Research paper

Downgrading of detonation properties of ammonium nitrate using calcium carbonate, dolomite, and fly ash

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Abstract

A process has been developed for minimizing the detonation hazard of ammonium nitrate that is used as a chemical fertilizer, by adding calcium carbonate, dolomite, and fly ash. The detonation enthalpies and velocities of the obtained ammonium nitrate derivates were measured, revealing their suitability for application in fertilizer production. These results showed that, for a pure ammonium nitrate solution, coating with 0−20 wt% fly ash and adding a maximum of 25 wt% limestone and dolomite would eliminate the detonation problem associated with ammonium nitrate. It was also revealed that chemicals such as lead azide, lead styphnate, and mercury fulminate, which normally increase the detonation velocity of ammonium nitrate, did not do so when it contains $CaCO_3$ (12.5%), $CaMg(CO_3)_2$ (7.5%), or fly ash (0−20%). Even with the addition of lead salts and mercury fulminate, the detonation velocity of calcium ammonium nitrate continues to decrease. Thus, the detonation hazard of calcium ammonium nitrate can be mitigated.

Keywords: ammonium nitrate, calcium carbonate, dolomite, fly ash, detonation

1. Introduction

Ammonium nitrate (AN) is widely recognized as an important fertilizer. Increasing consumer demands have further stimulated the production of AN as well as the modification of various properties of this compound. However, AN is inexpensive and readily available, and can be easily triggered to undergo explosion; hence, there is an increased concern regarding the possible misuse of this compound as an explosive for terrorist activities. For this reason, the governments of many countries have imposed strict limitations on the industrial-scale production and the use of AN, leading to consumer demand for fertilizer not being satisfied. This has also led to the increased cost of AN-based fertilizers, thus limiting their use in agriculture.

Several formulations and processes aimed at suppressing the detonation probability of AN have been proposed by the past researchers[1]. Although various chemical compositions have been designed and applied to degrade the detonation properties of this compound, they are not intended to satisfy consumer requirements. In another study, Taulbee et al.[2] developed a method to reduce the detonation enthalpy of ammonium nitrate. In

this method, various fly ash compounds were used to decrease detonation enthalpy and they have concluded that such a measure decreases the detonation enthalpy of ammonium nitrate[2]. Resende et al. studied the detonation properties of mixture of ammonium nitrate and various materials such as biodiesel and sugar cane and they have found that the detonation velocities of these mixtures had been mitigated[3]. They also replaced the fuel oil in commercial ammonium nitrate/fuel oil (ANFO), which is a widely used bulk industrial explosive, with rice straw, corn cob, sugarcane bagasse, and biodiesel[3].

Zygmunt and Buczkowski studied the explosive properties of ammonium nitrate with ANFO[4]. According to this study, the porous structure of ammonium nitrate has a significant influence on the detonation properties of ANFO explosives. As the porosity of ammonium nitrate increases, the detonation velocity of ANFO increases. Therefore, to limit the detonation sensitivity of ammonium nitrate, the porosity of ammonium nitrate should be decreased. To better understand these properties, they investigated the oil adsorption capacity of the porous structure of ammonium nitrate[4]. In another study,

Buczkowski and Zygmunt attempted to suppress the detonation probability of AN by diluting it with different concentrations of dolomite[5]. Experiments show that even mixtures of milled fertilizers containing 40% dolomite and aluminum can detonate[5]. Bohanek et al.[6] studied the detonation properties of ANFO explosives using penthrite. They reported that detonation velocity decreases with an increase in penthrite[6].

On the other hand, to measure the detonation velocity, a different method was developed by Miyake et al.[7]. In their study, the detonation velocity of an ANFO mixture was measured using JIS G3454 steel tube. This tube had a 35.5 mm inner diameter, a 42.7 mm outer diameter and it was 400 mm in length. The ANFO was detonated in this tube and the detonation velocity was recorded[7]. They prepared ANFO samples using the same AN pore diameter and pore volume and found that the detonation velocity (3.85 km s^{-1}) was the highest for those particles with the smallest diameter (< 0.85 mm). After aging for 12 months, the ANFO detonation velocities decreased, suggesting that the ANFO reaction was influenced by the physical and chemical properties of the AN particles and oil during storage.

