

HAZARDOUS REACTIONS OF ALUMINUM POWDER WITH WATER IN THE PROPELLANT, EXPLOSIVE and PYROTECHNIC (PEP) INDUSTRIES.

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Although aluminum powder has been successfully used in propellant, explosive and pyrotechnic (PEP) for generations, there are hazards associated with allowing the material to become wet. Unfortunately, many of the normal industrial operations, such as the use of water traps on vacuum collectors, may allow wet aluminized PEP to accumulate, resulting in a hazardous event. This paper investigates the reaction phenomena and provides some test data to qualify the hazard.

BACKGROUND

Aluminum metal has been used in the propellant, explosive and pyrotechnic (PEP) industries for slightly more than 100 years³. Prior to discovery of the Hall - Heroult electrolytic process for reducing aluminum from bauxite ore in 1886, the cost of aluminum per kilogram exceeded that of most precious metals. As late as World War I the cost of aluminum was prohibitively high, which significantly limited the use of the metal in explosive mixtures. It was not until the mass production of aluminum structural metals prior to the Second World War that the use of powdered aluminum in torpedoes, bombs and pyrotechnics became widespread. The annual US military consumption during World War II was estimated at 40,000 metric tons per year and the German consumption about 25,000 tons.

The addition of aluminum powder substantially increases the blast radius in aluminized explosives and increases the brisance by about 10%. In pyrotechnics, the addition of aluminum provides a brilliant white light with a substantial heat release. Aluminum powder is often added to explosives to provide an additional incendiary effect that results from the massive release of energy as the aluminum reacts with oxygen to form the stable aluminum oxide. This reaction yields more than 225 kcal per mole. Aluminized solid propellants utilize this substantial heat release, and after World War II large rocket boosters took advantage of this fact by using aluminum as an additive. Aluminized propellants are still currently used in the solid rocket boosters for the NASA Space Shuttle.

The current US explosive inventory has numerous aluminized explosive formulations. The principal aluminized explosive compositions are listed in Table 1. In the realm of pyrotechnics,

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³Davis, Tenney L.; Chemistry of Powder and Explosives, John Wiley and Sons, NY, 1941; pg. 62.

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the use of aluminum can be found in almost any composition from display fireworks to anti-missile flares. Likewise, the use of aluminum in the solid propellant industry is widespread and can be found in a very large number of compositions.

Table 1
Common US and Former Soviet Union
Explosives Containing Aluminum Powder

<i>US Materials</i>	<i>FSU Materials</i>
Comp A3/Al	A-IX-2
DBX	A-IX-20
H-6	Akvatol
HBX-1	Alyumotol
HBX-3	Grammonal
HTA-3	Granulity
Minol	TGA-6
Torpex	TGAF-5
Tritonal	

Aluminum powder used in the PEP industry varies in both size and shape depending on the specific purpose that the metal is to perform. In the pyrotechnic fields the use of flaked and grained aluminum in addition to atomized materials is common, while in the solid propellant and explosive compositions the atomized variety is almost always used. The manufacturing techniques of these powders substantially contribute to the behavioral characteristics. For some specialty pyrotechnic flake powders, sheets of aluminum are repeatedly hammered in stamping mills until the resultant metal is reduced to both the desired thickness and size. Aluminum flake powder made for the industry today is typically ball-milled instead of stamped. Surface coatings, such as greases and waxes, inhibit the oxidation of the surface and allow for thinner platelets to be formed without agglomerating. Flaked aluminum is also used in the formulation of many paint pigments and is often called “aluminum bronze powder” as slightly different alloys allow the paint pigment to simulate various metallic hues. Aluminum flake made to the US military specifications⁴ ranges in size from 20 to 325 (44 μ) mesh and can range in thickness down to 4 microns.

Grained aluminum is formed by grinding aluminum stock to form fine particles that are roughly spherical in nature. Although this process is still recognized by the US military as being an acceptable production process, the economics of the process is not as favorable as atomization. Although not recognized by the US military specifications, the commercial mining industry often uses reclaimed aluminum fines and turnings⁵ from machine shops in the production of aluminized watergel explosives.

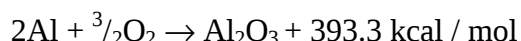
⁴Military Specification MIL-A-512A; Aluminum Powder, Flaked, Grained and Atomized; US GPO; 11 June 69

⁵Fletcher, L.; *Personal Communication*; US BuMines, Minneapolis Research Station, Mpls, MN.

