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Final Report to Orica

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**Final Project Report to
ORICA, USA**

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Executive Summary

A novel nano-composite energetic material consisting of a nano-porous xerogel resorcinol-formaldehyde (RF) framework containing the inorganic oxidizer ammonium nitrate (AN) is described. Several formulation routes were investigated to attain an oxygen-balanced energetic formulation that consisted of 90% by weight AN 10% by weight RF, which is optimized with respect to oxidizer/fuel ratio. Initial studies showed this material to have a high energy content by calorimetry as well as good small-scale safety characteristics. From those studies one formulation route, using the base catalyst sodium carbonate with no solvent wash, was selected and scaled to the 50-gram level. Sufficient drying of the material at the scaled up level was challenging and a process involving ambient and elevated temperature drying as well as ball-milling was developed to produce powders of the composite energetic powder. These powders were then pressed to higher densities for detonability experiments. In such experiments a 2.54 cm x 15.25 cm steel cylinder, fitted with crush pins and placed on a dent plate was filled with energetic nano-composite. Three detonability experiments were executed at different densities (1.6 1.4 and 0.92 g/cm³, respectively) of nano-composite. The assembly was initiated with a RP-1 detonator and boosted with a 23-gram charge of Composition B. Only the lowest density composition was able to detonate and did so with a detonation velocity of 2.92 km/sec.

Objective

The replacement of a monomolecular explosive as booster charge with a sol-gel derived nano structured binary material consisting of resorcinol-formaldehyde (RF) sol-gel and ammonium nitrate (AN). Tasks to be completed by LLNL in support of this objective: 1) Establish a robust process for the preparation of a binary booster charge scaled to the one-pound quantity level 2) Perform detailed small-scale thermal and micro-structural characterization of the candidate material 3) Perform a precision cylinder test with the material to enable a determination of its utility for the sponsor and 4) Provide a written final report of process methodology and performance findings will be provided to ORICA.

Experimental

Formulation of RF/AN

Using input and guidance from ORICA, LLNL has performed synthesis and characterization of sol-gel RF/AN composites with weight percentage ratio of 10% RF/90% AN. This particular formulation is of particular interest as it is oxygen balanced. The formulation procedure was based on that provided by ORICA, USA contact, Mr. David Johnson.

The reagents used in this study are detailed here. The resorcinol ($C_6H_6O_2$; F.w. = 110 g/mol) used was obtained from Aldrich Chemical company, ACS quality grade, and 99% + in purity. The formaldehyde (F.W. = 37 g/mol) was from Aldrich and was in 37% by weight in solution with water. Ammonium nitrate (NH_4NO_3 ; F.W. = 80 g/mol) used in this study was from Sigma-Aldrich Chemical, Co. (98%) as was the sodium carbonate (Na_2CO_3 ; F.W. = 106 g/mol) used. In some experiments an acid catalyst, glacial acetic acid (F.W. = 60 g/mol) was used.

A typical 50-gram formulation was prepared as follows. A 3.103-gram portion of resorcinol (0.028 moles) was dissolved in 50 mL of de-ionized water and 4.67 grams of a 37% by weight solution of formaldehyde (0.057 moles) was added to give a 1:2 ratio of resorcinol to formaldehyde. In that solution 0.15 grams of Na_2CO_3 (0.0014 moles) was dissolved to give a resorcinol/catalyst (R/C) ratio of 20. The solution was then diluted to 100 mL with more de-ionized water. A tightly capped vial of this solution was heated in an oven to 60°C and held for three hours. The resulting solution was red and clear, it was then allowed to cool to room temperature. In some instances no catalyst was used, which used the identical procedure as above, with the exception that the Na_2CO_3 was not used. A similar procedure was also used for acid catalysis of RF using CH_3COOH at an R/C ratio of 16.

A 60% by weight solution of AN, in water, was made by dissolving 44 grams of AN in 33 mL of H_2O . The heat of solution of AN is endothermic and thus this solution get quite cool on dissolution. This solution is allowed to come to room temperature. Once at that temperature the solution was mixed with the RF solution above with strong stirring. This produced a turbid orange solution shown in Figure 1. This solution was transferred to polypropylene vial, which was capped and then heated at 75°C in an oven for three days. During that time the solution formed a very weak gel with a layer of clear colorless solution on top, see Figure 2 for an image of the material in this state.



Figure 1. Photo of a freshly mixed solution of AN/RF (90/10) being stirred, total volume ~ 150 mL.



Figure 2. Photo of the AN/RF (90/10) gel with a clear colorless solution layer on top.

After gel formation and subsequent additional aging at the elevated temperature the cap was removed from the vial and the sample was dried for several days at 75°C. This resulted in the formation of a monolithic block of AN/RF composite that is shown in Figure 3.



Figure 3. Photo of AN/RF monolith from a typical 50-gram scale up experiment. The monolith was 3.6 cm in diameter and 2.1 cm in height, which gave a density of 1.35 g/cm^3 .

Drying yielded a somewhat heterogeneous product. While the major portion of the composite was a monolith some portions of the beaker contained a white solid (ammonium nitrate) that had phase separated. This was observed in nearly every formulation attempted. From the mass of the monolith and the known amounts of R, F, and AN used one can determine the mass percentages of AN/RF in the homogeneous composites. Quite consistently monolithic materials from this process were determined to be 84% AN and 16% RF. The additional phase separated AN was included in the subsequent steps of processing.