Another study on reducing the detonation enthalpy and velocity of ammonium nitrate was performed by Adamo et al.[8]. In that study, calorimetric experiments were performed and during the ammonium nitrate degradation, role of water was investigated as the degradation progressed. In addition, the possibility of the reaction between ammonium nitrate and the sodium salt of dichloroisocyanuric acid as a rate-limiting step was investigated. In another study that measured the detonation velocities of ammonium nitrate mixtures, Van der Steen et al.[9] measured those of non-ideal, low-density ammonium nitrate by using tubes with different diameters and wall thicknesses. Also, they determined that the tube diameter has a much greater effect on the detonation velocity than the confinement[9]. The interferometer acted on those elements resulting in the failure of the detonation velocity testing procedure[10]. In another ammonium nitrate detonation study, in order to understand the detonation mechanism of ammonium nitrate with the ultimate aim of prevention, Na_2SO_4 in KCl aqueous solutions were studied. The study attempted to prevent the thermal decomposition of the ammonium nitrate[11]. In another study, Taulbee set out to reduce the explosive potential of ammonium nitrate by applying a mixture of urea and ammonium nitrate[12]. The surface of the ammonium nitrate was coated with gypsum, calcium sulfate hemi-hydrate, calcium carbonate, calcium nitrate, soda lime, potassium sulfate, magnesium sulfate, bentonite, silica gel, potassium phosphate, potassium nitrate, potassium chloride, sodium sulfate, ammonium sulfate, sodium silicate, dolomite, anhydrite, sulfur, polyurethane, isobutylidine diurea, ureaform, methylene ureas, and urea-formaldehyde polymers[12]. In that study, 20% of urea to ammonium nitrate solution and 0.1% of other above-mentioned compounds were added onto the ammonium nitrate particles through a coating process. For this case, it was observed that a decrease in water absorption by ammonium nitrate particles was prevented thereby reducing physical contact between the ammonium nitrate particles and ultimately resulting in a reduction in the detonation potential[12]. Ledoux and De Moor prepared an ammonium nitrate mixture in which the explosive material contained urea calcium nitrate (UCaN), urea magnesium nitrate (UMgN), urea calcium phosphate (UCaP), urea magnesium phosphate (UMgP), urea superphosphate (USP) and mixtures thereof to minimize the detonation capacity[13]. As a result, they were able to limit detonation energy of the ammonium nitrate. Their study provided an important insight into understanding the detonation properties of ammonium nitrate with other explosive materials. Gezerman and Çorbacıoǧlu studied means of minimizing the antisocial use of ammonium nitrate by mixing it with dolomite and calcium carbonate, and also coating it with fly ash (10−50%). They successfully maintained the nitrogen concentration (26%) in the ammonium nitrate fertilizer while simultaneously mitigating the detonation velocity[14]. Gezerman, in another study, increased the concentration of the fly ash (max 20%) and combined dolomite and calcium carbonate with ammonium nitrate[15]. Detonation tests on ammonium nitrate were conducted using the Dautriche method, revealing that the detonation velocity was reduced[15].

