements a good knowledge base about the normal variation in the process is needed.

In spite of the limitations mentioned above it can be concluded that DSC combined on need basis with the use of a pressure reactor measurement forms a rapid and simple screening method which for the DSC part can be used even at site in order to increase the fertilizer process safety.

SYMBOLS

A	**Arrhenius frequency factor (mol/(kg·h))**
bp	**Boiling point (K)** of the reaction mass
c_p	**Heat capacity (kJ/(kg·K))** of the reaction mass
E_a	**Activation energy (kJ/mol)**
ΔH	**Heat of reaction (kJ/kg)** of the reaction mass
k	**Reaction rate coefficient (mol/(kg·h))**
R	**Gas constant (8.314 J/(mol·K))**
T	**Temperature (K)**
ΔTad	**Adiabatic temperature rise (K)** resulting from the release of the energy potential of the decomposition reaction. This is simply calculated from $\Delta H/c_p$ for the measured decomposition reaction.
T_{max}	**Maximum temperature of the reaction (K).** In the initial screening procedure, this should be taken as either the process temperature T_p plus the adiabatic temperature rise of the desired reaction i.e. $T_{max} = T_p + \Delta H/c_p$ or the maximum temperature of the heating medium, which ever is the greater.
T_{onset}	**Onset temperature of decomposition reaction (K)** at which the exothermic activity is first detected.
T_p	**Process operating temperature (K)** under normal conditions
T_{peak}	**Temperature at DSC peak maximum (K)**
TMRad	**Time to Maximum Rate under adiabatic conditions (h).** This gives an indication of the time available, at a particular temperature, to take corrective actions.

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