While monoliths could be achieved by this approach their quality was not ideal nor highly reproducible that would enable consistent shape casting and use in formulations for further. At this point after discussions with ORICA, USA there was interest in utilizing the material as a powder that could then be pressed to density for use in detonability tests. The monolith obtained on drying was subsequently broken in several pieces and ball milled for 24 hours. The materials were milled in a 500 mL milling jar with aluminum oxide milling media. The milling jar was rotated at ~ 100 RPM for a 24 hour period in 25 gram lots of material. The milled sol-gel composite was further dried for ~ 24 hours at 80°C to give the final powder.

Candidate powders were pressed to different densities using a hydraulically driven ram press. Powders were pressed at 30,000 psi through two cycles and held for 3 minutes on each cycle at room temperature. The diameter of parts was 2.5 cm and the length 2.5 cm. Powders were pressed to parts with densities of 1.65 g/cm^3 (97% TMD) and 1.41 g/cm^3 (80% TMD) respectively. The pour density of the RF/AN powder was 0.92 g/cm^3 (54% TMD). Photos of pressed parts of AN/RF (90/10) are shown in Figure 4.



Figure 4. Photo of pressed sol-gel AN/RF (90/10) composites pressed to a final density of 1.6 g/cm^3 .

A flowchart summarizing the processing overview is shown in Figure 5.

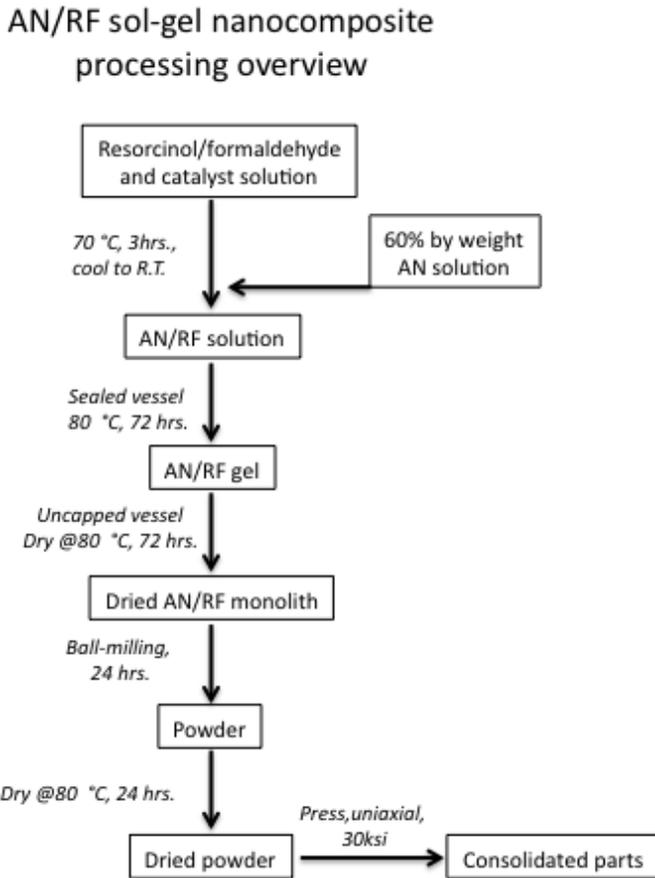


Figure 5. A process overview flow chart for the processing of AN/RF material used in this study is shown here.

Thermal Analysis

We performed DSC safety assessments for these materials using a TA Instruments DSC Q2000 using a temperature ramp from room temperature to 550°C at linear heating rate of 10°C/min with an ultrapure-nitrogen purge flow of 50ml/min. Analyses were performed using standard aluminum crimped type pans supplied by TA Instruments. Runs were performed with pans of this type with and without a pinhole punched in it. The pinhole pan is designed for solids that are non-volatile. Hermetically sealed pans are used to more accurately capture thermal events for materials with volatile components.

We performed TGA/DSC analysis of AN/RF composite materials using TA Instruments SDT Q600 Simultaneous TGA/DSC. Samples were heated in an alumina crucible at a linear heating rate of 10°C/min with a 100 mL/min. flow of ultra high

purity nitrogen. This analysis was used to determine residual moisture content as well as evaluate the fuel/oxidizer balance in the composite materials.

Detonability experiments

Experiments consisted of 80-125 grams of AN/RF powder loaded into a 1" diameter x 6" long non-precision stainless steel cylinder mounted vertically and set at the center point of a 6" diameter x 1" thick mild steel witness plate --- and fired with 4 shorting pins mounted along the length of the cylinder for detonation velocity. The main charge was initiated with a 1" x 1" Composition B booster and a RP-1 detonator. The schematic for the experiment is shown below in Figure 6 and photos of the actual experimental set up are shown in Figure 7.

