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Literature review on demilitarization of munitions

Document prepared for the RIGHTTRAC Technology Demonstration Project

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Defence R&D Canada – Valcartier

Technical Memorandum

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Abstract

The Canadian Forces (CF), as well as the United States Army and other military organizations, have a large inventory of munitions to support a multitude of tasks and missions, including training to ensure operational readiness. Throughout the life cycle of the munitions, items may become deteriorated, obsolete or declared surplus to requirement, and safe disposal options are then needed. This disposal should ensure that the items are rendered unusable for their intended military or strategic purpose and should be irreversible. Disposal should be carried out in accordance with regulations and safety and environmental requirements. This technical memorandum will present a literature review of the main technologies available in the demilitarization area. The classical destruction methods, such as open burning, will be reviewed, as well as new technologies that offer a more environmentally friendly way to dispose of munitions and methods that allow the recycling of the explosive content for other applications.

The design of future weapons is currently ongoing, for example through the RIGHTTRAC project. This design requires the use of explosive and propellant formulations having characteristics such as: enhanced performance, reduced vulnerability during storage and transportation, improved mechanical properties, decreased signature, extended service life and reduced environmental impact in manufacture, use and disposal. As demilitarization is a part of the life cycle of munitions, it must be addressed early to influence the design and positively impact future demilitarization execution. The up-front design for demilitarization (“Design for Demil”) is a new trend seen not only in the RIGHTTRAC project, but also in other organizations. This report will present an overview of the technologies, either present in the market or still in the laboratory in the development process, that deal with demilitarization.

Résumé

Les Forces canadiennes (FC), ainsi que l'armée américaine et les autres organisations militaires ont un large inventaire de munitions pour supporter une multitude de tâches et missions, incluant l'entraînement pour s'assurer que les troupes soient prêtes pour toutes les opérations. Tout le long du cycle de vie des munitions, des articles peuvent se détériorer, devenir périmés ou être déclarés non requis et ceux-ci nécessitent des options sécuritaires pour procéder à leur élimination. Cette élimination doit faire en sorte que les articles sont désormais rendus inutilisables à des fins militaires ou stratégiques et doit également être irréversible. Une telle élimination doit être faite suivant les exigences réglementaires, sécuritaires et environnementales. Ce mémorandum technique présente une revue de la littérature couvrant les principales technologies disponibles dans le domaine de la démilitarisation. Les méthodes classiques de démilitarisation, telle que la détonation à aire ouverte seront présentées, ainsi que les nouvelles technologies qui permettent une façon plus écologique de détruire des munitions, ou des méthodes qui permettent le recyclage des contenus explosifs pour d'autres applications.

La conception des futures munitions est présentement en cours, par exemple dans le cadre du projet RIGHTTRAC. Cette conception nécessite l'utilisation d'explosifs et de poudres à canon ayant des caractéristiques telles que : performance accrue, vulnérabilité réduite durant l'entreposage et le transport, propriétés mécaniques améliorées, signature réduite, vie utile étendue et impacts environnementaux réduits pendant la fabrication, l'utilisation et l'élimination. Puisque la démilitarisation fait partie intégrale du cycle de vie des munitions, on doit aborder cette question tôt afin d'influencer la conception et d'avoir un effet positif sur son exécution future. La conception a priori de la démilitarisation est une nouvelle tendance qui est non seulement présente dans le projet RIGHTTRAC, mais aussi au sein d'autres organisations. Ce rapport présente une revue de la littérature des technologies, actuellement sur le marché ou encore au stade du développement en laboratoire qui traitent de démilitarisation.

Executive summary

Literature review on demilitarization of munitions: Document prepared for the RIGHTTRAC Technology Demonstration Project

Isabelle Poulin; DRDC Valcartier TM 2010-213; Defence R&D Canada – Valcartier; November 2010.

All military organizations, as for example the Canadian Forces and the US Army, keep a large inventory of munitions to support their tasks, both in missions and in training. Through the life cycle of the munitions, items may become deteriorated (through ageing), obsolete (due to development of new weapon systems), or declared surplus to requirement (due to changes in requirements or destruction provisions of international treaties). This creates a costly (both in terms of money and storage space) backlog of excess, obsolete and unserviceable munitions. There is an important need for safe and cheap disposal options. In Canada, as of August 2006, more than 15,000 tonnes of obsolete, surplus or deteriorated ammunition-related items awaited disposal. In the US, as of 2009, 450 million kg of obsolete and unserviceable munitions items were in storage. These obsolete munitions should be demilitarized, i.e., disposed of in accordance with all legal and regulatory requirements and policies relating to safety, security and the environment. Disposal should render the items unusable for their intended military or strategic purpose and should be irreversible.

A new trend of “Design for Demil” has also been on the rise in the last few years. The key element of this concept is to incorporate demilitarization considerations early in the development of new munitions to mitigate impacts and cost while not affecting mission capability. The RIGHTTRAC Technology Demonstration Project is applying this strategy and this memorandum is a part of it.

This memorandum will present an overview of the demilitarization processes available or at the development level. The disposition of obsolete munitions by open burning/open detonation (OB/OD) is the most widely known technique, but it is less used nowadays due to environmental pressures. Many alternative procedures are currently under development by various organizations and researchers to remove, reclaim and reuse explosives and propellants from various military munitions. New and innovative solutions are being developed by many groups. They will be summarized in this publication.

Sommaire

Literature review on demilitarization of munitions: Document prepared for the RIGHTTRAC Technology Demonstration Project

Isabelle Poulin; DRDC Valcartier TM 2010-213; R & D pour la défense Canada – Valcartier; Novembre 2010.

Toutes les organisations militaires, par exemple les Forces canadiennes et l'Armée américaine, gardent un large inventaire de munitions pour supporter leurs tâches, en mission et à l'entraînement. Tout le long du cycle de vie des munitions, des articles peuvent se détériorer (durant le processus de vieillissement), devenir périmés (à cause du développement de nouvelles munitions) ou déclarés non requis (en raison de changements dans les exigences ou d'une convention de destruction en raison de traités internationaux) et ceux-ci nécessitent des options sécuritaires pour procéder à leur élimination. Cette situation crée une accumulation de munitions en surplus, désuètes et inutilisables qui est dispendieuse, au point de vue monétaire et espace de rangement.

Il existe un besoin criant pour une option de destruction sécuritaire et à faible coût. Au Canada, en date du mois d'août 2006, on compte plus de 15 000 tonnes d'articles liés aux munitions sont périmés, en surplus ou détériorés et en attente de destruction. Aux États-Unis, en 2009, 450 millions de kg de munitions périmées ou hors service sont présentement entreposées. Ces munitions périmées devraient être démilitarisées, c'est-à-dire détruites selon les exigences réglementaires et les politiques de sécurité et relatives à l'environnement. Cette destruction doit faire en sorte que les articles sont désormais rendus inutilisables à des fins militaires ou stratégiques et doit également être irréversible.

Une nouvelle tendance de conception avant démilitarisation ("Design for Demil") est apparue au cours des dernières années. La clé de ce concept est de songer à la démilitarisation tôt dans le développement des nouvelles munitions pour permettre d'atténuer les impacts et les coûts tout en n'affectant pas les capacités. Le projet de démonstration technologique RIGHTTRAC applique cette stratégie et ce mémorandum en fait partie.

Ce mémorandum présente un survol des procédés de démilitarisation disponibles ou au stade de développement. La destruction des munitions périmées par détonation ou brûlage est la technique la plus connue, mais elle est de moins en moins utilisée à cause des pressions environnementales. Plusieurs options de rechange sont présentement en cours de développement par plusieurs organisations et chercheurs pour retirer, traiter et réutiliser les explosifs et poudres propulsives des diverses munitions militaires. Des solutions nouvelles et innovatrices sont en développement par plusieurs groupes. Elles sont résumées dans cette publication.

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1 Introduction

The Canadian Forces (CF), as well as the US Army and other military organizations, have a large inventory of munitions to support a multitude of tasks and missions. In Canada [1], this inventory is composed of reserve stocks, forming the immediate capability for the CF and the Department of National Defence (DND) to operate in a conflict, and of free stocks, used primarily to train DND/CF personnel to ensure operational readiness. Through the life cycle of the munitions, items may become deteriorated (through ageing), obsolete (due to development of new weapon systems), or declared surplus to requirement (due to changes in requirements or destruction provisions of international treaties). This backlog of excess, obsolete and unserviceable munitions is large and storage is costly, so there is a need for safe disposal options. In Canada, as of August 2006, [1] more than 15 000 tons of obsolete, surplus or deteriorated ammunition-related items awaited disposal. In 1997, the backlog of the US Department of Defense was over 380 million kilograms in the Resource Recovery and Disposition Account, and this quantity was projected to increase substantially due to the retirement of weapon systems and downsizing of the military [2]. As of 2009, 450 million kg of obsolete and unserviceable munitions items are currently in storage and waiting for demilitarization [3].

In the USA, Department of Defense Instruction Number 5000.02 (December 8, 2008) [4] stated: “At the end of its useful life, a system shall be demilitarized and disposed of in accordance with all legal and regulatory requirements and policy relating to safety (including explosives safety), security and the environment”. The obsolete weapon platforms and ammunition end up in the demilitarization stock pile, but it decays and creates hazards and environmental and security problems. Moreover, to store, secure, maintain and inventory obsolete ammunition is a waste of money and resources, such as storage space [5]. In the case of storage space in particular, the munitions to be demilitarized are taking up valuable storage space in DND facilities and will eventually restrict or curtail the DND/CF ability to receive and store new munitions [6]. All these reasons call out for disposal through demilitarization. This process can be defined as: “destroying the military offensive or defensive advantages ... to prevent the further use” [7], or, according to the Canadian Controlled Goods Directive [6]: “action that renders an item unusable for its intended military or strategic purpose and that is irreversible”. In Canada, the Canadian *Controlled Goods Regulations* [6] and the US *International Traffic in Arms Regulations* (ITAR) [1] require that DND/CF take responsibility to demilitarize ammunitions.

The NATO Standardization Agency has published STANAG 4518, which suggests that any NATO participating country developing a munition shall implement the design and assessment principles of demilitarization [8]. Unfortunately, it seems that Canada is behind other NATO countries with respect to demilitarization practices [1]. NATO STANAG 4518 [8] defines demilitarization as: “The act of removing or otherwise

nullifying the military potential of a munition. Such action is to be carried out in a safe, cost-effective, practicable and environmentally responsible manner. Demilitarization is a necessary step for military items prior to their release to a non-military setting”. Unfortunately, the information included in this STANAG is brief and is not considered to provide a true guide for demilitarization of munitions [9].

The most widely known demilitarization procedure is disposal of the obsolete munitions by open burning/open detonation (OB/OD) or functioning. It is still identified as the main disposal technique in Canadian Forces Technical Orders (CFTO) [10]. OB/OD has been used for many years and is still used today, but this procedure is known to induce many environmental effects such as contamination with energetic materials (EMs) and metals. Open detonation can also generate large shock waves that can damage property (civilian or military) and the fragments produced can fly over long distances and harm or kill people. Moreover, this procedure is becoming more and more unacceptable and is facing close scrutiny by environmental agencies and the public. Another way to dispose of obsolete munitions was sea dumping, but this procedure is no longer used. Many alternative procedures are currently under development by various organizations and researchers to remove, reclaim and reuse explosives, propellants and pyrotechnics from various military munitions. New and innovative solutions are being developed by many groups. Open detonation should be limited to cases where ammunition is not safely approachable, such as for unexploded ordnance (UXO) on ranges.