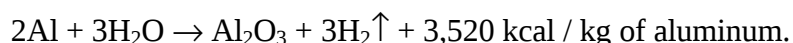
Atomized aluminum is made by spraying liquid aluminum in a large chamber that allows the surface tension to pull the individual droplets into spherical shapes. The size of atomized aluminum can be controlled by modifying the spray geometry to allow for the production of aluminum in a very wide range of sizes. One critical property of the atomized aluminum is the surface chemistry of the droplet. Aluminum atomized in air forms a thick layer of oxide or oxidizes completely while material atomized in inert gases may have pristine surfaces that will react exothermally when exposed to air. For these reasons the aluminum industry often uses small amounts of oxygen, in an otherwise inert atmosphere, to atomize the aluminum as the low amount of oxygen provides for a controllably thin oxide layer. Typical oxygen concentration is in the 3% to 7% range for non-specialty aluminum powder.

Aluminum powder becomes more reactive with increased surface area per unit mass. The generally accepted transition for the point at which aluminum powder becomes reactive to handling is in the 40 micron range. Material larger than the 40 micron size is too large to easily react unless an abnormal situation exists. The range of atomized aluminum used in propellants, explosives and pyrotechnics is generally much smaller than the 40 micron size. In the production of Tritonal, a TNT/Al mixture, the US military specification⁶ requires an *average* size of 27 +/- 7 microns with substantially smaller sizes implied.

The hazard of powdered aluminum in air causing a dust explosion is well recognized by the explosive safety community. The resultant dust explosion from as little as 35 grams of aluminum powder per cubic meter of air can yield overpressures in the order of 0.6 million Pascals⁷ (MPa). Potentially as dangerous as the dry aluminum reaction with oxygen is the wet aluminum reaction with oxygen. From the classical chemical standpoint, the reaction of aluminum with air is given as:



while with water the reaction is very similar:



The oxidation of aluminum in water releases, according to Cook, “2.5 times as much heat as is generated from pure nitroglycerin”⁸ plus the reaction adds a plume of fine hydrogen bubbles that can further sensitize the mixture. Aluminum is intentionally added to many commercial watergels for the specific purpose of generating hydrogen bubbles as it is well demonstrated that fine bubbles significantly increase the sensitivity of the explosive mixtures. To make the ammonium nitrate based explosive mixtures more likely to detonate, glass microballoons are often added to commercial explosives in order to sensitize those mixtures.

⁶MIL-A-512A, Op Cit; Type III, Grade F, Class 7.

⁷Explosion Venting Guide, Article 68, Table 5; National Fire Protection Association, Batterymarch, MA.

⁸Cook, Melvin A.; The Science of High Explosives; American Chemical Society Monograph No. 139, Van Nostrand Reinhold Co., NY; 1958; pg. 304.

The reaction of aluminum powder and water is not well documented and is even denied by some people outside of the commercial blasting industry. Weingart described the fine pyrotechnic aluminum powders as being “unaffected by water”⁹ and Federov downplays the reaction of aluminum in water by stating:

“An important reaction of metallic aluminum is its behavior with oxygen or water. Under many conditions the reaction is self-stopping because of the formation of an impervious film of aluminum oxide.”¹⁰

Others, such as Shidlovskii, recognized that wet aluminum¹¹ powder would spontaneously heat. Indeed, the US Government recognizes that the proper shipping classification¹² for certain grades of aluminum powder is *Class 4.3 - Flammable Solid, Hazardous When Wet*. Yet, for reasons of safety, much of the PEP industry uses water on aluminized materials in order to reduce the hazard of ignition from static electricity or from sparks.

In addition to flooding aluminized materials for safety, many ammunition loading operations use wet collectors in their vacuum lines to trap the explosive fines generated during loading operations. Although these production operations have a very good safety record, several incidents have occurred that point out that the reaction of aluminum with water can easily happen. Conversations with US ordnance safety personnel have identified numerous events involving aluminum and water in the United States as well as literature documenting some of the more significant events. The US Army¹³ researched the reaction of wet aluminized TNT (Tritonal) in loaded bomb incidents and the Swedish¹⁴ have presented the destruction of a facility of the Swedish Match Company from an aluminum water reaction. Although unpublished, the loss of structures at the Salt Lake City rocket facility and the Joliet Army Ammunition Plant have demonstrated the potential danger of wet collectors in production operations.

The many hours of operational experience with using wet collectors without event appears to contradict the equaling compelling evidence that allowing water to mix with aluminum powder is hazardous. Resolving this apparent contradiction has become even more critical as new methods of demilitarization utilize high-pressure water or steam to remove old aluminized explosives in an environmentally safe manner. It was this area of uncertainty regarding the reaction of aluminum powder and water that Ana Navarro chose as her area of research for the 1996 International Science and Engineering Fair (ISEF) competition.