Chaturvedi and Dave proposed reaction mechanisms occurring during the detonation of ammonium nitrate[16]. During the detonation reaction, the temperature increased to 230 °C and nitrogen oxides, such as NO and NO_2, were created as thermal decomposition products[16]. Several studies have addressed the limiting effects of different materials such as Al powders on the detonation properties of ammonium nitrate[5]. One such study found that the addition of a 30% concentration of aluminum powder (with a particle size of 6 μm) to an ammonium nitrate solution decreased the detonation energy dramatically[5]. Leong et al.[17] presented a patented method for preventing CAN fertilizer from being used as a precursor for explosives, e.g., for terrorist attacks. The CAN fertilizer was reacted with an organic polymer, producing a hydrogel that does allow the fertilizer to detonate. They used an organic polymer mixture of polyethylene glycol (PEG), hydroxyethyl cellulose (HEC), carboxymethyl cellulose (CMC) and cellulose gum for this process. Cranney et al.[18] produced non-detonable AN prills using surfactants such as non-polymeric polyisobutylonene succinic anhydride (PIBSA)-based polymeric emulsifiers, which react with the kaolin used to coat the surface of the AN (to suppress oxidation), thus decreasing the heat of detonation of the CAN. In another study examining the detonation, NaCl was added to the ammonium nitrate solution, and with the different mixing methods (15 wt% NaCl was added for solution mixing, and 35 wt% NaCl was added for mechanical mixing). However, when 40% NaCl was added, exothermic peaks were observed at even higher temperatures, i.e. 307.39 °C and 309.80 °C for solution mixing and mechanical mixing, respectively[19]. Detonation tests were performed using two methods, namely, the
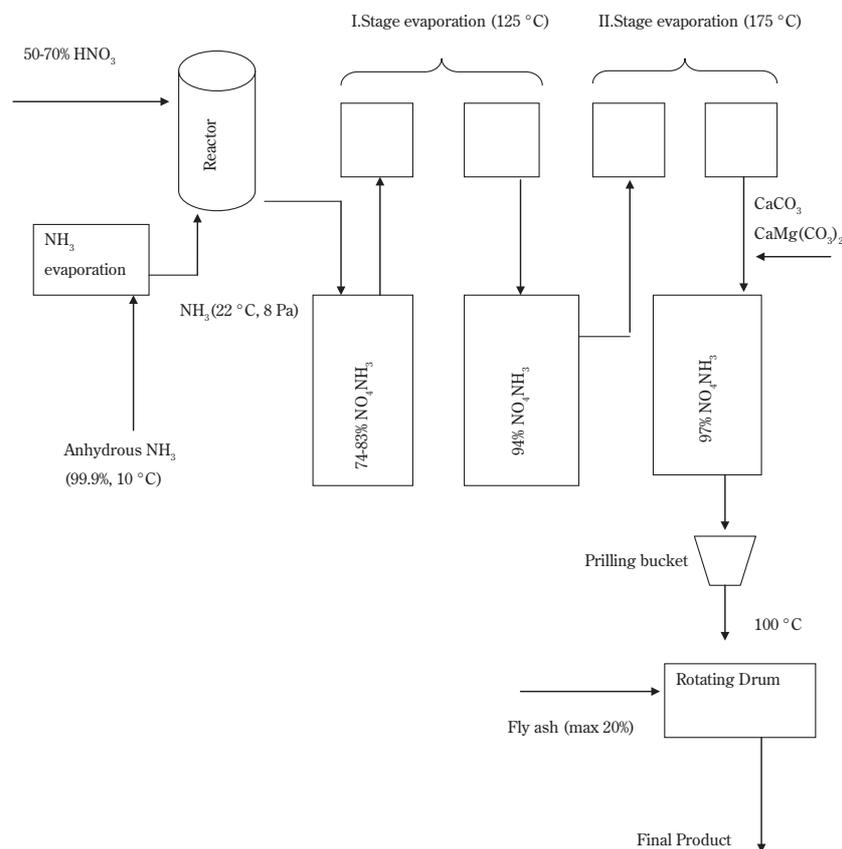
Figure 1   Fertilizer manufacturing process involving two evaporation stages.

Koenen and UN gap tests. Ammonium nitrate concentrations of 15−40% were investigated; for contents > 25%, the AN/ANFO mixture detonated[19]. In the patent of Highsmith et al. regarding the reduction of the detonation properties of ammonium nitrate, it is noted that 5−10% of additives, such as ammonium phosphates or ammonium sulfate, can desensitize ammonium nitrate and render it resistant to flame and detonation[20]. Another study which aimed to minimize the detonation risk presented by ammonium nitrate was performed by Han et al.[21]. Here, the detonation process resulting from the decomposition of ammonium nitrate was studied by investigating the reactions between ammonium nitrate and various additives (such as sodium sulfate and potassium chloride). In addition, the decomposition mechanisms were studied considering parameters such as the onset temperature and pressure. A previous study showed that the presence of sodium sulfate can increase the onset temperature of AN decomposition, thus inhibiting thermal decomposition of AN, while potassium chloride tends to decrease the onset temperature, promoting the thermal decomposition of AN[21]. Boyars[22] showed that the risk of accidental detonation of large masses of commercial AN during handling and storage under normal climatic conditions can be reduced by replacing a given amount of AN with a solid solution of potassium nitrate (0−50 wt%). Another study addressing the detonation properties of ammonium nitrate set out to observe the effect of adding a 50 wt% urea solution to the ammonium nitrate solution to investigate the thermal

