

# FINAL REPORT

## In-Situ Electrochemical Remediation of Underwater Unexploded Ordinance

SERDP Project MR18-1466

NOVEMBER 2018

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U.S. Army Corps of Engineers, ERDC-CERL

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## List of Acronyms

3-NT	3-nitrotoluene
AUV	autonomous underwater vehicle
DNT	2,4-dinitrotoluene (DNT)
NG	nitroglycerin
UXO	unexploded ordnance
HMX	cyclotetramethylenetetranitramine (HMX)
PTEN	pentaerythriol tetranitrate
RDX	cyclotrimethylenetrinitramine
TNT	trinitrotoluene
RDX	cyclotrimethylenetrinitramine
TAT	triaminotoluene
PDMS	Polydimethylsiloxane
LC	Liquid Chromatography
MS	Mass Spectrometer

## **Keywords**

In-Situ electrochemical remediation of munitions, Underwater unexploded ordnance (UXO), Leak free in-situ remediation of UXO, Secondary explosives, Dual working electrode, Flow through electrode, Chemical milling, Convective chemical milling

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## *1. Abstract*

Objective: This project focused on the development of technology for safe and cost effective remediation of unexploded ordnance (UXO) in the underwater environment with depths up to 35 meters using electrochemical reduction. The proposed technology is well suited for the in-situ remediation of the secondary explosives contained in UXO and discarded munitions underwater. The proposed methods provided a safe means for UXO remediation without accidental detonation or leakage of toxic chemicals. The objective of this proposal is to evaluate the proposed processes by obtaining the critical data needed to evaluate their potential for success in this demanding real-world application and to remediate munitions including small projectiles and mortars to small bombs.

Technical Approach: Two key processes were investigated through this SEED project to provide proof of concept for an electrochemical remediation system for underwater UXO. These processes are 1) the electrochemical transformation of nitro containing explosives into stable compounds, and 2) the formation of an access hole through the munition casing by a gentle process of chemical machining.

Low-cost, high-surface area dual working electrode system for TNT and RDX reduction was developed that is highly compatible with in-situ remediation. The dual working electrode system contains both solid electrodes for implanting into explosive material along with a flow through electrode for high efficiency reduction of solution phase material. The entire electrode was encased in a stainless tube to provide mechanical strength to the electrode. The tube also served as the counter electrode for the electrochemical system. The optimal conditions for the dual working electrode system were determined by studying the major variables, such as particle size of graphite particles used for fabricating the flow through working electrode, solution flow rate through the flow-through working electrode, supporting electrolytes, and the impact of binder on electrode fouling. The electrochemical reductions were performed by cyclic voltammetry and optimal scan rates for reducing/degrading the explosives up to 99% were determined. To measure reduction efficiency, the explosives and their by-products were measured before and after the electrochemical remediation process using LC-MS (Liquid Chromatography-Mass Spectrometer).

A chemical milling method was developed that optimized speed while providing sufficient hole quality to allow formation of a reliable seal around the access hole. The process we aimed to develop was speed over quality of finish. The main focus of this objective was to determine the etch rates and hole morphology for Si-steel and low carbon steel as a function of the etchant composition, convection, and temperature. The etch rates was significantly increased by supplying high rates of convection during the chemical milling process, which is in great contrast to conventional static chemical milling. Coaxial tubing system was developed for the high rates of convection where chemical milling solution was introduced through the center of the coaxial interface, and the spent solution extracted along the periphery. A negative pressure and suction was created by keeping the flow rate through the periphery greater than the coaxial. A soft suction cup formed a seal and suction held in place. The flow rates, etchant composition, effects of ions and temperature were optimized for fast chemical milling process.

Results: Different explosives including TNT, DNAM, DNT, RDX were successfully reduced. With our dual electrode flow system, the time for electrochemical reduction has been significantly

shortened. We can electrochemically reduce any dissolved TNT, RDX solution within 100 cycle, which could be completed within 25 min. We were also able to determine that aqua regia was ideal as the milling solution due to its effectiveness and versatility amongst various metal types. Furthermore our development of the coaxial tubing system was successful in securely attaching to metal surfaces and pump through the milling solution. The most crucial result was being able to chemical mill and punctures the wall of a 75mm artillery shell with our system in less than 2 hours. The results we have gathered so far can be developed further into a complete functioning system to effectively neutralize UXOs.

Benefits: Safe methods for in-situ remediation of underwater UXO are needed. The proposed technology has the potential to form the basis of a remediation system that is safe, nearly leak-free, energy efficient, and contains the waste in a relatively small volume. A safe approach will protect humans and the environment from unintended detonation of old and unstable munitions. Removal of these objects will protect people from accidentally coming into contact with UXO. Development of a virtually leak-free process will prevent the release of toxic chemicals into sensitive underwater ecosystems. Additionally, important process attributes that can lower remediation costs will be evaluated.

## **2. Objective**

This project focuses on the development of technology for safe and cost effective remediation of unexploded ordnance (UXO) in the underwater environment. The system will be particularly well-suited for use in shallow regions for depths up to 120 ft and beyond. The remediation of the underwater UXO was performed by electrochemically transforming the secondary explosive or high explosive into an inert compound and removing the inert compound in an aqueous solution. The operation will be performed in-situ without moving or shifting the UXO from the location and position in which it is found. The remediation will be performed through the use of a remotely operated vehicle, which will provide a safe work environment. The chemical machining process and decomposition of the secondary explosive will be extremely gentle, reducing the potential for inadvertently triggering the fuze and detonating the device. The characteristics of the process are well-suited for the subsequent generation of a leak free remediation system. The proposed method is generally applicable to the nitro-containing explosives, including but not limited to highly nitrated compounds trinitrotoluene (TNT), 78-11-5, cyclotrimethylenetrinitramine (RDX), pentaerythriol tetranitrate (PETN), and cyclotetramethylenetetranitramine (HMX), ammonium picrate (Explosive D), 3-nitrotoluene (3-NT), 2,4-dinitrotoluene (DNT), and nitroglycerin (NG).

The objective of this work is to investigate the suitability of chemical and electrochemical processes to convert the secondary explosives in underwater UXO to an inert compound and to remove the inert compound from the UXO casing, which will provide us with cost effective and safe munitions remediation process. While these processes are well characterized and used for industrial applications, they are yet to be applied to the remediation of underwater UXO.

Our long-term goal is to develop a method to remove the secondary explosive from underwater UXO without *leakage* or *detonation*. Our method used a new approach for in-situ decomposition of the secondary explosive that uses: 1) electrochemical processes to chemically neutralize or decompose the secondary explosive, and 2) chemical drilling to breach the metal casing of the UXO. The primary objective of this project was to characterize the electrochemical decomposition process and design suitable electrodes for the process. The secondary objective was to develop a chemical drilling method to provide a safe and effective means to put an access hole through the UXO casing. Therefore, this project focused on these two fundamental processes that provide the main hurdles that must be demonstrated before further development. Moreover, the basic attributes of these two processes are very well-suited for designing a system that is virtually leak free. Namely, the system works at negative pressure, at very low solution flow rates, and remediates the secondary explosive within the shell casing. After demonstration and characterization of these two fundamental processes, the project will naturally progress to an engineering development project to produce the equipment that provides a leak-free and safe means to inert underwater UXO in-situ. The outcomes of the technical objectives directly addressed two critical questions: 1) how fast is the chemical drilling through the UXO casing, and 2) how much energy is required for the reduction of the secondary explosive? The envisioned system will be operated remotely by an autonomous underwater vehicle (AUV).

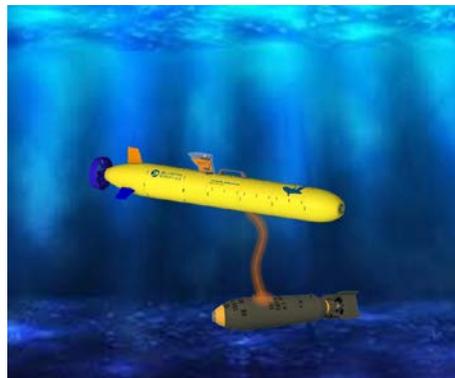


Figure 1. Overview of the AUV system envisioned. The chemical drilling and electrochemical remediation will be performed through a sealed umbilical connection.

Future development of a system that can provide leak free in-situ remediation of the secondary explosives from underwater UXO is envisioned. It is recognized that leakage of the untreated secondary explosive can be very damaging to the environment. Many characteristics of this technology reduce the possibility for leakage. First, the primary explosives are relatively insoluble in water, and the soluble fraction of the explosive will be continually transformed into less toxic compounds as it dissolves. Second, the system will be operated at negative pressure with suction providing continual removal of the products allowing the shrouded interface to suction itself directly to the UXO. Third, low volumes and low flow rates will be utilized to decrease the chances of inadvertently developing a positive pressure and to reduce the amount of material lost if a leak should occur. Fourth, additional electrode layers can be easily integrated into the system to provide additional layers of containment. Fifth, only a small hole will be opened through the casing, which will reduce any spillage, if a mishap should occur.

The electrochemical reduction and low flow rates used will decrease the overall cost of the removal by producing relatively benign inert compounds and reducing the volume of waste solution. Additionally the electrochemical reduction increases the solubility of the compounds in water, allowing the inert compounds to be easily removed in a small volume of water-based solution.

### ***3. Background***

#### ***3.1 Overview***

Present methods for UXO remediation in the underwater environment are not suitable for routine use. Consequently, blow in place methods are frequently used. However, in many locations, particularly in sensitive ecological systems, blow in place methods are not suitable for the remediation of underwater UXO due to damage caused by the blast and toxins released by the incomplete consumption of the energetic material. Additionally, many of the underwater UXO date back to World War II and have been in the ocean for many decades. Consequently, their body or casing materials are highly corroded adding to the dangers inherent with removing UXO. Therefore, a great need exists for a method that can remove high explosive materials from underwater UXO. Two very important considerations for UXO remediation is the need to prevent detonation and leakage of the secondary explosives and contaminants from the casing. As previously described the proposed method is well suited to prevent both detonation and leakage of the explosives and their degradation products. A schematic representation of the chemical drilling and electrochemical reduction are shown in Figures 2 and 3.