METHODOLOGY

⁹Weingart, George; *Pyrotechnics*; Chemical Publishing Company, NY, Second Ed., Revised, 1947; pg. 10.

¹⁰Fedoroff, Basil T. ed.; *Encyclopedia of Explosives and Related Items*; Picatinny Arsenal, NJ 1960; Vol. 1, pg. A143

¹¹Shidlovskii, A. A.; *Principles of Pyrotechnics*; Third Ed. Moscow, USSR, 1964. (AD A001 859), pg. 229.

¹²Title 49 *Code of Federal Regulations* (CFR): Department of Transportation, Section 172, Hazardous Materials.

¹³Hendrickson, John R.; *The Tritonal-Water Reaction as a Possible Explanation of M117 750-Pound Bomb Incidents*; Picatinny Arsenal, NJ; 1968..

¹⁴Johansson, Stig R. and K. Goran Persson; *Explosion Hazards of Pyrotechnic Aluminum Compositions*, in *Pyroteknikdagen*, Stockholm, Sweden, 1971.

In order to test the reaction of aluminum in water, seven experiments with replicates were conducted over a period of several months. These experiments were conducted in the laboratories of Alliant Techsystems in Hopkins, Minnesota. The tests were arranged as follows:

Test #1	1 gm Aluminum powder in 10 ml deionized (DI) water
Test #2	20 gm Al in 25 ml DI water
Test #3	1 gm Al w/ 1 gm ammonium nitrate in 10 ml DI water
Test #4	1 gm 80/20 Al/TNT ¹⁵ in 10 ml DI water corrected to the following pHs • pH 5 • pH 5.5 • pH 6.0 • pH 7 • pH 8 1 gm 80/20 Al/TNT in 10 ml aluminum corrosion inhibitor ¹⁶
Test #5	1 gm Al in 10 ml DI water
Test #6	20 gm Al in 25 ml DI water
Test #7	1 gm Al in 10 ml DI water

The first three tests utilized 40 micron nominal aluminum powder while the last four series utilized Mil-A-512A Type III, Grade F, Class 7 with a nominal size of 27 microns. The particle size analysis¹⁷ for the Mil-A-512A material is presented in Figure 1. No particle analysis was performed on the larger 40 micron material. The test tubes were loaded with the dry powder weighed out on a Mettler digital analytical balance and the liquid added to the test tubes prior to being plugged with a single hole rubber stopper. Each test tube was instrumented with a AWG 30 Type K thermocouple that was coated in polyurethane to prevent secondary reactions between the thermocouple and the aluminum. The thermocouples were attached to an Omega OM-500 data recorder for data-logging every 15 minutes. In order to prevent temperature fluctuations in the building from affecting the test results, an isothermal block of polystyrene was constructed that measured approximately 0.5 meters on each side and the test tubes were nested in individual holes separated from each other.

Each test was run for at least 168 hours and the test data entered into a personal computer for data analysis. Visual observations of the liquids were reserved until after the scheduled time interval to prevent influencing the test results. The test tubes were not cleaned after each test, but were accumulated to allow longer term visual observation of the reaction and by-products.

RESULTS

The reaction of aluminum with water occurred in every test sequence and became quite violent with even the one gram samples. The reaction with the 20 gram sample was significantly violent as it forcibly ejected some of the contents with sufficient force to embed it into the box cover. All tests after this point, with the exception of Test #6, were restricted to 1 gram samples to

¹⁵The test sequence that utilized TNT was prepared by G. Wittmer, Principal Chemist, on Ana's behalf as it is against Alliant Techsystems policy to allow students to handle energetic materials.

¹⁶Opti-Shield; Commercially available aluminum corrosion inhibitor used in high energy laser cooling systems.

¹⁷Particle size analysis was performed by Gradient Technologies, Andover, MN.

prevent damage to the laboratory setup. All of the test tubes with aluminum powder reacted with visible bubbles present in the aluminum mass appearing in the bottom of the test tubes. None of the control test tubes loaded with only DI water showed any rise in temperature or presence of bubble formation.