decomposition of the ammonium nitrate[23]. Detonation tests in that study were conducted using the Koenen and UN gap tests[23]. In this study, the effect of urea on the thermal stability and detonation properties of ammonium nitrate was investigated. In addition, the thermal decomposition temperature and surface morphology were examined. From the investigations, it is seen that an increase in urea content results in an increase in thermal stability (i.e. resistance to degradation with temperature) of the ammonium nitrate while resulting in a decrease in its thermal sensitivity (i.e. ignition with temperature). It is seen that for 50% urea-ammonium nitrate mixtures, the urea does not reduce the detonation capacity of the ammonium nitrate. Ammonium nitrate that contains 50% urea has a stable detonation capacity[23]. However, the detonation problem was not completely eliminated in any of these studies as none of the proposed additives or strategies were fully effective. Thus, in the present study, it was attempted to decrease the detonation velocity and heat of explosion of AN by adding calcium carbonate, dolomite, and fly ash, which are easy to handle and readily available. Calorimetry analysis was performed to confirm the effectiveness of the aforesaid chemicals in preventing the detonation of AN.

2. Experimental
2.1 Details of AN production for use as a fertilizer
In a typical process, hot (55 °C) 50−70% nitric acid solution and ammonia gas (6 Pa, 10 °C) are mixed to produce AN (Figure 1). Then, calcium carbonate or

Table 1 Experimental vs. calculated heats of explosion of ammonium nitrate mixtures containing $CaCO_3$, dolomite, and fly ash, along with their nitrogen concentrations.

Calcium carbonate [kg $CaCO_3$/ton AN]	Dolomite [kg dolomite/ton AN]	Fly ash [%]	Heat of explosion [kJ kg^{-1}] (Experimental)	Nitrogen concentration [%]	Detonation velocity [m s^{-1}]	Density [kg m^{-3}]
250 (25%)	0	0	1480	26.25	2900	910
175	75	10	540	26.18	1322	905
175	75	20	320	26.12	752	900
125	125	10	270	26.11	503	896
125	125	20	0	26.05	0 (No detonation)	890

dolomite is added to the hot, highly concentrated aqueous solution of AN to obtain the desired composition as per the requirements of the agricultural industry[24]. Among the various methods adopted for suppressing the explosive nature of AN, dilution with calcium carbonate is the most commonly used[24]-[26]. After adding $CaCO_3$ (and/or $CaMg(CO_3)_2$), ammonium nitrate solution is introduced by prilling. Then, various coating materials such as silicon dioxide can be sprayed onto the ammonium nitrate prill surface in a rotating drum[27]. In this study, instead of using kaolin as a coating material, different concentrations (0–20%) of fly ash were sprayed on the surface of the prilled ammonium nitrate in the rotating drum.

CAN containing 26% nitrogen is the most commonly used fertilizer containing AN[28]. To produce CAN with 26% nitrogen, 250 kg of $CaCO_3$ is required per 1000 kg of AN[24]. In the present study, a 50 : 50 ratio mixture of calcium carbonate and dolomite was used so that the nitrogen content of the resulting fertilizer would not be reduced, given that granular products containing ammonium nitrate and either ammonium or calcium sulfate are also manufactured[29]. The amount of fly ash added to the rotating coating drum during prilling was within the range of 10–20 wt% with respect to CAN.

2.2 Analysis of detonation properties

The detonation properties, i.e. the detonation velocity and heat of explosion, of a mixture of AN fertilizer and fuel were calculated. In addition, the detonation velocities of such explosive mixtures were studied by means of the detonation test described in the Recommendations on the Transport of Dangerous Goods[30]. The theoretical energies of detonation and of expansion (Gurney constants of the explosive mixtures[31]) were determined based on the detonation velocity (Table 2).