#### ***3.2 Secondary Explosives***

A number of different materials have been used by the military as secondary explosives, which are also referred to as high explosives. Common secondary explosives used by the U.S. military include, trinitrotoluene (TNT), pentaerythriol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), and cyclotetramethylenetetranitramine (HMX), ammonium nitrate, and ammonium picrate. The explosive filler material contained within the ordnance casing is often a mixture of more than one material. Additional materials often include agents to increase the heat including powdered aluminum and phlegmatizing agents, such as paraffin wax. Phlegmatizing agents decrease the sensitivity of the filler to impact, to decrease the chances of accidental explosion. The secondary explosives do not exist as pure compounds in munitions. The desired component in military grade TNT is 2,4,6-TNT. Military grade TNT will contain a number of contaminants, including the other five TNT isomers, the six DNT isomers, and various other compounds such as 2,4,6-trinitrophenol, and 2,2',4,4',6,6'-Hexanitrobiphenyl.<sup>1</sup> An example of a secondary explosive fill material is tritonal which contains 80% TNT and 20% aluminum powder. Others such as composition B and composition C include TNT, RDX, and paraffin wax. Composition H-6 includes aluminum powder in addition to TNT, RDX, and paraffin wax.

#### ***3.3 Electrochemical Reduction***

Electrochemical reduction has been previously performed to remove nitrates from drinking water and wastewater. Additionally, electrochemical reduction of nitro- explosives, including TNT, has been used to successfully remediate contaminated industrial waste water.<sup>2</sup> This study found the electrochemical reduction of TNT to be kinetically fast and limited by mass transport of the explosive molecules to the electrode surface. Electrochemical reduction chemically reduces the nitro functional group to an amino functionality and therefore is generally

applicable to all nitro containing explosives. Electrochemistry has long been used to detect explosive compounds such as trinitrotoluene (TNT) because these compounds are strong oxidizers and thus easily reduced. The electrochemical detection by reduction of 10 common military explosives including TNT, RDX, PTEN, and HMX has been reported.<sup>3</sup> In environmental settings, few compounds are readily reducible and thus selectivity can be quite good. In-situ remediation of underwater UXO, however, is ideally suited for electrochemical remediation because reduction inerts the

explosive compounds and allows them to be removed in a water based solution. Additionally, the system is relatively simple and can be operated from an AUV.

The electrochemical reduction of both TNT and RDX requires  $18e^-$  and  $18H^+$  along a reaction pathway that proceeds through a water soluble hydroxylamine intermediate to produce the highly soluble triamine final product as shown in below. The product triaminotoluene is highly soluble in water with a solubility near 1000 g/L. It is important to note that, as the explosives are reduced from nitro to their amine containing forms, their water solubility greatly increases. This increase in solubility allows for easy removal of the degradation products of the secondary explosive in the aqueous solution. This reduction occurs at negative potentials with the specific potential dependent on the electrode material. For carbon electrodes the reduction potential varies from -300 to -1000 mV.

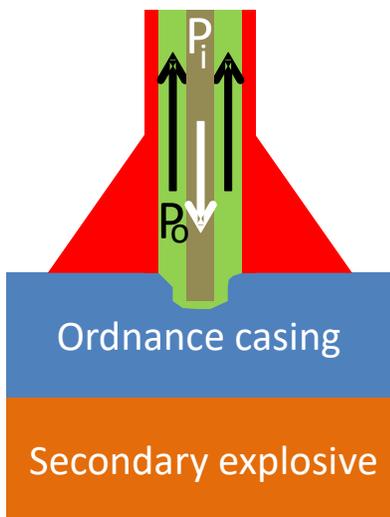


Figure 2. The chemical drilling solution will be introduced through the center of the coaxial interface, and the spent solution extracted along the periphery. A negative pressure and suction will be created by keeping  $P_o > P_i$ . A soft pliable gasket will form a seal and suction will hold it in place. To compensate for leakage, the volume of solution removed by the outflow will be increased.

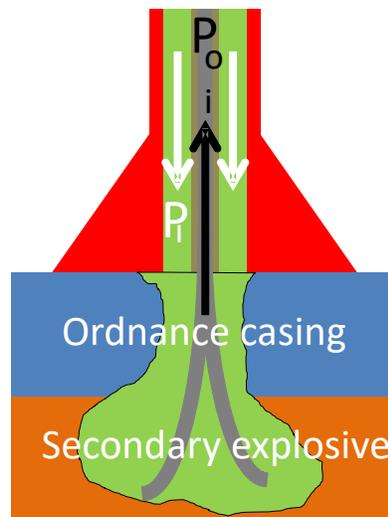
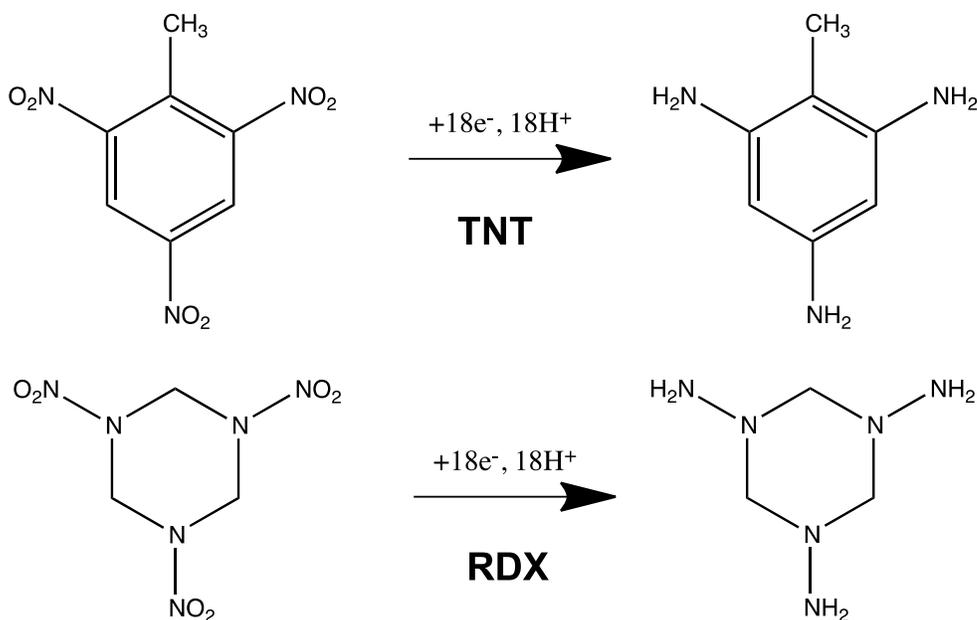


Figure 3. After the hole is opened the electrode(s) is inserted and the rapid random motion of the electrodes eventually fills the void in a manner similar to duct cleaning. The secondary explosive is rapidly inerted and its solubility in water increased through the electrochemical reduction. The solution with inerted explosive is extracted through the electrodes.



### 3.4 Chemical Milling

A safe and low impact approach to open an access hole through the shell casing is chemical milling. Although not required for this application chemical milling is proposed here for two reasons: 1) the process will be free of mechanical shock and therefore the risk of unintentional detonation is reduced, and 2) it is complementary to the remediation of the secondary explosive by electrochemical reduction.

The process of chemical milling can be used to safely create an access hole through the casing without shock or other mechanical disruption that might cause unintentional detonation. Chemical milling is not a new technique; it has been around for hundreds of years and likely started in the fifteenth century.<sup>4</sup> Chemical milling can be performed on a wide range of metals, including all types of steels, aluminum, magnesium, titanium, copper, brass, beryllium, magnesium, nickel, tantalum, uranium, and zirconium. Both large parts, such as airframes, and very small parts, such as electronics are machined through chemical milling. Typically, the emphasis in chemical milling is on exacting precision to meet tight tolerances and create smooth, defect free surfaces on articulated parts. To control the process evenly over large areas, dip tanks with little or no solution flow are used. In the aerospace industry tanks in excess of 44,000-L have been used. Although the rapid drilling of holes is very feasible, some process optimization will be required to meet the needs of the current application. Our approach will utilize chemical milling with solutions that contain significant portions of concentrated acid. Concentrated acids have been chosen because they are compatible with all the nitro-containing explosives, such as TNT and RDX. In fact, TNT is synthesized with by the addition of nitric acid to toluene, which demonstrates the stability of the nitro- containing explosives in concentrated acid solutions.

Cleaning of the parts before chemical machining is typically performed with a nitric or sulfuric acid solution and is referred to as pickling. The cleaning process will be an important task in proposed method, because large amounts of oxide, such as rust on a steel casing, will be present along with other possible components and organisms of the sea floor.

A wide variety of munitions are present as underwater UXO and must be remediated. Common small munitions found include grenades, intermediate size munitions include mortars and projectiles, and larger munitions include Mark 84 bombs. The munitions have different casing or body materials and the explosives vary as well. Most of the munitions present as underwater UXO have steel skins<sup>5</sup> that are either Si-steel or C-steel. Low steels, such as Si-steel<sup>6</sup> and C-steel and a wide range of other metals can all be chemically milled with the same solution. In conventional chemical milling, the solutions are often tailored to the alloy being machined to maximize the control and quality of the surface finish. However, in this application maximum control and surface quality are not needed and a single chemical drilling solution should be effective over a wide variety range of munition casings.

### 3.5 Fuze Sensitivity

One of the major complexities of dealing with UXO pertains to the various fuze types that trigger the devices. UXO fuzes can be commonly categorized into contact and proximity based. One of the most ubiquitous kinds of contact fuzes includes glass vial protuberances on the explosives that when broken, causes a chemical reaction resulting in a battery powered explosion. Proximity fuzes can be anything from microphone sensors attuned to the frequency of engines or magnets that are triggered when anything magnetic passes by. Fuze-specific UXO remediation techniques include a mechanical devices that can knock off impact fuzes or a cocktail of corrosive chemicals to degrade the trigger. These kind of techniques severely limit the application of explosives remediation tools due to all the different types of explosives found underwater today.

Due to the wide variety of fuzes, it is difficult to develop a singular method that can address the multitude of triggers. That is why most techniques of remediating UXO just involve setting off the devices in a controlled environment despite the negatives of the situation. Some of the most versatile ways of not using blow in place techniques include using supercooling equipment to freeze the entire UXO. Another method uses Abrasive Water Suspension Jets (AWSJs) to cut through UXO material and minimizes triggering the fuze because the technology does not have a thermal influence and the system does not contain air, therefore making sparks impossible.