Moreover, the design of future weapons is currently ongoing, for example through the RIGHTTRAC project. This design requires the use of explosive and propellant formulations having enhanced performance (energy output) and reduced vulnerability during storage and transportation, for example. Design considerations for such formulations include improved mechanical properties, decreased signature, extended service life and reduced environmental impact in manufacture, use and disposal [11]. Demilitarization is a part of the life cycle of munitions. In any program aimed at developing new munitions, demilitarization should be included as a system engineering requirement. Demilitarization must be addressed early in order to influence the design and positively impact future demilitarization. Early design for demilitarization may lead to low cost changes that do not detract from achieving item performance [7]. Up-front design for demilitarization (“Design for Demil”) is a new trend seen not only in the RIGHTTRAC project, but also in other organizations ([5, 7]). Design considerations in Design for Demil, according to Mescavage [7], include i) easy disassembly; ii) easy access to and removal of energetics; iii) materials & components that are reusable, recyclable, and non-hazardous; iv) accommodates existing demilitarization capabilities; v) minimizes the need for special tools; vi) considers demil operator involvement. Again, the key is to incorporate Design for Demil considerations early on, in order to mitigate the impacts and cost while not affecting mission capability.

This report will present an overview of demilitarization technologies, either available on the market or still in the laboratory in the development process. Among them, the R3 plan

(resource recovery and reuse) for explosives will be discussed. Note that this report will NOT deal with the demilitarization of chemical, biological or nuclear warfare agents. In the first part, a short description of two explosives used as insensitive munitions will be given. Then, the techniques available to open the projectiles to gain access to the explosive material will be presented. Then, methods to remove the explosives from the casings will be discussed. A section on the techniques available to destroy EMs will be presented. As one of the goals of the RIGHTTRAC project is to recycle explosives, a section on the potential markets for reused explosives will be presented, followed by the methods used to extract and recover energetic materials from explosives and propellants. The last section will present briefly the basic characterization techniques that aid in determining the purity of the recycled compounds. This literature review is not intended to be exhaustive.

2 Insensitive munitions for use as main charge explosives

In the RIGHTTRAC project, some properties are sought for main charge explosives: insensitivity, recyclability and low toxicity or non-toxicity for ecosystems. The insensitivity properties refer to a munition that is stable enough to withstand mechanical shock, fire and impact by shrapnel or bullets but is still able to explode as intended in order to destroy its target. Two main charge explosives are considered in the project: the first is a plastic bonded explosive (PBX), the other is based on an energetic thermoplastic elastomer (ETPE). Both will be described in this chapter.

2.1 Plastic bonded explosives

A plastic (or polymeric) bonded explosive (PBX) is an explosive material in which the explosive ingredient is suspended in a matrix of polymeric binder. The synthetic polymer is usually in small quantities (typically 5–10% by weight). The polymeric compounds are cast-cured and chemically reticulated (thus irreversibly), and the compositions are insoluble and non-recyclable. The polymer is an elastomeric rubber which absorbs and dissipates the energy from hazardous stimuli.

Inert binders such as those based on HTPB (hydroxyl-terminated polybutadiene) were used in early formulations. The crosslinked binder is made from the reaction of HTPB with an isocyanate, and it also contains a plasticizer such as dioctyl adipate. This binder acts as a protective agent; it tends to absorb shocks, making PBX less sensitive to accidental detonation. These formulations present the advantage of low viscosity before the addition of the curing agent and a large capacity to hold solid particles. PBX can be pressed into a particular shape and is safe to machine. However, these polymers are inert, thus decreasing the overall energetic yield of the explosive. A trade-off has to be made between sensitivity, performance and viscosity in order to obtain a formulation that is insensitive, mechanically processable and with performance comparable to that of regular explosives [12]. Other polymers include carboxy-terminated polybutadiene (CTPB) and hydro-terminated polyethers (HTPE) [11].

2.2 Thermoplastic elastomers

Thermoplastic elastomers (TPEs) are polymers having superior strain capability in low temperature regions like elastomers, while they can be processed as thermoplastics at elevated temperatures. Conventional elastomers need to be chemically crosslinked into a three-dimensional network structure to provide structural integrity resulting in thermosetting characteristics, while TPEs involving physical crosslinks, i.e., intermolecular forces of attraction, to form a three dimensional structure can be softened at elevated temperatures and processed like thermoplastics as they regain their original physical characteristics on cooling [13]. The binders, or TPEs, are copolymers of type ABA, AB or $(AB)_n$, where A and B are the hard segment and the soft segment, respectively. The hard segment is capable of crystallization or association and gives the copolymer its thermoplastic behaviour. The soft segment gives elastomeric behaviour. Physical crosslinking (dipole-dipole interaction, hydrogen bonding, etc.) in the polymer results in a rubber-like behaviour at room temperature. Because these crosslinks are reversible, the TPE can be melted or dissolved in a solvent [14], which is a huge advantage for recycling.

Industrial processes to produce TPE can be classified in four categories: a) thermoplastic styrene-diene block copolymers, b) thermoplastic polyurethanes, c) copolyester ethers, and d) polyolefin thermoplastic elastomers. However, the presence of the inert polymer decreases the energetic yield of the explosive. To increase the energy of the composition, many efforts have been deployed to develop energetic thermoplastic elastomers (ETPEs).

2.2.1 Energetic thermoplastic elastomers

These polymers still reduce the sensitivity of explosives but without reducing their energetic yield. For the purpose of realizing formulations with superior energetic yield, various ETPEs have been synthesized (see review in Reference [13]).

In the early 2000s, Defence R&D Canada – Valcartier scientists developed a melt-cast explosive containing energetic thermoplastic elastomers [15]. The most promising ETPE is based on glycidyl azide polymer (GAP, see Figure 1). This ETPE is a copolymer of AB type having a molecular weight of 2800 g/mol (ETPE 2000, see Figure 1). The polymer is highly soluble in melted trinitrotoluene (TNT) and its introduction in the formulation yielded more desirable properties, such as low viscosity (as conventional melt-cast explosives, they can be processed in existing facilities), insensitiveness to external stimuli, and recyclability. Because the formulation is meltable, the need for solvents during casting is eliminated. No other chemical crosslinking agent is added, thus making processing easier. The superior processing qualities and the ease of recycling make these materials a much more environmentally sound choice for energetic binders.

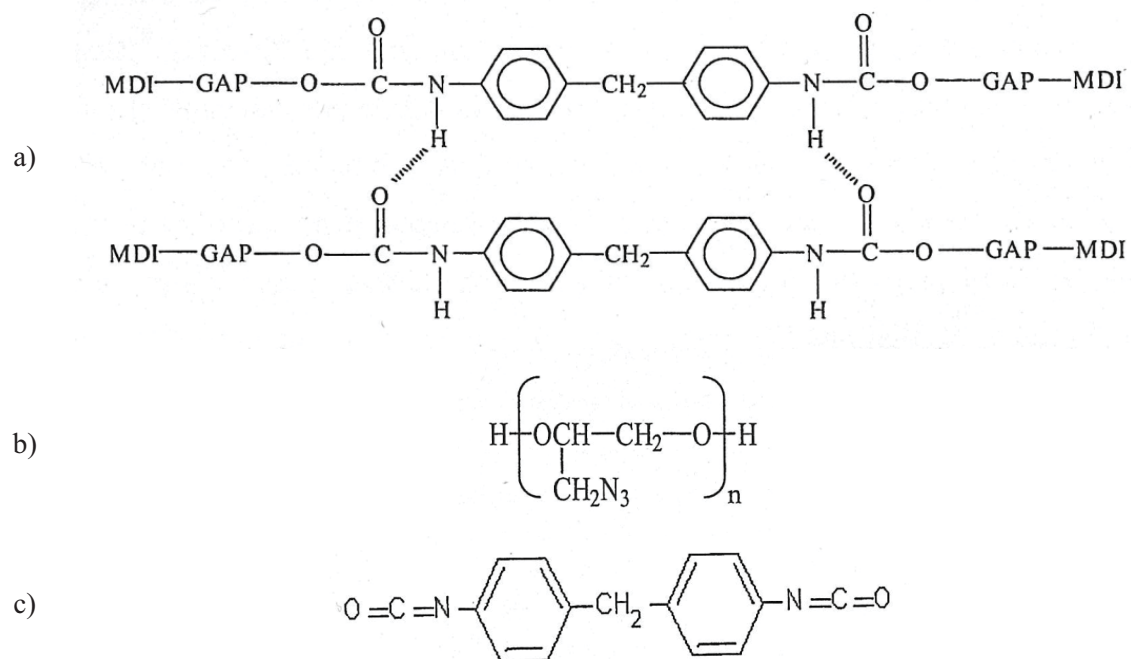


Figure 1: Structure of a) ETPE, with b) GAP segment and c) MDI

3 Demilitarization and disposition processes

The process of demilitarization will result in the neutralization of the military potential of the munitions to prevent reuse, misrepresentation or misidentification of the residue for military or terrorist activities [8]. The actions taken in demil processes should make the item unidentifiable as a munition. The main processes of demilitarization are presented in Figure 2. Most of these steps will be described and discussed in this report. It must be noted that not all of these steps are required, for example munitions could be destroyed without disassembly. Removal from storage and transportation will not be discussed in detail here.

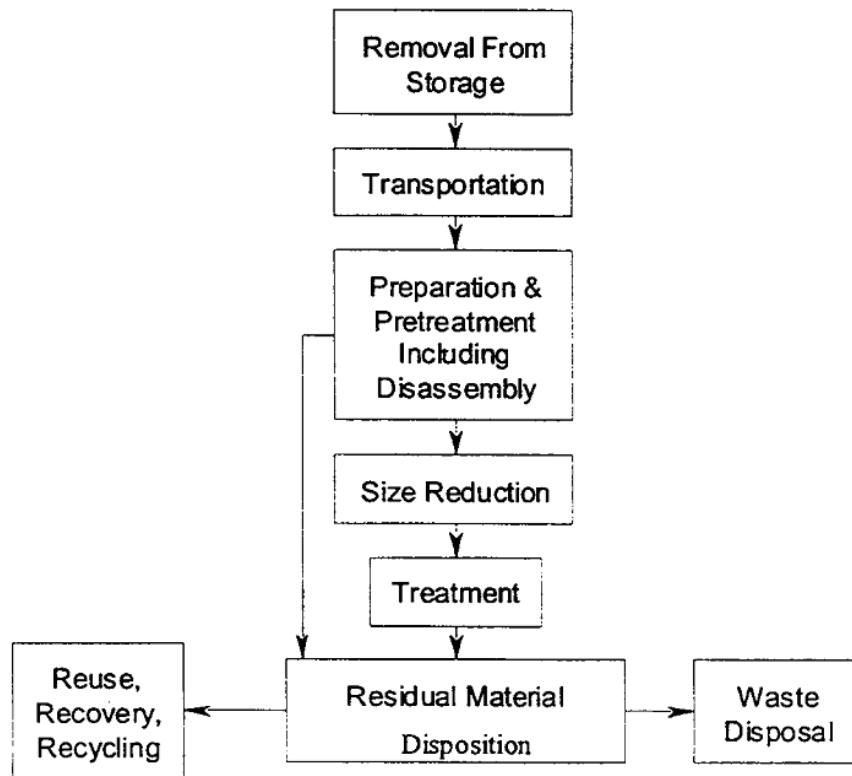


Figure 2: Demilitarization and disposal process [8]