The detonation test results for various mixtures of AN and calcium carbonate, dolomite, and fly ash are listed in Table 2. In the UN detonation test[30], a steel cylinder with an inner diameter of 50 mm, an outer diameter of 60 mm, and a length of 500 mm is used. An electrical wire of known impedance is stretched along the entire length of the cylinder. The change in impedance across the wire when it comes into contact with the shock wave is measured, in addition to the length of the tube and the damage pattern observed on the tube. The bottom of the tube is closed by a booster of hexocire[32], which is a mixture of RDX and beeswax used in detonation testing. This was done to simulate real conditions and to minimize possible pressure loss during detonation thereby allowing for the best results[33]. The cylindrical booster has a diameter of 60 mm and a height of 50 mm[32]. A thin plastic film is introduced between the booster and the contents of the cylinder to avoid leakage of the liquid onto the booster and/or to prevent undesired chemical reactions[32]. The booster is initiated by a priming tube (U8) connected to the bottom of the tube[32]. The priming tube is initiated electronically[32] from the bottom and then sparked by a booster. The entire system is enclosed in a protective outer ring and placed in a pillbox capable of withstanding the shock waves that may be generated by the chemical reaction[32].
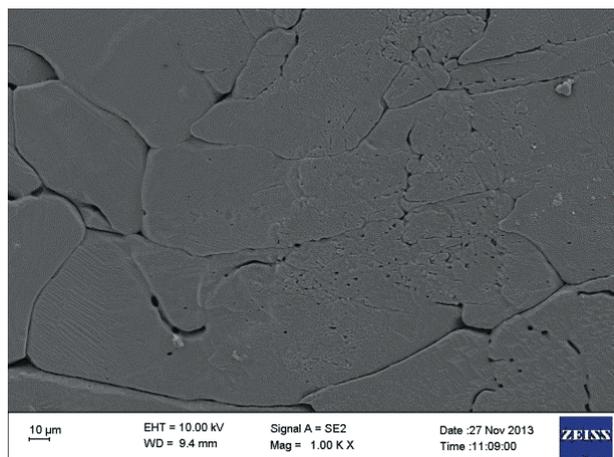
2.3 Detonation velocity

The detonation velocity is an important parameter that serves as a measure of the detonation performance of an explosive. Typically, 250 kg of $CaCO_3$ is used in the production of 1000 kg of CAN, implying that $CaCO_3$ constitutes 25% of the product. Under the present operation conditions, the amount of $CaCO_3$ can be decreased from 25% to 20% when $CaMg(CO_3)_2$ is added during the ammonium nitrate production process. $CaMg(CO_3)_2$ was added during the dilution stage of the ammonium nitrate production process in order to reduce the detonation enthalpy of the ammonium nitrate to 50%. Under these conditions, the nitrogen concentration did not fall below 26%, as shown in Table 1. Dolomite can be used for dilution because it decreases the heat of explosion of CAN. However, given the cost of the material, the amount of dolomite is minimized to 7.5%. Commercial CAN mixtures were used, i.e. AN mixtures of various compositions were prepared by dilution with calcium carbonate or dolomite and with the addition of fly ash.

The compositions of the AN mixtures and the detonation results for different dilution ratios are listed in Table 2. The physical aspects of an explosive material, such as its porosity, significantly affect its detonation properties. These effects are especially pronounced for CAN and its non-explosive mixtures. The most important parameters that can help improve the detonation properties of CAN and CAN-based materials are prill
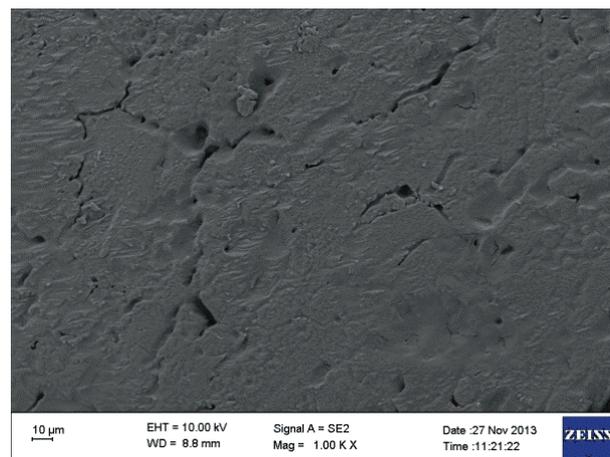
Table 2 Experimental vs. calculated heats of explosion of ammonium nitrate mixtures that contain CaCO₃, dolomite, and fly ash.

