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**Reaction of Large Volume GB with $\text{Li}_3\text{N}+\text{H}_2\text{O}$
and Unresolved Issues for the Tactical
Disablement Project**

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PREFACE

The work described in this report was authorized under project no. CB10412. The work was started in February 2019 and completed in March 2022.

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REACTION OF LARGE VOLUME GB WITH $\text{Li}_3\text{N}+\text{H}_2\text{O}$ AND UNRESOLVED ISSUES FOR THE TACTICAL DISABLEMENT PROJECT

1. INTRODUCTION

As part of the Tactical Disablement Project, neat weapons-grade isopropyl methylphosphonofluoridate (sarin; GB) was reacted with lithium nitride (Li_3N) and water (H_2O) in glass or steel reaction containers using up to 1 L of GB by volume. Products were analyzed, and reaction schemes are provided to explain the products. Solid product was formed under some reaction conditions. To find the best conditions for solid formation, studies were done using similar volumes of dimethyl methylphosphonate (DMMP) as a simulant. Some complications with Li_3N reagent in this volume size are discussed.

The objective of this tactical disablement project was to use a minimal amount of reagents to make bulk chemical agent (CA) unusable as a threat through the neutralization or solidification of the bulk agent. Wet chemical reactions were performed in the simulated CA storage container without any mechanical mixing, excessive agitation, or external heating. The goal was to avoid the need to transport the storage container or transfer the chemical out of the container into a reactor.

A previous study¹ demonstrated a method to perform the neutralization reaction of bulk GB CA in a glass jar that simulated a storage container using a small volume of GB. Solidification of the product was observed, although the amount of solidification varied, and the mechanism is not well understood.

Reaction of GB with several reagents were studied in preliminary surveys. The most effective reagents were Li_3N and H_2O . These reagents form a strong base, and decontamination occurs by basic hydrolysis to form isopropyl methylphosphonic acid from GB. A detailed study was done to narrow down the range of reagent ratios. A 100 mL scale reaction and multiple smaller runs were done, and the products were analyzed.¹ The minimal quantities of chemical reagents were typically 15% by weight of the amount of CA. The amount of reagent was determined by the stoichiometry of the reaction and by the addition of enough reagent to form a solid product.

Previous studies used the same reaction conditions for *O*-Ethyl-*S*-(2-diisopropylaminoethyl) methylphosphonothiolate (VX),² *O*-(2-diisopropylaminoethyl) *O'*-ethyl methylphosphonite (QL),³ methylphosphonic difluoride (DF),⁴ and pinacolyl methylphosphonofluoridate (GD).⁵ Neutralization of a CA was required to greatly reduce the toxicity of the chemical. However, it was not anticipated that an environmentally approved decontamination method such as that which was required for the destruction of the U.S. CA stockpile would eliminate toxicity. This study did not require a method for trace detection of residual GB in the reaction products to determine residual amounts of agent or final toxicity.

Further studies were performed on the process of forming solid products to make the results more reproducible. Some reaction runs were done using the simulant DMMP, which

is less reactive than GB. Solidification was observed with DMMP, so it was found that a reactive CA or the formation of acid products was not needed to obtain solidification. These simulant studies provided valuable information about the limiting conditions that are required to make the products solidify.

This report discusses scaling up the reaction to a 1 L volume. Additional studies with DMMP were also done at this scale. Reaction to decontaminate the GB was still observed, but the problem of mixing the reagents became more complex for larger volumes. The original goal of the project was to minimize physical mixing of the reaction mixture to reduce the amount of manipulation required for the reaction. Without mixing, however, there was significant variation among the reaction runs. The problem of inhomogeneous reaction mixtures was also more significant for large volumes than for small volumes because diffusion is not as effective at mixing large volumes. Because one reagent was the solid Li_3N , the amount of settling varied from a powder that was fairly evenly dispersed for long time periods to pellets that tended to sink quickly to the bottom or sometimes float on the surface.

The issues related to using Li_3N as a reagent at the large reaction scale will be discussed in this report along with other topics that need further study before the decontamination method can be fielded.

2. EXPERIMENTAL RESULTS OF LARGER SCALE REACTION STUDIES

2.1 Chemical Sources

The GB reaction runs were done with technical grade, stabilized GB, and the 1 L reaction was performed in a glove box at U.S. Army Chemical Transfer Facility (CTF; U.S. Army Combat Capabilities Development Command [DEVCOM CBC]; Aberdeen Proving Ground, MD). The GB contained unknown dissolved metals or metal particles that gave it a dark color. All reactions were sampled to determine residual GB using ^{31}P NMR. Reaction times between sampling varied, and kinetic time points were not measured at frequent time intervals to determine rate information for the samples.*

DMMP (>98% purity, Chemical Abstracts Service [CAS] No. 756-79-6; part no. D169102) was purchased from Millipore Sigma (St. Louis, MO).

Sandia National Laboratories (SNL; Albuquerque, NM) purchased Li_3N (99.4% purity; CAS No. 26134-62-3; part no. 35479) from Alfa Aesar (Tewksbury, MA). The powder was pressed into pellets in a glove box at SNL. Pellets were stored in screw cap vials under Ar gas for shipment and until use.

**Caution:* The use of GB in these procedures should only be performed by trained personnel using applicable safety procedures and approved engineering controls. Regulations for use and decontamination of a 1 L quantity of GB are stringent and based on national and international laws.

Water (H₂O) was obtained from an in-house distilled deionized (DI) source. Deuterated water (D₂O) and deuterated chloroform (CDCl₃) for use as NMR lock solvents were obtained from Millipore Sigma.

2.2 General Considerations for Reagent Addition

As reported previously,¹ a variable amount of product solidification for GB and DMMP reactions was observed in multiple trial reactions. DMMP is less reactive to hydrolysis compared with GB, but it is used as a nontoxic simulant. Initial small-scale studies formed solidified products with GB and DMMP, but other studies failed to produce solidified products.

Several different reaction conditions were studied that were dependent upon the order and method by which reagents were added: (1) Add Li₃N powder or pellets to CA first, followed by slow addition of water using a pipet or syringe. (2) Add Li₃N first, followed by fast addition of water in the measured amount without mixing, which could form a local high concentration of water at the surface. (3) Add water to CA first and mix so the liquid was homogeneous, followed by addition of Li₃N powder. (4) Add water quickly, then add Li₃N pellets.

The major difference among these methods was the amount of mixing of the liquid reagents. If water is added quickly, it can form a layer on the surface of the denser CA. In addition, the solid can settle on the bottom or stay suspended in the partially mixed liquid. Water can react faster if it is in contact with the solid or slower if the solid settles at the bottom while the water is on top. Pure water can react quite vigorously with solid Li₃N powder, as discussed in more detail in previous work,¹ whereas water that is premixed as 10% in CA reacts slowly. These differences can significantly affect the speed and progress of the reaction. If the reaction is vigorous enough to generate a temperature increase in the liquid, the reaction accelerates in a nonlinear way. This accelerated reaction can be difficult to control or reproduce.

Method 1, using Li₃N pellets, was studied most extensively. Reagent tablets were anticipated to have a practical advantage over powder because they are simpler to handle and store. Pellets were easily formed from commercial Li₃N powder by compression in a pellet press. This method slowed down reactions by decreasing the surface area of the solid relative to a fine powder. However, there was a competition between reaction and settling out of the Li₃N reagent onto the bottom of the reaction container. Settling further slowed the reaction.

Method 2 was the best method for causing rapid and complete solidification. Solid Li₃N came into contact with relatively pure water, which caused rapid reaction and heating of the liquid. However, there could be catastrophic effects. With methods 2 and 4, it was possible for some pellets to float on the layer of water. These pellets got red hot when exposed to pure water if they were not submerged (see section 3.1.2). Powder that was exposed to water could form red-hot sparks capable of igniting any flammable organic compound that is present.

When the water was added rapidly but the pellets and powder were submerged, it was possible to achieve boiling of the solution at a temperature of 90–100 °C because the reaction of water with the Li₃N solid was accelerated.