3.1 Preparation and pre-treatment

The munitions that are stored in military facilities and are removed from service usually come in packaging made of various materials. Most of them are safe, such as wood,

```
graph TD; A[Unpack Munitions] --> B[Disassemble]; A --> C[Shell and Explosive]; A --> D[Packing Material]; B --> E[Extract Explosive]; C --> E; E --> F[Scrap Brass]; E --> G[Scrap Metal]; E --> H[Recycling Process]; D --> I[Reuse or Energy Recovery];
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The flowchart illustrates the recycling process for munitions. It begins with 'Unpack Munitions', which leads to a 3D illustration of a munition. From this illustration, three arrows branch out: one to 'Disassemble', one to 'Shell and Explosive', and one to 'Packing Material'. 'Disassemble' leads to 'Extract Explosive'. 'Shell and Explosive' also leads to 'Extract Explosive'. From 'Extract Explosive', three arrows branch out: one to 'Scrap Brass', one to 'Scrap Metal', and one to 'Recycling Process'. Finally, 'Packing Material' leads to 'Reuse or Energy Recovery'.

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3.1.1.1 Manual disassembly

This technique involves the use of human resources to manually dismantle the munitions using simple hand tools. This process will likely follow the reverse order of assembly used in production. The capital investment is minimal, but it is labour-intensive with a very low throughput. The method requires well-trained semi-skilled staff [17] and health hazards are high.

3.1.1.2 Mechanical disassembly

Mechanical disassembly involves the use of mechanical systems to physically dismantle the munitions. The conventional treatment for munitions includes the reverse assembly or reverse engineering with specialized equipment, such as automated robots. The separation of the projectiles from the cartridges, the defuzing and the removal of the explosives from the projectiles are carried out [18]. A mechanical system can also pull apart the pieces and remove the fuze and primer from the munition [17]. In some cases, both the EM and the metal casing can be reused. A variety of methods exist, but equipment for reverse engineering is usually designed to work well for specific munitions and does not adapt easily to different configurations [16]. Nevertheless, reverse assembly is applicable to most regular munitions [19]. The advantages are high production rate, low staff requirement and current availability of the technology. On the other hand, the investment in capital is high [17] due to the mechanical systems. Other mechanical disassembly methods involve the opening of the munition by cutting the casings and other parts. In the next subsection, some of these technologies will be presented: water jet cutting, cryofracturing, cutting with a high-pressure ammonia jet, femtosecond laser cutting and acid dissolution.

3.1.1.2.1 Water jet cutting

The technique of water jet cutting (or fluid jet cutting) involves the opening of the munitions by using a highly pressurized water jet and some abrasive material, like garnet. It was disclosed in US Patents No 5363603 and 5737709 [20, 21]. It is a powerful alternative to the conventional metal cutting tools. It is a relatively safe method as the water cools the metal and possible ignition of the explosive is suppressed. This technique can be utilized on those munitions that cannot be opened by reversed assembly (irregular munitions or in bad conditions). This technique has been tested on many different calibers, from 20mm to very large bombs, mortars and pyrotechnic flares [19] and on very sensitive parts (fuze and igniter) and the process did not cause any undesirable reaction. The shell can be cut longitudinally so that most of the components will be available for removal, but for safety reasons, a preferred option is to cut around the fuze until it is free from the casing [22]. The munitions need to be cut underwater to avoid the

noise and spread of abrasive and debris around the area [23] and also avoid the production of sparks due to metal to metal contact. The water contaminated by explosives is collected and can be used again after filtering [19, 24], but ultimately has to be treated as explosive-containing waste [23]. According to Galecki [23], the cost evaluations for water jet cutting are:

- Abrasive cost: \$US 0.60/lb
- Abrasive disposal: \$US 2.40/lb (flash, landfill)
- Water cost: \$US 1.80/kgal
- Water disposal: \$US 0.04/gal (carbon treatment)
- Energy cost: \$US 0.20/kWhr.

This technology is actually commercialized by various companies, such as Gradient Technology (Elk River, MN) [25].

3.1.1.2.2 Cryofracturing

One technique used to open the containers and extract the EM is fracturing at cryogenic temperatures [16, 26-29]. It involves the cooling of the device in a liquid nitrogen bath followed by crushing with a hydraulic press. It takes between 30 minutes and 4 hours to cool the munitions [1]. Both the casing and EM are brittle after being cooled in liquid nitrogen, so the device fractures into pieces when crushed. A simple mechanical shear or a press can be used [17]. The fragments can be processed to recover the EM by solvent extraction, melting, gravity or magnetic separation, or they can be destroyed by incineration or other techniques. Needless to say, in this case the casing cannot be refurbished. With this process, all munitions handling can be performed remotely by controlled robots and automated conveyors. Other attractive characteristics are: i) minimum contaminated area (contained within the equipment); ii) simple system processing a variety of munitions; iii) complete destruction of the munitions; iv) high throughput, v) flexible process which is not sensitive to munition design or condition, such as rusted munitions, and vi) system easy to operate. A schematic of the process is presented in Figure 4. As there is no waste stream, such as contaminated water, the final disposal costs are lowered. This technique is particularly effective for munition items that are difficult to disassemble or are likely to detonate during the demilitarization process. In the event of a detonation, safety is assured by the presence of a explosive-containment chamber [30]. The investment seems low for the set-up, but the costs for operation with a lot of liquid nitrogen can rise rapidly. General Atomics (San Diego, CA) seems to be the leader in the development of this technology [30]. They are developing a transportable unit of this device [31].

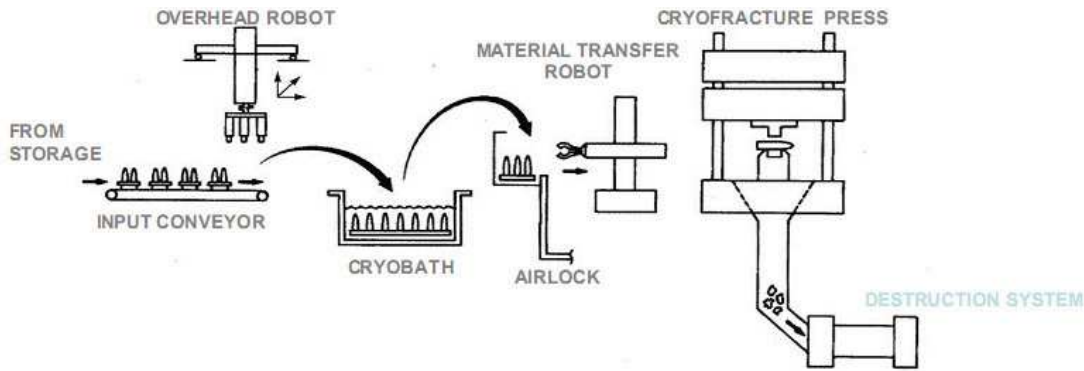


Figure 4: Schematic of the munition cryofracture process (from [31])

3.1.1.2.3 Cutting with high-pressure ammonia jets

It has been shown in Reference [32] that it was possible to demilitarize munitions, i.e., M55 rockets, using ammonia. The procedure developed uses an abrasive liquid ammonia jet to cut the casings. Ammonia is a good solvent for demilitarization as it dissolves and desensitizes some military explosives. Cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) are dissolved and are stable in ammonia, while nitroglycerin (NG) and TNT are decomposed through ammonolysis. This technique can also be used to remove explosives from the casing. At room temperature and at 0.78 MPa, ammonia exists as a liquid. In the cutting and washout process, ammonia could be recycled.

3.1.1.2.4 Femtosecond laser cutting

In order to access the interior of the munition, the casing must be opened, but conventional machining techniques may lead to high risks of explosive reaction due to an increase in temperature caused by machining with cutting tools. Rowske [33] demonstrated that it was possible to use a femtosecond laser to ablate metals and energetic materials. It is an attractive alternative since the absorption of the ultra-short laser pulse occurs on such a short time scale that the material is ablated with virtually no heat transfer to the surrounding material, resulting in a “cold” laser cutting process. The main disadvantages that the author of this report sees with this technique are very low throughput, i.e., one munition at a time, very high investment necessary to buy a femtosecond laser, and the need for highly trained personnel to operate and maintain this sophisticated system.

3.1.1.2.5 *Acid dissolution*

Another solution for the treatment of whole unserviceable munitions is acid digestion/dissolution. In this process, the complete munition is immersed in acid. The casing is dissolved, thus liberating the internal components. The acid action rapidly renders the fuze safe by dissolving the metal parts of the system. As soon as the casing is dissolved, the explosive is removed from the acid. This procedure was presented at a conference by Wynne [34], and is currently being implemented in a field demonstration by Battelle Memorial Institute (Maryland) [1]. Munitions as large as 105 mm can be opened with nitric acid dissolution. Due to the digestion of the steel munition body, the waste stream contains significant amounts of ferrous and ferric nitrates, which can be treated for the production of ammonium nitrate fertilizer.

3.1.2 Comparison of technologies

The technologies presented are summarized in Table 1 to make the comparison easier.

Table 1: Overview of the technologies for disassembly of munitions

Technology	Mechanical system	Applicable to various calibres	Capital investment	Throughput	Worker requirement	Health hazards	Current industry technology?	Other comments
Manual disassembly	None – everything is done by hand with simple tools.	Yes	Minimal	Very low	Labour-intensive	High	Yes, but in poor countries. Becoming less common.	
Reverse assembly – reverse engineering	Can be automated.	Is adapted for most regular munitions, but does not adapt easily to different calibres.	High	Medium	Medium	Medium	Yes	
Water jet cutting	Automated	Yes	High (US\$25M for a fixed water jet system) [37]	Medium (1600 rounds of 3-in. per shift)	Medium	Low	Yes	Resulting contaminated water needs to be treated.
Cryofracturing	Simple mechanical shear or press can be used. Can be fully automated. Can be transportable.	Yes	Low for set-up, but operating costs with a lot of liquid nitrogen can rise rapidly (US\$1-5M for the cryofracture system only).	High (depending on munition type, e.g. 360 ADAM mines/hour)	Low	Low	Yes, but not widespread.	Minimal contaminated area, no waste stream
Cutting with high-pressure ammonia jet	--	Yes	High	--	--	Medium	--	Ammonia dissolves or decomposes explosives. Ammonia can be recycled.
Femtosecond laser cutting	Femtosecond laser	Yes	High	Low	Medium, but highly trained personnel needed to operate and maintain.	Low	No, still in the labs.	
Acid dissolution	Acid bath, conveyor. Can be automated.	Yes	??	Depending on size of acid bath and number of rounds. Expected to be low.	Low	High (handling UXO and concentrated acid)	No	

3.2 Size reduction: Removing the explosive from the casing

As seen in Figure 2, once the ammunition is open, the explosive has to be taken out in order to be further processed. Depending on the properties of the explosive (easily melted, hard and brittle, etc.), different processes can be used. These processes help in reducing the size and volume of the complete munition. The separation of the components should be followed by further processes, which vary according to the material. The techniques presented in the next subsection are applicable to the projectile, the propellant casing or both, depending on the caliber and design.

3.2.1 Removal by melting

The energetics in many conventional munitions are melt-cast, therefore these munitions can be demilitarized by heating the filler sufficiently to cause it to melt and flow out of the munition. The explosives that melt at relatively low temperatures are, for example, Composition B (80°C) and TNT (80°C) [35]. The melting can be done using direct heat: steam, autoclave [8] or a hot bath [36]. The applied heat liquefies the explosive which is poured out of the casing [16]. Melting can also be done by inductive heating [37], where a magnetic field is applied around the metal casing, by the use of a coil around the casing in which alternating current is applied. The resulting changes in the magnetic field induce a current and therefore heats up the casing [9]. Often, drilling holes does not allow complete removal and some form of cutting or reverse engineering is required [9]. The molten TNT flows into a granulator, which is a metal container filled with water and an agitator. TNT is insoluble in water, so the stream of liquid explosive is transformed into pellets [38] when it comes in contact with the water. The use of steam and hot water washout is not effective in removing the explosive when it is composed of cast-cured energetics or PBX. Therefore, munitions containing PBX cannot be demilitarized using melting and steamout [36].

3.2.2 Water jet washout

Water jet washout was developed by the Royal Dutch Navy with the assistance of TNO-PML (The Netherlands Organisation for Applied Scientific Research - Prins Maurits Laboratory) [19]. By means of a high pressure water jet, the explosives can be removed from the munition casing. As opposed to water jet cutting, there is not always a need for an abrasive in the water. Advantages over the standard melt-out technique are: i) less time needed to remove the explosive from the projectile, ii) applicable to all explosives including PBX, iii) less energy needed compared to melt-out, iv) less pollution because

the water is reused, and v) less TNT vapour, so lower health hazard to personnel in the building. In the melt-out process (presented in subsection 3.2.1), a TNT film remains on the walls of the projectiles; but with the water jet technique, removal is more complete. There are disadvantages in this technique. For example, waste water is generated and there are hazards related to the explosive properties of the compounds (detonation can occur in pipes) and to their pyrophoric properties (e.g., with aluminized explosives).