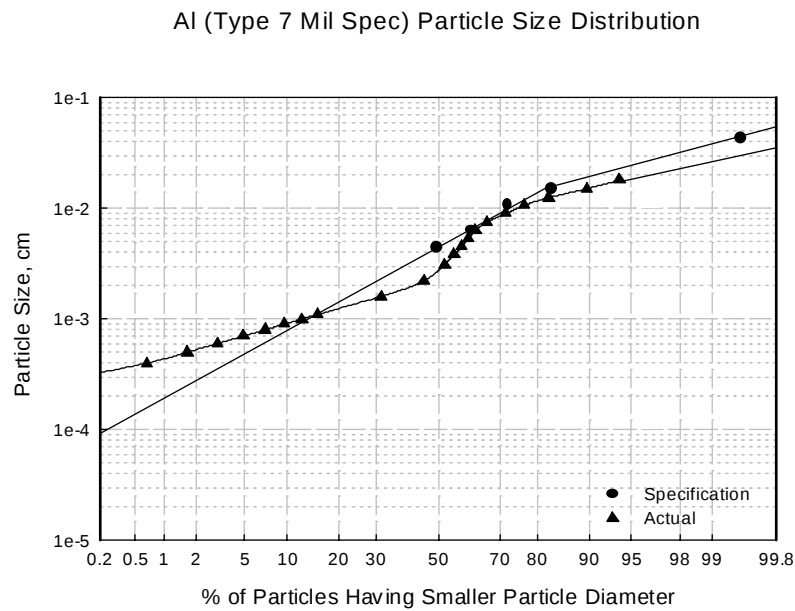


Figure 1
Particle Size Analysis of Aluminum
Powder Meeting Mil-A-512A Type III
Group F, Class 7

In those test tubes that contained aluminum and TNT, the test tubes were significantly discolored and changed from a light tan to black. The commercial corrosion inhibitor also reacted with the explosive mixture to form the same burnt toast color. The time and temperature curves are attached as an appendix.

Most significant in the results of the testing was the length of time that the reactions took to occur. The testing resulted in average time to peak reaction of over 50 hours. Another interesting phenomenon was the difference in the rates of reaction. The test results, when plotted as time versus temperature, showed great differences between tests. Some materials would react all at once while other materials would gradually ramp up to a plateau and then hold constant for a longer period of time before exhausting the reaction. The plateau type of reactions were similar to the one presented by Shidlovskii¹⁸ for wet aluminum powder, while the more dramatic rise in temperature corresponded to the temperature curve presented by Johansson and Persson.¹⁹

In the Al/TNT tests, the pH was varied to investigate the affect that pH had on the reaction. In the region where the water was neutral with a pH of 7.0, the reaction was significantly more exothermic than in either the more acidic or basic solutions. Nevertheless, the visible color change in the test tubes mentioned above showed that all materials had reacted and gone through degradation.

In the Al/water reaction tubes, the reactants were still reacting several months after being removed from the test box. In some cases the entire water content was consumed or evaporated while in the controls the water content was still present. The reaction of the aluminum powder in water also broke several of the Pyrex test tubes, probably from the physical expansion of the ceramic oxide that formed a hard, fused cake. One test tube, however, was broken but the aluminum oxide powder that was formed was free flowing.

There appeared to be a definitive mass effect as the two tests that were the most dramatic were the tests using the larger quantities of aluminum in water. This would be logical as the larger masses were contained in larger test tubes and had less surface area from which to reject any heat build up. This spontaneous heating of aluminum and water contradicts Johansson and Persson²⁰ who stated that the presence of nitrates was necessary for self-heating compositions but confirms their observations that mass effect was critical.

DISCUSSION

As shown by the testing, the reaction of aluminum powder and water does exist and is an exothermic reaction that presents a significant hazard if the reaction rate generates heat faster than the environment can remove it. The degradation of the TNT in the test sequence #4 shows that there is a definite interaction with the explosive during the reaction of aluminum in water. This co-reaction was discussed by Shidlovskii²¹ who wrote about the reactions between the aluminum and water decomposing the alkali metal nitrates into hydroxides.

¹⁸Shidlovskii, Op Cit.; Fig 12.1, pg. 230.

¹⁹Johansson and Persson, Op Cit.; Fig 3, pg. 79.

²⁰Ibid; pg. 84.

²¹Shidlovskii, Op Cit.; pg. 232.

The mass effect that was observed was also observed by Shidlovskii²² and Johansson and Persson²³ who showed that with larger quantities of material the composition would proceed to auto-ignition. Johansson and Persson further demonstrated that, under the right conditions, the aluminum / water reaction could proceed past ignition to deflagration and potentially detonation. Their testing was in response to the detonation of 12 kg of aluminized pyrotechnic composition in water that exploded and destroyed a production building.²⁴

One further area that should be of concern is the introduction of foreign materials into the aluminum or water that may accelerate the reaction. Shidlovskii mentions that contamination of the aluminum with magnesium, copper, mercury or lead will lead to a rapid increase in the reaction rates as these materials, and very likely many others, create galvanic cells with the aluminum powder.²⁵ The problem of contamination is of particular interest to those involved with the demilitarization of ordnance as the chemical composition of the materials being reclaimed is not always known and the process of reclamation often introduces materials that would not normally be there during the original production operation. The introduction of water from steam or waterjets also may introduce with it any contaminant that may be in the water or in the plumbing. With steam especially, the water is often treated with a wide variety of chemicals to prevent damage to the steam boiler that may be reactive to the aluminum.

