



## The mechanism of the spontaneous detonation of ammonium nitrate in reactive grounds

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### ABSTRACT

The mechanism of the decomposition of ammonium nitrate fuel oil (ANFO) and of ammonium nitrate (AN) emulsions has been investigated. The formation of NO gas bubbles at the end of an induction period was observed, which led to the evolution of brown NO<sub>2</sub> gas on contact with air. Inhibition of the decomposition reaction could be achieved by reducing the NO concentration in the gas phase, with inhibitors not in physical contact with the reaction mixture. NO adsorbing clay minerals (hydrotalcite) were effective inhibitors, indicating multiple mechanisms of inhibition. A central role is assigned to nitrous acid (HNO<sub>2</sub>): sequestering NO prevents its formation, base inhibitors keep it in the non-reactive form of the nitrite ion (pK<sub>a</sub> of HNO<sub>2</sub> ~ 3), and urea in acidic conditions decomposes it to harmless N<sub>2</sub>. Our results have implications in industries where NO<sub>x</sub> emissions can cause significant environmental problems for both aquatic and marine life as well as for human health.

### 1. Introduction

Ammonium nitrate, or AN (NH<sub>4</sub>NO<sub>3</sub>), is the basis of most explosives used in the mining industry. Its detonation usually must be deliberately initiated, but there have been a number of instances when it has spontaneously exploded, at great risk to life and property. One of the causes has been identified as the presence of pyrite (Fe<sup>II</sup>S<sub>2</sub>) in contact with the explosive. Another is the presence of naturally high temperatures in the ore body, from some geothermal source. These causes are termed ‘reactive ground’ and ‘hot ground’, respectively [1].

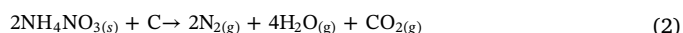
The explosives industry has developed emulsion explosives due to their superior water-resistance, and low environmental impact [2,3] over traditional explosives. However, when sulfide ores are present, or in hot grounds, inhibited emulsion explosives must be used to prevent premature detonation of the explosive. The explosives industry achieve this by the addition of urea, to extend the ‘sleep time’ of the product—the quiescent time between contact with the reactive ground and the exothermic process that leads to detonation [4,5]. The role of urea as an inhibitor was the original subject of this research. The work led to a new, alternative understanding of the mechanism of the spontaneous, and of the inhibited, decomposition reactions.

#### 1.1. Chemistry background

Ammonium nitrate decomposes in an exothermic reaction ( $\Delta H = -36 \text{ kJ mol}^{-1}$ ) to produce three moles of gaseous products for each mole of solid reactant:



The reaction can be made more exothermic ( $\Delta H = -280 \text{ kJ mol}^{-1}$ ), with more gaseous products, if some oxidisable fuel is added:



Hence, the standard ammonium nitrate explosive mixture is termed ANFO, for an ‘ammonium nitrate fuel oil’ mixture.

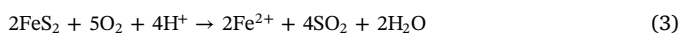
The decomposition temperature of pure ammonium nitrate is 170 °C, but recently Gunawan and Zhang [6] calculated that an intimate mixture of ammonium nitrate and pyrite can decompose at temperatures as low as 50 °C in blast holes more than 0.2 m in diameter. This is consistent with many field observations of detonations at low ambient temperatures. We have analysed the heat flow in these systems elsewhere [7].

The same initial reactions occur in acid mine drainage, which has

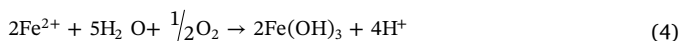
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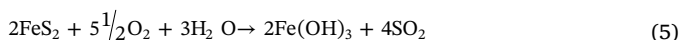
been extensively studied [8,9]. Parallels can be made between the two processes and analogies usefully drawn. Water is required in both cases, implying that soluble species are involved. The first step in the process is the oxidation of pyrite by air. The oxidation product of the sulfur could be various substances, such as  $\text{SO}_2$ ,  $\text{SO}_3$ , thiosulfate, etc. For illustrative purposes we choose  $\text{SO}_2$ , because it is detected as a product in reactive ground environments; however, this choice does not affect the conclusions of the argument. For example, oxygen from the air oxidizes the disulfide anion to  $\text{SO}_2$ :



The Fe(II) is further oxidised to Fe(III), which precipitates as the insoluble hydroxide in near neutral pH solutions.



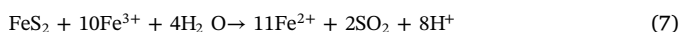
The sum of these two reactions neither consumes nor produces protons,



but the  $\text{SO}_2$  is readily soluble in water to produce sulfurous acid, with  $\text{pK}_{\text{a}1}$  of 2.



Both of the oxidation reactions above are relatively slow, but, as they proceed and the acidity increases, some of the  $\text{Fe}(\text{OH})_3$  begins to dissolve. It turns out that the oxidation of pyrite by Fe(III) is a lot faster than by oxygen [8,10,11].



The process now becomes autocatalytic, as more acid is produced and more Fe(III) dissolves. The rate-limiting step in this inorganic cycle then becomes the oxidation of Fe(II) to Fe(III) by oxygen, but in the field this is accomplished rapidly by bacteria. In mine sites where bacteria are present, pH values can range from 0.7–3.0 [12] and ferric (Fe(III)) concentrations from 1 to 20 g/L [13,14]. Such conditions have been shown to lower the thermal decomposition of ammonium nitrate [15,16].