The water jet washout technique has been used by Crane Division, Naval Surface Warfare Center (NAVSURFWARCENDIV Crane) in support of the US Navy Ordnance Reclamation Program and the Joint Service Large Rocket Motor Disposal Program, to remove and reclaim PBX-based energetics from munitions [2, 36, 39]. The goal was to demilitarize PBX-loaded munitions without creating undesirable pollutants and with the possibility to reclaim reusable materials. The use of high pressure water jets to remove PBX from ordnance was investigated, focusing on the safety of the operation and the design of an automated facility [40]. It was demonstrated that the pressure of the water jet has to be chosen with care, since PBX can detonate under high pressure water jet impact. Operating jet pressures of 35 to 175 MPa were sufficient to remove all of the PBXs of interest [36, 39]. In order to quantify the sensitivity of explosives and to determine the safety factors [41] during water jet impact, two tests were developed (Derringer test and shaped charge test). One of the main concerns was the processing of water in order to recirculate it back through the washout system. Some projectiles bodies were even returned for reloading.

3.2.3 Cryogenic washout

Cryogenic washout is a dry process that uses high-pressure jets of cryogenic liquid to embrittle and fracture the EM. With this process, a cryogenic medium such as liquid nitrogen is used to remove explosives from casings, and it then evaporates, eliminating aqueous wastestream. This process is believed to offer improvements in safety, waste minimization, protection of surface and groundwater and control of air pollution. Bench-scale testing has been performed with liquid nitrogen and liquid ammonia, and large-scale tests are planned [16].

In the report by Creedon [42], three propellant types were investigated: Class 1.1, composite modified double base (among the ingredients: nitrocellulose, nitroglycerin, inert triacetin plasticizer, ammonium perchlorate, aluminum, HMX), Class 1.2, crosslinked double base (PEG polymer, nitroglycerin, nitrocellulose, ammonium perchlorate, aluminum, RDX), and Class 1.3, hydroxyl terminated polybutadiene (HTPB) (polybutadiene, ammonium perchlorate, aluminum). For all the tests, no initiations of the explosives were detected. Impact, friction, low-level shock and electrostatic discharge sensitivity tests were conducted, and it was found that essentially no change in the sensitivity of the propellants occurs between ambient and cryogenic temperatures. The

bench-scale tests demonstrated the safety of liquid nitrogen washout and established parameter ranges for effective propellant removal. Removal rates of over 60 lb/hr were achieved for all propellant types. The prototype tests demonstrated cryogenic washout of several reduced-scale motors in a semi-automated process.

3.2.4 Ultrasonic separation

Research [43] has shown that it is possible to safely fragment and remove explosives from metal containers by the process of ultrasonic separation. The process uses ultrasonic waves in a fluid (alcohol or ketones for PBX) in which the munitions are immersed. When high-intensity ultrasound is applied to a liquid medium adjacent to a solid material, the stress produced by acoustic cavitation in the liquid causes fragmentation of the material. The stress (or pressure) produced by the cavitation of the liquid is a function of the properties of the liquid. High vapour pressure and surface tension greatly enhance the reaction [44]. The technology is especially well suited for cast-loaded explosives (TNT, Composition B (Comp B)), high melting point and polymer-bonded materials. It works for medium and large caliber munitions. The use of ultrasonic energy presented an unexpected outcome: with a suitable solvent and optimum filtration conditions, this process was able to separate some materials into their constituents, for example Comp B was separated into TNT and RDX, Octol was separated into TNT and HMX [45], and PBXN-101 was separated into HMX, laminac and styrene. Results showed that none of the materials presented signs of deterioration upon sonication. The process was tested by TPL, Inc. in a small pilot plant with great success [43, 46].

3.2.5 Dry ice blasting

Dry ice blasting (or CO₂ pellet abrasion) is a technique that uses high-velocity dry ice pellets to physically clean surfaces without damaging equipment or creating new waste streams, such as with the water jet washout technique. The process is dry, non-abrasive, non-conductive and does not change, alter or destroy the chemical structure of the material being processed. It uses a jet of solid CO₂ particles (pellets) fired at supersonic velocity and with great precision onto the area to be cleaned. One option is to use liquid CO₂ that is sent into a pelletizer, and upon expansion, the liquid CO₂ cools down and forms solid dry ice, which is extruded into rice-size pellets [47]. The other option is to use dry ice pellets and insert them into a pressurized air stream, which is directed at the surface to be cleaned [48]. This technique is mainly used for medium to large caliber munitions. Most of the energetic material in the munitions is first removed with a contour drill and vacuum system, and the residual material on the wall is removed by carbon dioxide blastout [3].

Dry ice pellets cannot remain solid when exposed to atmospheric pressures and temperatures. Because of the temperature difference between the dry ice and the surface to be treated, thermal shock occurs during the blasting process. In other words, when the dry ice pellets penetrate the contaminant and hit the substrates, friction slows them down and they begin to warm up. As the pellets warm up, they sublime (solid to gas phase) very quickly. The expansion forces the contaminant – which is no longer solidly bonded – to detach from the substrate. The dry ice vaporizes, and the safe and non-toxic CO₂ gas is simply released into the atmosphere after the cleaning process [47, 48]. This technique is not commercially used [3, 16].

3.2.6 Cryocycling

In the cryocycling technique [49], the propellant is cycled repeatedly between ambient and cryogenic temperatures. During both the freezing and warming phases of the process, fractures develop in the propellant grain material, and as the fractures intersect through repeated cycling, the bulk material is reduced to relatively uniform-sized rubble, i.e., thermal stress causes the material to break into pieces and it can then be either recovered or destroyed. Cryocycling is sufficiently dust-free to eliminate any requirement for dust collection from the propellant handling systems. This process will not work on all explosives and propellants, and it was first developed for the demilitarization of triple base propellant [1].

3.2.7 Comparison of technologies

The technologies presented are summarized in Table 2 to make the comparison easier.

Table 2: Overview of the technologies for removing explosive from casings

Technology	Mechanical system	Applicable to various calibres	Capital investment	Throughput	Staff requirement	Health hazards	Current industry technology?
Melting	Steamer, autoclave, coil, etc.	The explosive must melt (e.g. TNT)	Low	Medium	Low	Low	Yes
Water jet washout	Pressurized water (with or without abrasive)	Yes, but easier for large calibres.	--	--	--	--	--
Cryogenic washout	Pressurized liquid nitrogen to embrittle and fracture material.	Yes, easier for large calibres.	--	--	--	Low	No
Ultrasonic separation	Ultrasonic probes immersed in organic solvent.	Yes. Tested on 81-mm rounds.	US\$200,000	Low: 50 lbs TNT per day for 81-mm rounds. Could be increased by adding probes.	Low (two persons)	Low	Still at the prototype stage.
Dry ice blasting	Accelerated dry ice pellets	Yes. Easier on large calibres	--	--	Low	Low	No
Cryocycling	Cycling: immersion in liquid nitrogen and back to room temp. with warm air.	Not suitable for some explosives/propellants.	US\$1-3M	High: 400-500 rocket motors /day.	Low: two persons	Low (oxygen monitoring and explosive precautions)	--

3.3 Treatment

Following the demilitarization processes scheme in Figure 2, once the casings are open and the explosive filling is removed, it needs to be treated. Either high explosive in projectile or gun propellant in casings must be carried out with special care, depending on their nature. Treatment may include destruction and waste handling, as well as reuse, recovery and recycling. This section will present the technologies available for treatment.

3.3.1 Destruction technologies for energetic materials

Even though the aim of the RIGHTTRAC project is to recycle explosives, this section will cover the most popular destruction techniques for energetic materials. After being processed with these technologies, the end-products are completely non-energetic, and have lost all commercial value. The explosives are often transformed mainly into combustion gases. Any remaining material should be disposed of according to regulations. In the case of inert materials, some can be disposed of in landfills, but in the case of hazardous compounds, special disposal methods must be considered. The following section is not intended to be exhaustive, but the most common techniques for explosive destruction will be discussed.

3.3.1.1 Open burning and open detonation

Open burning and open detonation (OB/OD) operations are conducted to destroy unserviceable, unstable UXO or unusable munitions and explosive materials. It is the least expensive and technologically simplest disposal method available. In OB operations, explosives or munitions are destroyed by self-sustained combustion, which is ignited by an external source, such as flame, heat or a detonation wave. In OD operations, detonable explosives and munitions are destroyed by a detonation initiated by a disposal charge. OB/OD operations can destroy many types of explosives, pyrotechnics and propellants. OB areas must be able to withstand accidental detonation/deflagration of any or all explosives being destroyed, unless the characteristics of the materials involved are such that orderly burning without detonation can be ensured.

OB and OD can be initiated either by electric or flame ignition systems. In general, electric systems are preferable because they provide better control over the timing of the initiation. In an electric system, electric current heats up a bridge wire, which ignites a primary explosive or pyrotechnic composition, which in turn ignites or detonates the

material to be burned or detonated. If necessary, safety fuzes are used to initiate the burn or detonation [50].

Although OB/OD can effectively destroy munitions, they fail to meet the challenge of minimizing waste by-products in a cost-effective manner. Such methods of disposal are undesirable from an environmental point of view because they cause pollution. For example, OB/OD produces relatively high levels of undesirable airborne pollutants, such as nitrogen oxides (NO_x), acidic gases, particulates of various types, including metal, as well as many pollutants on the soil surface (metals, explosive residues and combustion by-products). However, it is believed [51] that it is possible to meet the emission requirements for the destruction of some munitions, with OD likely to be a cleaner process [9]. But incomplete combustion products can also leach into the soil and contaminate ground water from the burning pits used for OB methods. The surrounding soil and ground water often needs to be remediated after OB/OD to meet environmental guidelines. OB/OD for disposing of munitions is becoming impractical owing to increasingly stringent federal and other environmental protection regulations [22], as well as the limited availability of incineration sites and the hazards associated with transportation of large quantities of propellants or explosives [52]. Moreover, these operations are resulting not only in losses due to wastage of valuable materials, but also in high costs for transportation to the destruction area and the destruction process itself [53]. The noise from open detonation in particular is difficult to mitigate. Due to all these factors, it is recognized that there is a need to move towards a large reduction in environmental emissions from open burning [54] and to develop more environmentally sound means of demilitarization.

3.3.1.2 Closed detonation

The Swedish firm Dynasafe builds static detonation chambers [55] that allow the complete destruction of explosives, with the advantage of little or no need for disassembly prior to feeding. Munitions are fed in and heated until detonation occurs. The detonation chamber is indirectly heated from outside the inner chamber where the destruction takes place. Consequently, no gases from the heat generation will be mixed with gases from the destruction process. The ammunition or explosives fed into the inner chamber are destroyed through burning, deflagration, detonation on a hot scrap bed. A customized off-gas treatment system makes environmental requirements achievable. The detonation chamber is available in a mobile version that can easily be trucked from one destruction site to another. The mobile unit offers a solution to expensive and unsafe transportation of munitions. The chamber is heated above the auto-initiation temperature of all known explosives and propellants, thus ensuring complete destruction in one step. There is no need for counter charge [56, 57]. NAVSEA Warfare Center (Indian Head – in collaboration with others) also has a contained detonation facility that offers an alternative to open detonation. In this facility, particulate emissions are controlled.

3.3.1.3 Detonation chambers

Controlled detonation of munitions can be performed in detonation chambers, such as those manufactured by CH2M Hill (Englewood, Colorado [1, 58]) and by Kobe Steel (Japan [59, 60]). The munition to be destroyed is put in the chamber with donor charges for detonation. In the case of the DaVinch system by Kobe Steel [59, 60], the chamber is under vacuum. The destruction is carried out in a single-step process. The chamber is designed to withstand the detonation pressure and fragmentation. The system also includes an expansion tank to control overpressure and air pollution. The solid waste (airborne particulates collected on filters and residues in the chamber) is considered as hazardous waste. The system can be transportable or fixed.

3.3.1.4 Incineration

