Detonability of Ammonium Nitrate Solutions

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ABSTRACT
Tests were performed under various conditions to determine whether aqueous solutions of ammonium nitrate could be detonated when shock-initiated using a high explosive. The solutions were contained in six-inch diameter stainless steel tubes with one-half inch thick walls. Variables in the test series were: solution density (varied with air bubbles, 0.8 - 1.4 g/cm$^3$), ammonium nitrate concentration (80 - 95%), temperature (127 - 152°C), and pH (approximately 0.5 - 8). Nineteen tests were performed, five of which resulted in detonations. One out of four tests on 83% solution with bubbles detonated.

These data are compared to previously published results. The relevance of these results to potential explosion hazards in ammonium nitrate production plants is discussed.

INTRODUCTION
The detonability of aqueous ammonium nitrate (AN) solutions has not been thoroughly investigated although large quantities of such solutions are produced. In general, it has been assumed that solutions containing about 17% or more water could not detonate. Bubbles have been assumed to play an important role in the explosion hazards of AN solutions, as they do in other liquid explosives. This work was performed to clarify the concentration limits and the effects of bubbles, temperature, and pH on the detonability of AN solutions.

BACKGROUND
The detonation characteristics of anhydrous molten ammonium nitrate have been studied by several researchers (King et al., 1978 and references therein), but fewer data are available on the detonability of AN solutions in water.

ICI performed some tests in 1939 and 1947 on solutions with concentrations between 80 and 100% (cited by Groothuizen, 1979). They concluded that under low confinement in cylinders with 2.5 inch diameter, the solution had to have a concentration of about 90% at a temperature of 150°C to be detonable.

The Bureau of Mines (Van Dolah et al., 1966) tested molten AN in glass and steel vessels at 180 to 220°C. No gas bubbles were added to the melt. They obtained detonations for pure molten AN at 220°C in heavy walled steel tubes of 1.63 inch inside diameter and in low confinement glass vessels with diameters greater than 4 inches.

Groothuizen at TNO in the Netherlands (Groothuizen, 1979) studied AN solution detonability in tubes with inside diameters of 50 mm (1.97 inch). These tubes were comprised of an inner stainless steel tube with 6.5 mm wall surrounded by a concentric steel tube with 9 mm wall thickness. Thus, the overall wall thickness was 15.5 mm or 0.61 inch. No gas bubbles were added to the solutions. They obtained detonations only for AN with 1% or less water, measuring reaction wave velocities between 1.8 and 2.1 km/s. The detonations were obtained at temperatures of greater than 209°C. Two similar tests at 204°C and 205°C did not detonate.
King and coworkers at Queen’s University performed minimum priming tests on AN and AN solutions (Bauer et al., 1981). These tests were not detonability tests but were sensitivity tests. When detonations were obtained, the tests show that the material was detonable under those conditions. Failures, however, do not necessarily show that a material was not detonable because small explosive boosters were used. Adding glass microballoons lowered the density of the solutions. They obtained detonations in minimum priming tests performed in 150 mm (5.9 inch) diameter schedule 40 steel pipes on 93% AN solution at a density and temperature of 0.81 g/cm$^3$ and 160°C, and on 90% solution at 0.8 g/cm$^3$ and 100°C and 0.83 g/cm$^3$ and 130°C. The initiating charge weight for these detonations was 0.8 g. Tests on 80% solution at 0.8 g/cm$^3$ and 127°C using a 71 g explosive booster failed to detonate.

Some of the sensitivity results on molten AN from various authors have been discussed in terms of the variation in sensitivity with temperature. However, as shown by King and co-workers, AN begins to thermally decompose at temperatures higher than about 220°C, producing gaseous reaction products that form bubbles in the melt. Therefore, even when bubbles are not added to molten AN, at high temperatures they are formed internally by thermal decomposition and contribute to increasing the observed sensitivity of the material to shock initiation. Above about 230°C, molten AN is observed to become significantly more shock sensitive than at lower temperatures (King et al., 1982).

**EXPERIMENTAL PROCEDURES**

Detonability tests were performed by subjecting AN solution contained in a steel cylinder to a strong shock wave initiation stimulus. The experiments were performed to answer the question “Can the solution detonate?” rather than other questions about the initiation sensitivity or critical diameter of solutions.