CONCLUSIONS

Production and safety personnel should recognize that the reaction of aluminum and water is a real potential whenever those two materials are in contact. The reaction of the two materials can be controlled if held in either sufficiently small quantities or there is adequate heat removal. That the reaction does not take place immediately should not be the basis for a false sense of security. Additional precautions should be taken to prevent the introduction of secondary contaminants into aluminum compositions that would accelerate the reaction process.

Comment by Paul Miller

This paper was adapted from Ana Navarro's presentation to the International Science and Engineering Fair this last May where she took second place internationally for Engineering. Alliant Techsystems has made it a practice to assist talented students and has a goal to encourage women and minorities students in the fields of science and engineering.

²²Ibid; pg. 230.

²³Johansson and Persson; Op Cit; pg. 81.

²⁴Ibid; pg. 79.

²⁵Shidlovskii, Op Cit; pp. 233 and 236.

Figure 2
Test #1 Al/Water

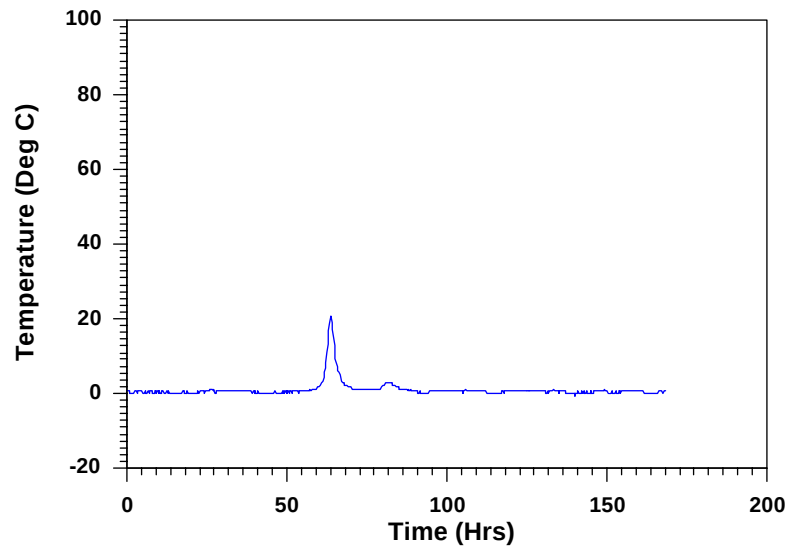
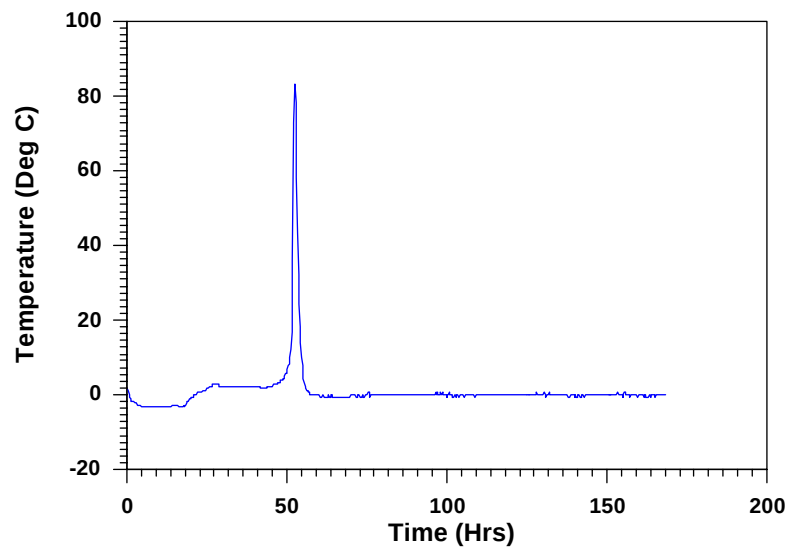


Figure 3
Test #2 Al/Water



Note: All figures in this appendix are drawn from the temperature differential when corrected for ambient changes in the test box temperature.