Different incineration systems are already in use for the disposal of propellants and explosives: rotary kiln, fluidized bed incinerator, plasma arc thermal treatment, flash furnace, deactivation furnace [61]. In the burning of propellants and explosives, toxic gases are always produced, such as HCN (this is oxidized with excess oxygen), NO_x, hydrochloric acid (HCl) and soot in considerable quantities, so that a technical and costly fume cleaning process is necessary. Some incineration plants are mobile [62] and can recover the energy for heating or electricity generation. Rotary kiln, fluidized bed combustion, plasma arc treatment and flashing furnace will be described in the next subsections.

3.3.1.4.1 *Rotary kiln*

In 1989, Germany acquired 300 000 tons of old and substandard munitions when the former German Democratic Republic was reunited with the Federal Republic of Germany. Some authors [63] believe that the idea of converting high explosives into inert products first occurred at that time. The disposal program that was undertaken concluded that it is feasible to reformulate the surplus energetic materials for either civilian or military applications. Incineration of the surplus munitions in rotary kilns was found to be the most efficient mode of destruction that also complied with German air quality standards [63, 64]. Rotary kiln or deactivation furnace seems to be a very mature technology; it has a long and proven history of treating a wide variety of explosive waste. It consists of an unlined cylindrical rotary furnace (combustion chamber designed to withstand detonations) inclined slightly to the horizontal which is rotated slowly about its axis. The material to be processed is fed into the upper end of the cylinder. The kiln contains internal spiral flights, which move the waste in an auger-like fashion through the retort as the kiln rotates [17]. As the kiln rotates, material gradually moves down towards

the lower end, and may undergo a certain amount of stirring and mixing. Hot gases pass along the kiln and burn the energetic wastes. The furnace is equipped with conveyors and feed systems, and most are also equipped with air pollution control equipment to limit gaseous pollutant emissions (i.e., remove particulates and hazardous gaseous wastes such as acid gases (HCl, NO_x and SO_x), which are neutralized and removed). Typical equipment includes an afterburner, a dry scrubber, a cyclone particle separator, a gas cooling system and a filter. The operating temperature of deactivation furnaces is approximately 650° to 820°C [50].

3.3.1.4.2 *Fluidized bed combustion*

TNO [19] developed an alternative method for the incineration of explosives that is safe and environmentally acceptable. It consists of burning the explosives in a fluidized bed furnace. Fluidized bed incinerators possess a high potential in the specific control of the incineration process [61].

In fluidized bed combustion, a bed of crushed solid particles (usually 6 mm or less) is made to behave like a fluid by an air stream passing from the bottom of the bed at sufficient velocity to suspend the material in it. The bed material is often coal and sand [65]. Due to the action of hot air flow, the particles of the bed float like a liquid. The fuel is injected into this floating bed in the form of fine droplets to ensure optimum mixing with air. Particles react completely before they reach the top of the bed [19].

In van Ham's paper [19], the explosive fillings and pyrotechnics (washed out by water jet) are first milled under water and transformed into a stable slurry (concentration of approximately 50% of the explosive weight). Separate water-based slurry is made for propellants. The slurry is then treated in the furnace.

The advantages of this combustion are: i) explosives can react portion by portion with excess air and yield "clean" combustion products; ii) the amount of explosives present in the furnace at a given time can be regulated, to avoid pressures that can damage the furnace. Special care should be taken in the cleaning of the exhaust gases created in the fluidized bed furnace. The solid reaction products can be collected in a cyclone or a bag house, whereas the gaseous products are emitted through the exhaust stack. Gaseous products include CO₂ and H₂O, and other compounds such as NO_x, CO, HCl, HF and SO₂ may be created (depending on the composition of the explosive). In the case of NO_x, careful tuning of the gas equilibrium can considerably reduce NO_x emissions. The use of a catalyst may decompose the NO_x. However, there is still a need for additional exhaust cleaning, with scrubbing for example.

3.3.1.4.3 *Plasma arc thermal treatment*

A plasma arc [3, 66-68] operates on principles similar to an arc-welding machine, where an electrical arc is struck between two electrodes. The high-energy arc creates a high-temperature, highly ionized gas enclosed in a chamber, i.e., plasma at a temperature over 12,000°F. Waste explosives are fed into the chamber where soil was previously added and melted in a crucible. The intense heat of the plasma melts the inorganic constituents of the munitions into a homogeneous slag. The organic components are fully oxidized in the slag. In a carefully controlled process, these atoms recombine into harmless gases such as carbon dioxide. The soil is melted to form materials, similar to hardened lava, in which toxic metals are encapsulated. With plasma arc technology there is no burning or incineration and no ash. The main concern is to ensure that gaseous emissions are kept to a minimum and cleaned (combustible gas is oxidized to CO₂ and H₂O in ceramic bed oxidizers) before being released. However, the potential for air pollution is low due to the use of electrical heating in the absence of free oxygen. The inorganic portion of the waste (molten slag) is periodically poured from the chamber, cooled and collected as a stable, leach-resistant, homogeneous solid slag which meets the Environmental Protection Agency (EPA) requirements for a non-hazardous waste. It is focused on the destruction of small caliber and hand held completely assembled pyrotechnic, smoke and dye ordnance which cannot be processed in a conventional deactivation furnace because of high heat and smoke generation. It is a completely destructive technology; there is no way to recycle or reuse the energetic components. On a more practical basis, the chamber for the plasma treatment is not designed to withstand detonations, so it can treat only unconfined explosives.

3.3.1.4.4 *Flashing furnace*

The flashing furnace is a system that destroys energetic materials at high temperature. For example, the El Dorado flashing furnace [69] has a heat cycle time of 45 to 90 minutes (depending upon load size and type) and the operating temperature ranges from 1000° to 1600°F. Fuel oil is fed to the burners for heating and the debris are put in a high-temperature resistant basket before they are inserted in the furnace. This technology is mainly used for the treatment of potentially explosive contaminated materials or small arms ammunition. For example, metal range debris from range clean-up and contaminated inert material from decommissioned ammunition plant (pipes, valves, equipment) can be treated by thermal decontamination, so scrap metal could be certified clean enough and sold for recycling to industry without restriction. The technology was adapted in a transportable unit. The manufacturer claims that this unit is robust, easy to use, has a high throughput capability, inherent safety and is very versatile. Demonstrations at various sites were successful.

3.3.1.5 Chemical and biological disposal

One method to dispose of nitrocellulose (NC) and NG, two ingredients in propellants, is the combination of the rapid chemical destruction by base hydrolysis (see subsection 3.3.1.5.1) and the biological degradation of the mixture. This process of chemical and biological disposal is suitable for all explosives containing NC as a major component. The chemical treatment of energetic materials to generate a biodegradable reaction mixture is an alternative to incineration for NC-based materials [61, 70, 71]. After alkaline hydrolysis, the degradable mixture will then go through two more steps, i.e., anoxic biological treatment (denitrification) and normal aerobic biological treatment.

3.3.1.5.1 *Base hydrolysis*

Base hydrolysis is being studied as a chemical conversion method for the destruction of EMs. Many energetic materials can be rendered non-energetic via reaction with highly concentrated bases (sodium hydroxide, potassium hydroxide, ammonia (ammonium hydroxide), sodium carbonate) and at elevated temperatures (80° to 150°C, use of a pressurized reactor if needed – note that the hydrolysis under high temperature and pressure accelerates the reaction by a factor of 8 to 10 as compared to room temperature and atmospheric pressure). In order to reduce mass transfer resistance to reactions, other solvents may be used, either neat or in combination with the main solvent, for example ethanol and dimethylsulfoxide (DMSO). They will also help to swell the binder to allow base access to the explosive.

Many reactions occur in the process, including hydrolysis, oxidation/reduction and substitution/elimination. These reactions usually produce a stream of small molecules: simple carboxylic acids, amines, sodium salts, nitrites, nitrates, ammonia and gaseous products such as NO_x, but additives (diphenylamine (DPA), graphite) remain as residues [61, 70, 72]. For example, it has been shown that 1.5 M sodium hydroxide (NaOH) solutions at 85-90°C readily breakdown many explosives and PBX formulations to non-explosive hydrolysis products [16]. It should be noted that products from the base hydrolysis, although non-energetic, still require additional processing before release to the environment. Base hydrolysis has been successfully transitioned to large scale operations [72].

3.3.1.5.2 *Supercritical water oxidation*

At the supercritical state, a fluid has a density between that of water vapour and liquid at standard conditions, and exhibits high gas-like diffusion rates along with high liquid-like collision rates [73]. For water, this state is obtained at temperatures and pressures above

its critical point, i.e., $> 374^{\circ}\text{C}$ and 218 bar. The process of supercritical water oxidation relies on the fact that solubility behaviour is reversed in the supercritical state, so that hydrocarbons become soluble in water. In the process, the organic wastes are destroyed using an oxidant in supercritical water. In these conditions, organic materials and gases become highly soluble and this makes it possible to carry out rapid, complete oxidation using water as a carrier medium [74]. The reversed solubility also causes salts to precipitate, meaning they can be treated using conventional methods for solid-waste residue. Because the temperature of supercritical water oxidation is much lower ($400\text{--}650^{\circ}\text{C}$) than conventional incineration, there is no accompanying generation of NO_x or SO_x and much less energy is required to operate the system [3].

The technique is effective in destroying a range of agents, from “regular” explosives to toxic and hazardous compounds of pyrotechnic ammunition including carcinogenic/toxic smoke and dye compounds. Especially chloro-organic compounds can be destroyed in an environmentally safe way [75]. Most organics are oxidized to CO_2 , H_2O and inorganic acids or salts with no production of SO_x , dioxins or furans [76]. The technique exhibits unparalleled environmental compliance capabilities, without the need for a pollution abatement system [77]. The principle is already being used commercially for the treatment of toxic organic waste [78]. A process developed at Parsons uses hydrogen peroxide as an oxygen source [79]. In trials conducted at Aberdeen Proving Ground in Maryland in 1994, conversion rates of 99.999 percent were achieved. The destruction conditions were 250 bar and 400°C . The exothermic reaction raised the temperature further, to 600° to 650°C , which increased the reaction rate [74]. Supercritical water oxidation has the advantage of being a single-phase, closed process, avoiding the need for further treatment of toxic gaseous or solid products. It is also rapid. However, the environment is extreme, and explosion is possible if firm control is not maintained on the temperature. In addition, a leak in the reactor would release highly toxic products under high pressure. The environment is also highly corrosive, forcing designers to use expensive materials to construct the pressure vessels. Inorganic salts can also form sludge with the potential to block valves and pipes. The development of this technique has been undertaken by a number of organizations, including General Atomics and Lockheed Martin [74].

3.3.1.5.3 *Molten salt process*

In the molten salt process, the explosive wastes are combined with water to form a slurry that is introduced with air into a crucible in which sodium, potassium and lithium carbonates are melted (operating temperature: $600\text{--}900^{\circ}\text{C}$) [16]. Even though the oxidation is thermal, it is a flameless technology. The organic components in the waste react with oxygen from the air to produce carbon dioxide, nitrogen and steam. As a result of wetting and dissolution, the inorganic components (ash) are captured in the molten salts. If halogenated compounds are present in the mixture, the acid gases created are scrubbed by the alkaline carbonates, producing carbon dioxide and the corresponding

salt. The gases in the crucible exhaust line are monitored and a cold trap acts as a filter if necessary. The emissions are sent to atmosphere, with lower amounts of nitrogen oxides than when produced by incineration. The molten salts mixture can be separated (carbonates, ashes, non-carbonates), and the carbonates can be reused. The ashes can be disposed of. Lawrence Livermore National Laboratory scientists have received many patents for this process and their technology was successfully demonstrated. Among the advantages over incineration is the absence of an open flame and operation at lower temperatures [80, 81]. It can treat many different waste streams including explosives and propellants, chemical warfare agents, and hazardous organic liquid wastes such as chlorinated solvents and PCB-contaminated oils [3].