Each test included about 50 pounds of AN solution of the selected concentration, pH, and temperature placed in a six inch inside diameter, sixty inch long schedule 40 stainless steel tube as shown in Figure 1. A 12 inch square, 0.625 inch thick steel witness plate covered the top end of the tube. The bottom of the tube was closed using 0.018-inch thick stainless steel sheet. Electric tape heaters were wound around the outside of the tube to heat it to the selected temperature, between 127°C and 152°C, measured using two stainless steel sheathed K-type thermocouples inserted through the wall into the center of the solution. The tubes were insulated using ceramic wool. Some of the tests were performed with the solution under a static pressure of five psig, representing a head of about eight feet of AN solution.

In most tests, air bubbles were blown through porous stainless steel tubes into the solution to increase its sensitivity to shock initiation. The percent of air bubbles was measured by determining the density of the solution in place with bubbles present. In practice, a weighed quantity of AN solution was loaded into the tube so that the desired density was obtained when sufficient air bubbles were added for the bubble-containing solution to just fill the tube. The AN solutions were tested at densities of approximately 0.8 g/cm$^3$, 1.0 g/cm$^3$, or 1.2 g/cm$^3$ when bubbles were present. The airflow duration was limited, typically to much less than a minute, to minimize any effects on the solution concentration, temperature, or pH.
A one-pound booster (454 g) charge of Composition C-4 explosive was used to initiate the solution. The difference between a detonation and a non-detonation of the AN solution was identified by three means. First the tube wall would be completely fragmented into relatively small pieces if the booster initiated a detonation of the AN solution, but the tube wall would be partially “banana-peeled” if the detonation died out along the tube length. An example of a “no-go” or non-detonation result is shown in Figure 2. When the AN solution detonated, the stainless steel tube was fragmented into many pieces, and typically only a small percentage of the tube metal was recovered from the surrounding area. Second, the steel witness plate located at the end of the tube was perforated and usually fragmented by detonation reactions but not by failing reactions. Third, the velocity of the reaction wave was measured using six time-of-arrival detectors spaced at eleven-inch intervals along the tube length. When a detonation reaction occurred in the AN solution, the velocity of the reaction wave near the end of the tube was approximately 2.3 km/s (greater than the speed of sound in the solution which was roughly 1.1 km/s). Detonation velocity data were not obtained when the test did not detonate because the wave was not sufficiently strong to trigger the detectors. In every test, whether a detonation occurred or not was unambiguously determined, using these three indicators.

Solutions were prepared using high purity crystalline AN and purified water. Nitric acid or ammonium hydroxide was added to alter the pH of the solution.

The experiments were performed at the New Mexico Tech, Energetic Materials Research and Testing Center’s explosive test range in Socorro, NM.

RESULTS

Nineteen detonability tests were performed, five of which resulted in detonations. The test data are shown in Table 1, sorted in order of increasing AN concentration. Although there are an insufficient number of tests to unambiguously define the effect of each of the variables of interest, the data show trends. The same test result was not always obtained for seemingly identical conditions. This behavior is often seen in detonation testing, probably due to test-to-test variations in bubble size or fraction near the booster end of the test vessel, or other random variations in test parameters. To show whether a material is detonable, typically several negative (no-go) results are needed, whereas only one positive (go) result is required to show that a material is capable of detonating under a given set of conditions.

No detonation was obtained in any test without the presence of bubbles in the AN solution. Only solutions with density 0.8 g/cm$^3$ detonated.

As expected considering previous work, solutions with higher AN concentrations were found to be more likely to detonate. Figure 3 shows the data for solutions with density of 0.8 g/cm$^3$ plotted versus AN concentration. Solutions with concentrations of 83% and higher exhibited detonations. The one test at 80% AN did not detonate. The “Fraction Detonations” in Figure 3 is the ratio of the number of detonation results divided by the number of tests performed for each AN concentration. It should be noted that these results should not be interpreted to guarantee
that AN solution with concentration less than 83% cannot detonate -- only that the likelihood of detonation appears to becomes quite low for concentrations less than 83%.