The thermal profile of the decomposition process comprises three stages: an induction period, an intermediate stage and the final highly exothermic decomposition. (Fig. 1) The reactions described above could explain the observation of the induction period in the thermal decomposition of ammonium nitrate explosives caused by reactive ground. Some preliminary studies have indicated an inverse correlation between initial acidity and the induction time. According to Rumball, acid accelerates the rate of the initial stage and has little or no effect on the intermediate stage [17]. The initial stage of the process is

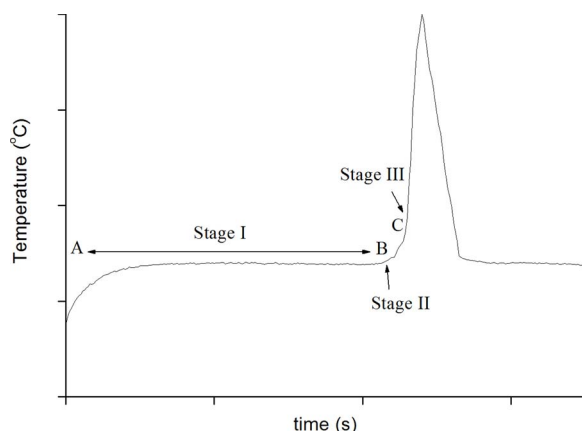
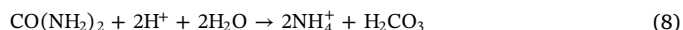


Fig. 1. Typical temperature versus time trace for reaction between pyritic black shale and AN. A-B is the initial stage (the induction stage or Stage I), B-C is the intermediate stage, or Stage II. Ignition stage starts at C (Stage III). After Rumball (1991) [17].

interpreted as the slow reduction in pH until the rapid and exothermic oxidation by Fe(III) accelerates.

The preferred method of controlling both acid mine drainage and reactive ground has been to maintain a high pH through the use of alkaline substances. The use of solid bases, such as limestone, is not effective, however, as the Fe(III) precipitates on the surface and passivates the remaining solid base, a process termed ‘armoring’, rendering it ineffective.

Accordingly, the use of urea is preferred, which homogeneously generates the weak bases ammonia and carbonate by hydrolysis, and hence consumes protons (Eq. (8))



There is compelling empirical evidence in the industry that urea is an effective inhibitor of the thermal decomposition of AN in reactive ground. The mechanism of this inhibition is uncertain. The hydrolysis of urea is known to be a slow reaction, which proceeds at a rate that is independent of pH [18]. The length of the induction period could be limited by the total consumption of the urea. Alternatively, if the rate of acid generation is greater than the rate of urea hydrolysis, then the pH of the system could slowly drop, despite the partial neutralisation by the urea hydrolysis, until it reaches an acidic condition that allows an autocatalytic runaway decomposition. Finally, the urea could act as an inhibitor by a mechanism not involving its acid-base chemistry. This third alternative is in fact our preferred explanation from the evidence we have accumulated.

## 2. Experimental

### 2.1. Materials

Several sources of pyrite were used. RG1 was supplied by Dyno Nobel and is a reactive grade ground sample containing ~2.50% by weight of adsorbed water, and a pyrite content of less than 10 wt%. The remaining material is a mixture of clays, quartz and organic matter. The particle size is less than 50  $\mu\text{m}$  on average. Pure pyrite (PY) was obtained from Spectrum Chemicals and is 100% oxidized pyrite with a grain size of 200–400  $\mu\text{m}$ .

Ammonium nitrate, AN, (Acros Organics, 99 + %) was used as received but was ground in a mortar prior to use to break up any large clumps. Dodecane (Sigma,  $\geq 99\%$ ), iron (II) sulfate 7 hydrate (BDH, > 99.5%), iron (III) sulfate 5 hydrate (Fluka), urea (Ajax chemicals, 99.5%), hydrazinium sulfate (Ajax chemicals, > 99.5%), zinc oxide (Aldrich, 99.9%, < 1  $\mu\text{m}$ ), kaolin (Kaolin Australia, Pty Ltd, Eckafine BDF), hydrotalcite (Sigma) and Basolite C300 (BASF) were used as received. Sodium nitrite (Mallinckrodt), diacetyl monoxime, DCM (Fluka), thiosemicarbazide, TSC (BDH), phosphoric acid (85%, Ajax Finechem Pty. Ltd), sulfuric acid (96%, Ajax Finechem Pty. Ltd), iron (III) chloride 6 hydrate (Merck), and PIBSA-DEEA (Clariant) were also used as received.

### 2.2. Urea determination

Urea was determined by UV-vis spectroscopy at a wavelength of 525 nm using diacetyl monoxime, DCM and thiosemicarbazide, TSC [19]. An acidic ferric solution was made containing phosphoric acid (100 ml), sulfuric acid (300 ml), water (600 ml) and ferric chloride (0.10 g). DCM and TSC were mixed (0.50:0.01 g) and made to volume (100 ml). When ready to use, the chromogenic reagent containing the acid solution (2 parts) and DCM/TSC solution (1 part) were mixed. Urea stock solutions were prepared containing ~ 20 ppm urea.

Standard urea solutions were prepared by diluting stock urea solutions in water. The urea solution (0.32 ml) was mixed with the chromogenic solution to 10 ml, covered with aluminum foil and heated in boiling water for 10 min. The sample was cooled rapidly in ice and the UV-vis spectrum was measured from 400 to 600 nm.

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