The reaction usually progressed slowly when method 3 was used on a 10 mL volume of DMMP or GB. However, method 3 unexpectedly ignited flames in one trial when a test volume of 100 mL DMMP was used. The ignition may have been caused by fine powder being added quickly to the liquid. Fine particles became red hot from fast reaction with water, which ignited the DMMP vapor above the liquid. This mechanism is not likely to be a problem for CA compounds because they do not have a flashpoint and do not ignite with a spark.

It is difficult to determine the best method for adding reagents that optimizes the reaction rate of the CA and is also safe for operators.

2.3 Study of the Solidification Process Using DMMP up to 1 L Volume

It was necessary to perform trial runs at a variety of volumes because the amount of reagent mixing could depend strongly on the total volume. In particular, diffusional mixing is less effective for large volumes. A full 1 L run consumes significant amounts of reagents and generates a volume of waste; therefore, the number of 1 L runs was minimized, and conditions were chosen for demonstration purposes that were expected to be appropriate for field use.

The first 1 L DMMP reaction run was done in a steel container. Reagents were added to the container, and a pressure gauge and steel plug were used to seal the container. DMMP was added first, followed by water (10% or 100 mL) and Li_3N pellets (5% by weight or 50 g).

It was not possible to observe mixing within the steel container. The container was agitated to mix the DMMP with water, which should be similar to method 3 but was more likely similar to method 4. When the Li_3N pellets were added, flame was generated at the top of the container from ignition of the DMMP vapor (**Error! Reference source not found.1**). It is possible that there was Li_3N powder on the threads of the container that contacted water and was hot enough to generate a spark.

After the reagents were added, a pressure gauge was used to seal the container. The reaction mixture heated up, and the temperature on the outside of the steel container reached 170 °C within 30 min after the reagents were added. The flame generation and energetic reaction are assumed to be a result of the reaction of nearly pure water with the Li_3N pellets, indicating that the water was not well mixed with the DMMP. The pressure increased to at least 250 psi. (The pressure gauge read at its maximum, so the actual pressure may have been higher.) By the next morning, the reaction was finished, the container had cooled off, and the pressure had returned to ambient.

The advantage of this approach was that the reaction appeared to be complete and the product thoroughly solidified in less than 24 h. A photograph of the solid inside the steel container that was taken using a fiber-optic borescope is shown in Figure 2. However, there are safety concerns in having personnel work with a hot reaction mixture that generates flame. This could present a dangerous situation for an untrained operator in the field. From an engineering and procedural perspective, it must also be determined how to generate the same conditions on a reproducible basis.



Figure 1. Addition of Li_3N pellets to a 1 L DMMP reaction in an open pressure vessel. Reaction of Li_3N with water generated a spark that ignited the DMMP vapor. The image is a still frame from a video recording.



Figure 2. Borescope photograph of solidified reaction product inside the steel container. The solid is white and flaky.

To address some of the questions, another 1 L DMMP reaction was performed using a larger 2 L steel container. A pressure gauge with a higher scale was also used to prevent it from being maximized. Reagents were added in accordance with method 3; pellets were used,

and some mixing was performed. Concentrated potassium hydroxide (KOH solution) in water (100 mL) was used instead of water. (A comparison of KOH solution to water is discussed by McGarvey et al.¹ and in Section 3.) For this run, no temperature increase or flame were observed. The pressure gauge did not show a pressure increase. The contents of the steel container were poured into a glass beaker after a week of reaction, which thoroughly mixed the liquid contents but did not cause a visible reaction or increase in temperature. The solidification process continued for more than one month in the beaker. Figure 3 shows the reaction product in the beaker after three weeks of reaction time.

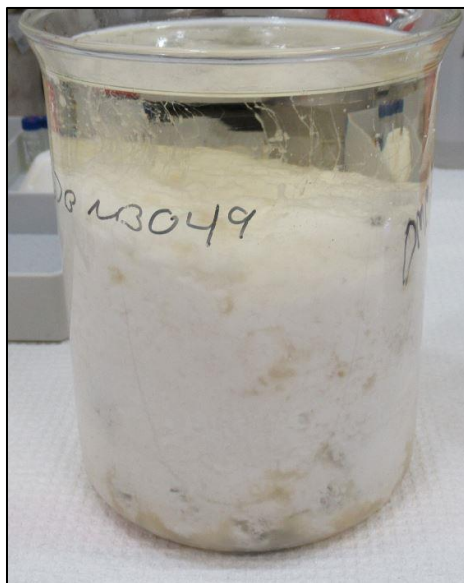


Figure 3. Reaction products of 1 L DMMP reaction after three weeks of reaction time. Most products were solidified, but a layer of liquid was still present on top.

Another 0.5 L DMMP reaction was performed using the 2 L steel container. Reagents were added in accordance with method 3; pellets were used, and some mixing was performed. For this run, 50 g of Li_3N pellets were added followed by 100 mL of water. A small temperature increase to 32 °C was observed, but no detectable pressure increase or flame were observed. The contents of the steel container were poured into a glass beaker after 24 h, so the reagents were well mixed. The reaction progress could be observed directly in the glass beaker. The solidification process continued for more than one month. Photographs of each stage of the process are shown in Figure 4.

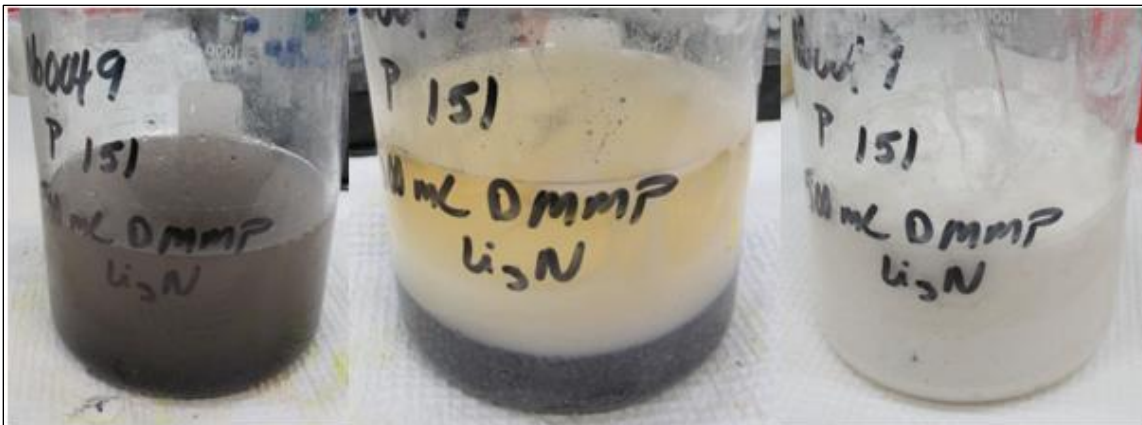


Figure 4. Reaction product of 0.5 L DMMP with Li_3N . Reagents were mixed in a sealed steel container. After one day of reaction, the mixture was poured into a glass beaker. Left: immediately after the mixture was removed from the steel container, with liquid mixed and residual brown Li_3N suspended in liquid. Center: after two more days, the Li_3N settled to the bottom, and white solid began to form on top. Right: after three weeks, the Li_3N was completely consumed, and the product was entirely solidified.

2.4 Study of the Decontamination and Solidification Process Using GB at 1 L Volume

One 1 L reaction study was performed with GB.[†] The 1 L GB reaction was performed at the DEVCOM CBC CTF because that facility had the capability to handle 1 L of nerve agents in a certified glove box. The instructions included in the Appendix were used to perform the reaction.

The goal of the study was to demonstrate that a 1 L reaction could be completed successfully, not just to vary parameters or determine the best approach. The reaction was carried out in a 2 L steel pressure vessel. A pressure gauge was connected after the reagents were added in accordance with the instructions in the Appendix. The temperature on the outside of the container was monitored using an infrared thermometer.

After the reagents were added, there was a small temperature increase to 30 °C but no measured pressure increase.