The effect of temperature cannot be easily separated from that of AN concentration, since higher concentration solutions were only tested at higher temperatures.

The effect of the pH of the solutions on their detonability is not clear. Of the five detonations, two solutions had pH of 8, while three solutions had relatively low pH values of 2 to 2.5. None of the three tests on pH 0.5 solutions detonated. Further work would be necessary to clarify the effect of pH.

Detonation velocity data are shown in Table 1 for the tests that detonated. No data were obtained for tests that failed to detonate. The values shown in the table are for the final velocity measured in each test. The average velocity for all five detonations was 2.25 km/s.

Figure 1. Schematic Drawing of Detonability Test Apparatus
Figure 2. Vessel After Failure or No-Go Reaction of AN Solution
<table>
<thead>
<tr>
<th>AN Concentration (Weight %)*</th>
<th>Density (g/cm³)</th>
<th>Bubbles</th>
<th>pH</th>
<th>Temperature (°C)</th>
<th>Applied Pressure (psig)</th>
<th>Result</th>
<th>Detonation Velocity (km/s)</th>
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<td>0.80</td>
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<td>126.6</td>
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<tr>
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</tbody>
</table>

* Aqueous solutions.
Figure 3. Detonability Data for Aqueous AN Solutions Containing Bubbles at Density 0.8 g/cm³.

The fraction of detonations was obtained from small numbers of tests:

- At 80%, 0 out of 1 test detonated;
- At 83%, 1 out of 4 tests detonated;
- At 84%, 1 out of 4 tests detonated;
- At 88%, 2 out of 5 tests detonated;
- At 95%, 1 out of 1 test detonated.
DISCUSSION

The current data show AN solution detonations under conditions where previous workers have concluded that such solutions were not detonable. However, examining the data from ICI and TNO (Groothuizen, 1979), only two tests were done using AN solutions with concentrations less than 85% and only four tests with concentrations between 85% and 90%. The tests in the new work reported here were performed at a larger scale, slightly higher temperatures, under high confinement, and using air bubbles directly blown into the solution. The scale and confinement of the current work were intended to investigate detonability of industrial quantities of such solutions. We believe these results to be relevant to the safe design and operation of ammonium nitrate production.

Bubbles are important in detonation hazards of all liquid energetic materials. As discussed by Lee, homogeneous and heterogeneous explosives show notable differences in their initiation mode by shocks (Lee, 1987). In homogeneous explosives, such as bubble-free liquids or molten or single crystal solids, initiation is caused by homogeneous thermal heating due to compression by the shock. Initiation of heterogeneous explosives, such as polycrystalline solids or liquids with bubbles, occurs at hot spots created by the interaction between physical imperfections and the shock wave. Although this picture may be an oversimplification of what actually occurs, it serves as a framework for analyzing initiation of energetic liquids.

Without bubbles, liquids such as AN solutions usually require extremely high shock initiation pressures to produce sufficient homogeneous compression to heat the material. On the other hand, when bubbles or other discontinuities are present, much lower shock initiation pressures can initiate a self-sustaining detonation reaction. Practically, we can consider aqueous solutions of AN to be non-detonable without bubbles to lower their initiation sensitivity and critical failure size.

The bubbles used in this work were comprised of air, whereas in AN neutralizers the bubbles are composed of mainly water vapor. The difference between air and steam bubbles could have some effect on AN solution sensitivity, but it is not expected to alter the general conclusions from this work.

Glass or plastic microballoons are often used to sensitize AN emulsion explosives. In the work reported here, the bubble size or size distribution are not known experimentally, but the air bubbles were probably quite large compared with typical microballoon size (microballoons typically have diameters of the order of 80 µm). The larger diameter air bubbles in our work might be expected to be less effective in sensitizing the solutions, but, on the other hand, the void fraction in producing an AN solution with density of 0.8 g/cm³ is quite high, greater than 40%, and many bubbles would be present.