Our UXO remediation method is designed to minimize the sensitivity of the fuze with a

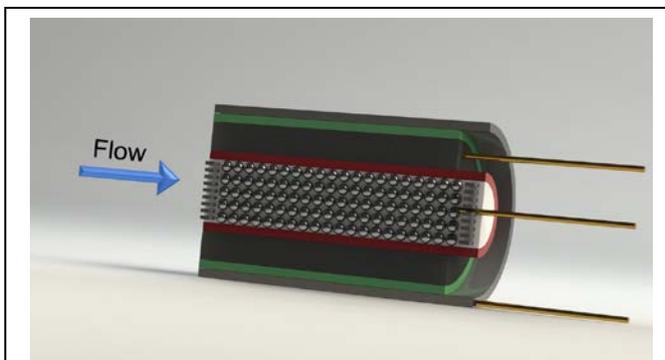


Figure 4. Schematic drawing of the proposed electrode system.

combination of controlled chemical milling and electrochemical reduction of the explosive chemicals. Our techniques minimizes any mechanical byproducts found in conventional drilling that can set off fuzes. Furthermore we are able to control the temperature and pressure difference to minimize any thermal based sparking or triggers and pressure-driven triggers. Overall, our methods of neutralizing UXO involves precise activity that provides a safe, controlled environment, thus quelling any inadvertent explosions due to fuze sensitivity.

#### 4. Materials and Methods

Graphite, powder, <150  $\mu\text{m}$ , 99.99% (Sigma-Aldrich), Graphite, powder, <45  $\mu\text{m}$ , 99.99% (Sigma-Aldrich), Graphite, powder, <20  $\mu\text{m}$ , 99.99% (Sigma-Aldrich), TNT (2,4,6-Trinitrotoluene solution), 10 mg/mL in acetonitrile (Sigma-Aldrich), RDX (Hexahydro-1,3,5-trinitro-1,3,5-triazine solution), 10 mg/mL in acetonitrile (Sigma-Aldrich), DNT (2,4-Dinitrotoluene) (Sigma-Aldrich), Iron chloride, sublimed grade, 99.99% (Sigma-Aldrich), Aluminum chloride, anhydrous, powder, 99.99% (Sigma-Aldrich), Sea salts (Sigma-Aldrich), Paraffin wax, low viscosity (Sigma-Aldrich).

Fabrication of dual working electrodes system. A low-cost high-surface area electrode system for electrochemical reduction of explosives has been fabricated. The entire electrode was encased in a short metal tube (Aluminum) to provide mechanical strength to the electrode while allowing overall flexibility to be maintained (The figures shown below is one unit of the electrode system).

The tube will also serve as the counter electrode for the electrochemical system. An insulating layer between metal tube and graphite tubing was made of epoxy and will serve to isolate the graphite electrode from the metal tube. Electrical connections was made at the back



Figure 5. Fabricated one unit of the electrode system.

side of the system. The porous electrode was made from 1/8" OD PEEK tubing packed with particulate graphite (20  $\mu\text{m}$  i.d.). To keep particles in place, commercially available filter screens was placed at each end of the tube. Chemicals used for chemical milling experiments are all from Sigma Aldrich. For the milling solutions, we used three unique formulas. The first was the 1:1:1 molar ratio of sulfuric acid, nitric acid, and deionized water. The other was nicknamed the "patented solution" with nitric acid (25 wt%), stannic chloride (5 wt%), sodium bifluoride (5 wt%), ferric chloride (10 wt%), oxalic acid (2.5 wt%), acetic acid (2.5 wt%), and deionized water (50 wt%). The final milling solution tested is aqua regia with 1:3 molar ratio of nitric acid and hydrochloric acid. The metal coupons were obtained from McMaster-Carr (Elmhurst, IL) and all had dimensions of 6" by 6" by 3/8". Three materials were tested: low-carbon steel, 304 stainless steel, and impact-resistant A516 Carbon steel. For the PDMS (Polydimethylsiloxane) wells, the PDMS was made using Dow SLYGARD 184 silicone elastomer kit. The 0.5mL wells were created by punching an 8mm diameter hole using a biopsy punch from Integra Miltex. The PDMS wells were secured onto the metal coupons using Dow Corning 3140 Silicone adhesive. To perform milling using the PDMS well setup, each well was filled completely with the respective milling solution. 4 time points were used: 30 minutes, 1 hour, 1.5 hour and 19 hours and each time point was repeated 3 times to obtain measurements. To neutralize the milling reaction, the PDMS and adhesive was peeled off and the well was cleaned with deionized water and dried. The coaxial tubing system was constructed with two Tygon 2375 Ultra Chemical Resistant tubes from US

Plastic Corp. One tubing had an inner diameter of 5/32" and outer diameter 7/32", while the outer tubing had an inner diameter of 1/4" and outer diameter of 3/8". The coaxial tubing system was secured together by Gorilla Glue Epoxy. At the opening of the coaxial tubing system, a Blue Vinyl Vacuum suction cup from All Vac Industries was also secured with Gorilla Glue Epoxy. This coaxial tubing system was run through a peristaltic pump (Masterflex L/S Digital Drive, from Cole Parmer) for the milling solution to flow through the entire system. Due to the speed of the peristaltic pump, it was able to create seal between the metal coupon and coaxial tubing opening. Each metal coupon was milled with the coaxial tubing system and aqua regia for 19 hours. A 75mm artillery shell (M337 A2) made with aluminum and brass with a wall thickness of 1.75mm was milled with the coaxial tubing system. The system was ran until complete penetration of the artillery shell wall for about 2 hours.

For all the milled metal coupons, each area of the coupon that was milled was analyzed using a 3D laser scanning microscope: Keyence VK-X100. This determined the depth for which each condition that the metal coupons were milled.

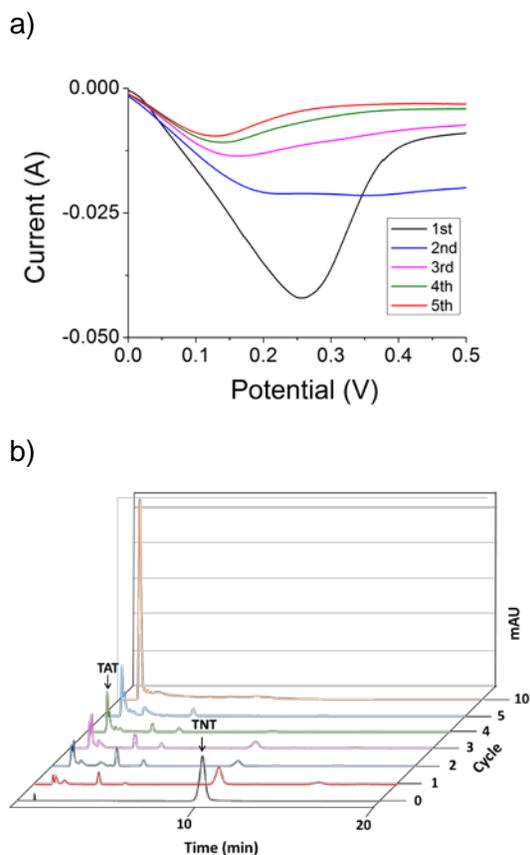


Figure 6. a) Cyclic voltammograms for the electrochemical reduction of TNT to TAT. b) Liquid chromatography of the electrochemical transformation of trinitrotoluene (TNT) to triaminotoluene (TAT).

## 5. Results and Discussion

### 5.1 Electrochemical Explosives Neutralization

#### 5.1.1 Electrochemical Reduction of different explosives with Pt electrode.

Electrochemical reduction was conducted to reduce the nitro functional groups in TNT to an amino functionality. In order to mimic seawater salinity, 1 mL aqueous solution of 0.2 g/L TNT (solubility 0.1 g/L) dissolved in 3.5 wt% sodium chloride was prepared. A platinum working electrode, a platinum counter electrode and a Ag/AgCl reference electrode were placed in the trinitrotoluene (TNT) solution. Electrochemical reductions were performed by cyclic voltammograms between 0.5 V to  $-0.2$  V versus Ag/AgCl at  $10 \text{ mV s}^{-1}$  using a potentiostat (CH Instruments, Inc.). As the potential became positive, the nitro groups were reduced to amino groups at a potential of  $\approx 0.15$ - $0.25$  V, resulting in the reduction peak in every reduction sweep of the cyclic voltammogram. Due to the decreased amount of TNT in the electrolyte, the reduction peak current of each sweep was also gradually decreased. After 24h, electrochemical reduction was repeated to further reduce TNT to triaminotoluene (TAT). The experiment was ended till cyclic voltammogram was

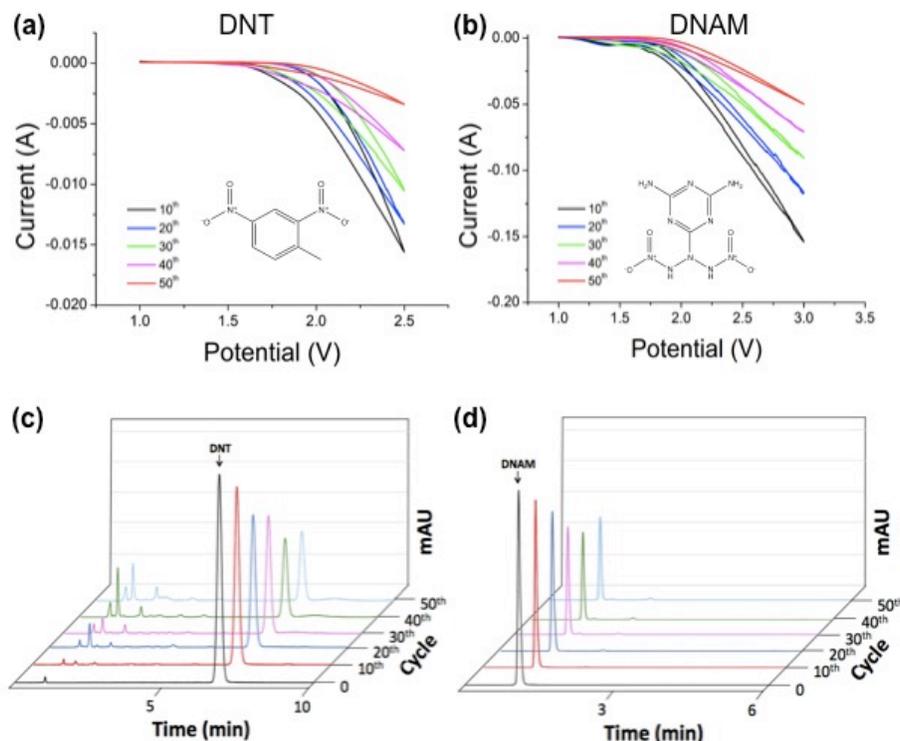


Figure 7. Cyclic voltammograms for the electrochemical reduction of a) DNT; b) DNAM. Liquid chromatography of the electrochemical transformation of c) DNT; d) DNAM.

featureless with no characteristic reduction peaks. The chromatogram shows the electrochemical reduction of the nitro- functional groups of TNT to amino- groups through 10 cycles of electrochemical reduction. The intermediate compounds of this reaction, such as 4-amino-2,6-dinitrotoluene and 2,4-diamino-6-nitrotoluene, are not labeled. Sample separation was carried out on a 1120 Compact liquid chromatography (Agilent Technologies) with an Eclipse Plus C18

column (150 mm length x 4.6 mm i.d., 5 $\mu$ m particle sizes, Agilent). An isocratic method for this analysis consisted of a mobile phase of 40% methanol and 60% trifluoroacetic acid (0.1%) in water at a flow rate of 1.5 mL min<sup>-1</sup>. Samples were analyzed by a UV-Vis detector set at a wavelength of 280 nm.