Samples of about 1 mL of liquid were removed at intervals of 1, 3, 7, and 71 days after the reagents were added and analyzed for residual GB using ^{31}P NMR. An internal standard of triethyl phosphate was added during sample preparation, and the amount of GB was measured by comparing the signal for GB relative to the internal standard signal in the same spectrum. The weight percentage of the residual GB as a function of time is shown in Figure 5.

[†]Caution: This reaction is extremely hazardous and must be done only in an approved facility by trained operators.

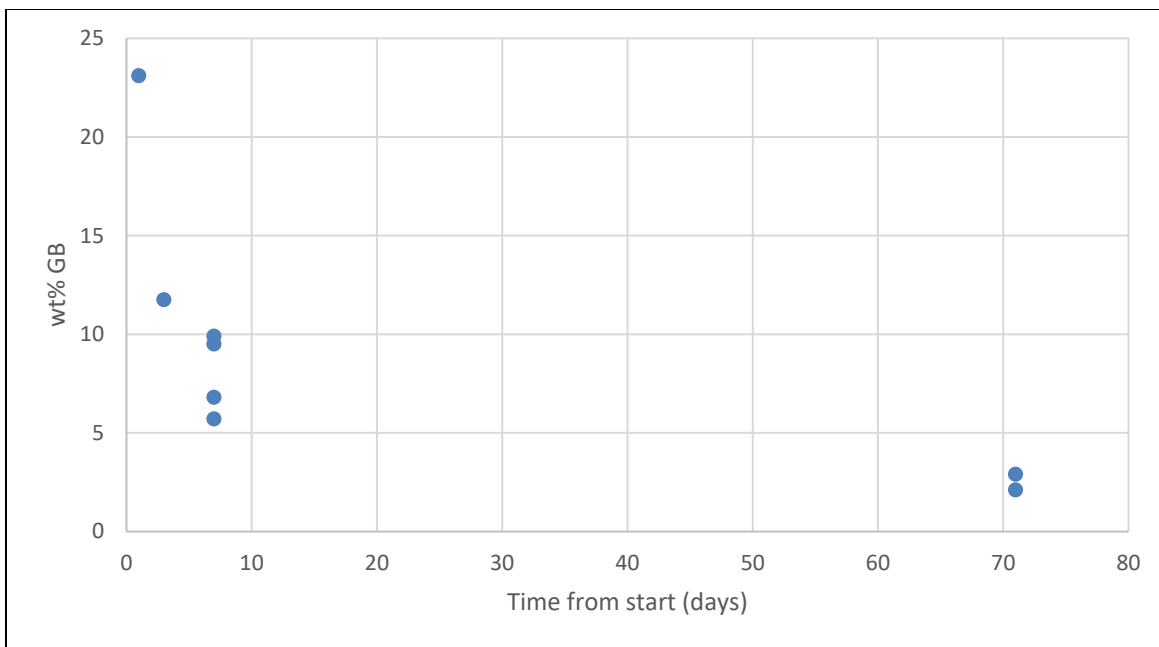


Figure 5. Plot of the residual GB (wt % GB) remaining in the 1 L GB reaction mixture versus time (days).

On day seven, samples were taken from both the top and bottom of the container; the samples were not found to be significantly different. Samples were also prepared with and without the addition of diethyltriamine (Millipore Sigma ReagentPlus, 99% purity; part no. D93856). The additive was used to reduce NMR peak broadening, which was caused by low-purity GB containing paramagnetic metal impurities, most likely iron, that interfered with the NMR measurement. An amount of 10 μL of the additive was mixed in 400 μL of sample. The NMR lines were narrower with the additive, which made it simpler to positively identify the GB lines and integrate the peaks. The additive either complexed with the metal ions or changed the pH of the sample so that the metals precipitated. The integration results showed a slightly higher weight percentage value with the additive. In either case, the amount of GB was less than 10 wt % after seven days of reaction. The reaction slowed down but reduced the residual GB to 2.9 wt % by day 71.

The solidification reaction for this run was not effective. After 71 days, a borescope was used to photograph the contents of the steel container (not shown), and a camera was used to photograph the contents again after they were removed to a glass jar (Figure 6). In both cases, most product material, probably >90%, remained liquid, and little solid was observed. It is not clear whether the brown color resulted from residual Li_3N or GB impurities. Close to 1 L of liquid remained, although it was not measured. Clearly, the solidification of the reaction products was not effective.

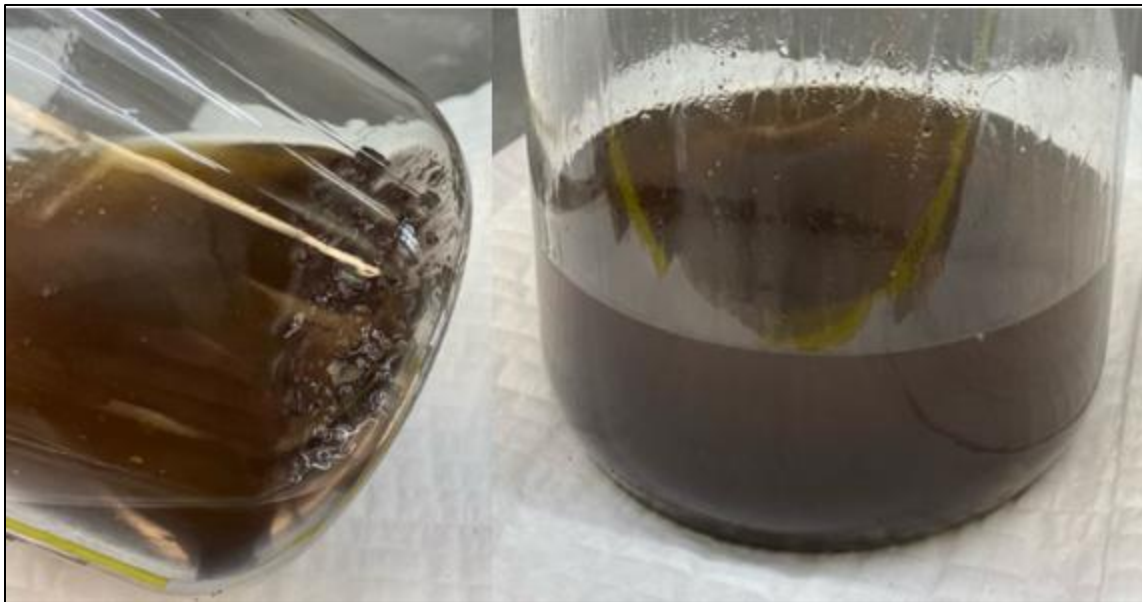


Figure 6. Product of 1 L GB reaction run, photographed after removal from the steel reaction container to a gallon jar after 71 days of reaction.

3. ISSUES RELATED TO $\text{Li}_3\text{N} + \text{H}_2\text{O}$ REAGENTS

For these reaction studies using $\text{Li}_3\text{N} + \text{H}_2\text{O}$ with GB as well as previous studies with GB, GD, VX, QL, and DF,¹⁻⁵ the CA or simulant was added to a container, and Li_3N pellets or powder and water were added. However, even with only three ingredients, the reaction effectiveness depended sensitively on the method for adding reagents. The dependence appeared to be due to the mixing or lack of mixing of the reagents in the inhomogeneous mixture.

A goal of the study was to add the reagents without external mixing to simulate addition to a munition or large container for which mixing may not be an option. However, the reactions were not reproducible, which made it difficult to accurately measure reaction kinetics. A significant amount of study was devoted to determining a method for adding the reagents that was effective without extra mixing. Even without mixing, if the reaction was given enough time, decontamination of the agent took place, although solidification of the products did not always take place.

3.1 Reaction Properties of Li_3N Reagent

3.1.1 Li_3N Reaction Mechanism

Li_3N was selected as a reagent because of its strong basicity (after reacting with water to form LiOH) and low molecular weight, although it is not widely used as an aggressive chemical synthesis reagent.^{6,7} The reaction of Li_3N and H_2O was expected to form LiOH and NH_3 (or NH_4OH in aqueous solution):⁸



It appears from experiments that not much of the ammonia generated from the reaction was in the form of NH_3 gas. When the bulk liquid reagents were not hot enough to boil, the reaction did not produce significant amounts of vapor pressure or visible bubbling, except for some microbubbling that could have been from air displacement in the pellets. When DMMP reactions were performed in a closed pressure vessel, there was little pressure increase that could be attributed to NH_3 gas production. For some reactions, a pressure increase was observed, but it was attributed mostly to DMMP vaporization at elevated temperature, and the pressure decreased when the reaction cooled back down to ambient temperature. A literature publication⁹ indicated that NH_3 should be a major product, but that study may have used different reaction conditions.