3.3.1.5.4 *Solvated electron technology*

Solvated electron technology is a patented non-thermal process (ambient temperature) for the treatment of a wide range of organics. The process uses solvated electron solutions to reduce organic compounds to metal salts and the parent (de-halogenated) molecule. Solvated electron solutions, which are strong reducing agents, are formed by dissolving alkali or alkaline earth metals such as sodium or calcium in anhydrous liquid ammonia. The operating pressure is around 110 to 167 psi. The solid and liquid residues from the process are first hydrolyzed with water to destroy the excess sodium. The hydrolysate is then oxidized with sodium persulfate or hydrogen peroxide to form more environmentally benign effluents [82]. The technique was evaluated for energetics (TNT, RDX, tetryl, M28 propellant and Comp B) and indicated that destruction efficiencies greater than 99% can be achieved routinely for all energetics [83].

3.3.1.5.5 *Biological treatment*

Some energetic materials can be destroyed by biological means. The biological treatment is mainly known for the treatment of contaminated soils, in which case it is called bioremediation. Waste water contaminated with energetic materials is also a good candidate for this kind of process. Biodegradation involves an oxidation reduction reaction and the breaking of bonds in organic energetic materials. However, unlike chemical oxidation, this occurs due to the action of microbes [9]. As for the advantages of bioremediation, it is viewed by the public as a natural process, unlike incineration and other chemical techniques; it operates at ambient temperature and pressure; and the by-products are fewer and generally non-toxic. Moreover, in the case of bioremediation, soil and groundwater can be treated in-situ. The processes should be customized for particular energetics (for example, nitroguanidine degrades anaerobically while NG biodegrades aerobically), and they are often harder to control to completion than chemical methods. For example, biodegradation techniques can be subject to toxic upsets which cannot occur with chemical oxidation techniques [9].

3.3.2 Resource recovery, reusing and recycling technologies for energetic materials

Explosive formulations include valuable materials that may be reused, recovered or recycled by various techniques. According to NATO [8], reuse can be defined as “the alternative use of a munition or its components, for example change from operational to training use”; recovery is “the process of extracting serviceable and economically repairable components and material from excess or surplus munitions”; and recycling is defined as “the use in a different item of materials recovered from a munition”.

In order to develop a resource recovery and reuse (R3) plan for explosive waste, some basic features are required. First, the safety of all personnel involved in the processes should be ensured. Second, the processes should recover valuable energetic materials for reuse and/or produce high-value by-products. Third, the processes should be environmentally safe, i.e., no discharge of toxic materials to the environment – ground, water or air. However, a careful evaluation of the cost and environmental consequences should be carried out because the goal in demilitarization is not always to attain the highest degree of recovery [8]. Finally, the processes should be cost-effective and capable of high throughput for bulk processing [75, 84]. In the case of HMX, for example, the cost of recovered HMX versus virgin is expected to be approximately half [85].

There are two main alternative approaches in recycling EMs. The first and simplest involves the recovery of the energetic ingredients and their use for other purposes with little or no modification, i.e., process, separate and recover the EM to remanufacture new explosive products. For example, propellant can be reused with or without physical alteration for commercial or military use. It allows potential waste material to be recovered as high-value product and avoids the necessity of using new resources to manufacture explosives [86]. The reclamation, reuse and/or recycling of explosives saves a lot of money versus the production of new material. These savings do not include the intangible environmental impact mitigation achieved by not destroying explosives by burning. Moreover, the use of reclaimed materials in lieu of new materials results in significant time and effort reductions as well as negating the addition of materials to an already overburdened demilitarization stockpile [87]. In order to be cost-effective, the ideal process for reusing explosives or propellants should be readily scalable [88]. Wulfman [88] also suggested that the end-product should either fill a known need or compete with existing technologies on the products’ own merits. On the other hand, there are several problems associated with the recovery and reuse of explosives. These include [88] requalification to meet military specifications; disposal of non-usable material and waste streams; technical problems related to the category of explosive and due to the available energy content and low activation energy of the materials processed, all

processing of EMs requiring careful attention to safety precautions to avoid initiation of high-energy release events [16, 88].

Another alternative is to transform the reclaimed EMs into new products, but with chemical modifications that eliminate the explosive characteristics of the material.

Recovery and reuse methods should be applied only to munitions that have documented histories. Documentation should include the method of manufacture and the composition of all energetic materials in the device. Note that the primary explosives and initiating explosives (e.g., lead azide or metal fulminates) are generally not good candidates for recovery and reuse due to their sensitivity [16] and the small amount of explosive material does not economically justify their dismantling and reuse [35].

The explosives used by the US Department of Energy and the Canadian Department of National Defence are manufactured by the private sector under contract. This same contractor may be considered as the primary industrial contact for receipt of DOD/DND reclaimed explosives. Other commercial explosive manufacturers may be interested in receiving the recovered explosives for use in a variety of applications, but, as highlighted by Pruneda et al. [89], there are several disadvantages that the private sector faces with regard to acceptance of these materials. First, the legal liability issue of ownership if an accident or unexpected violent reaction occurs in processing these “previously owned” explosives. Second, concerns arise from guaranteeing a consistent source supply for receipt by the industrial sector. Third, even if maximum shipments were made reliable, the quantities envisaged may be too small to make a significant impact on the commercial sector. On the other hand, there are advantages for industrial participation: for minimal cost, high quality explosives are available to interested parties, and in the interest of waste minimization, valuable energetic compounds can be recycled for reuse or for other applications rather than being destroyed.

3.3.2.1 Scrap metal recovery

Probably the easiest form of resource recovery is the reuse of scrap metal from munitions. Before being released to the general public, scrap from munitions must be proven to be free of EM. A heat treatment is often used. In the US, the Army system for material safety hazard classification describes four levels of contamination [9]:

- 1X – articles which have only been subjected to routine, after-use cleaning and therefore substantial contamination continues to exist. They must remain under government control.
- 3X – articles where surface contamination has been removed but sufficient contamination may remain in ‘less obvious’ places to present an explosive safety hazard. They must remain under government control.
- 5X – articles where there is not enough remaining contamination to present an explosive safety hazard. They may be released for unrestricted use (e.g., recycling) [90].

- 0 – articles that were never contaminated.

In addition to heat treatment for 5X cleaning, munition casings are often mutilated using a large shredder [91]. Mutilation renders the munitions unrecognizable as munitions, preventing reassembly, future use for original purpose, or reverse engineering for duplication [92].

3.3.2.2 Reuse of components for other explosive products (non-military applications)

The option of reusing EMs in explosive products is very attractive. However, success depends on the size of the potential market. Civilian explosives are generally cheap, and if military explosives and propellants are to be competitive in this market, then the cost needs to match that of the satisfactory materials available [86]. Recovery and reuse of explosives from ordnance can also reduce the need for foreign sources, which may be affected by foreign, domestic or transportation issues.

3.3.2.2.1 Commercial mining explosives

One possible way to use reclaimed explosives in a feasible and environmentally safe manner is as an ingredient in commercial blasting explosives [53]. Many companies were involved in the feasibility studies, including Technology Development Inc. (TDI) of Rolla, Missouri. They studied the market potential of reclaimed explosives and propellants for the mining industry [2, 93]. In mines, ammonium nitrate and fuel oil (ANFO) is the explosive of choice due to its low price and relative insensitivity. The use of demilitarized explosives offers a tremendous potential to the mining industry because the converted explosive could reduce the costs associated with blasting operations. This is accomplished by developing a more effective explosive which could reduce the diameter and/or the relative spacing of the boreholes. TDI performed tests in a mine in Missouri with reformulated PBX explosives and demonstrated that they presented better or equal performance than ANFO. The reformulated explosives could be used as a booster for ANFO or as a stand-alone commercial mining explosive [94]. Reclaimed TNT and RDX could also be used as blast charges and boosters for rock blasting. It was confirmed that they could be applied in quite a wide range of operating conditions [95]. A system developed by TPL [96] manufactures a high propellant content (double and triple base propellant [1]) blasting agent for the mining and quarry industry. Two processes are available: i) repacking the propellants from bulk containers and artillery propellant storage cans into bags that are compatible with on-site mining operations, and ii) conversion of propellant to blasting gel that is then loaded into customer-specified down hole bags, ready for direct use in mines.

Universal Tech Corporation (Riverton, KS) has successfully demonstrated that several new blasting products were developed with reclaimed propellant grains (M1, M6, M16, M30, M26, M14 and LKL) [97]. In Georgia (former Soviet Union), a project was aimed at developing a low-cost and ecological industrial explosive based on recycled military explosives (NC and NG) reclaimed from various calibers (122-mm artillery shells for example) [98]. To obtain good explosive properties to use in the mining industry, ammonium nitrate was added to the mixture. Other countries (Belarus and Ukraine [99], as well as Poland [53]) also recover propellants and high explosives to use as blasting agents in the mining industry. Considering the difficult economic position of the mining industry in these countries, the availability of effective and cheap high explosives recovered from military stores could provide a substantial supply source for the domestic mines. Propellant containing NC can also be used as an additive in civilian explosives for road construction [35].

3.3.2.2.2 *Explosive welding*

Explosive welding, also called explosive metal brazing, explosive cladding or explosive metal bonding, is a commercial process that is used to weld similar and dissimilar metals at any temperature (process usually performed at room temperature). The weld is generated over the entire surface of the two plates after one of them was explosively accelerated toward the other. The process removes the oxide layer of both metals at their line of contact and under the high collision pressure, a metallurgical bond is created. The welds produced are very strong (usually stronger than either of the metal plates), are gas-tight and show optimal electrical and heat conduction across their interface [100]. TPL, Inc. (Albuquerque, New Mexico) has developed metal brazing explosives from reclaimed PBX [2]. This company has demonstrated in preliminary studies that the bonding of 1 cm stainless steel to 3.5 cm carbon steel presented outstanding interface and bonding characteristics. TPL [101] also performed tests with LX-14 scrap and they believe that this explosive, combined with diluents (sand for example), can be used as a blasting agent for explosive cladding.

3.3.2.2.3 *Oil and gas industry*

In 1993, TPL, Inc. (Albuquerque, New Mexico) identified the perforating charges for the oil and gas industry as a large-scale user of reclaimed HMX from Class 1.1 explosives [102]. Perforating charges are employed to penetrate wellbore casings and connect the producing reservoir to the wellbore. They also studied the possibility of using gun propellant as a gas generation device for oil and gas well simulation [2]. This technique involves the rapid gas generation capabilities of gun propellants to fracture geologic formations containing fossil fuels. They have demonstrated that dry wells can be made productive utilizing the tailored pulse fracturing technique.

3.3.2.2.4 Small arms powders