Electrochemical reduction was conducted on DNT (2,4-dinitrotoluene). 5mL aqueous solution of 0.1 g/L of DNT (solubility 0.3 g/L) dissolved in 3.5 wt% sodium chloride (seawater salinity) was prepared. Three electrodes system: a platinum wire working electrode, a platinum wire counter electrode and a Ag/AgCl reference electrode was applied in the solution to electrochemically reduce the nitro functional groups in DNT to an amino functionality. Electrochemical reductions were performed by 50 cyclic voltammograms cycles between 1.0 V to 2.5 V versus Ag/AgCl at 0.1 V s<sup>-1</sup> using a potentiostat (CH Instruments, Inc.). CV and chromatogram data was collected at every ten cycles. As the potential became more positive, the nitro groups were reduced to amino groups, resulting in the reduction peak in every reduction sweep of the cyclic voltammogram. Due to the decreased amount of DNT in the electrolyte solution, the reduction peak current of each sweep was gradually decreased accordingly. The experiment was ended till the reduction peak started to overlap. In order to fully reduce DNT, electrode with larger surface will be applied next. The LC chromatogram (Fig. 7c) showed the electrochemical reduction of the nitro- functional groups of DNT to amino- groups through 50 cycles of electrochemical reduction. DNT intermediates are not labeled (retention times between 1-2 min) in this figure. Separation was carried out as described above apart from the isocratic method used. The mobile phase for DNT separation consisted of 50% methanol and 50% trifluoroacetic acid (0.1%) in water at a flow rate of 1.0 mL min<sup>-1</sup>, with UV-Vis analysis of 280 nm. Electrochemical reduction of DNAM (dinitaminomelamine) was performed by cyclic voltammograms between 1.0 V to 3.0 V versus Ag/AgCl at 0.1 V s<sup>-1</sup>. 5mL aqueous solution of 0.1g/L of DNAM (solubility 3.2g/L) dissolved in 3.5wt% sodium chloride (seawater salinity) was prepared. Similarly, DNAM was successfully electrochemically reduced as the potential became more positive. Due to the decreased amount of DNAM in the electrolyte solution, the reduction peak current of each sweep was gradually decreased from -0.15A at 10th cycle to -0.04A at 50th. The electrochemical reduction of DNAM was monitored by LC using the same isocratic method as DNT (above). While intermediate compounds can be seen in the reduction of DNT, DNAM intermediates were not easily observed. Therefore, only the decrease in DNAM concentration was observed in the LC chromatograms.

### ***5.1.2 Electrochemical reduction of different explosives using dual working electrode system.***

The dual working electrode system will be able to provide higher efficiency for electrochemical reduction of explosives since inner working electrode has much larger surface area by packing graphite powders in it. Two different size of electrode systems have been prepared (Figure 8). The larger electrode system encapsulated with 1" OD stainless-steel tubing for both good mechanical and corrosion resistance properties in seawater. It will also serve as the counter electrode for the electrochemical system. 0.75" OD purified graphite tube was inserted into and insulated from outer stainless-steel tube. The graphite tube provides excellent conductivity and works as a large outer working electrode. The porous inner working electrode was fabricated with 0.5" OD tygon tube which packed with different sizes of graphite particles (20, 45, and 150  $\mu$ m). This inner working electrode adopted interchangeable design for flow rate study as shown in Figure 8. Efficacy of the electrode system was tested by running cyclic voltammetry and reduction efficiency of the electrode system was obtained.

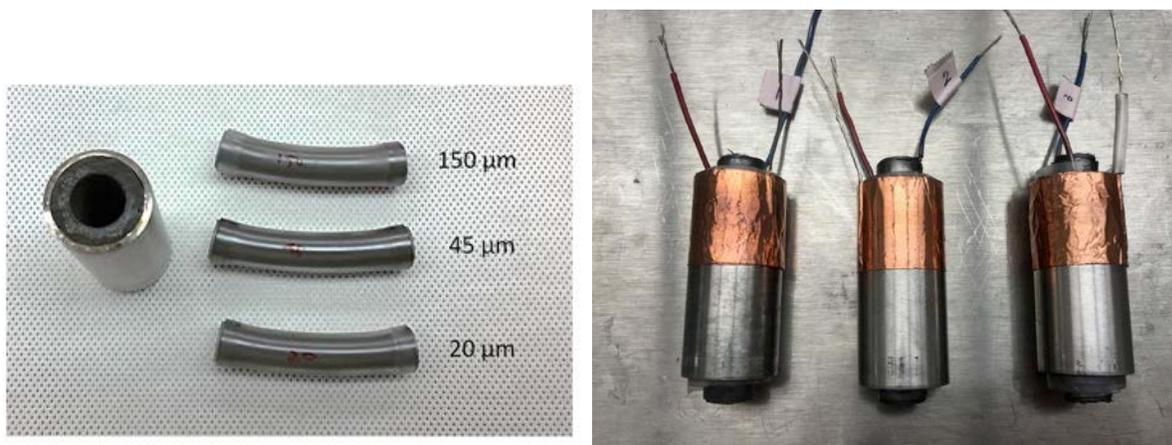


Figure 8. Fabricated electrode systems with different size of graphite.

Electrochemical reduction was conducted to reduce the nitro functional groups in DNT to an amino functionality. In order to mimic seawater salinity, the aqueous solution of 1 mg/mL DNT (solubility 0.3 mg/mL) dissolved in 3.5wt% sodium chloride was prepared.

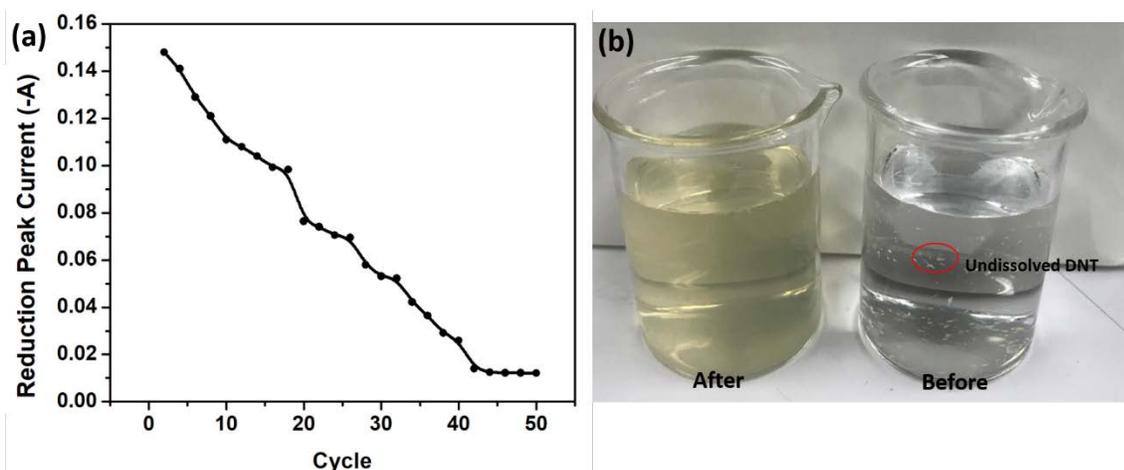


Figure 9. (a) Reduction peak current evolution of 50 cycles from cyclic voltammograms for the electrochemical reduction of DNT. (b) DNT solution before and after electrochemical reduction.

The dual electrode as working electrode, a platinum counter electrode and a Ag/AgCl reference electrode were placed in the DNT solution. Electrochemical reductions were performed by cyclic voltammograms between 1.2 V to 2.4 V versus Ag/AgCl at  $100 \text{ mV s}^{-1}$  using a potentiostat (CH Instruments, Inc.). As the potential became positive, the nitro groups were reduced to amino groups resulting in the reduction peak in every reduction sweep of the cyclic voltammogram. Due to the decreased amount of TNT in the electrolyte, the reduction peak current of each cycle was also gradually decreased shown in Figure 9a. The experiment was ended at 50 cycles with no further reduction current change. From Figure 9b on the left side, it is observed that DNT was not

dissolved in the original prepared solution due to the DNT solubility of 0.3 mg/mL. However, after DNT was electrochemically reduced after 50 cycles on the right side, the solution turned clear yellow with intense odor with no solid DNT observed. It is concluded that while applying electrochemical reduction, the solid DNT was continuously dissolved and eventually reduced after 50 cycles. The LC chromatograms (Figure 4) show the progression of the nitro-functional group reduction of DNT through 50 cycles of electrochemical reduction. With ~80% reduction of DNT, intermediates were observed to increase in concentration, seen at retention times between 3-5 minutes.

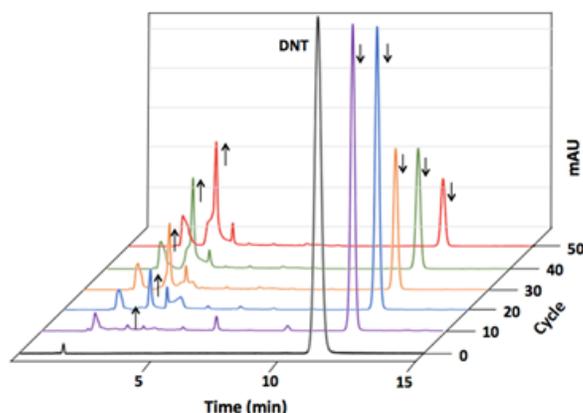


Figure 10. Liquid chromatography of the electrochemical transformation of DNT.