It is possible that nitrogen remains in solution as $\text{NH}_4\text{OH}(\text{aq})$, but the final nitrogen-containing products were not determined. It is not clear whether the nitrogen products contributed to solid formation of the product. The caustic ammonia in solution could contribute to decontamination of CAs. Phosphoramidate compounds that could be reaction products were not identified.

The proposed reaction mechanism of the reaction of $\text{GB} + \text{Li}_3\text{N} + \text{H}_2\text{O}$ is shown in Figure 7.

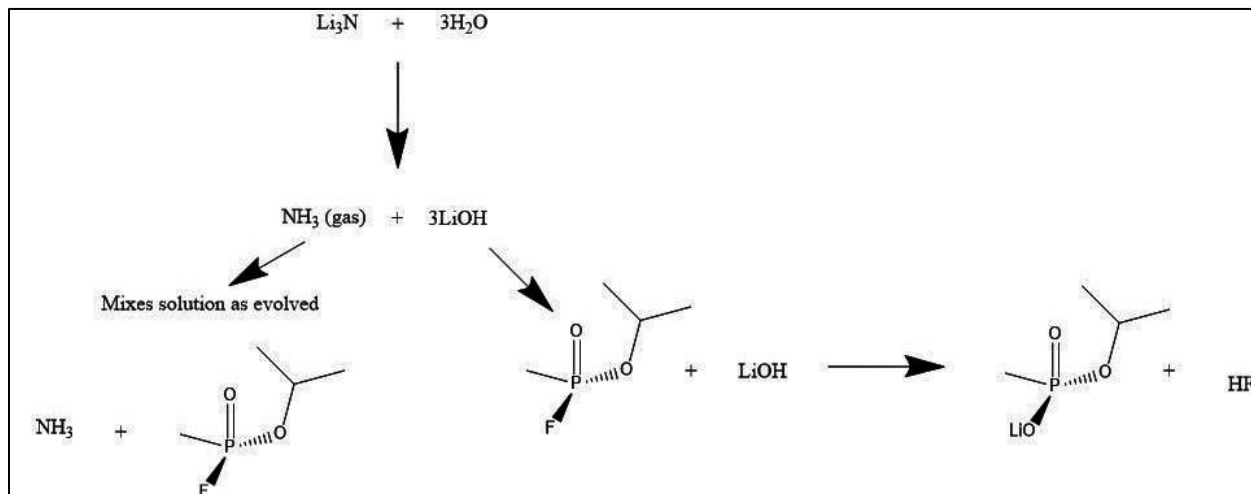


Figure 7. Proposed reaction mechanism of $\text{GB} + \text{Li}_3\text{N} + \text{H}_2\text{O}$. The products can form an ionic solid, which may account for the formation of solid material.

3.1.2 Li_3N Spark Generation

Reaction of Li_3N with pure water was observed to be very energetic and to generate considerable heat. Pressed pellets of Li_3N sometimes floated on the surface of liquid water and could become red hot from the reaction, as shown in Figure 8. The generation of glowing hot material seems to be dependent on the pellet not being submerged in liquid to cool it down. Depending on the density or porosity of the pellet, it can sink in water, which prevents it from getting red hot. In that case, it only forms a steady stream of bubbles from the reaction. A similar effect was observed when using Li_3N powder. The much smaller powder particles also

could glow red hot and generate hot spots in air or on the surface, but not when well mixed in liquid.

The effect of Li_3N pellets floating versus sinking creates significant uncertainty about their use and makes it difficult to predict the safety of the reaction. When pellets are added to organic agent without water present, the pellets may float for a short time, but they ultimately sink to the bottom as air in the porous material is displaced. It is recommended that a few minutes be allowed to elapse after pellets are added to organic agent so the pellets can sink before liquid water is added.

The simulant DMMP, which is nontoxic and less reactive from alkaline decontamination compared with GB, was used in a number of reaction runs. In terms of chemical reactivity, DMMP is not very similar to GB. The lack of reactivity eliminated one variable from direct reactions with Li_3N . However, no reaction was observed even between GB and Li_3N when water was not present.

One significant difference between GB and DMMP is that DMMP has a closed cup flashpoint of $69\text{ }^\circ\text{C}$.¹⁰ In comparison, GB does not have a flashpoint and is classified as nonflammable.¹¹ As a result, DMMP vapor is subject to ignition in a container if oxygen and an ignition source are present.



Figure 8. Pellets of Li_3N floating in water. Pellets can become red hot when they are not submerged in liquid.

When glowing hot Li_3N is present from reaction with water, it can serve as an ignition source, and there were experiments in which the DMMP was ignited. Ignition of DMMP vapor that caused a flash of flame was observed, as shown in **Error! Reference source not**

found.1. This can occur if water is added to DMMP in such a way that the water forms a layer on the surface and then Li_3N pellets or powder react with the layer of water. The heat from the reaction can produce sparks that can ignite any chemical with a flashpoint.

Even if the pellets do not get hot enough to ignite, the reaction can be strongly exothermic. Significant heat can be generated if Li_3N pellets contact nearly pure water. This can cause the chemicals and water to boil, as reported previously.¹ The GB decontamination reaction appears to be accelerated by high temperature; it was complete and a solid was produced within a few minutes.

3.1.3 Order of Reagent Addition

Using DMMP as a simulant, the reagents were added using various approaches so that the best method could be found. Several of these experiments using up to 100 mL of DMMP were discussed in a previous report.¹ The experiments included adding DMMP followed by Li_3N pellets and then water, or DMMP followed by water and then Li_3N pellets. Significant differences and safety hazards were observed even with simple changes in the order of addition. The only energetic reaction was between Li_3N in pellet or powder form with liquid water. When water was mixed with an unreactive liquid, the reaction was considerably slower. This study sought to identify methods that would not generate an immediate hazard but would react quickly to decontaminate chemical warfare agents. The effort was only partly successful because there appears to be a narrow range of conditions that excludes hazards but also allows for fast reaction and solid formation. Reactions that take weeks or months and involve only partial solidification are much easier to achieve.

If water was thoroughly mixed with DMMP before Li_3N was added, ignition was not observed. Reaction of Li_3N with a well-mixed DMMP–water mixture, particularly if the pellets or powder were dispersed in the liquid and not floating on the surface, was unlikely to produce sparks. In this case, the reaction still produced heat, but it resulted in a moderate temperature rise. In a closed container, DMMP vapor can cause a pressure increase until the reaction is finished. After the reaction is complete and the mixture cools to ambient temperature, the pressure also returns to ambient.

3.1.4 Li_3N Saturation with Organic Compounds

The reactivity of the Li_3N pellets can vary because the pellet can be passivated by organic compounds. The pores in the pellets can absorb unreactive compounds, which decreases the reactivity of water to the Li_3N . This effect may be due to the restriction of diffusion of water into reactive sites of the Li_3N solid. This is a particular problem if Li_3N is added to a nonpolar liquid with low water solubility, so that the liquid tends to exclude water from the pores of the solid material. This problem was noted in experiments at SNL using diphenyl chlorophosphate as a simulant. Because CWA liquids can have a wide range of polarity, the effect can cause a significant reduction in reactivity for some agents or simulants. There was no effective method for quantitatively measuring the passivation effect. The effect seemed to be particularly large for reactions of HD (sulfur mustard), for which no measurable reaction was observed between Li_3N ,

water, and HD.¹² Even a compound like DMMP may have caused some passivation of the Li₃N, but this deactivation was not measured.