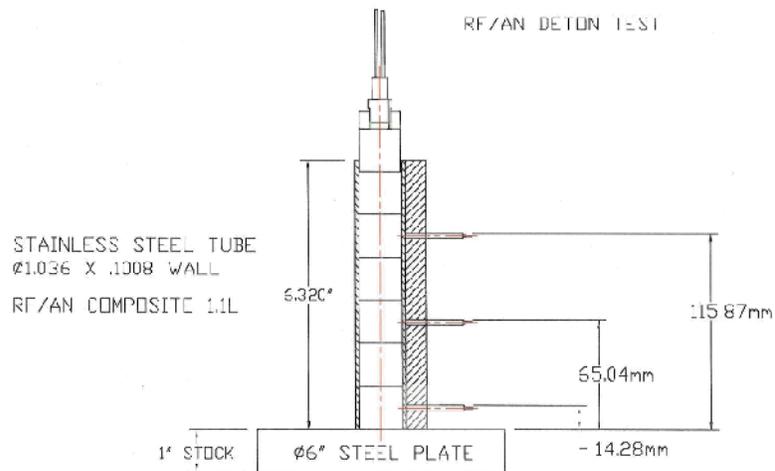


Figure 6. Drawing of the detonability test set up used in this study to evaluate AN/RF nano-composites.

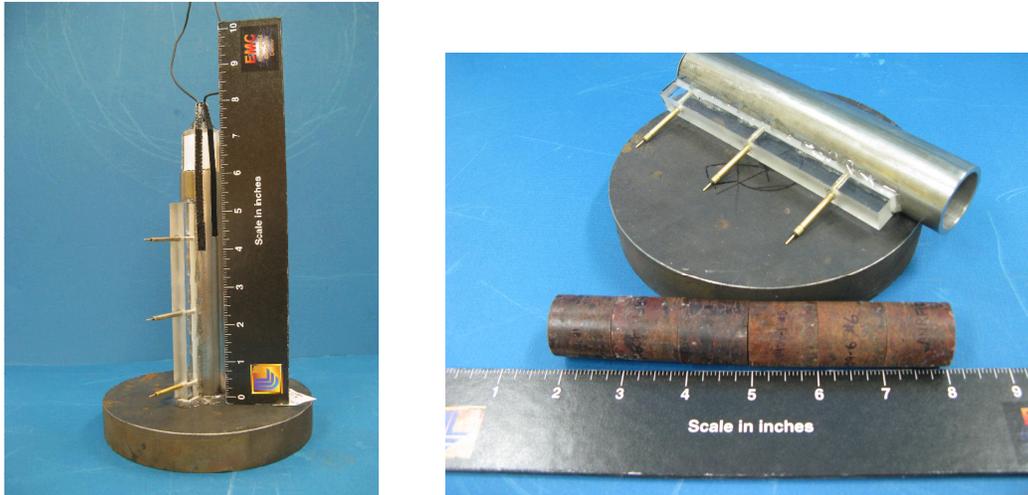


Figure 7. Photos of detonability test components used in this study. The red/brown cylinders in the figure on the right are the pressed energetic materials.

Small scale safety testing

The response of AN/RF energetic composites to friction was evaluated using a BAM high friction sensitivity tester. The tester utilizes a fixed porcelain pin and a movable porcelain plate that performs a reciprocating motion. Weights are attached to a torsion arm allows for the applied force to be varied from 0.5 to 36 kg. The measure of frictional sensitivity of a material is based upon the largest pin load at which less than two ignitions occur in ten trials. The friction tester results are compared to an RDX calibration sample, which was found to be zero events in ten trials at 16.0 kg.¹

The sensitivity of AN/RF energetic composites toward electrostatic discharge was measured on a modified Electrical Instrument Services electrostatic discharge tester. A small pile of AN/RF energetic composites powder (0.4 cm diameter) was loaded into Teflon washers and covered with 1 mm thick Mylar tape. A spark discharge of variable energy is sent from a movable electrode tip to the sample. The sensitivity is defined as the highest energy setting at which ten consecutive “no-go” results are obtained. A “go” result is obtained with visual observation of flash or burn residues. The energy setting for this instrument was 1 J.²

The impact sensitivity of AN/RF energetic composites were evaluated with an Explosives Research Laboratory Type 12 Drop Weight apparatus. The instrument is equipped with a Type 12A tool and a 2.5 kg weight. Thirty-five milligrams of AN/RF energetic composites was placed on a piece of carborundum paper on a steel anvil and the weight dropped on them. The operator made visual evaluations for “go” and “no-go” events. The mean height for “go” events called the “50% Impact Height” denoted DH_{50} was determined using the Bruceton up-down

method. Results were compared to calibrated samples of PETN, RDX, and Comp-B whose DH_{50} values are 15.5 cm, 34.5 cm, and 41.4 cm respectively.³

Results and Discussion

Synthesis and Formulation

An initial technical challenge in this effort involved the formulation of high oxidizer content gel composites via ambient evaporative drying techniques. Composites with a high oxidizer/fuel ratio have been demonstrated by Tappan *et al.* using a flash freezing/sublimation approach to achieve cryogels.⁴ Several points bear consideration here.

- 1) Large amounts of oxidizer in gel composites present significant issues regarding drying, mechanical properties of the final part, and general tractability of the process and sol-gel binary energetic composites. The desired composition contains such levels of oxidizer that it makes the feasibility of monolithic parts challenging.
- 2) Scale up of any energetic material from the gram bench scale to hundred gram quantities has its own set of unique issues. In most cases it is not as simple as increasing the amounts of composite materials.
- 3) It is highly desired that the large booster piece be a monolith derived by drying of the wet gel composite. This can be a challenge as drying of sol-gel materials is a complex process with many competing factors such as the vapor pressure, surface tension, and polarity of the solvent as well as solids loading, all of which affect the final mechanical properties of the material. It is important that this process be robust and practical for industrial use.