TPL, Inc. has looked at using reprocessed gun propellants for small arms powder. The commercial small arms smokeless powder market is approximately 20 million pounds per year (US value, 1997) [94]. Also this company is developing a small arms ammunition powder with low flash characteristics, which could benefit warfighters by: i) reduced detection through smaller muzzle signature; ii) improved effectiveness through increased night-firing rate; and iii) no interference with night-vision devices [96]. The system is still at the prototype development level [1].

3.3.2.2.5 Synthesis of TATB

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) was synthesized from TNT with the goal of developing a less costly production process [64, 103]. TATB is a reasonably powerful high explosive with considerably greater thermal and shock stability than that of any other known material of comparable energy. It is used in military applications because of its significant insensitivity to thermal and shock environments. In the civilian sector, Schlumberger has designed perforating guns containing TATB for deep oil well explorations where heat-insensitive explosives are required [64].

The procedure uses hydrogen sulfide which partially reduces TNT to 4-amino-2,6-dinitrotoluene (ADNT), which is then treated with nitric acid in sulfuric acid to provide pentanitroaniline (PNA) via an unexpected oxidative nitration of ADNT (see Figure 5). Treatment of PNA with ammonia provides TATB in addition to polynitrophenol by-products. The conversion of TNT to TATB results in 44% overall yield. Although all of the reactants are relatively inexpensive, the cost of pollution abatement ultimately prevented the industrial scale-up of this process.

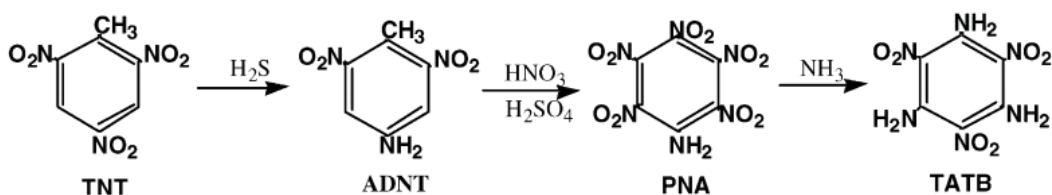


Figure 5: Atkins synthesis of TATB from TNT [64]

3.3.2.3 Reclaiming components for use as non-explosive products

Even though the conversion of explosives of considerable value into other non-explosive products such as fertilizer and other chemicals is not competitive with the material it replaces, and sometimes at considerable expense, this section will present some potential avenues for reclaimed explosive components into non-explosive products.

3.3.2.3.1 *Fertilizer*

Propellants and explosives can be rendered non-energetic by transformation into fertilizer [35]. TPL, Inc. has conducted preliminary experimentation and showed the feasibility of using ingredients extracted from NC-based gun propellant (single and triple base) as a specialty fertilizer for agriculture applications (tests performed at New Mexico State University) [2, 39]. The estimated material cost for the denitrification and additives for a complete fertilizer was estimated at \$35 per 100 pounds [104]. The NATO Maintenance and Supply Agency has put in place a rocket propellant recycling facility in Azerbaijan, in which rocket propellant is converted to fertilizer [105].

The American company Arctech [106, 107] has a patented and established technology called Actodemil™ that transforms propellants, energetics and explosive wastes into humic-rich organic fertilizer. The technology is based on naturally occurring coal-derived humic acid. It is optimized to achieve a series of useful reactions in the decomposition of highly toxic or hazardous chemicals. Humic acid is a water-soluble colloidal medium which, being a reducing agent, promotes reductive hydrolysis. It has a strong affinity for organic molecules and metal ions; therefore, it is effective in absorbing reaction products. The active material is a proprietary reagent. The system is remotely controlled and operates at atmospheric pressure and a temperature of 160 to 180°F. Following completion of the reaction (between two and four hours), the residue is neutralised by phosphoric acid and can be safely used in applications such as fertilisers or other means of safe disposal [108]. This technology does not produce any waste by-product or toxic emissions and is more cost-effective than thermal treatment technologies for energetics [107]. It can process 1 ton per 10-hour and can handle single, double and triple base propellants [109] as well as explosives, except ammonium picrate and explosives containing ammonium perchlorate [1]. For each ton of explosive, 800 gallons of fertilizer (liquid) is expected to be produced. Their technology is available on the market.

3.3.2.3.2 *Animal feed*

Tests conducted at New Mexico State University [39] have demonstrated the concept of using the NC recovered from single base propellants as an animal feed supplement. The digestibility of NC was similar of cottonseed meal, an accepted animal feed supplement. Feeding of a sheep with NC showed increased food consumption. Although the initial results were promising, this research was abandoned in favour of the fertilizer concept, which would provide greater results in terms of faster transition to commercialization [94]. No information was found on the chemical process used.

3.3.2.3.3 *Production of ethanol*

In a patent by Kim et al. [110], a method was described to dispose of waste nitrocellulose by converting it into glucose and further into ethanol. The nitrocellulose was treated with acid in a hydrolysis process to break the nitrocellulose down to glucose, recovering most of the acid by electrodialysis, neutralizing the remainder of the acid, and fermenting the glucose to convert the glucose to ethanol.

The reaction with hydrochloric acid (HCl) converts most (typically, in excess of 60%) of the nitrocellulose to glucose, or sugar oligomers. At 90°C, the hydrolysis reaction requires about nine minutes to reach the maximum glucose yield of about 85%, by weight, of the nitrocellulose in the reactor. At 60°C, the hydrolysis reaction requires about 63 minutes to reach maximum glucose yield (85%). Acid concentrations of 19%-38% have been utilized. Tests have shown that the reactions are faster at higher acid concentrations. The effect on hydrolysis of various ratios of acid to nitrocellulose has also been investigated, including ratios of about 5-1 to 30-1. The results have indicated that the higher the ratio, the faster the degradation of nitrocellulose. Preferably, hydrolysis is conducted with an acid concentration of greater than 20% and a temperature of about 60°C. The ratio of acid to nitrocellulose affects the rate of degradation, but not the glucose yield. The hydrolyzate, with substantially no active HCl remaining therein, is fermented for conversion of the glucose to ethanol by micro-organisms. *Saccharomyces* were particularly efficient in converting sugars to ethanol and are not as strongly inhibited by high ethanol concentrations as are other microbes.

3.3.2.3.4 *Coating industry*

Nitrocellulose propellants (mostly single base) can be reprocessed in the coating industry to produce compounds such as varnish or lacquer NC [75]. The propellant has to be ground, dissolved in acetone, then the NC is precipitated and separated. The crucial step is boiling the NC in ammonia to reduce its nitrogen content to below 12.6%. The

viscosity is reduced with a lower degree of nitrification [35]. Care has to be taken to control the molecular mass of the NC. One of the problems with the reuse of NC to make varnish is that the end-product contains impurities such as diphenylamine and decomposition products [61] (diphenylamine being considered as toxic [35]). Another problem is that whereas pure NC is colourless, reclaimed NC is slightly yellow. It therefore cannot be used as a base for colourless furniture varnish [35]. Other potential markets include the biomedical industry [84].

3.3.2.3.5 *Chelating resins*

According to Mitchell et al. [103, 111], TNT could be used as a source for the production of chelating resins. The multi-step reaction will not be described here, but the final product is a resin that should provide chelators of heavy metals since it is chemically close to the aminopolycarboxylic acids which are effective chelating ligands for copper, iron and other heavy metals that have been employed to remove heavy metals from industrial waste streams.

3.3.2.3.6 *Conversion into chemical raw material*

One of the biggest challenges in chemically converting surplus energetic materials is to yield commercially viable products. But from a chemical point of view, most explosives are highly nitrated aromatic compounds, highly nitrated heterocycles or nitric acid esters. Due to the large number of reactive functional groups, surplus high explosives could obviously be regarded as a valuable raw material for chemical synthesis. Chemical reactions are in most cases reduction, oxidation or hydrolysis of a molecule. In the case of nitroaromatics, only the reduction process renders a valuable product [63]. There are a number of proposals on the use of TNT as a chemical raw material.

3.3.2.3.7 *Isocyanates*

TNT can be hydrogenated into triaminobenzene (TAB), then TAB is phosgenated into isocyanates. This reaction was demonstrated at the lab scale, but the industrial market does not really exist [61, 75]. TNT can also be converted into 2,4-diaminotoluene, a toluene 2,4-diisocyanate (TDI) precursor. TDI is the basic raw material for the production of polyurethane foams. TNT can also be used to produce nitrotoluene diisocyanate (NTDI) [103].

3.3.2.3.8 *Phloroglucinol*

The process for converting TNT to phloroglucinol [64] (1,3,5-trihydroxybenzene) was developed at the end of World War II. Phloroglucinol is used in the pharmaceutical (e.g., treatment for gastrointestinal disorders), cosmetics, textile-dyeing and photographic industries (2002 bulk price: US \$50/lb [64], priced in 2008 at Can\$112/100 g, purity $\geq 99\%$ [112]). TNT is first oxidized to 2,4,6-trinitrobenzoic acid (TNBA, 82%) in the presence of sodium dichromate in concentrated sulfuric acid (50° – 60°C). The TNBA is thermally decarboxylated to 1,3,5-trinitrobenzene (TNB) and reduced by iron in hydrochloric acid (90°C) to 1,3,5-triaminobenzene (TAB, 95%) without isolation of TNB. Hydrolysis of TAB in hydrochloric acid (105°C) produces phloroglucinol (75%). The reaction is presented in Figure 6. The conversion of TNT to phloroglucinol results in about 58% overall yield. This process was discontinued in the USA in the 1970s due to environmental problems associated with the disposal of waste products acid liquors, iron, chromium and ammonium salts.

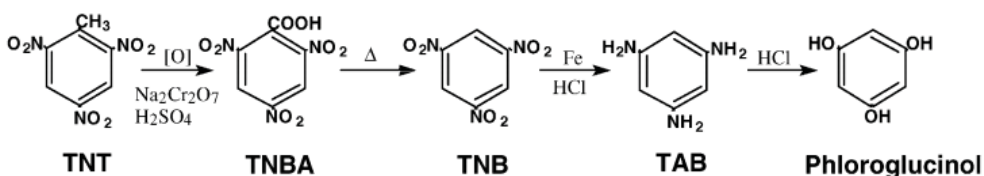


Figure 6: Commercial production of phloroglucinol from TNT [64]

3.3.2.3.9 *Benzenehexamine*

As seen in subsection 3.3.2.2.5, TATB can be synthesized from TNT. TATB can be used as the starting material to produce benzenehexamine, an intermediate in the synthesis of new advanced materials. Benzenehexamine has been used in the preparation of ferromagnetic organic salts and in the synthesis of new heteropolycyclic molecules such as 1,4,5,8,9,12-hexaazatriphenylene (HAT) that serve as strong electron acceptor ligands for low-valence transition metals [113]. In addition, the use of TATB to prepare components of liquid crystals for use in display devices is the subject of a German patent. TATB was priced at US\$20 to \$50/lb before industrial production ceased in the US at the end of the 1980s. In 2002, TATB was available to customers outside the US Department of Energy (DOE) for US\$100/lb [64].

3.3.3 Comparison of technologies

The technologies presented are summarized in Table 3 to make the comparison easier.

Table 3: Overview of the technologies to recover, reuse and recycle energetic materials from munitions

Technology	System	Applicable to various calibres	Capital investment	Throughput	Staff requirement	Health hazards	Current industry technology?	Other
Scrap metal recovery	Decontamination and shredding of casings.	Yes	?	High	Low	Medium	Yes	
Commercial mining explosive	Conversion of propellants.	Yes	?	30K to 50K pounds/day (TPL system)	Approx. 10	Low (fire hazard)	Yes	
Explosive welding	Welding of metals at any temperature.	Tested with PBX	?	?	?	?	No	
Oil and gas industry	Perforating charges	Tested with reclaimed HMX.	?	?	?	?	No	
Small arms flashless powder	Powder formulated with demilitarized triple base propellant.	Triple base propellant only.	?	?	?	Low (fire hazard)	No	
Synthesis of TATB	TATB used as a high explosive.	Uses reclaimed TNT.	Reactants inexpensive, but pollution abatement systems are expensive.	?	?	?	No	
Fertilizer	Actodemi® reactor: hydrolysis of explosives/propellants and neutralization.	Yes (except ammonium picrate and ammonium perchlorate)	US\$2M plus \$1/lb for chemicals.	High: 1 ton/10 hours.	Low: three persons.	Low (handling of chemicals).	Yes	Fertilizer could be sold to help offset the costs.

Legend: ? = information not available

Table 3 (continued): Overview of the technologies to recover, reuse and recycle energetic materials from munitions

Technology	System	Applicable to various calibres	Capital investment	Throughput	Staff requirement	Health hazards	Current industry technology?	Other
Animal feed	NC used as feed supplement. NC digestibility is similar to cottonseed meal.	Tested with reclaimed NC from single base propellants.	?	?	?	?	No	Research was abandoned in favour of fertilizer.
Production of ethanol	Waste NC converted to glucose, then ethanol.	Patented for NC	Low	?	?	?	No	
Coatings industry	NC reprocessed into lacquer.	Used with NC.	?	?	?	?	?	Problems: impurities and colour.
Chelating resins	TNT processed into resins for metal adsorption.	Needs TNT.	?	?	?	?	No	
Conversion to raw chemicals	TNT transformed into other products such as isocyanates, phloroglucinol and benzenehexamine.	Needs TNT.	?	?	?	?	Not on large scale.	

4 Extraction technologies to recover energetic materials for reuse and recycling

Recovery and reuse of explosives are the most attractive alternatives to disposal by destruction. For some compositions, most of the components can be recovered with very little waste generation. The technologies are state-of-the-art and have the potential of meeting the recovery and reuse goals of demilitarization in a cost-effective environmentally acceptable manner [22]. Recycling EMs offers a route to reusable ingredients that is worth exploring where high-value compounds are concerned. However, the materials will need to be processed to extract the compounds of interest from the matrix, and will need some reassessment and requalification before they can be reused. This section will present some technologies available for selective recovery of components.