3.1.5 Li₃N Oxide Passivation

The Li₃N solid material can also have a passivation layer of oxide or hydroxide on the surface. The Li₃N pellets made at SNL were stored under argon gas in glass vials, which reduced the reaction with atmospheric oxygen and water. They were pressed under air because the ambient moisture helped the powder to better bind into a pellet.

It was important that the reagents be handled in air to show that special handling was not required and that this method of decontamination could be implemented in the field. In general, it is not hazardous to handle Li₃N in air, and doing so did not present any safety problems. However, in one instance, dispersal of Li₃N powder or dust into a fume hood while it was being transferred between containers generated a flash of flame when the dust was exposed to humid air. In most cases, there may have been enough passivation on the solid to prevent fast reaction with water vapor.

3.1.6 Li₃N Binders

The addition of various binders or additives to the Li₃N reagent pellets was also studied. The binders had a dual purpose of increasing the cohesion of the pellets to prevent them from breaking up or generating powder during dry handling. Once they were added to liquid reactions, the binders should help the pellets break up into smaller pieces to decrease the particle size and increase the reactivity.

Capsules: Li₃N powder was packed into capsules made of cellulose (called vegetarian) or gelatin.¹ The cellulose capsules dissolved in a solution of DMMP and 10% water to release the powder, which reacted effectively to solidify the reaction mixture. The use of capsules could be effective to minimize passivation and make the reagent easier to handle. Further study is needed to determine the best way to pack the capsules and whether they can be used effectively for reactions.

LiAlH₄: Lithium aluminum hydride (LiAlH₄) was studied as a potential reagent with nerve agent decontamination, but it was not effective.¹ Another application for the chemical was as a binder by adding it at 10% to Li₃N. It was hoped that the LiAlH₄ would generate gas to assist in the break-up of the pellets to provide more surface area. However, studies with these pellets did not demonstrate that they had any performance advantage over the pellets without a binder.

Wax: Hydrocarbon wax was added to the Li₃N as a binder. It was expected that the wax would dissolve in organic chemicals so the pellet would break up. Several wax-containing pellets were studied, but no advantage was observed.

3.2 Reaction Properties of Water Reagent

3.2.1 Water Solutions to Control Density

As discussed previously, the presence of a pure water layer could affect the reaction with Li_3N . The Li_3N pellets react rapidly and get red hot if they are dropped on top of the water layer. Alternately, if the pellets are on the bottom and water is on top, the reaction is minimal, and little decontamination takes place. This difference can cause a wide variation in the reaction rate.

The density of the aqueous solution can be controlled to intentionally bring the pellets and water into contact. If the Li_3N pellets sink to the bottom of the container, using a denser aqueous solution that also sinks can bring the two reagents into closer contact and cause more reactivity. The reactivity is influenced by the physical properties of the density of the water phase. Water is less dense than DMMP, so when water is added, it tends to form a concentrated layer on the surface until mixing by diffusion or agitation of the mixture takes place. Caustic solution (10% NaOH) was used instead of water for the solidification reaction when using DMMP as a simulant. The caustic solution may slow down the reaction of water with Li_3N because of its high hydroxide content, but it also provides more caustic conditions for the decontamination reaction.¹ It was visually observed that dense aqueous solutions tended to sink to the bottom as expected.

Researchers at SNL sought to optimize the reaction using bis(2-chloroethyl) ether (BCEE) as a simulant for HD; both BCEE and HD are much denser than water. A study was done to increase the aqueous solution density using a saturated solution of potassium carbonate (K_2CO_3 ; 112 g in 100 g DI water), thereby improving liquid contact with the pellet (Figure 9).

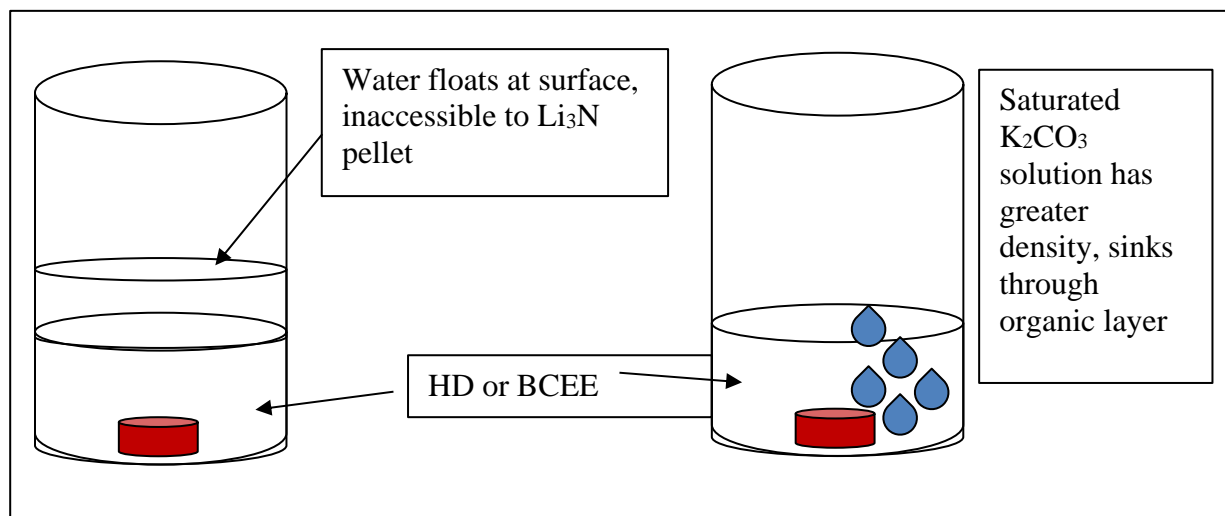


Figure 9. Use of high-density salt solutions to overcome mixing limitations of water and HD or BCEE.

Initial efforts with potassium chloride (KCl) produced limited success. The solution reached the pellet, but it did not substantially react with the Li_3N . An attempt with saturated K_2CO_3 was more successful, for several reasons. First, K_2CO_3 is highly soluble in water, to a literature value of 112%. Second, K_2CO_3 produces a moderately basic solution (pH 10–11), which may enhance the hydrolysis rate.

The reactions of saturated sodium chloride (NaCl), saturated potassium hydroxide (KOH), and distilled DI water solutions with GB were compared. The reactions were done side-by-side using three 10 mL vials of GB. The reaction solutions were sampled at one day, two days, and one week. GB destruction rates were similar for all three runs, with 9–12% GB remaining in two days and 1–2.6% remaining in one week. The decontamination rates show that GB reaction is not strongly affected by the density of and solutes in the water reagent, at least for this volume of reagents.

All three solutes produced at least partial solidification. Reaction vials are shown in Figure 10. Sample P149A (left photo, rightmost vial), which used pure water as the reagent, had the most rapid initial reaction, even though the water layer was less dense than the GB. In the photo on the left, with 5 min reaction time, formation of some white solid is visible on the surface layer, and vapor condensation due to heating and evaporation of the liquid is visible on the glass vial.