Electrochemical reduction was conducted to reduce the nitro functional groups in TNT and RDX to an amino functionality. In order to mimic seawater salinity, the aqueous solution of 1 mg/mL DNT and RDX dissolved in 3.5 wt% sodium chloride was prepared.

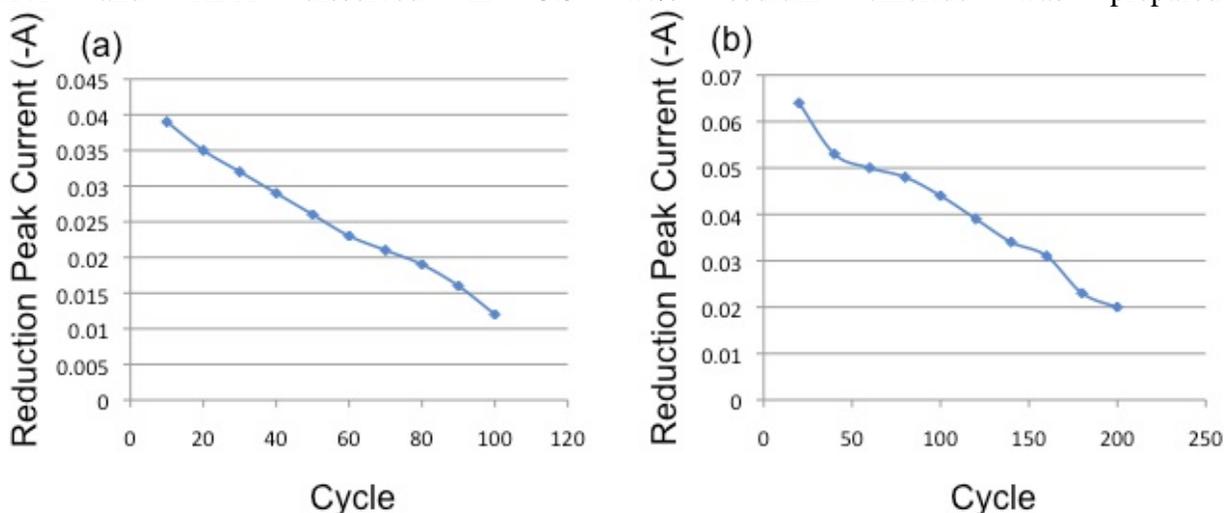


Figure 11 (a) Reduction peak current evolution of 100 cycles for TNT. (b) Reduction peak current evolution of 200 cycles for RDX.

The dual electrode as working electrode, a platinum counter electrode and a Ag/AgCl reference electrode were placed in the DNT solution. Electrochemical reductions were performed by cyclic voltammograms between 1V to 3V versus Ag/AgCl at 100 mV s<sup>-1</sup> using a potentiostat (CH Instruments, Inc.) for TNT and 1.5V to 3V for RDX. As the potential became positive, the nitro

groups were reduced to amino groups resulting in the reduction peak in every reduction sweep of the cyclic voltammogram. Due to the decreased amount of TNT and RDX in the electrolyte, the reduction peak current of each cycle was also gradually decreased shown in Figure 4. The experiment was ended at 100 cycles for TNT and 200 cycles for RDX. The LC chromatograms (Figure 11) show the progression of the nitro-functional group reduction of DNT through 50 cycles of electrochemical reduction. With ~80% reduction of DNT, intermediates were observed to increase in concentration, seen at retention times between 3-5 minutes. Through further studies, these intermediates will be identified using a ThermoFisher Velos Pro ion trap mass spectrometer.

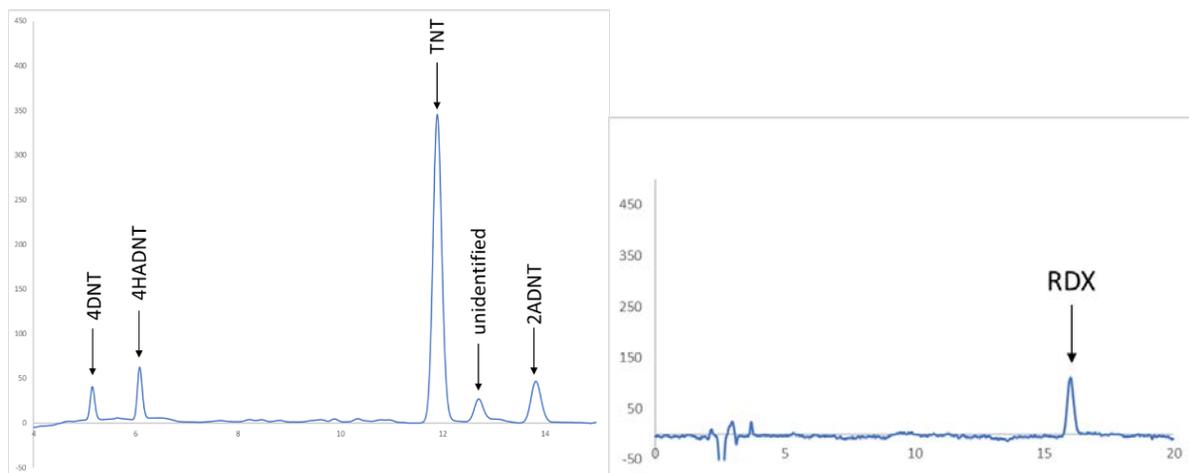


Figure 12. LC of TNT (left) and RDX (right).

The LC chromatogram (Fig. 12 left) shows the typical electrochemical reduction of the nitro- functional groups of TNT to amino- groups through multiple cycles of electrochemical reduction. Intermediate compounds of this reaction include 4-hydroxylamino-2,6-dinitrotoluene (4HADNT), 4-amino-2,6-dinitrotoluene (4DNT), and 2-amino-4,6-dinitrotoluene (2ADNT). Sample separation was carried out on a 1120 Compact liquid chromatography (Agilent Technologies) with an Eclipse Plus C18 column (150 mm length x 4.6 mm i.d., 5 $\mu$ m particle sizes, Agilent). An isocratic method for the analysis of TNT consisted of a mobile phase of 50% acetonitrile and 50% formic (0.1%) in water at a flow rate of 1.0 mL min<sup>-1</sup>. Samples were analyzed by a UV-Vis detector set at a wavelength of 210 nm. Intermediates were identified by LC-MS (not shown). Figure 12(right) illustrates a typical RDX electrochemical reduction. Unlike TNT, intermediates are rarely seen in the reduction of RDX. Separation was carried out as described above apart from the isocratic method used. An isocratic method consisting of a mobile phase of 30% acetonitrile and 70% formic (0.1%) in water at a flow rate of 1.0 mL min<sup>-1</sup> was used for the analysis of RDX. Samples were analyzed by a UV-Vis detector set at a wavelength of 210 nm.

### 5.1.3 Electrochemical Reduction of different explosives with flow system.

To optimize the overall system for maximum efficiency, we pulled the solution through the inner working electrode using a peristaltic pump. The pressure will be monitored using a pressure gauge. We optimized the two major variables, i.e., particle size and solution flow rate. As a starting point, we compared tubes packed with one of three sizes of graphite particles, <20 microns, <45 microns, or <150 microns, to provide optimal packing densities and back pressures. For flow rate studies, we pumped from the outlet side of the inner working electrode tube, which packed with different diameter of graphite mentioned above to ensure the cavity remains at reduced pressure.



Figure 13. Flow system with dual electrode system

The optimized flow rate was 0.5 mL/min with 150 microns of graphite particle. To simulate convection caused by moving the electrode within the shell interior, we performed the experiments in stirred solutions.

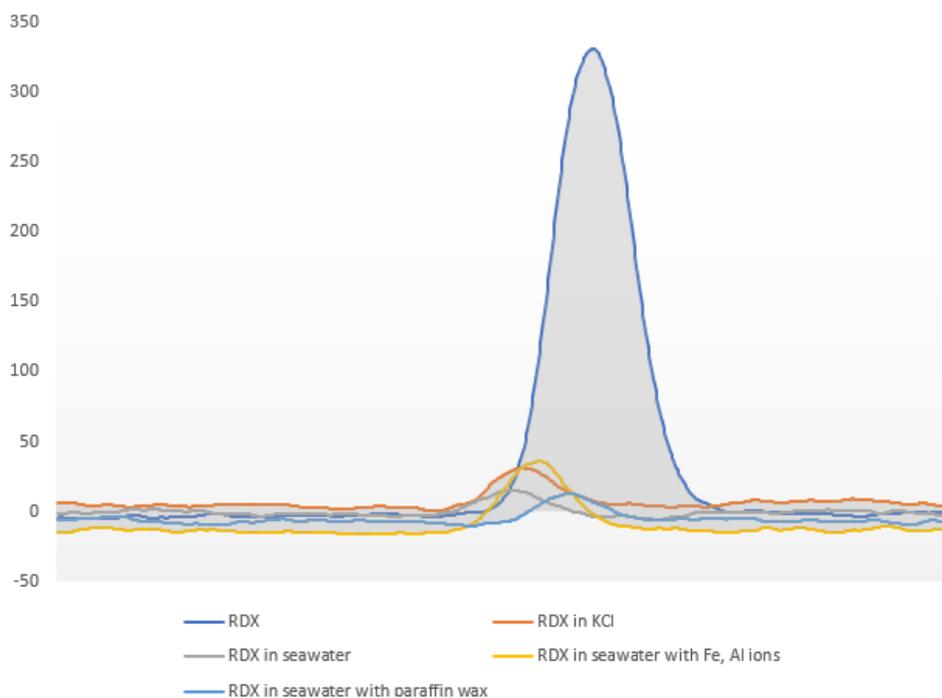


Figure 14. LC of RDX at different conditions

The following explosives with different condition were electrochemically reduced using the flow system. 1) RDX in KCl (0.3M); 2) RDX in seawater (0.3wt%); 3) RDX in seawater (0.3wt%) with Fe and Al ion (5wt% each); 4) RDX in seawater with paraffin wax (20wt%); 5) TNT in KCl (0.3M); 6) TNT in seawater (0.3wt%); 7) TNT in seawater (0.3wt%) with Fe and Al ion (5wt% each); 8) TNT in seawater with paraffin wax (20wt%).