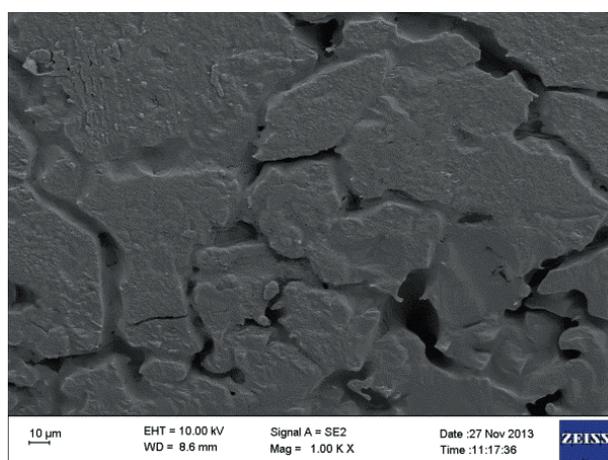| Calcium carbonate [kg CaCO$_3$/ton AN]	Dolomite [kg dolomite/ton AN]	Fly ash [%]	Heat of explosion [kJ kg^{-1}] (Experimental)	Gurney's energy-heat of explosion [kJ kg^{-1}] (Calculated)	Detonation velocity [m s^{-1}]	Density [kg m^{-3}]
250 (25%)	0	0	966	1480	2900	910
175	75	10	440	540	1322	905
175	75	20	250	320	752	900
125	125	10	167	270	503	896
125	125	20	0	0	0	890
					(No Detonation)	

(a)

(b)

(c)

Figure 2 SEM images of crushed fertilizer. Mixtures of CAN containing (a) 25% calcium carbonate (CaCO₃); (b) 17.5% calcium carbonate (CaCO₃), 7.5% dolomite (CaMg(CO₃)₂, 10% fly ash; (c) 12.5% calcium carbonate (CaCO₃), 7.5% dolomite (CaMg(CO₃)₂, 20% fly ash.

formation and particle size.

Prilled samples were ground in a lab-scale grinder to prepare for the detonation test. Before grinding, the size of the prilled ammonium nitrate particles averaged 2 mm. The ammonium nitrate particles were ground before the detonation test, because it is known that ammonium nitrate particles have been ground for anti-social purposes[14]. CAN-based mixtures are crushed to the desired sizes to enhance their detonation properties. In the present study, the CAN particles were finely ground with a maximum particle size of 750 μm before the detonation test to attain a better understanding of the detonation velocity. Figure 2 shows SEM images of the particle surfaces of CAN mixtures. In all the mixtures, the particle sizes are approximately 1 mm or smaller. Some of the particles have smooth surfaces, while others have rough, non-uniform surfaces. The density of the samples after treatment with calcium carbonate, dolomite, and fly ash is 1020 kg m^{-3}. The surface areas of the finely ground calcium carbonate, dolomite, and fly ash are 10−70, 50−100, and 28 cm g^{-1}, respectively. The ground CAN samples were mixed with fuel oil (10%, w/w) for the detonation

tests.

The detonation velocity was tested by the cylindrical test in the UN guidelines and calculated using Guerney's energy (E_G) equation[34] (Equation (1)) as follows, where ϕ and D are given by equations (2) and (3) [35], respectively to compare the theoretical and experimental values.

$$\sqrt{2\,E_G} = \frac{D}{3} \tag{1}$$

$$\phi = NM^{1/2}Q^{1/2} \tag{2}$$

$$D = 1.01\phi^{1/2}(1 + 1.3\,\rho_0) \tag{3}$$

where N is the number of moles of gaseous detonation product per gram of explosive, M is the average molecular weight of the gaseous detonation products, Q is the chemical energy of the detonation reaction (kJ kg^{-1}) (Equation (2)), and D is the detonation velocity (Equation (3)).

2.4 Heat of explosion

In this study, ammonium nitrate solutions were diluted with CaCO₃ and dolomite materials to obtain 84−95% ammonium nitrate solutions. Then, the ammonium nitrate solutions were granulated using a prilling bucket. The heats of reaction for different concentrations of fly ash, calcium carbonate, and dolomite in the CAN solution are listed in Table 2. A steel vessel with an inner volume of 5.6 dm³ was used for the calorimetric tests. The spherical volume of the bomb was filled with 2.0 MPa compressed Ar gas, and the detonation velocity and heat of explosion were determined. During detonation of the CAN, as a result of the decomposition of ammonium nitrate, gaseous products evolved, resulting in an increase in the detonation velocity. These gaseous compounds reacted with the fly ash and it then caused detonation energy and velocity to increase. This resulted in an increase in detonation enthalpy (Table 2). Therefore, two detonation tests were performed to verify the method used and for ensuring reliability of the results.