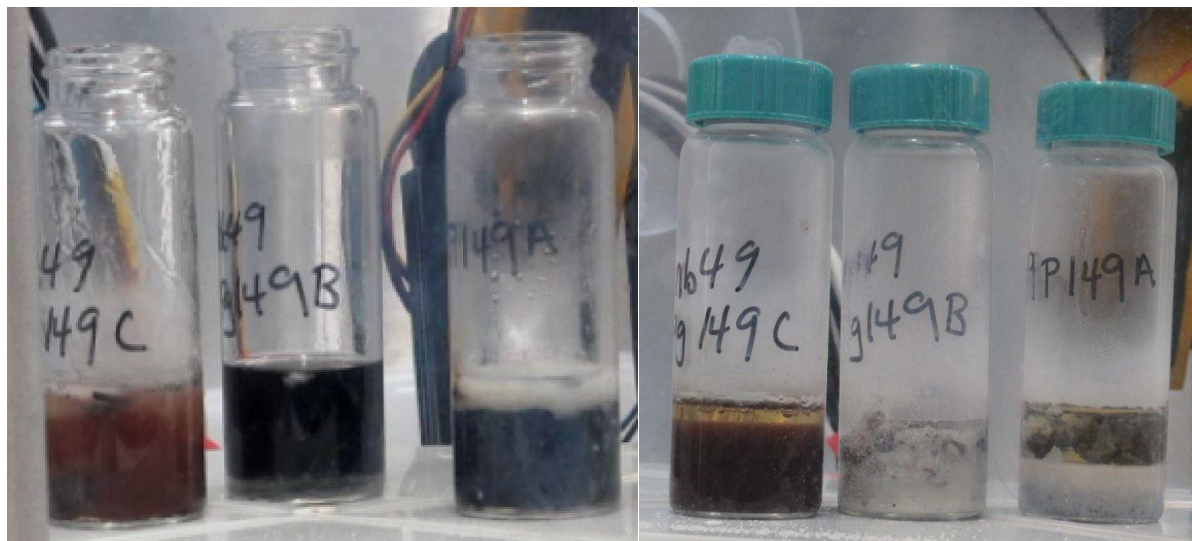


Figure 10. Three reactions of GB with Li_3N ; (left) after 5 min. reaction time, still image from a video, and (right) after one month. Sample P149A (right side vial of both photos): 10 mL GB + 0.5 g Li_3N + 1 mL H_2O . Sample P149B (center vial): 10 mL GB + 0.5 g Li_3N + 1 mL saturated NaCl in H_2O . Sample P149C (left vial): 10 mL GB + 0.5 g Li_3N + 1 mL saturated KOH in H_2O . For all three reactions, GB was added first, then pellets, and finally the aqueous solution. The GB was initially black colored.

After three weeks, sample P149B, which used saturated NaCl solution, was completely solidified. The photo on the right was taken after the reaction had proceeded for a month. Both samples P149A and P149C were partly solidified, but a significant amount of liquid remained. All three samples were stirred once during sampling to test for residual GB after the first day of reaction.

Another experiment was performed using DMMP and a 15 or 30% NaOH solution, rather than a saturated solution. For prior reactions with saturated NaOH, the reaction of the Li_3N pellets seemed suppressed. When Li_3N pellets were added directly to the 15 or 30% NaOH solution, the pellets showed signs of vigorous reaction. However, when either NaOH solution was added to DMMP without any mixing, the NaOH solution formed a layer that did not appear to be miscible with the DMMP. When pellets were added, they tended to stay at the interface between the two layers and have little interaction. The high salt concentration may have decreased the solubility of DMMP in the solution and created enough surface tension to prevent the pellets from mixing well.

It is worth pointing out that using a solution instead of water adds another logistical requirement for the use of this approach to decontaminate unknown chemical agent containers in field trials. It is simpler for warfighters to carry only the Li_3N pellets and use whatever water is available onsite, including undrinkable brackish water or seawater, without needing to prepare a solution of a particular salt. These experiments show that there is no general advantage to using a salt solution.

3.2.2 Use of Nonaqueous Solvents

Nonaqueous solvents were tested for further improvements in density match and miscibility with BCEE. Simple alcohols, ranging from those with short chain lengths (methanol) to surfactant-like (dodecanol) were used as the solvent and Li_3N reaction activator. Reactivity with the Li_3N powder was inversely proportional to chain length; methanol produced a violent reaction, and dodecanol produced no perceptible reaction. The reaction with alcohols was expected to produce lithium hydroxide and the corresponding trialkylamine (Figure 11). An example reaction for BCEE, propylene glycol, and methanol is shown in Figure 12. Polyols, including propylene glycol and glycerin, were used as reagents to improve miscibility and produce multidentate alkylamines as a product. Viscous mixtures of solvent afford some degree of control and miscibility with Li_3N because they do not immediately react on contact. Analysis of reaction products via Raman spectroscopy indicates partial consumption of BCEE.

Methanol was found to be an effective reagent to activate Li_3N when used as an organic solvent in place of water. HD (or simulants) should be slightly more soluble in methanol and other alcohols than water. In addition, the alkyl products produced from hydroxyl cleavage should produce alkylamines as opposed to ammonia. The alkylamines were expected to be more reactive (due to greater contact time) with the HD or simulants than gaseous or aqueous ammonia.

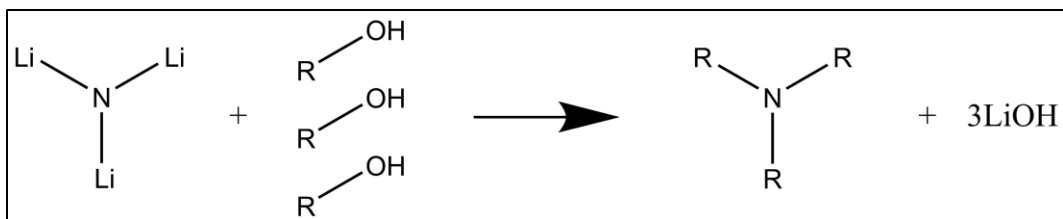


Figure 11. Hypothesized reaction of Li_3N and alcohol.

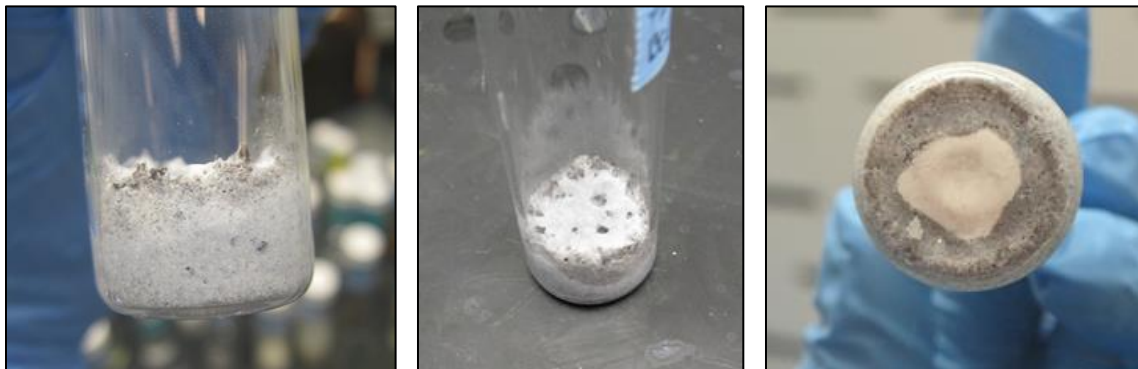


Figure 12. Solidified reaction products from Li_3N with propylene glycol and methanol equimolar mixtures.

Reactions using methanol as the solvent were effective for the decomposition of chloroethyl phenyl sulfide (another HD simulant). The reactivity was measured from the decline of a C–Cl peak via Raman spectroscopy. Results are shown as a function of reaction time in Figure 13. A greater reaction rate was achieved by adding sodium dodecylsulfate (SDS) as a surfactant to the solution. Methanol, ethanol, and an equimolar mixture were used as solvents for comparison with water, all with added SDS to enhance solubility. The ethanol–SDS solution exhibited the greatest decrease in the chlorine peak.

Pyridine was studied as another candidate solvent because it could function both as solvent and reagent via the cyclic amine functional group. In place of water, a solvent mixture of pyridine and methanol was added to Li_3N and BCEE. The alcohol activated the Li_3N . In contrast to typical reactions between Li_3N and water, this reaction did not cause any noticeable exothermic temperature increase. After reacting overnight, the entire system formed a translucent gel (Figure 14).

To further elucidate reaction behavior, neat pyridine was added to BCEE. A pink solution developed and evolved to dark red after 16 h, eventually resulting in a dark red precipitate. The addition of a small amount (5 vol %) of water in a subsequent reaction reduced the reaction rate, and a pink color took five days to develop. Extraction with water resulted in the pink solution migrating into the aqueous phase.