It should be emphasized that the presence of bubbles tends to increase the sensitivity of aqueous AN solutions with respect to shock initiation and detonation. The bubbles do not necessarily make the solutions thermally unstable or increase their sensitivity to thermal decomposition.
INDUSTRY APPLICATION

The industry has known from prior experimental work that bubbles can sensitize AN solutions at concentrations of 90% and above. The recent work discussed here shows that bubble sensitization extends to a lower range of concentrations than previously known, as demonstrated at 83% AN. Typically the industry treats AN solutions with caution and, if needed, will dilute and cool the AN solution by adding water to reduce potential hazards. Safeguards including control measures to insure safe pump operation, careful and complete monitoring, and other actions as part of a plant safety hazard review are typically applied to even more dilute AN solutions in manufacturing plants. Operation and design decisions can reduce the occurrence and the volume of AN solutions at reduced densities, especially during upset or unknown conditions.

As indicated earlier, there is nothing to suggest that bubbles alone could initiate a detonation event or that bubbles increase sensitivity to thermal decomposition or self-heating. Bubbles are a normal part of most safely operating AN production processes. These detonability tests used a one-pound explosive booster to initiate the detonations in the bubbled solution. The work confirms the importance of avoiding strong initiating events, particularly in contact with bubbled ammonium nitrate solution that may lead to a sympathetic detonation.

Part of industry practice is to identify and avoid such sources of strong initiation triggers in handling ammonium nitrate. Thermal runaway reactions are well known hazards in the production and storage of energetic materials. AN, like other energetic materials, can generate internal heat due to slow decomposition which, under confinement, may lead to a runaway reaction leading ultimately to a deflagration-to-detonation transition (DDT). This is essentially a burning to detonation, which is the cause of many industrial detonations in condensed phase materials. Because of the significant water content, AN solutions exhibit a high degree of thermal stability. Under some conditions, particularly when physically confined and thermally confined or heated, AN solutions can decompose violently and deflagrate. The transition to detonation in hot AN without bubbles, however, is difficult to achieve as has been shown by Van Dolah (1966), US Bureau of Mines. In the absence of substantial confinement or source of contamination, the risk of DDT in normal AN processes appears to be remote. Additional work by Bauer et al (1979) indicates there are several hurdles that must be overcome before molten AN will achieve a deflagration-to-detonation transition. Knowing and utilizing this type of process safety information provide reliable and safe operation of ammonium nitrate plants. Industry practices closely guard against contamination, overheating, and confinement, as well as eliminating high-energy initiating sources needed for sympathetic detonation of bubbled ammonium nitrate.

Another possible source of initiation for AN solution is bullet or fragment impact initiation. Bauer and co-workers performed impact tests on molten AN and 95% solution (Bauer et al., 1981). Molten AN at 260°C was initiated by impact of a 150 mm diameter projectile traveling at 190 m/s, corresponding to an impact shock pressure of about 1 kbar (14,500 psi), whereas 95% AN solution was not initiated by an impact pressure of 1.9 kbar (27,500 psi). The tests of Bauer et al., therefore suggest that as the solution concentration decreases, it becomes more difficult to detonate and requires a higher energy impact. In a plant environment, AN solutions are contained in pipes and vessels and therefore protected from direct impact of projectiles. Also,
such pressures are unlikely to result from mechanical events such as falling objects because the velocities are too low.

The results presented here and in previous work point out that there are areas where ammonium nitrate safety could be better understood as it applies to plant operation and product handling. A few examples follow:

While these results and previous work provide some clear results (for example, the effect of AN concentration), the tests also suggest but do not clarify some other trends. Further work would provide statistical support for establishing firm relationships between test parameters and results.

Questions have been raised regarding the application of this work (which used air bubbles) to solutions containing bubbles of steam or other gasses typically found in operating plants.

Questions have been raised regarding the effect of the size of the bubbles used in this work compared to those found in operating plants.

Tests on mixtures of AN with other products would provide insight on safe operation of general use fertilizer products, such as urea ammonium nitrate solutions.

CONCLUSIONS

Ammonium nitrate solutions with concentrations as low as 83% were found to be detonable when they contain a large number of gas bubbles, which increases their shock sensitivity. Initiation of a detonation reaction in such solutions requires a powerful trigger mechanism, which is unlikely to be present in normal AN processes. However, sensible control measures are warranted to guard against potential initiation sources and avoid such an event, and AN plant operators are encouraged to consider the data presented here in future AN plants reviews.
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REFERENCES