Figure 4
Test #3 Al/ NH_4NO_3 /H₂O

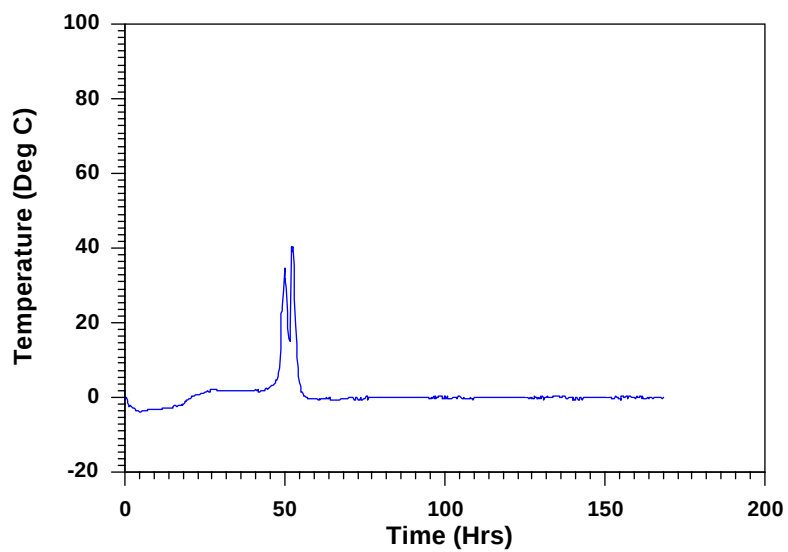


Figure 5
Test # 4 80/20 Al/TNT pH 5.0

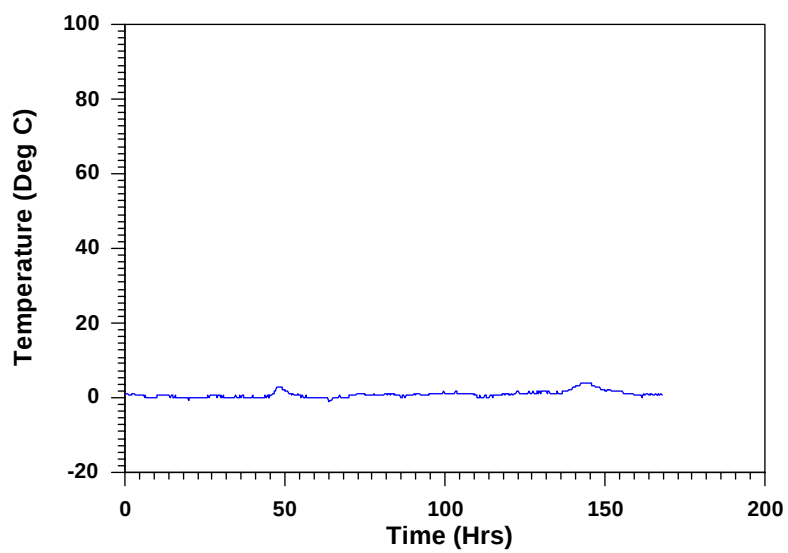


Figure 6
Test # 4 80/20 Al/TNT pH 5.5

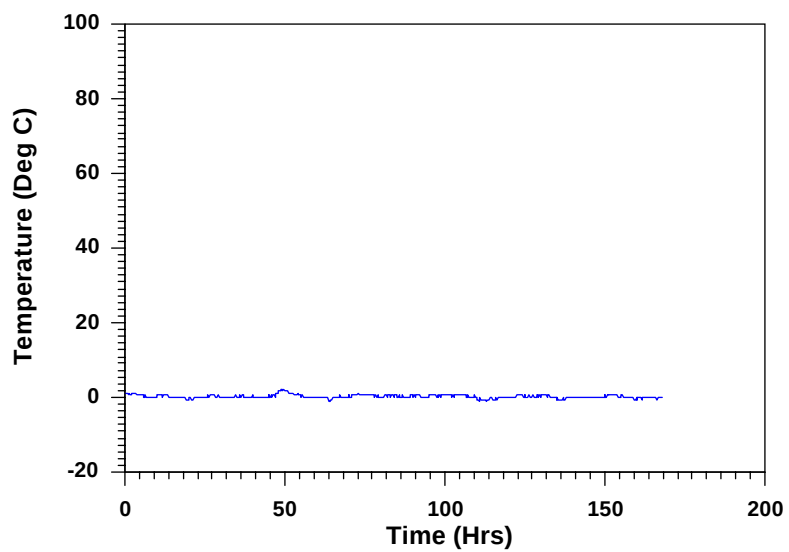