While the effort to prepare a single as-dried monolithic article for use is important it is more critical that the detonation parameters of the nano-mixed fuel and oxidizer system (RF/AN) be fully evaluated. With that in mind we performed performance tests on any material, be it a monolith or pressed or packed mixture of sol-gel processed nano-mixtures. To get to that point larger quantities of sol-gel RF/AN material must be prepared.

One of the tasks on this effort was to develop a robust and reliable formulation method for the production of AN/RF composites with high solid oxidizer loading levels.⁵ One can imagine this is challenging as appropriate levels of solid oxidizer are in the 85-90% by weight range, comparably there is very little RF present to help bind the nano-composite together. Understandably a number of different approaches were attempted in an effort to come up with an optimal method. A summary of those approaches is shown in Table 1.

Table 1. Results from series of RF/AN sol-gel energetic material formulations under different conditions.

Sample	AN/RF Ratio	Target Amount (grams)	Amount recovered (g)	Catalyst	Density (g/cm ³)	Comments
1	90/10	10		Na ₂ CO ₃	NA	
2	90/10	1		Na ₂ CO ₃	NA	
3	50/50	1	0.57	none	NA	
4	90/10	1	0.64	CH ₃ COOH	NA	Acetone wash appeared to remove AN
5	50/50	1		CH ₃ COOH	0.28	
6	75/25	1	0.25	None	NA	Acetone wash may have removed AN
7	50/50	1		None	NA	
8	66/33	1	1	CH ₃ COOH	0.91	No acetone wash, monolith 61% TMD as dried
9	90/10	50	~50	Na ₂ CO ₃	1.37	No Acetone wash; Monolith appears to be 85/15 (AN/RF)
10	90/10	50	~50	Na ₂ CO ₃	NA	No Acetone wash
11	90/10	50	~50	Na ₂ CO ₃	NA	No Acetone wash
12	90/10	50	~50	Na ₂ CO ₃	NA	No Acetone wash
13	90/10	50	~50	Na ₂ CO ₃	NA	No Acetone wash
14	90/10	50	~50	Na ₂ CO ₃	NA	No Acetone wash
15	90/10	50	~50	Na ₂ CO ₃	NA	No Acetone wash
16	90/10	50	~50	Na ₂ CO ₃	NA	No Acetone wash

Inspection of Table 1 indicates that formulation # 9 gave reasonable material and that was repeated on several occasions (formulations 10-16) to obtain a suitable amount of material for detonability tests.

In general some observations on formulation include:

- 1) Both the base catalyzed and composites, with the balanced AN/RF (90/10) formed with no catalyst formed very weak gels that dried to give highly cracked weak RF monoliths that were somewhat heterogeneous and contained regions of phase separation (see Figure 3).
- 2) Composites formed with lower weight percentages of AN relative to RF (e.g., 50/50, 66/33, 75/25) stronger more homogeneous gels, see Figure 6a (AN/RF (50/50)). These wet gels were readily dried to give nice monoliths with reasonable mechanical properties, see Figure 8b (AN/RF (50/50)).

- 3) Composites formed using the acid catalyzed formation of RF gave the most robust monoliths, see Figure 8c, seen in this study. These parts were $\sim 0.9 \text{ g/cm}^3$, which is 61% of TMD. These were very hard monoliths that have impressive mechanical properties for porous energetic composites. While monoliths were readily formed using this synthetic process it was only limited to compositions up to 66% AN and 33% RF by weight.
- 4) Early in this study acetone was used to exchange with the water in the gel composites before drying. In some initial experiments we noted a significant difference between the recovered amount of composite and the target mass of each formulation. Note samples 3,4, and 6 in Table 1 for examples of this. It was determined that in our hands the acetone appeared to be washing some fraction of the AN out of the gel structure. While acetone is not a strong solvent for AN mixtures of acetone and water (which is effectively the situation described here) will solubilize AN. It is worth noting that when acetone washing was removed from the processing that recovered yields were consistent with target ones (see samples 8-16 in Table 1).

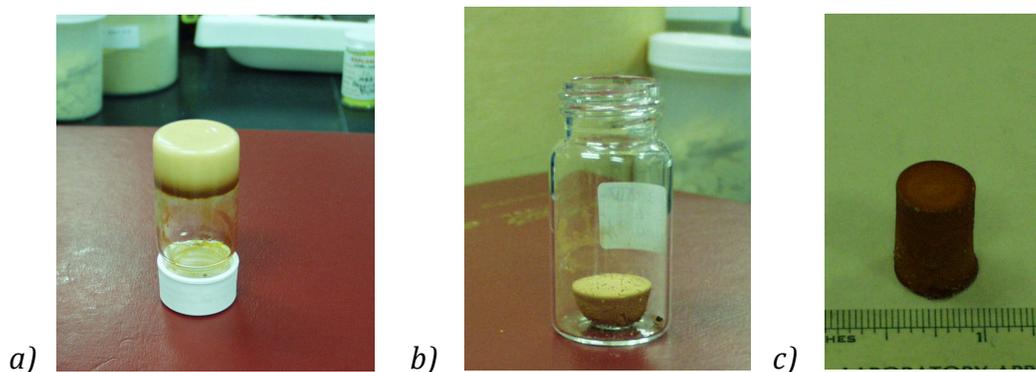


Figure 8. Photos of gel and dried gel monoliths from small-scale formulation experiments.