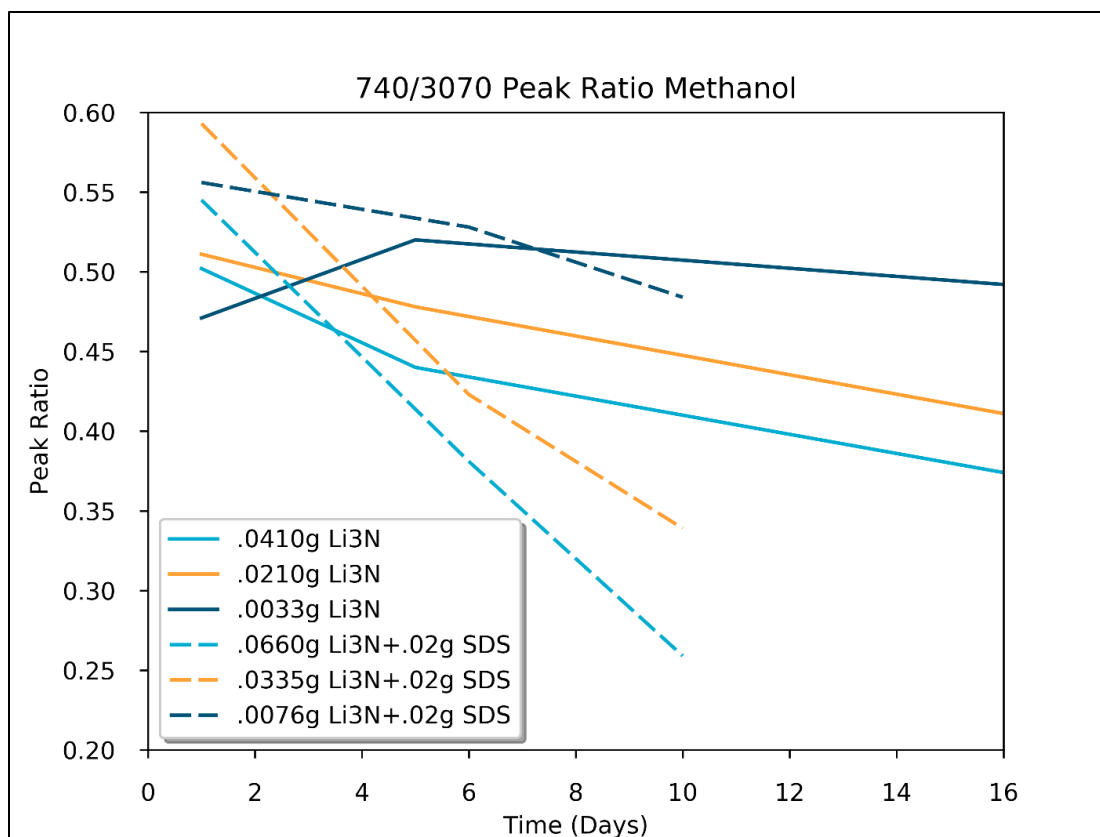


Figure 13. Peak ratio of C–Cl (730 cm^{-1}) to C–OH (3070 cm^{-1}) signals measured by Raman spectroscopy for methanol at varying ratios of Li_3N . Solid lines are neat solvent reactions; dashed lines are solvent with surfactant reactions.



Figure 14. Gelled BCEE– Li_3N –pyridine–MeOH reaction after reacting overnight. Typical LiOH reaction products (gray and white powder) did not form.

3.2.3 Water Encapsulation to Control Reactivity

Previously, experiments were described in which capsules were used to contain Li_3N powder.¹ It is also possible to encapsulate the water reagent. It was hypothesized that water encapsulation would prevent reaction immediately after the reagents were added, thereby allowing time for safety measures such as closing a container. The water could then be released in a burst to provide a faster reaction. In addition to vegetarian and pullulan (polysaccharide polymer) capsules, some types of polyethylene and polypropylene plastic bags were tested. These barriers contained the water or aqueous solution and prevented immediate reaction with the solid Li_3N reagent. The contents of the encapsulated containers eventually leaked or diffused into the DMMP bulk liquid. However, none of these containers released the water quickly enough to reliably accelerate the reaction.

3.2.4 Mixing and Stirring

Diffusional mixing became less effective as reagent volumes increased, even when the solution was soluble in the bulk agent. It is expected that it would be difficult to mix a container in the field without extra equipment, so physical mixing was minimized for most of the testing during this study. The slowest reactions likely resulted at least in part from the lack of mixing. For early feasibility testing of the reactions on small 1 mL scale, the mixing of vials or tubes of reagents was almost unavoidable. In these cases, mixing problems were not noted.

When reactions were performed on 100 mL volumes, the mixing issues became apparent. The reaction can be very sensitive to whether the reagents come into contact, which was dependent on how the reagents were added. In some cases, the reagents were separated in a way that reduced mixing, and the reaction did not take place rapidly as a result.

As a test for the effectiveness of mixing, a reaction of DMMP was performed with constant stirring on a stir plate with a magnetic stir bar. The reaction was performed using 25 mL of DMMP to which 2.5 mL of water was added. The solution was well mixed, then 1.2 g of Li_3N pellets were added. The Li_3N pellets broke up and were well distributed after 5 min of vigorous stirring, giving the liquid a brown color (Figure 15, left). After 20 h of reaction, the product was thoroughly solidified (Figure 15, right).

The result indicates that the reaction is effective enough to take place in <20 h when the solution is well stirred. This implies that the previous reaction trials that took weeks or months were slower because of a lack of mixing or failure of the pellets to break up. However, the results have also shown that scaling up the reaction to 1 L or larger volumes can present unforeseen changes, so it would be worth doing the same stirred reaction at different scales to make sure the results are comparable.

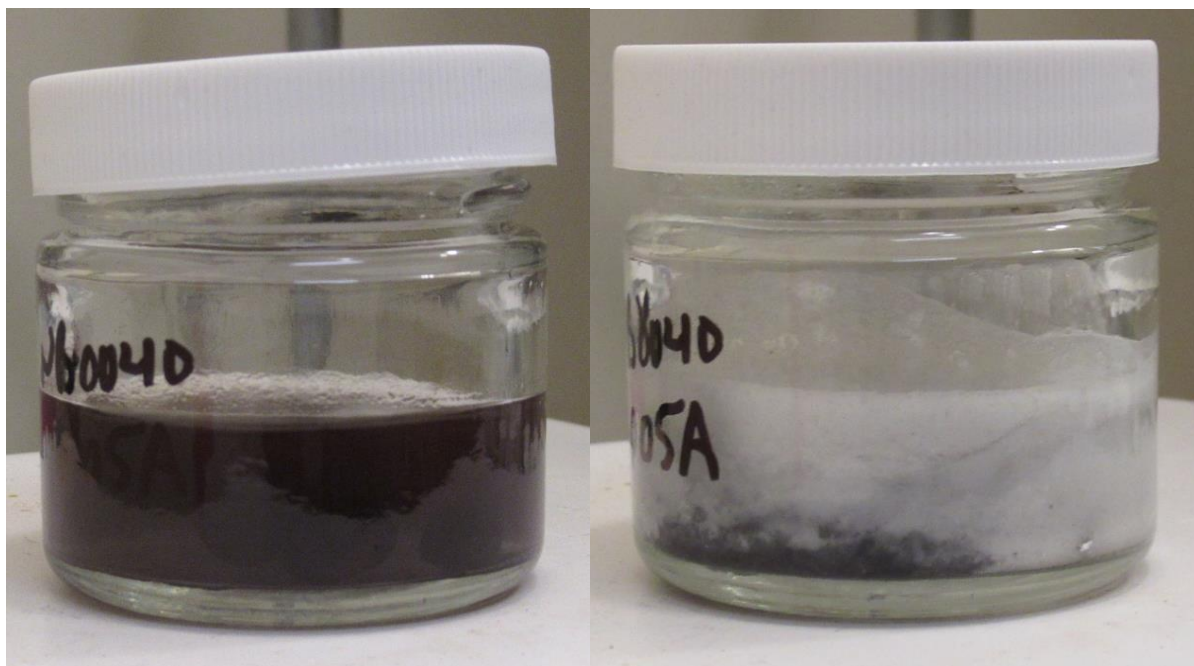


Figure 15. Reaction of DMMP + Li_3N + H_2O with stirring. Left: all reagents, on a stir plate 5 min. after addition. Right: After 20 h of reaction.