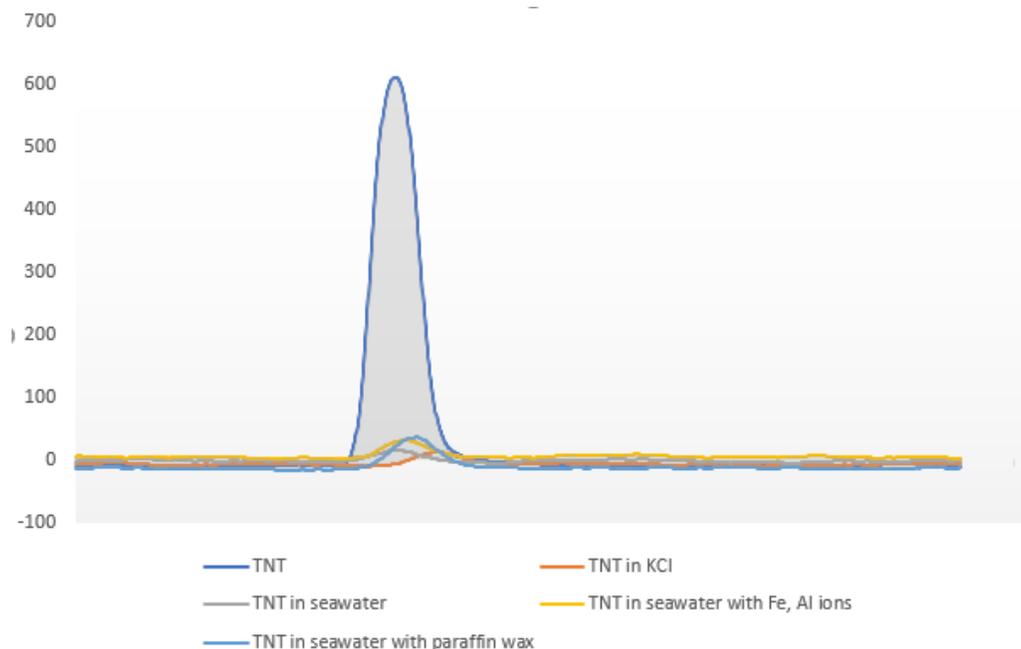


Figure 15. LC of TNT at different conditions

150 mL aqueous solution of 0.1 mg/mL of TNT or DNT dissolved in different solution as described was prepared. Three electrodes system: a dual working electrode, and a Ag/AgCl reference electrode was applied in the solution to electrochemically reduce the nitro functional groups in either explosive to an amino functionality. Electrochemical reductions were performed by voltammograms cycles between 1.5 V to 3 V versus Ag/AgCl at  $0.1 \text{ V s}^{-1}$  using a potentiostat (CH Instruments, Inc.). As the potential became more positive, the nitro groups were reduced to amino groups, resulting in the reduction peak in every reduction sweep of the cyclic voltammogram. Due to the decreased amount of explosive in the electrolyte solution, the reduction peak current of each sweep was gradually decreased accordingly. Each experiment was ended till the reduction peak started to overlap. LC results of before and after electrochemical reduction for both were shown in Figure 14 & 15. It was confirmed that more than 99% of explosive were electrochemically reduced.

RDX in different solutions	Cycles
<b>RDX in KCl</b>	<b>69</b>
<b>RDX in seawater</b>	<b>75</b>
<b>RDX in seawater with Fe and Al ion</b>	<b>75</b>
<b>RDX in seawater with paraffin wax</b>	<b>98</b>

Table 1. No. of voltammograms cycles applied to each conditions for RDX

TNT in different solutions	Cycles
TNT in KCl	25
TNT in seawater	31
TNT in seawater with Fe and Al ion	32
TNT in seawater with paraffin wax	41

Table 2. No. of the voltammograms cycles applied to each conditions for TNT

Table 1 and 2 listed the number of the voltammograms cycles that needed in order to electrochemically reduce >99% of explosive for each experiment. From the comparison, with seawater present, it will need more time in electrochemical reduction. Metal ions did not have any noticeable impact on number of the voltammograms cycles. However, with 20wt% paraffin wax in the solution, the number of the voltammograms cycles increased. The optimal scan rate can be increased to  $0.5 \text{ Vs}^{-1}$ , which could reduce the time to 10 min for more than 99% of both RDX and TNT to be electrochemically reduced.

## 5.2 Chemical Milling (Drilling)

### 5.2.1 Chemical Milling Solution

To construct a milling system for the UXOs, various chemical milling solutions were tested on 3 types of metal coupons: low carbon, high carbon, and high silicon. Based on literature research, we found that combination of sulfuric acid, nitric acid, and water (1:1:1 molar ratio) was apt for milling Si-steel, Aqua Regia solution (Nitric acid/Hydrochloric acid, 1:3 molar ratio) was suitable for carbon steel, and versatile chemical milling solution that uses less volatile chemicals to mill various steels is summarized in Table 1. The versatile chemical milling solution was given the nickname “patented solution.”

Chemical	Wt%
Nitric Acid	25
Stannic Chloride	5
Sodium Bifluoride	5
Ferric Chloride	10
Oxalic Acid	2.5
Acetic Acid	2.5
Water	50

Table 3. Versatile chemical milling solution

For systematic study of acid composition/concentrations and time-dependent milling depth of metal coupons in static state, a PDMS well system was constructed. Each well was filled with a designated milling solution and milled the metal for a time of 30 min, 1hr, 1.5hr, or 19hrs. Figure 16 shows an example of low carbon steel coupons milled with the 3 chemical milling solutions at the 4 time points.

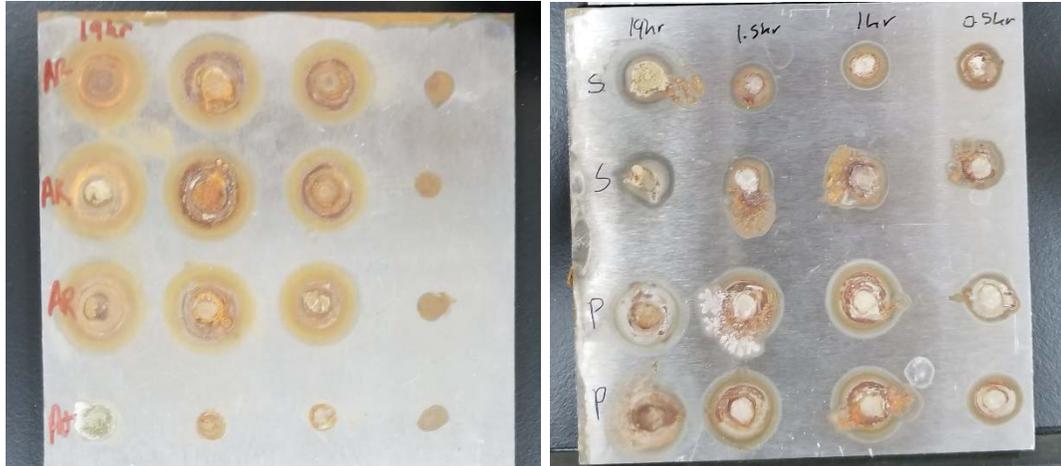
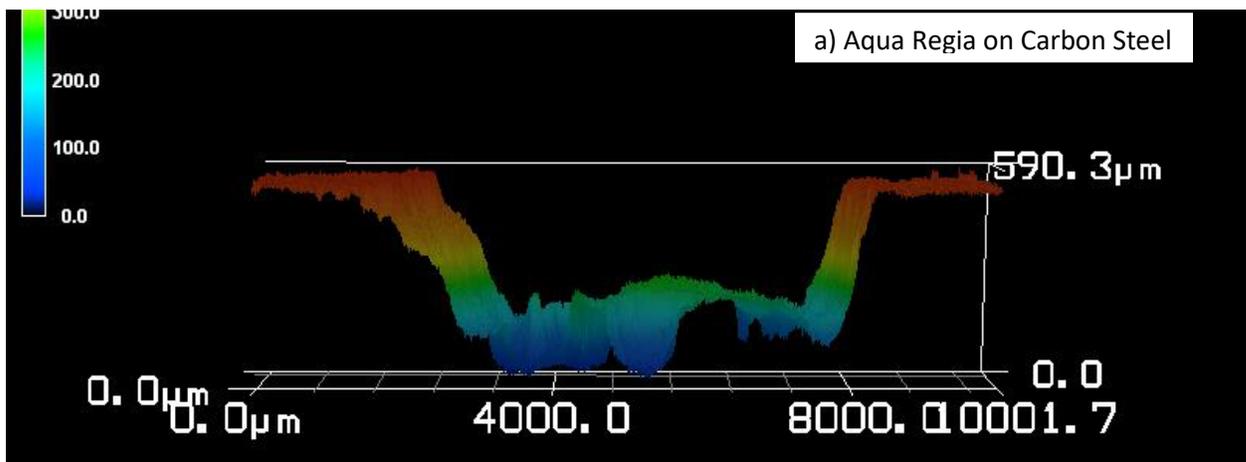


Figure 16. Low carbon steel milled with aqua regia, sulfuric/nitric acid, and patented solutions at 19hr, 1.5hr, 1hr, 0.5 hr.

For a precise measurement of the milling depth of each condition, a 3D Profilometer laser microscope was used. Based on the initial results, it became clear that Aqua Regia was the most powerful in milling all three types of metal coupons. Therefore we attempted to modify Aqua Regia with iron and tin salts, which have been known to improve chemical milling efficiencies. We performed milling tests with this modified Aqua Regia on the same three types of metal coupons. The summary of the milling after 19 hours depth data is shown in Table 2. Examples of the 3D Profilometer images of all the chemical milling solutions on carbon steel after 19 hours are shown in Figure 17.