Thermal Analysis

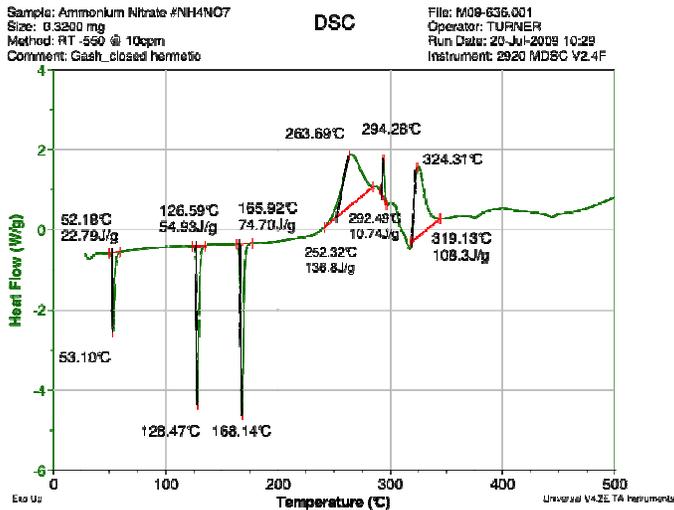
Differential scanning calorimetry (DSC) measures the difference in heat flow between a sample and an inert reference measured as a function of time and temperature. In the LLNL thermal analysis laboratories, DSC analysis is used to characterize thermal properties of energetic materials. Under our standard experimental protocols, decomposition of conventional explosives is indicated by exothermic events which typically have enthalpies on the order of 10^3 J/g and onset temperatures below 350°C . Oxidation is normally indicated by exothermic events

which have exothermic onset temperatures above 350°C. Other common phase transitions (e.g. melting, evaporation, or sublimation) are indicated by endotherms; glass transitions and changes in heat capacity are generally indicated by step-wise events. General features of the DSC curve may also indicate complexity of the decomposition pathway.

Simultaneous thermo gravimetric analysis TGA/DSC measures both heat flow and weight changes (TGA) in a material as a function of temperature or time in a controlled atmosphere. Measurement of these two material properties improves productivity and simplifies interpretation of the results. The complementary information obtained allows differentiation between endothermic and exothermic events which have no associated weight loss (e.g., melting and crystallization) and those which involve a weight loss (e.g., decomposition). TGA is commonly employed in research and testing to determine characteristics of materials to determine degradation temperatures, absorbed moisture content of materials, the level of inorganic and organic components in materials, decomposition points of energetic materials and residual solvent levels. It is also often used to estimate the kinetics of high temperature oxidations.

The DSC scans of pristine AN in sealed and pinhole provide insights for the interpretation of the corresponding DSC scans of AN/RF energetic composites. It is well known that when AN is heated two reactions dominate: 1) Dissociation to ammonia and nitric acid and 2) Decomposition to N₂O and H₂O.⁶ The first reaction is endothermic and the second is exothermic. Figures 9 and 10 below are a summary of the thermal analyses performed on AN in this study.

a)



b)

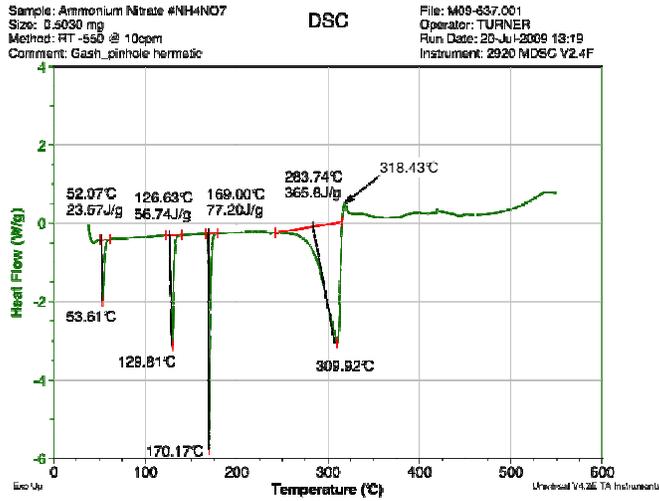


Figure 9. DSC scans for the base ammonium nitrate oxidizer, in a) hermetically sealed pan and b) pinhole hermetic pan, used in this study.

In confined conditions, like that encountered in the hermetically sealed DSC sample pan the second reaction is dominant and leads to further reaction with one another to form H_2O , N_2 , and NO , still further exothermic reactions.⁷ It appears that when AN is heated in an only partially confined system, like that of the pinhole hermetic pan, the endothermic process in the first pathway is dominant. This is further confirmed by an SDT DSC/TGA on the AN that shows complete mass loss at the endotherm at $310^\circ C$, shown in Figure 10.