Dolomite is used in addition to calcium carbonate for mitigating the detonation of CAN. However, given the high cost of dolomite, the present study aimed to use no more than 12.5% dolomite. To this end, instead of adding a large amount of calcium carbonate or dolomite to the CAN solution, the surfaces of the AN particles were coated with fly ash by a small amount (10−20%) to improve the operation and to prevent the health hazards associated with the use of fly ash. Thus, the average composition of the material was 25% calcium carbonate, 7.5−12.5% dolomite, and 10−20% fly ash.

3. Results and discussion

In this study, the interactions in ammonium nitrate samples with additives such as calcium carbonate, dolomite, and fly ash were investigated. The speed of detonation of CAN fertilizer samples was determined experimentally and theoretically (Table 2). The test results show that the detonation velocities of all the CAN samples continue to decrease with an increase in the amounts of additives. The highest detonation velocity of 3.3 km s^{-1} and Gurney's energy of 1580 kJ kg^{-1} are reported for ANFO[5]. With an increase in the amounts of dolomite, calcium carbonate, and fly ash, there was a decrease in both Gurney's energy and the detonation velocity. For CAN fertilizer mixtures containing 25% calcium carbonate, 7.5−12.5% dolomite, and 10−20% fly ash, the heat of explosion and detonation velocity dramatically decreased to less than 540 kJ kg^{-1} and 1322 m s^{-1}, respectively. The average values of the obtained heats of explosion are given in Table 2. The final heat measured in the calorimetric system decreased with an increase in the fly ash content of the CAN mixture. The obtained results can be evaluated as follows. The detonation enthalpy of high explosives such as AN can be decreased by adding materials that suppress the decomposition of AN.

The detonation velocity of ammonium nitrate is approximately 3.3 km s^{-1} [5], but when the calcium carbonate concentration in the ammonium nitrate is increased, the detonation velocity decreases. For example, the detonation velocity of calcium ammonium nitrate containing 25% CaCO₃ is approximately 2.9 km s^{-1} [14]. However, this poses a risk of the CAN solution becoming excessively diluted. This is because commercially available CAN fertilizer is marketed as 26% and 33% nitrogen. The excess calcium carbonate used to reduce the nitrogen content which means that it is degraded to a useless form for plants[36] during the industrial process, which minimizes the risk of explosion.

As more dolomite is added, the reaction enthalpy between the dolomite and the ammonium nitrate that contain calcium carbonate continues to decrease. The fly ash adheres to the prilled ammonium nitrate surface as a film layer. This film layer prevents potential surface reactions with external flammable products. In terrorism purposes, ammonium nitrate is grinded. With the aim of preventing terrorism activities, the ammonium nitrate that was coated by fly ash was grinded. Thus, the fly ash layer comes in contact with all parts of the ammonium nitrate resulting in non-sensitive ammonium nitrate and thus a further decrease in the detonation enthalpy of the ammonium nitrate[15].

Gezerman and Çorbacıoğlu studied the detonation mitigation properties of a mixture of CaCO₃ and CaMg (CO₃)₂, and they were able to successfully lower the detonation velocity[14]. In the present study, in addition to the detonation properties of a mixture of CaCO₃, CaMg (CO₃)₂, and fly ash, various military explosives, such as lead azide, lead styphnate mercury fulminate, both of which are very strong explosives, were examined. Very low detonation velocities for the ammonium nitrate and the other explosives were obtained (Table 3). Thus, AN mixtures with low detonation velocities were successfully obtained. This study proposes a reference method for the preparation of CAN mixtures and for the determination of detonation velocities of these mixtures. The tests show that detonation velocity and heat of reaction can be used to investigate various explosive mixtures of CAN.

Table 3 Detonation parameters of ammonium nitrate containing 12.5% CaCO₃, 12.5% CaMg(CO₃)₂, and 20% fly ash with the explosives used in the military.

Explosives	Detonation velocity [m s^{-1}]	Density [kg m^{-3}]	Heat of explosion [kJ kg^{-1}]
*CAN+lead azide	125	914	300
*CAN+lead styphnate	112	942	256
*CAN+mercuryfulminate	124	937	275

For comparison, the heat of explosion and volume of gases produced by the explosion were calculated using the heats of reaction of ammonium nitrate, fuel oil, fly ash, calcium carbonate, and dolomite, as summarized in Table 2.