Metal Coupon Type	Aqua Regia	Sulfuric/Nitric	Patented	AR w/ Tin and Fe
Stainless Steel	320.8 $\mu\text{m}$	242.4 $\mu\text{m}$	97.8 $\mu\text{m}$	207.4 $\mu\text{m}$
Carbon Steel	590.3 $\mu\text{m}$	44.0 $\mu\text{m}$	193.6 $\mu\text{m}$	175.7 $\mu\text{m}$
Low Carbon Steel	326.7 $\mu\text{m}$	92.2 $\mu\text{m}$	92.2 $\mu\text{m}$	216.1 $\mu\text{m}$

Table 4. Chemical milling depth data via 3D Profilometer



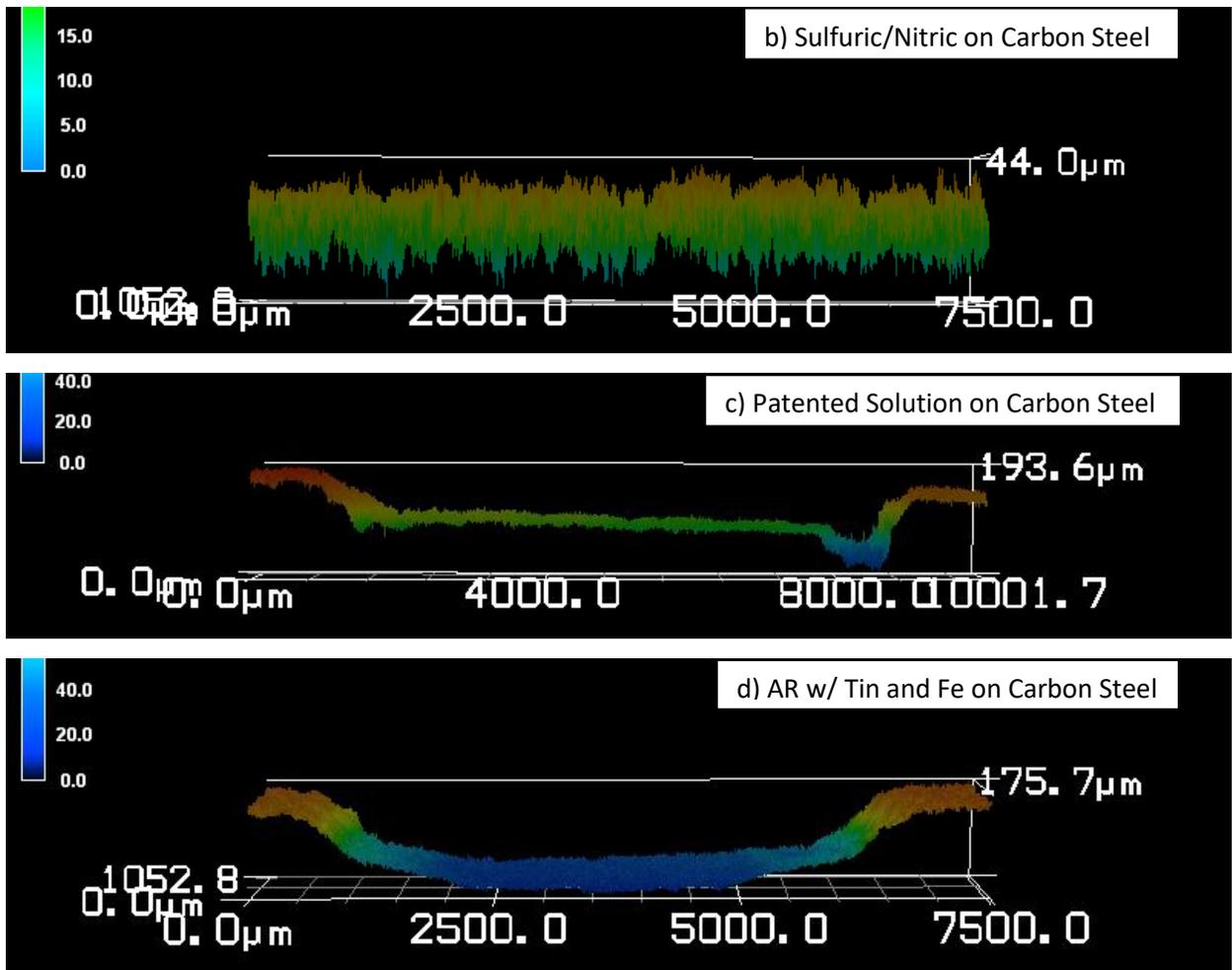


Figure 17. Images from 3D profilometer microscope to show milling over 19 hours on carbon steel with (a) Aqua Regia, (b) Sulfuric/Nitric acid, (c) patented, and (d) modified Aqua Regia with tin and iron solutions.

Overall, we performed 3 replications of each chemical milling conditions on the 3 metal coupons. We have determined that just pure Aqua Regia is this most versatile and efficient at milling metals. Therefore we will be continuing all experiments with Aqua Regia.

Given the expected colder conditions of actual UXOs due to being underwater in the oceans, we have begun testing aqua regia milling of metal coupons in colder conditions. Our experiments were conducted at 4°C and 15°C. As expected, the milling effectiveness was reduced at temperatures colder than room temperature as shown in the table below. These measurements were ascertained from a 3D profilometer.

Metal Coupon Type	Aqua Regia at 4°C	Aqua Regia at 15°C
Stainless Steel	213.9 μm	267.9 μm
Carbon Steel	221.6 μm	369.13 μm
Low Carbon Steel	243.7 μm	379.2 μm

Table 5. Chemical milling depth performed at 4°C and 15°C, data via 3D Profilometer

Our next plan is to determine the effect of salts (akin to found in sea water) on aqua regia's performance as a chemical milling solution.

### 5.2.2 *Delivery System for Chemical Milling (Drilling)*

To perform the milling on UXOs and appropriate conditions, we need to build a coaxial tubing system that can deliver the chemical milling solutions and at the same time vacuum out the used up solution. For this case, we combined tygon tubes and modified them so the inner tubing can essentially pump in solution while the outer tube pumps out the solution. Figure 18 shows the new tubing system that we have constructed and successfully shows that the solutions from the inner (green dye) and outer tubing (red dye) do not mix.

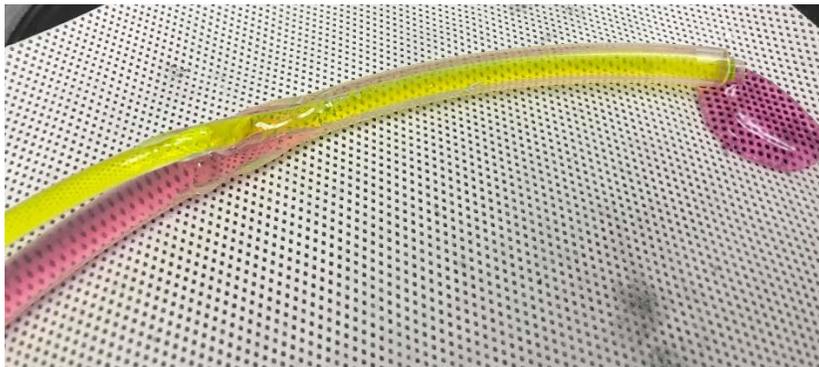


Figure 18. Tygon tubing modified for coaxial structure. The inner tube (green dye) and outer tube (red dye) do not mix as we expected.

Next we used a combination of a syringe pump for flowing solution in the inner tube and a peristaltic pump to vacuum out the solution. We held the tube against a flat glass surface and showed that our system works in Figure 19. Therefore we attempted to construct a junction that can affix the opening of the coaxial tubing to a metal surface for a complete, hands-free milling system. Our plan was to use a combination of adhesives and polymer-based connector with a suction-cup design. Then we plan to use Aqua Regia to perform chemical milling with the complete coaxial tubing system on metal coupons and eventually a sample UXO.

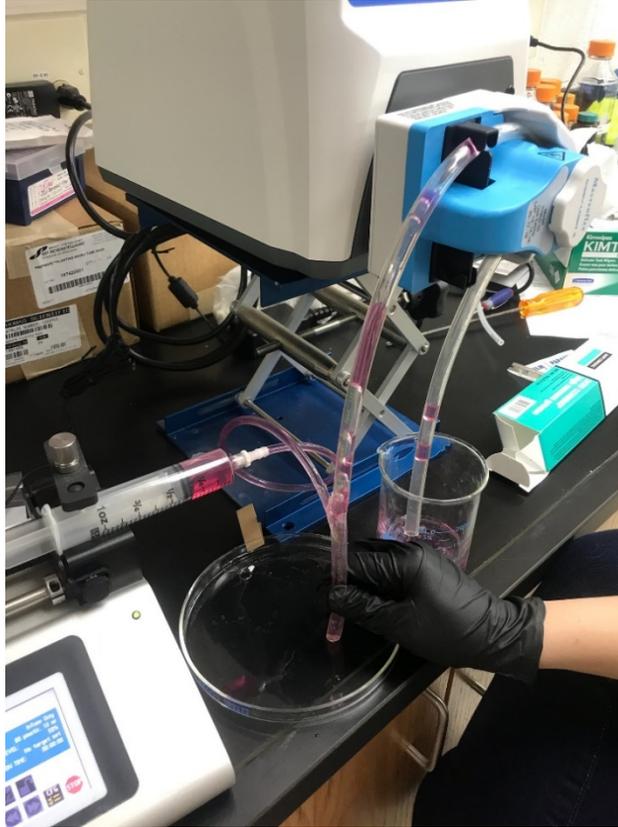


Figure 19. The coaxial tubing system combined with syringe pump and peristaltic pump to show the desired input and removal of solution.

Our first attempts to construct our own junction were unfortunately unsuccessful. Our designs produced leaks that made the idea ineffective as shown in an example in Figure 20.

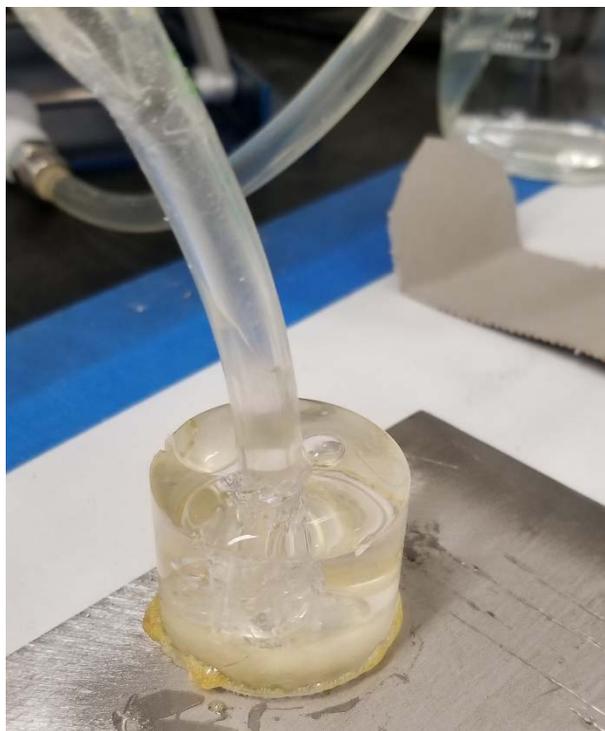


Figure 20. PDMS-based design of a junction to affix the coaxial tubing against a metal surface. Designs such as this one produced leaks.