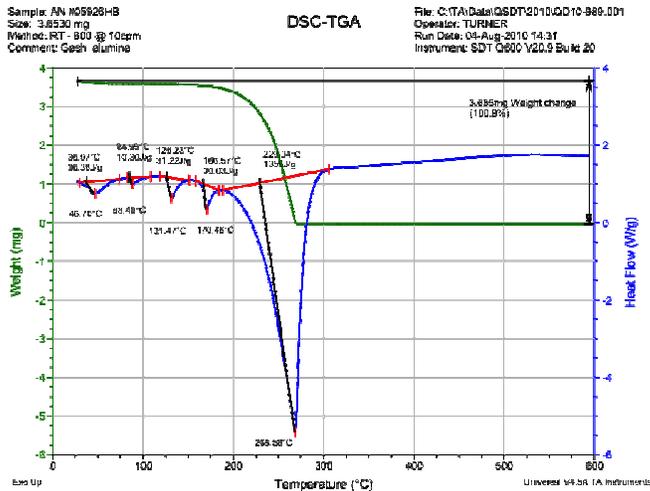
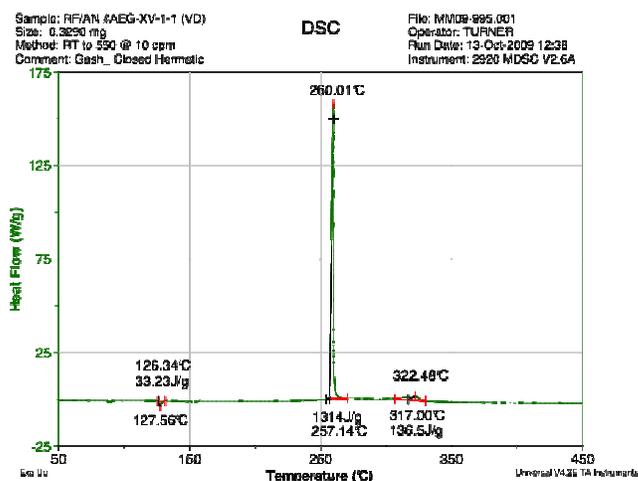


Figure 10. SDT scans (DSC and TGA) for the base ammonium nitrate oxidizer used in this study.

The DSC analysis of the ammonium nitrate used in this study is shown in Figure 9. The trace shows endothermic peaks at 53°C and 126°C which correspond to known solid phase transitions of AN from the orthorhombic to tetragonal polymorph and tetragonal to cubic polymorph, respectively. The endothermic peak at 168°C is attributed to the melting of AN. The largest peak in the scan is a broad exothermic one that occurs over the 250°C–290°C range and is the decomposition of AN to nitrous oxide (N₂O) and water. The exothermic event at 324°C may result from an alternative mechanism of AN decomposition at higher temperatures dominated by a free radical mechanism.

a)



b)

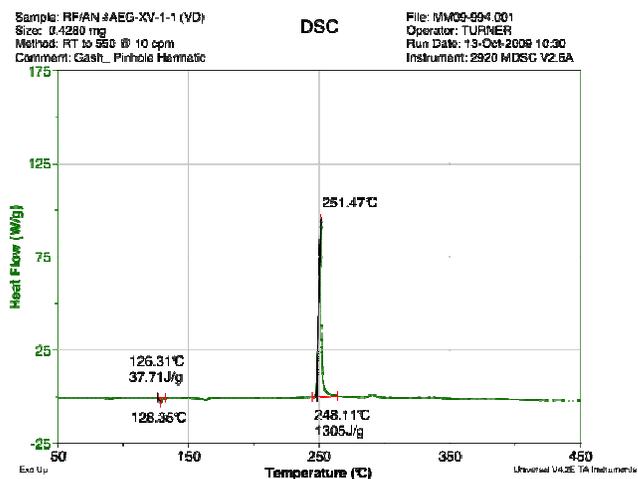


Figure 11. DSC scans of AN/RF (90/10) using a) hermetically sealed sample pan and b) pinhole hermetic sample pan are shown in this figure.

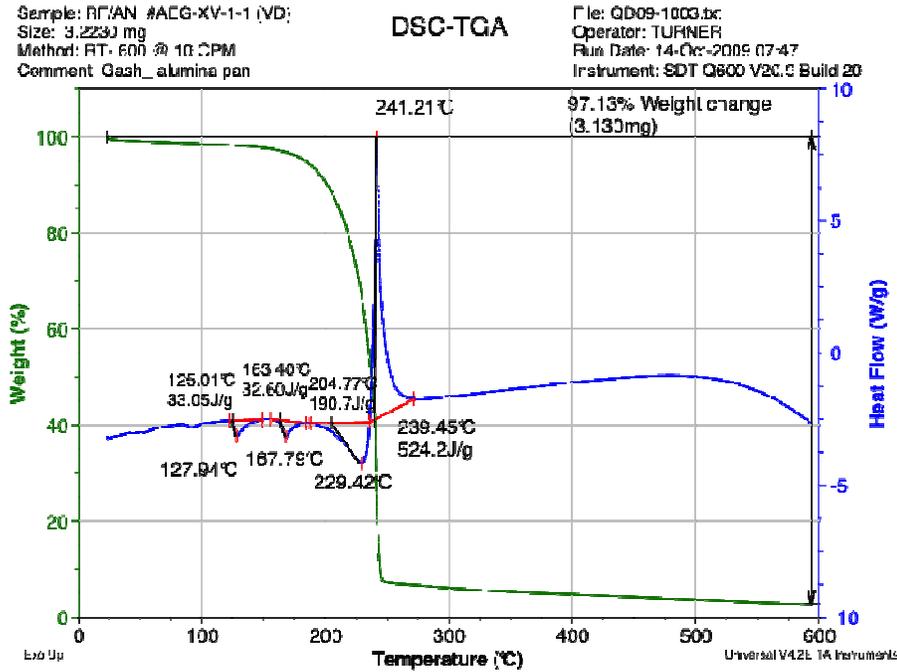


Figure 12. The simultaneous DSC/TGA analysis of an AN/RF (90/10) nano-composite is shown here.