It is still possible for an unstirred reaction to be faster than a stirred reaction. If the reagents Li_3N and water can be kept in proximity so that they react quickly and generate excess heat, the resulting vigorous reaction can be faster than a reaction with thoroughly mixed reagents. When the water is mixed with the unreactive agent, reactivity decreases substantially, and the reaction rate can decrease from minutes to months. In addition, the reaction exothermicity is enough to heat the liquid, and at higher temperatures, the reaction rate is accelerated. It is possible that a carefully engineered test system could take advantage of the lack of mixing and higher temperature to cause faster reaction. However, the conditions may only work for specific volumes and types of containers.

The reaction process that would be simplest and easiest to achieve under a range of conditions would probably not involve the optimal reaction conditions. In suboptimal reactions, it may take months for the reaction to complete, and liquid may remain mixed with the solid. This may not be a major consideration for CA in storage that may not be accessed for months.

The more complex approach to the reaction will probably involve stirring and mixing. This could involve using a mechanical apparatus to remove the liquid fill to another stirred reactor or adding a stirring device to the existing container. An added heating element could also help accelerate the reaction. Transporting and setting up this extra equipment could add complexity and extra labor to the operation.

An even more complex approach would involve a specialized mechanism that artificially mixes the Li_3N and water reagents to generate the maximum heat and reaction rate in

a way that is customized to the specific agent that is being decontaminated. The equipment would be optimized to variable viscosity of the starting materials and to the change of viscosity as the product solidifies. The equipment may have to be appropriate for the corrosivity of the waste products and to absorb or neutralize gaseous products. A flowing system is an option. The equipment to accomplish this goal would be more complex to set up and transport.

3.3 Other Potential Studies to Control Reaction Rate

Further studies could be done to understand the reaction, but they were beyond the scope of work of this project.

3.3.1 Transfer of Agent from Storage Container to a Reaction Vessel

A more controlled way to accomplish the decontamination reaction is to remove the fill from the container and treat it in a reactor. This approach, which is used for the Explosive Destruction System¹³ or the Field Deployable Hydrolysis System,¹⁴ allows the reaction to be carried out under controlled conditions.

3.3.2 Adding Mixed Powder and Pellets

Another possible approach would be to add reagents using a pump. The reactivity of the solid reagent could be adjusted based on the particle or pellet size, with a powder being more reactive. Adjusting the mixture before it is added to the chemical agent could allow more effective use of the reaction exothermicity to heat and mix the reagents.

3.3.3 Adjusting Reaction Temperature

If the reagents were transferred to a reactor, the reaction temperature could be better controlled using a thermostated heater. This would allow temperature to be an independent variable for controlling the reaction rate.

4. CONCLUSION

As part of the Tactical Disablement Project, neat weapons-grade GB was reacted with Li_3N and water. Reactions were performed up to a 1 L volume of DMMP or GB. Each reaction was photographed and recorded on video to document the solidification process of the products.

This study demonstrates a method to perform the neutralization and solidification of bulk GB CA that should also be effective in a long-term storage container or munition. The minimal quantities of chemical reagents are typically 15% by weight of the amount of CA, using 5% Li_3N and 10% water. This indicates that the Tactical Disablement goal of using a small amount of decontamination reagent to detoxify and render useless a container or munition of GB is achievable.

Several technical issues were addressed. GB was decontaminated by a commonly used caustic hydrolysis reaction, but the reaction was relatively slow because there was no mechanical stirring or heating and no large amounts of excess water and alkali. Regardless, the GB was usually destroyed in a week or less. The NMR method detection limits were relatively high. It was possible to determine residual GB in the reaction product to <1%. A more sensitive analytical chemistry method, possibly using gas chromatography/mass spectrometry will be required to determine whether trace amounts of GB remain in the product.

Experiments with CA amounts ranging from 1 to 100 mL showed similar reactivity, although some differences were observed for larger volumes. Solid product was not formed in a consistent way in all reaction conditions, so further studies were done using DMMP as a simulant to study the conditions that were needed for formation of solid products.

The method for adding the two reagents, Li_3N (powder or compressed pellets) and liquid water, caused a wide variation in the reaction rate. Addition of Li_3N powder so it is evenly suspended in liquid GB followed by rapid addition of water can cause very rapid reaction, boiling of the liquid, and solidification in minutes. Slower addition of water can give the Li_3N time to settle out of suspension so it is less likely to react, and the entire amount of agent may not be solidified. Experiments with DMMP showed that decontamination products are not necessary to produce a solid.

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ACRONYMS AND ABBREVIATIONS

APG	Aberdeen Proving Ground
BCEE	bis(2-chloroethyl) ether
CA	chemical agent
CAS	Chemical Abstracts Service
CTF	U.S. Army Chemical Transfer Facility
CWA	chemical warfare agent
DEVCOM CBC	U. S. Army Combat Capabilities Development Command Chemical Biological Center
DF	methylphosphonic difluoride
DI	deionized
DMMP	dimethyl methylphosphonate
GB	sarin, isopropyl methylphosphonofluoridate
GD	Soman, pinacolyl methylphosphonofluoridate
SDS	sodium dodecylsulfate
SNL	Sandia National Laboratories
QL	O- (2-diisopropylaminoethyl) O'-ethyl methylphosphonite
VX	O-ethyl-S-(2-diisopropylaminoethyl) methylphosphonothiolate

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APPENDIX

STEPWISE DIRECTIONS FOR 1 L GB + Li₃N REACTION

Developed by David McGarvey, William Creasy, and Rachel Knoebel,
Research and Technology Directorate, U. S. Army Combat Capabilities Development Command
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The NMR Laboratory will supply all equipment and materials except for the steel reaction container and GB.

1. Obtain a 2–2.88 L steel pressure reaction container. Make sure it is dry.
2. In a hood, add 1 L isopropyl methylphosphonofluoridate (GB; technical grade) to the container.
3. Set up video camera so it views the container and opening. The camera should be outside the hood, if possible, to avoid contamination. Start the video recording when ready to move to the next steps.
4. Add 50 g Li₃N pellets to the container. CAUTION: Pellets react vigorously with water, so avoid contact with liquid water. The pellets can generate powder, which is more reactive than the pellets. Dispersed powder can react with humid air to cause heat and start a fire with any flammable material. Avoid dispersing powder outside of a hood or inhaling any powder. Keep sand for fire suppression at hand.
5. Allow 1 min for the pellets to sink in the liquid GB. A borescope can be used to look inside the container to make sure the pellets have sunk to the bottom. CAUTION: The borescope probe will be contaminated with liquid GB, so do not remove the probe from the hood.
6. Add 100 mL concentrated KOH solution to the container. Record the time for the start of the reaction.
7. Screw the fitting with pressure gauge to the top of the steel container.
8. Measure the temperature of the outside of the container with a non-contact IR thermometer. Avoid contamination of the thermometer, if possible. Record time, temperature, and pressure readings.
9. When the temperature or pressure stop increasing (or at 15 min), stop the video recording. Record the time, temperature, and pressure readings.
10. After 24 h, determine whether the container has excess pressure by opening the valve or checking the pressure gauge and record the external temperature.
11. If the temperature and pressure are ambient, the threaded fitting can be removed. Use the borescope to obtain photographs of the container contents.
12. Remove a 0.5–1 mL sample of the liquid from the container and transfer it to a sample vial. Wipe the outside of the vial, double contain it, and notify the NMR laboratory to pick it up for analysis. Recap the container after the sample is obtained.

13. After 1 week, remove the fitting. Use the borescope to obtain a photograph of the container contents.
14. Remove a 0.5–1 mL sample of the liquid from the container and transfer it to a sample vial. Wipe the outside of the vial, double contain it, and notify the NMR laboratory to pick it up for analysis. Recap the container after the sample is obtained.
15. After sample analysis is complete and after consultation with the NMR laboratory, the container and contents may be decontaminated and discarded as waste using the appropriate procedure.
16. Remove the memory cards from the camera and the borescope and bag them separately in a non-static bag. Return the equipment. If any equipment is contaminated, perform surface decontamination and double bag it before returning it.

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