Instead, we have decided to use suction cups with customized dimensions that are available from a commercial vendor. These suction cups also ensure no reactivity with the aqua regia milling solution. The coaxial tubing with suction cups attached were then set up in a peristaltic pump that ran at 16 mL/min. The force of the pump allowed for the suction cup to remain secure on the metal coupon without any adhesives or assistance as shown in Figure 21. It also pulled solution through the inner tubing and out through the outer tubing. Figure 22 shows the complete system of aqua regia being pumped in through the inner tubing, coming in contact with the metal coupon and then out the outer tubing.



Figure 21. The tygon-based coaxial tubing system with a suction cup attached to the surface of a metal coupon, while aqua regia runs through the tubing.



Figure 22. The complete coaxial tubing system attached to the surface of a metal coupon and hooked up to the peristaltic pump, while aqua regia runs through the tubing in a complete loop.

The coaxial tubing system with aqua regia was tested on the three metal coupons. Figure 23a shows an example of stainless steel milled for 19hrs with this method, while Figure 23b shows the corresponding 3D profile to show the milling depth. Table 6 summarizes the data attained from the coaxial tubing system milling on the metal coupons and compares to the results from the milling done in the PDMS wells. The data clearly shows that the coaxial tubing system mills much more, most likely due to convection flow of the aqua regia combined with the milling solution being replenished constantly.

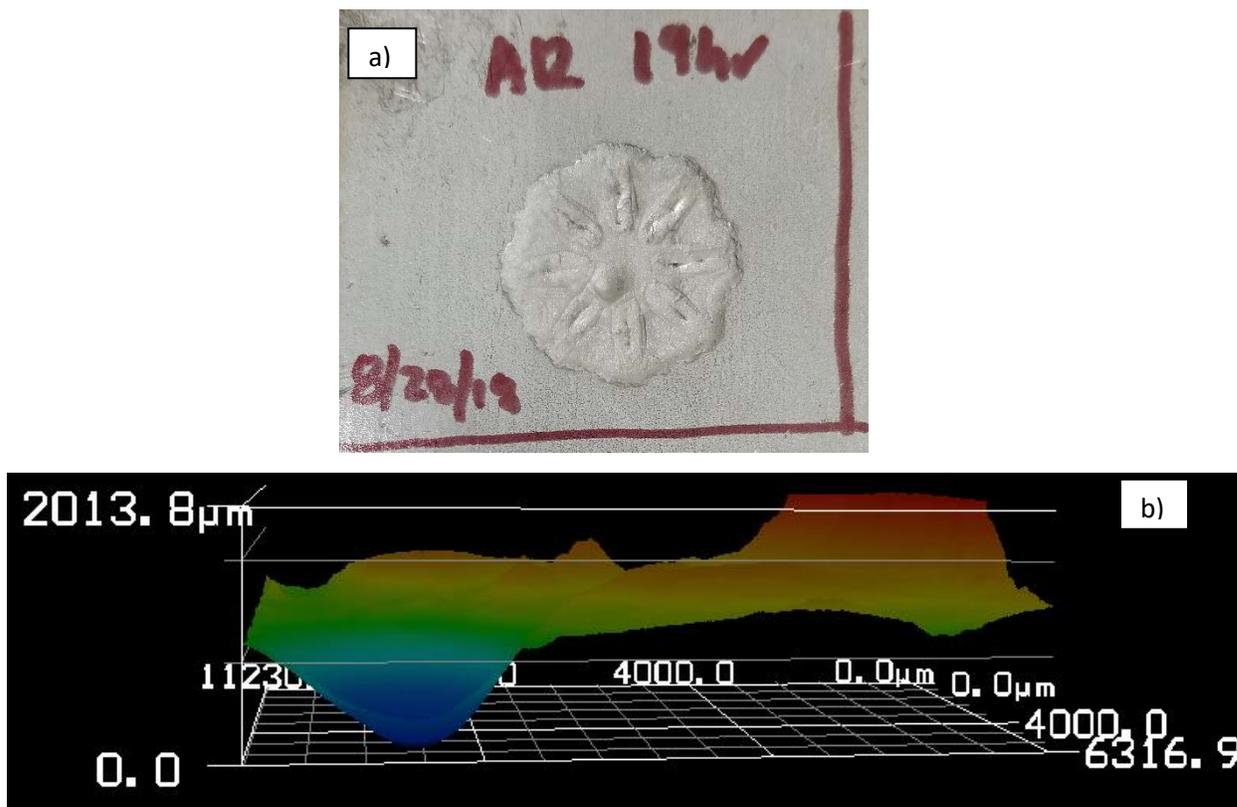


Figure 23. a) Stainless steel milled with aqua regia using the coaxial tubing system. b) The 3D profile from the center to the edge of the milled section of the stainless steel sample.

Metal Coupon Type	Aqua Regia in Well	Aqua Regia w/ Coaxial Tubing
Stainless Steel	320.8 $\mu\text{m}$	2013.8 $\mu\text{m}$
Carbon Steel	590.3 $\mu\text{m}$	3867.2 $\mu\text{m}$
Low Carbon Steel	326.7 $\mu\text{m}$	838.3 $\mu\text{m}$

Table 6. Chemical milling depth performed with aqua regia in a well vs. with the coaxial tubing system after 19 hrs.

Given our success with the coaxial tubing system, we decided to use the method to try and mill through an actual artillery shell. We ordered a 75mm shell made with brass/aluminum that is 1.75mm thick. Using the coaxial tubing system as shown in Figure 24, we successfully made a hole on the wall of the shell using aqua regia for only 2 hrs. Figure 25 shows the milled area of the artillery shell. Given our results, we feel that our coaxial tubing system combined with the use of aqua regia is the ideal method of milling UXOs.



Figure 24. A 75mm artillery shell with the coaxial tubing system attached via peristaltic pump.

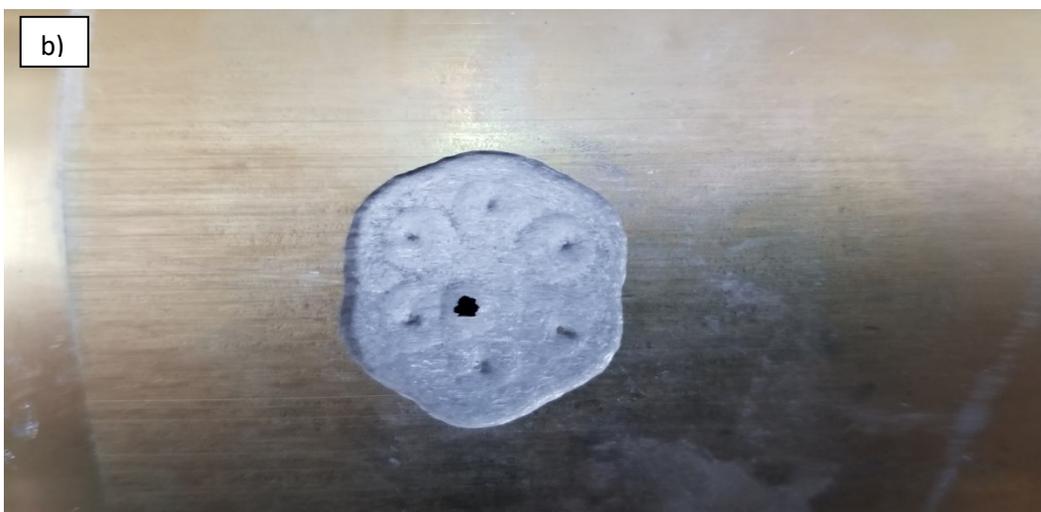


Figure 25. a) The artillery shell after being milled for 2 hrs with aqua regia in the coaxial tubing system. b) Zoomed in image of the hole created by the chemical milling.

## ***6. Conclusions and Implications for Future Research***

Our efforts in both electrochemical reduction and chemical milling during our SEED project yielded fruitful results. We were able to successfully reduce different explosives including TNT, DNAM, DNT, RDX. With our dual electrode flow system, the time for electrochemical reduction has been significantly shortened. It is expected that we can electrochemically reduce any dissolved TNT, RDX solution within 10 min with larger electrode system. We were also able to determine that aqua regia was ideal as the milling solution due to its effectiveness and versatility amongst various metal types. Furthermore our development of the coaxial tubing system was successful in securely attaching to metal surfaces and pump through the milling solution. The most crucial result was being able to chemically mill and puncture the wall of a 75mm artillery shell with our system in less than 2 hours. Furthermore we can optimize the milling process by reconfiguring the size of the coaxial tubing system. We believe the size of the inner tube dictates the speed and size of the milling area. The milling process could be sped up and enlarged by using larger inner tubing. The results we have gathered so far can be developed further into a complete functioning system to effectively neutralize UXOs. The major step to further develop this project includes physically combining the milling system and the electrochemical reduction components.

If requested, the second stage project will be to produce a remotely operated vehicle that can be piloted to known UXO. After finding the UXO the system will attach itself through an umbilical interface to the UXO and hold itself in place during remediation by suction. The suction will provide secondary containment to reduce the risk of leaking environmental toxins to very low levels practically achievable. The system can be equipped with emergency disconnect capabilities. At this point, it is unknown what size system will be needed to handle small, medium, and large UXO. However, our dual electrode can be easily scaled up to meet any size requirement of the system. The active surface area of dual electrode will be significantly increased with large outer metal tube and filled with more graphite beads. Also the volume of the flow per min will be largely increased so more explosive will be passing through the graphite beads. Thus the electrochemical reduction rate is expected to raise with the scale up system. The chemical milling process can also be further optimized with a better solution delivery method. We envision that replacing our laboratory-scale peristaltic pump with an industrial strength vacuum pump would make our system more efficient and applicable in a real-life situation for UXO remediation. The strength of an industrial strength vacuum pump will allow for better coaxial tubing and UXO interface sealing to allow for more directed delivery of the milling solution. Furthermore, scaling up the sizes of the coaxial tubing system will also speed up our milling process, while also increasing the limits of the milled hole size. This will also allow for better delivery of the dual electrode mechanisms. Systems can be envisioned in which the operation is performed completely by an underwater remotely operated vehicle and others in which the remotely operated vehicle attaches the umbilical, but the primary pumping and energy systems are on land or a small surface watercraft. While 100% success will be the objective, there will still be risk associated with any remediation endeavor. However, the processes laid forth in this project have characteristics that make them extremely well-suited for this application. I am certain that a system can be developed that can reduce the risk and impact compared to other strategies, including blow in-place and leaving the munitions undisturbed.

## 7. Literature cited

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