The SDT trace in Figure 12 above contains several features that are important to discuss in regards to the nature and characteristics of the AN/RF composite. It is interesting to note that there is no indication of the solid phase change for AN observed at 52°C in the baseline AN thermal analysis and tentatively assigned to the orthorhombic to tetragonal structure change (see Figure 9-10), in the DSC for the AN/RF composite. On the whole this endothermic peak was only seen occasionally in the thermal analysis of AN/RF composites. It is possible that in some combination of chemical processing conditions of composites enabled the stabilization the tetragonal phase of AN.

Both the TGA and DSC components of the data do not indicate any significant moisture content. The total mass loss up to ~ 120°C is only at the most 2 weight %. In addition, there is no evidence of a vaporization endotherm at 100 °C, which would be indicative of residual moisture.

The DSC endotherm at 127°C can be assigned to the crystallographic transformation of ammonium nitrate from its tetragonal to cubic structure.⁸ The DSC endothermic peak at 168°C is assigned to the melting of AN. The assignment of the two endothermic peaks is supported by no sample mass loss on the TGA curve, which would be expected for thermal events like structural transformation and melting. Both of these peaks were seen in all of the thermal analyses of AN/RF composites performed in this study, in contrast to the 52°C phase transformation only observed in some samples.

The major DSC exotherm at 241°C is thought to be that associated with the thermal reaction of the oxidizer and fuel phases of the composite. This can unambiguously be assigned to this reaction as its enthalpy (~ 2000 J/g, as observed in the DSC) is much higher than the value associated with decomposition of ammonium nitrate alone.⁷ Further still, this is supported by the massive mass loss recorded by the TGA curve at this point. One also will note the nearly quantitative mass loss of the sample in this region (97 %). This type of response is expected in a fuel oxidizer system that is oxygen balanced and lends some merit to the accuracy of the fuel/oxidizer balance in the AN/RF (90/10) composite system. The smaller enthalpy of reaction observed in the pinhole hermetic DSC (1400 J/g as opposed to 2000 J/g) relative to the hermetic pan DSC can be possibly be attributed to the competing thermal degradation pathways of AN under confined and semi-confined conditions discussed above. In the semi-confined pan there may be more significant loss of AN to dissociation and volatilization which results in less oxidizer for reaction with the RF fuel.

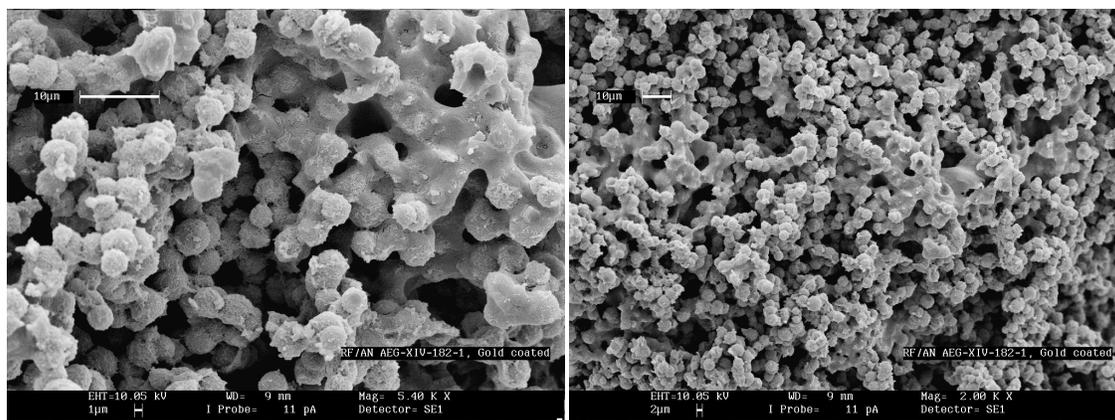


Figure 13. Scanning electron micrograph, at two different magnifications, of AN/RF (33 wt%/66 wt. %) nano-composite made with acetic acid catalyst.

Small Scale Safety Test Results

Small-scale safety analysis and thermal analysis was performed on the scaled quantities. The composite appears to be quite insensitive as the drop hammer results are $DH_{50} > 177\text{cm}$ which is the limit of the LLNL test instrument (for comparison RDX has a $DH_{50} = 32\text{ cm}$ on LLNL instrument), the spark results are negative in ten trials at 1 J total energy, and the friction results are negative in ten trials at 36 kg setting on the BAM friction apparatus.

Table 2. Results from LLNL small-scale safety tests on AN/RF (90/10) sol-gel composite formulation.

Sample	DH₅₀ (cm)	BAM Friction	Spark	DSC Exotherm (°C)	CRT (cm³/g)
AN/RN (90/10) sol-gel composite	>177	0/10 @ 36 kg	0/10 @ 1 J	250	0.11

The small-scale safety tests were performed at the 1-gram, 10-gram, and 50-gram scaled levels for the AN/RF (90/10) formulation and gave the same response results each time. These results indicate the very desirable (insensitive) safety characteristics of this material. The chemical reactivity test (CRT) is a LLNL test to evaluate the evolution of any gaseous species during a 22-hour thermal treatment at 80 in a sealed sample loop. Values above 4.0 cm³/g of material are considered thermally reactive. Samples are run by themselves and also with other materials that it may come in contact with (e.g., metals, polymers, adhesives). As can be seen in Table 2 AN/RF (90/10) has a very low CRT value as it does have in combination with both copper and steel.