Figure 7
Test # 4 80/20 Al/TNT pH 6.0

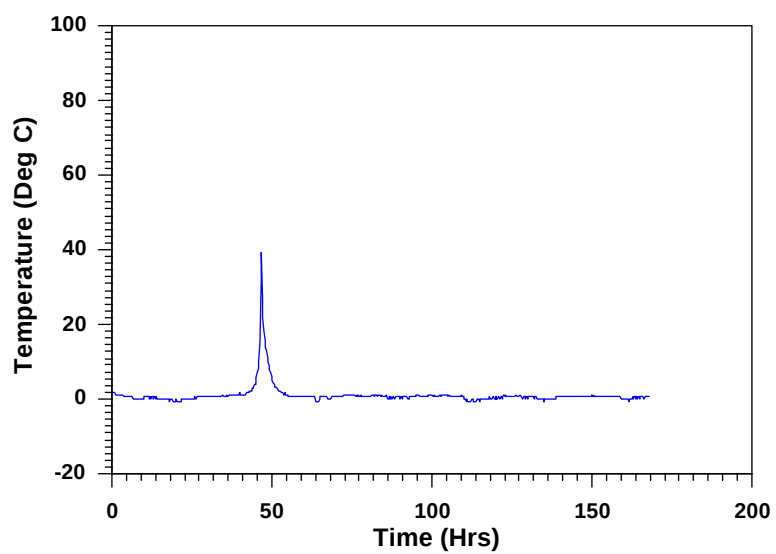


Figure 8
Test # 4 80/20 Al/TNT pH 7.0

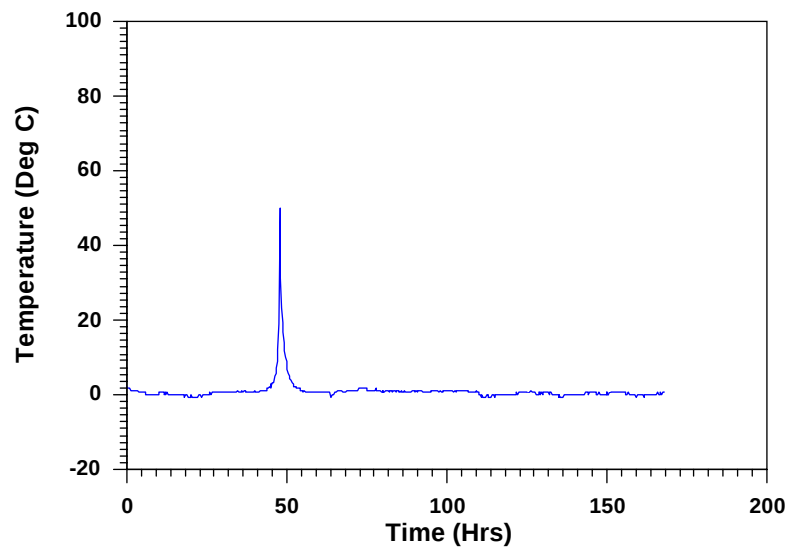


Figure 9
Test # 4 80/20 Al/TNT pH 8.0

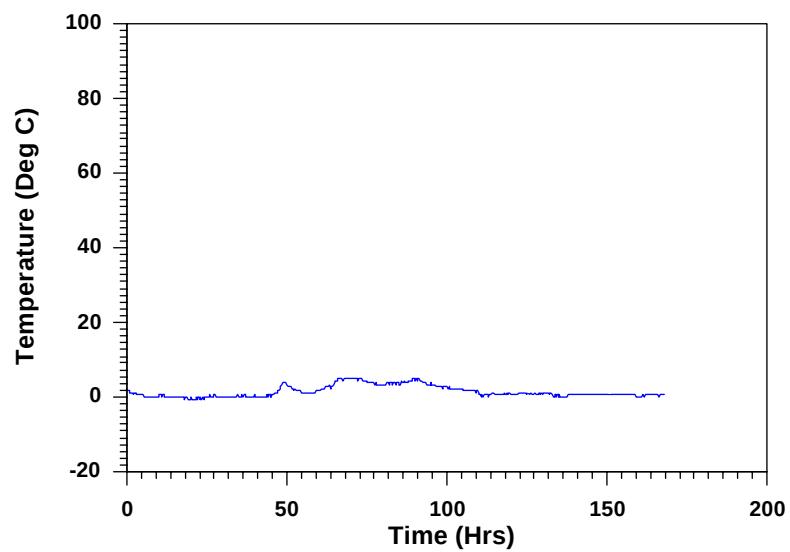