As can be seen in the table, the experimentally derived heat of explosion for AN mixtures containing CaCO₃ is 1480 kJ kg^{-1}. However, upon adding dolomite and fly ash, the heat of explosion decreases significantly (< 540 kJ kg^{-1}). Table 2 also shows that the addition of 12.5% CaCO₃, 12.5% dolomite, and 10% fly decreases the heat of explosion to 270 kJ kg^{-1}.

The effect of dolomite on the detonation properties of ammonium nitrate has previously been investigated[5]. It was shown that the detonation enthalpy of ammonium nitrate decreased depending on the dolomite and aluminum content (max. AN/dolomite 50/50 + Al or diesel oil)[5]. It was proposed that the increase in the amount of dolomite in the AN contributes to reducing the detonation enthalpy of AN[5]. The results of this study are particularly important to the prevention of the antisocial use of ammonium nitrate. For example, the detonation velocity of a mixture of 30% CaMg(CO₃)₂ and 4% diesel oil was found to be 0 km s^{-1} [5]. The addition of 40% dolomite to the AN solution decreased the detonation velocity to 1.94 km s^{-1}. These results are compatible with those reported in the literature[5].

To increase the detonation intensity of ammonium nitrate, chemical additives can be added. For example, in terrorism attacks or military exercises, lead azide, lead styphnate, or mercury fulminate are some of chemicals used[37]. In this study, the detonation performance of ammonium nitrate that contains CaCO₃, dolomite and fly ash is investigated. Furthermore, lead azide, lead styphnate, and mercury fulminate were added separately to the ammonium nitrate mixtures. Our experimental studies revealed that the detonation velocity was 125 m s^{-1} and, as determined by calorimetric tests, the heat of detonation was 300 kJ kg^{-1} (Table 3). With a decrease in the concentration of the CaCO₃ in the calcium ammonium nitrate, the concentration of CaMg(CO₃)₂ was increased (max 7.5%), such that the detonation velocity was reduced dramatically.

The heat of explosion determined from bomb calorimetric tests was lower than the calculated value. Pure AN has a high detonation enthalpy and this enthalpy value decreases with the addition of CaCO₃. The reaction between dolomite and ammonium nitrate that contains CaCO₃ is exothermic and this reaction has a lesser enthalpy value (< 440 kJ kg^{-1}) than ammonium nitrate that contains CaCO₃ (966 kJ kg^{-1}). With this, due to the fly ash, which is waste material in the thermal reactor, inorganic materials such as Mn and Fe in the fly ash decrease the detonation enthalpy of the ammonium nitrate that contains CaCO₃ and dolomite[1]. At this point during the detonation testing, the ammonium nitrate that contains dolomite and CaCO₃ and that is coated with fly ash is grinded. The ammonium nitrate particles were crushed during grinding, resulting in the fly ash having access to a higher surface area of ammonium nitrate, which in turn resulted in a decrease in the detonation enthalpy of the ammonium nitrate mixture. According to the experimental and calculated results shown in Table 2, when the concentration of fly ash in the ammonium nitrate increased, the enthalpy of the ammonium nitrate mixture decreased. In the case of adding dolomite, calcium carbonate, and fly ash content to the ammonium nitrate, it is thought that Mn (NH₄NO₃)₃ and Fe (NH₄NO₃)₃ compounds produced during the explosive reaction resulted in more intense endothermic reactions, which decreased the explosive tendency of AN. The use of dolomite, as outlined in this study, would be an important step towards enabling the preparation of CAN with a smaller risk of explosion.

4. Conclusions

The present study examined the use of additives such as calcium carbonate, dolomite, and fly ash in the industrial production of CAN to prevent detonation and its associated risks. With increasing concentrations of the additives, the detonation velocities of CAN mixtures were found to gradually decrease. The enthalpy decreased with the addition of fly ash and dolomite to CAN mixtures that had been diluted using calcium carbonate. The systems with these three additives produced less heat than CAN to which only calcium carbonate had been added.

Thus, with the aim of preventing the antisocial use of ammonium nitrate, this study has revealed that the addition of CaCO₃, CaMg(CO₃)₂, and fly ash decreased the detonation velocity and detonation enthalpy of ammonium nitrate when combined with lead azide, lead styphnate, and mercury fulminate. All these results were demonstrated by both calculations and experiments.

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