Detonability tests

The key task in this project was to evaluate the detonation characteristics of AN/RF nano-composite by a precision cylinder test. The sponsor to further evaluate the utility of AN/RF for their purposes would utilize data from the cylinder test. Due to the complexity and time involved in a precision cylinder test it was necessary for an evaluation of the rough characteristics of detonation of this composite material. While there was strong belief that this material would detonate, we have to keep in mind that the material is a new energetic material with no historical data to guide us. With that in mind we performed some detonability test with the material to evaluate the critical diameter and density of material that would in fact sustain a

detonation upon suitable initiation with a booster. Table 3 shows the important parameters in the three detonability tests performed in this study.

Table 3. Results from detonability experiments where a cylinder of material (2.54 cm x 15.25 cm) was initiated with a 23-gram booster charge of Composition B explosive.

Test	Date	Material	Density (g/cm ³)	%TMD	Detonation velocity (km/sec.)	Comments
1	11/04/09	AN/RN (90/10) sol-gel composite	1.6	97	NA	Detonation Failed
2	2/25/10	AN/RN (90/10) sol-gel composite	1.4	80	NA	Detonation Failed
3	4/12/10	AN/RN (90/10) sol-gel composite	0.92	54	2.92	Detonation propagated

One can see from the data in Table 3 that detonations were not sustained in AN/RN (90/10) material with densities of 1.6 and 1.4 g/cm³ (97% and 80% TMD), respectively. However detonation was sustained at a density of 0.92 g/cm³ (54% TMD and the pour density of the material) and achieved a final detonation velocity of 2.86 km/sec (with an average velocity of 2.92 km/sec.). The raw data for the crush pin times is given in Table 4.

Table 4. Raw data from detonability experiments of AN/RF (90/10)

Shot #	# Pin to # Pin	Distance (mm)	Time (μ sec)	Velocity (mm/ μ sec)
3	1 to 2	25	8.070	3.098
3	2 to 3	25.4	8.939	2.839
3	3 to 4	25.4	8.926	2.846
2	1 to 2	25	34.84	0.716
2	2 to 3	24.5	NA	Detonation failed to propagate beyond this point

The data in Table 4 enables a closer examination of what is occurring in the detonability tests. The data for shot #3 (the one that propagated a detonation) reveals that the transit time from pin 1 to pin 2 gave a detonation velocity of 3.098 mm/ μ sec and subsequent detonation velocity intervals (pin #2 to #3 and #3 to #4) of 2.839 and 2.846 mm/ μ sec, respectively. It is likely the first detonation velocity is a bit high and is likely overdriven by the Composition B booster charge. The subsequent two detonation velocity intervals indicate a wave that appears to have reached steady state. The data from shot #2 shows the very slow detonation velocity of 0.714 mm/ μ sec, for pin #1 to pin #2, in the higher density formulation (80% TMD), which is likely just driven by the booster charge output. This is further supported by the cessation of the detonation wave in the next interval.

Figure 5 contains the photos of the experimental hardware after detonability test #1. Note that the cylinder is partially intact (initiation was from the top of the cylinder in the photo). This indicates that the detonation wave did not propagate to bottom dent plate, also shown in the right side of the figure.



Figure 14. Photos of the experimental hardware after detonability test #1.

From this data it appears that AN/RF 90/10) nano-composite exhibits Group 2 explosive behavior as described by Price.⁹ Group 2 materials behave more ideally in detonation with higher porosities in contrast to Group 1 materials which behave more ideally at low porosities. For a given diameter there is a critical density above which Group 2 materials will fail in detonation. Failure behavior of this type is often attributed to explosives consisting of mixtures of fuel and oxidizers, and is commonly seen in formulations containing AN.^{9,10}

There are several reports on sol-gel energetic materials containing organic gel frameworks with inorganic oxidizers imbedded in them. Most of these studies involve the synthesis and formulation of these materials along with small-scale safety and thermal behavior.^{4,11,12} There is only one report of the detonation properties of sol-gel derived oxidizer fuel explosive networks. That work involves the use of RF as the fuel and ammonium perchlorate (AP) as the oxidizer.¹¹ A nano-composite consisting of AP/RF (80/20) (oxygen balance of -8.5%) was prepared using sol-gel chemical routes and dried using freezing and sublimation of the water solvent to give cryogel powders. These powders were cold pressed to a density of 1.68 g/cm³ and a cylinder test performed which gave a detonation velocity of 6900 km/sec detonation velocity. This detonation velocity was ~14 % less than that predicted by the CHEETAH code. This material has metal accelerating ability somewhat below that of TNT. In addition the small-scale safety characteristics of this material indicated it is a sensitive energetic material to friction and impact. This composite has a ignition impact energy of 4.0 J and friction ignition energy of 210 N compared to 7.5 J and 120 N for the explosive RDX respectively. This is significantly more sensitive than the composites described here, however AP formulations are often more sensitive than those with AN. It is worthwhile to note that the sol-gel organic/inorganic materials that have the more sensitivity and the reasonable performance are those prepared by freeze drying of composite materials. It

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