Figure 10
Test # 4 Test Control

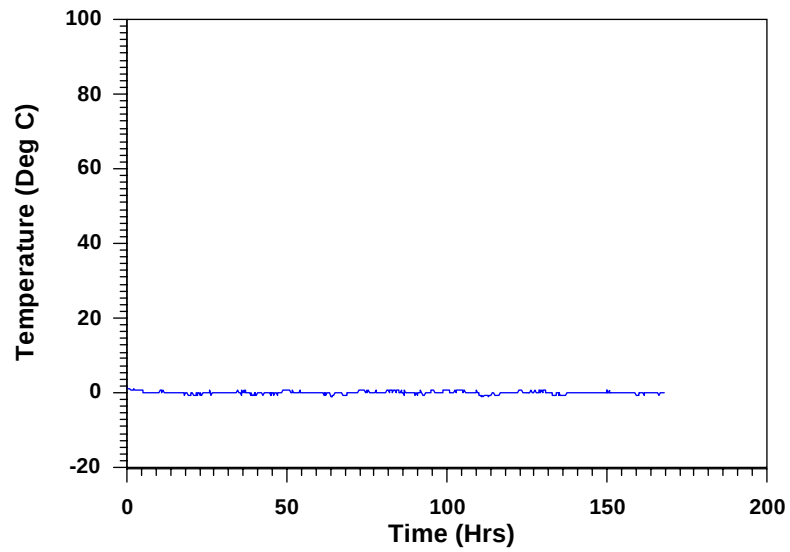


Figure 11
Test #5 Al/Water

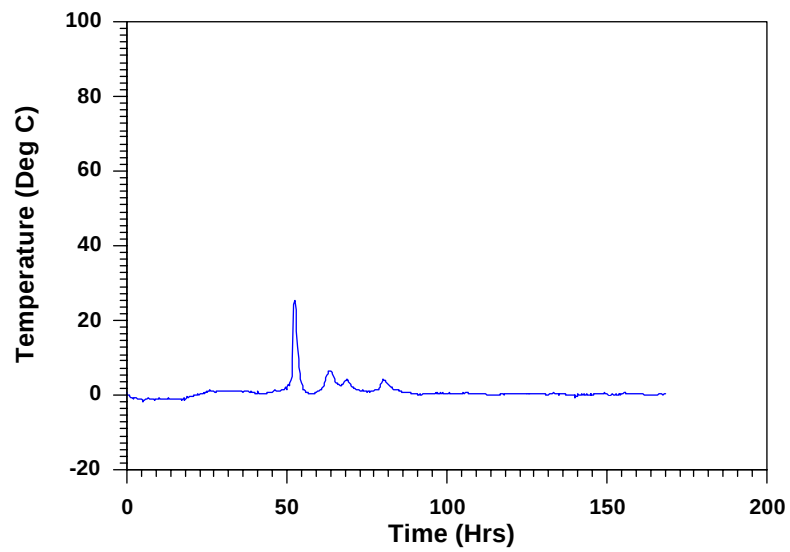


Figure 12
Test #6 Al/Water

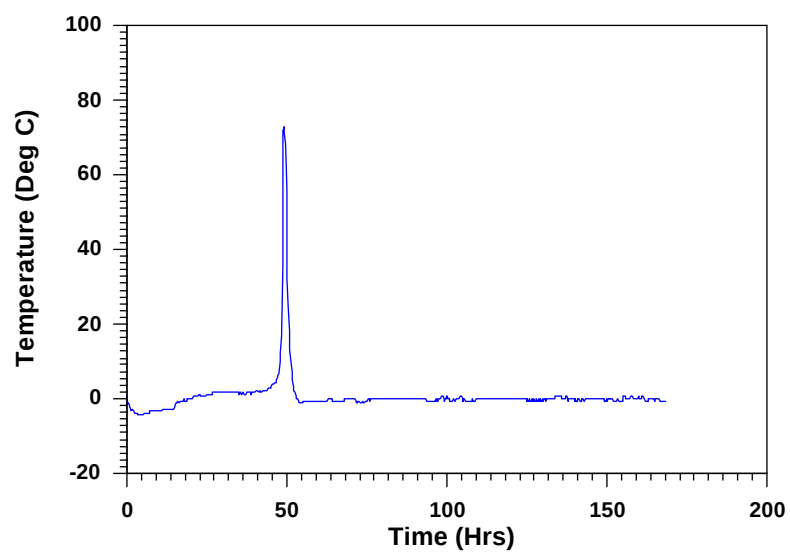


Figure 13
Test #7 Al/Water