The nitramines (RDX, HMX) are commonly among the most expensive and highly explosive ingredients of conventional energetic compositions, making their successful and efficient recovery for subsequent reuse highly desirable [114].

4.1 Supercritical fluid extraction

A supercritical fluid is any substance at a temperature and pressure above its thermodynamic critical point. It is neither liquid nor gas. It has useful physical properties, such as low viscosity and high diffusion rate; it can diffuse through solids like a gas; and dissolve materials like a liquid, especially organic materials. Close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties to be "tuned". Supercritical fluids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes. Carbon dioxide and water are the most commonly used supercritical fluids, being used for decaffeination and power generation, respectively [73]. Carbon dioxide is supercritical at moderate conditions ($T_c = 31.3^\circ\text{C}$, $P_c = 7.28\text{ MPa}$) and its noninflammability and chemical inertness make it an attractive alternative to hazardous organic solvents. The use of CO_2 is environmentally safe and economical [52], but the extractor could be expensive. Unfortunately, most of the primary propellant ingredients have limited solubility in supercritical CO_2 [52] due to the fact that CO_2 is a non-polar molecule. Nevertheless, several groups have attempted to use this technique to extract energetic ingredients.

Interesting results for the extraction of TNT from contaminated soils were shown by Gerber [115]. He showed that TNT could be extracted from contaminated soils with good yields. For other explosives (RDX, 3-nitro-1,2,4-triazol-5-one (NTO), pentaerythritol

tetranitrate (PETN), nitroguanidine (NQ)), the addition of modifying agents (e.g., acetone, acetonitrile, i-propanol) increased the extractability, but the yields were still not fully satisfactory. The solubility (or extractability) of explosives depends on pressure, temperature and modifying agents. For HMX, supercritical CO₂ seems to be a poor solvent [102].

At Aberdeen Research Laboratory [116-118], a supercritical fluid extraction system was operated to separate TNT and RDX from Comp B in demilitarized munitions. TNT is selectively solubilized by the solvent, which is neat carbon dioxide, then precipitated from the solution when the pressure is reduced. RDX is not solubilized, so it is removed from the extractor at the end of the process. The use of carbon dioxide, a solvent that is commonly used in supercritical fluid extraction, is generally accepted as an environmentally friendly processing solvent for green technologies, and is fairly inexpensive.

The same authors [119] used supercritical CO₂ to extract nitroglycerin from triple base propellant. Further extraction of nitroguanidine from the NG-depleted propellant was made using simple liquid extraction with hot water. The latter process will be described in section 4.3.

Morris et al. [52] used solvent-modified CO₂ to extract RDX from RDX-based LOVA gun propellant. The addition of acetonitrile as a modifier seemed to be the most effective among the solvents tested to increase the solubility of RDX in supercritical CO₂. On the other hand, the use of a modifier such as acetonitrile caused significant swelling of the propellant.

Subjecting energetic materials to a supercritical fluid environment poses potential safety hazards, in addition to those considered for conventional energetic material handling. Extraction in a supercritical fluid requires that the explosive be placed in a sealed vessel under pressure and at somewhat elevated temperatures. The initiation of even a small amount of material would be a very serious accident. A thorough study of the risks associated with this procedure was performed [118] and recommendations were made. Special precautions should be taken to ensure that no energetic material is trapped in the threads of the cap used to seal the extraction vessel.

4.2 Liquid ammonia extraction

Most plastic bonded explosives contain binders which are unlikely to be degraded by exposure to solvents or dilute acids or bases under practical demil conditions. In the late 1960s, the US Navy [120] began research on the demil of explosives by chemical and biological techniques. PBXs were found to be resistant to degradation because the polymer binders were insoluble in acids, bases and organic solvents. While crosslinking

binders can be degraded using high-temperature or reactive reagents, this is not a safe or practical approach because of the inherent reactivity of the energetic material in the composition. In the 1970s, Naval Air Warfare Center Weapons Division, China Lake, began research on the development of a binder which could be used to form PBXs and propellants that are degradable by soaking in aqueous ammonia. Such degradation by ammonolysis-hydrolysis of the binder to form relatively small molecules would allow the ingredients to be recovered. A number of different polyesters were investigated to achieve adequate processing, curing, mechanical, and hydrolytic and aging characteristics. Adipate esters were found to have the best properties (Note: adipic acid = $\text{HOOC}(\text{CH}_2)_4\text{COOH}$.) The best polyester synthesized is a polyethylene glycol (PEG) chain length of nine oxyethylene units (roughly commercial PEG 400). As the chain length increased, the rate of hydrolytic degradation in HMX-containing PBXs increased. This polyester was commercialized (in 1998 at least) by a private company (Witco Chemical) under the name 10PE-37. This binder can be hydrolyzed in aqueous ammonia, the HMX being recovered by filtration.

In another paper, Melvin [114] patented a method to extract and recover the nitramine oxidizers – which have a high commercial and military market value (e.g., HMX, RDX) – from solid propellant in liquid ammonia.

A pilot plant was built and the process was successfully demonstrated [121]. It consists in a closed-loop ammonia-based process in four steps: 1) propellant removal by cutting or erosion into small pieces; 2) solvation of the oxidizers by the liquefied gas solvent; 3) separation of the insoluble binder, metal fuel and additive components by filtration and recovery of the solid oxidizer by evaporation of the liquefied gas solvent ammonia; 4) recompression/liquefaction of the gas solvent for reuse.

The process is a closed system with no release of solvent to the environment. Washing the extracted ingredients in ethanol separates insolubles, nitramines and impurities from solubles, degraded nitroglycerin and other plasticizers. Standard acetone/water or cyclohexanone/water solution is employed for recrystallization of nitramines (HMX and RDX) which are recovered in high purity [114]. Further studies were conducted on the reclaimed explosives and they indicated that RDX can meet military specifications when recrystallized in accordance with their manufacturing processes. Recovered HMX performance was evaluated against virgin HMX with excellent results [121].

The problem anticipated with this method is the high capital cost of the equipment capable of operating at the high pressure needed. The presence of liquid ammonia creates a worker safety issue (skin contact or inhalation), and a fire hazard as liquid ammonia is slightly flammable in the presence of open flames and sparks. Moreover, handling explosives in pressurized environments increases the risk of accidental detonation [114].

4.3 Solvent extraction

Arcuri [22] patented a technique to reclaim RDX and TNT from composition B. Once the composition B is removed from the casings, it is put in contact with a solvent in which RDX has a low solubility and TNT has a high solubility (ethanol (most preferred), isopropyl alcohol, cyclohexanone, methanol, cold acetone, benzene, carbon tetrachloride, dimethylsulfoxide, ethyl ether, diethyl ether, isobutanol, methyl acetate, ethyl acetate, butyl acetate, xylene, toluene and mixtures of thereof). The slurry of dissolved TNT and RDX particles is allowed to settle and particles are extracted from the mixture, washed to remove any remaining TNT, washed again to remove any wax (with an aliphatic solvent such as hexane), and the RDX is ready to be reused upon determination of the purity. The slurry of TNT can be purified by adding a small amount of water to crystallize any RDX present. The solvent is then evaporated and the TNT recovered.

A soxhlet extraction apparatus could be employed to extract energetic materials with solvents. This technique is well characterized and has been scaled-up to large systems. Once the apparatus is set up, little operator intervention is needed. But this process is relatively slow, and even if the solvents are recycled during the process, they must be discarded at some point. This technique has been used to extract HMX from PBXW-114 (78% HMX/10% Al/12% HTPB binder) with DMSO. The HMX recovered was very pure [102].

Other research [39] is exploring alternative solvents to dimethylsulfoxide under increased temperature and pressure (1–5 atm). The solvent butyrolactone shows promise for extraction of HMX from reclaimed explosive materials.

RDX can also be extracted from Hexal (mixture of RDX and aluminum powder used in air defence ammunition) by using a solvent. Once the Hexal is removed from the casings using a high pressure water jet and dissolved (solvent not indicated), it can be recrystallized to a defined particle size and reused as a base component for new Hexal. This method is at least 10% less expensive than a new synthesis of RDX [122].

Wulfman [88] recovered high explosive in PBX with dichloromethane or methylchloroform, but these two solvents cause recognized health and environmental problems, or with dimethylsulfoxide, which also causes a recognized health problem, creating disincentives to using them.

It must be noted that all the work to extract energetics utilizing organic solvents to solubilize and separate the explosive from the binder system generated hazardous organic wastes which needed to be treated or destroyed [2].

Nitroguanidine was extracted from triple base propellant using simple liquid extraction using hot water [119]. The propellant tested was M30, composed roughly of 47%

nitroguanidine, 29% nitrocellulose, 22% nitroglycerin, 1.6% ethylcentralite and 0.4% cryolite. The propellant was first treated by supercritical fluid extraction to strip the nitroglycerin, then the remaining material was treated by simple extraction with hot water (95°C). The solution of extracted nitroguanidine was cooled to 1°C for at least 90 min for precipitation. Nitroguanidine was recovered with vacuum filtration.

4.4 Solvolytic extraction with mineral acids

On account of the chemical crosslinking of the polyurethane matrix of many PBXs, simple breakdown of the propellants by solvents is not possible. For a recovery of energetic materials, the choice has to be made between extraction with solvents and a solvolytic breakdown of the plastic binder with a release of the energetic material [123].

In 2002, a patent was awarded to Cannizzo and Huntsmann [114] for the development of a method for the recovery of nitramines in propellants, explosives and pyrotechnics in an inexpensive and efficient way, without the use of organic solvents. The process was applied to Class 1.1 solid rocket motor propellants.

The solvolysis extraction uses mineral acids to dissolve the nitramine from the binder in the explosive composition. The solution is filtered, leaving the product, HMX for example, in the liquid filtrate. The acids are relatively safe to use, easily neutralized – thus environmentally safe – and inexpensive. Suitable acids include hydrochloric, sulphuric, phosphoric, nitric and perchloric acid (or a combination). Nitric acid was the preferred one, at concentrations of 70 to 98% by weight. The formulation is agitated and the parameters (acid concentration, temperature, ratio of acid to oxidizer, particle size) have to be carefully controlled to avoid a long reaction time, since the nitramine can degrade. When using a highly concentrated acid (90-98%), the reaction is carried out at room temperature, but with lower concentrations (70-90%) the temperature is raised to 60° to 90°C. The nitramine will dissolve, leaving the binder behind. NO_x are produced during the process. The solution is then filtered and the filtrate is treated to induce precipitation of the nitramine, such as with water addition. The precipitated nitramine is recovered and purified [114]. The process does not usually need much operator involvement, as the extraction can be done in a passive mode: the feed stock can be soaked in the aqueous acid for several days before the extraction and separation are performed. Moreover, minimal mechanical processing is needed, and large pieces can be used. Care must be taken when metals such as aluminum are present in the explosive, as some acids cause an exothermic reaction and/or hydrogen gas can evolve [102].

Polyurethane-based polymers can be treated by hydrolysis at 230°C, causing the polyurethane groups in the binder to split. The mixture is then treated by solvent extraction to recover both the polyols and EM from the binder [16].

4.5 Solvolytic extraction with organic solvents and hydrogen containing compounds

Another method [124] uses organic solvents (toluene, dioxane, tetrahydrofuran) in conjunction with liquid active hydrogen containing compounds (alcohols, water, primary amines, secondary amines, ammonia and mineral acids – hydrochloric, sulphuric, phosphoric, nitric and perchloric acid) to separate the nitramine from the binder in PBX. The crosslinked polymer is decomposed by heating (50°–160°C, mostly 80°–120°C) in the presence of liquid active hydrogen containing compounds. The organic solvent accelerates the reaction by swelling the organic polymer components and/or by dissolving the filler material in the composition. Solvents include water, diethylbenzene, xylene, toluene, benzene, perchloroethylene, cyclohexanone, dioxane, ethylene glycol, cyclohexanone and tetrahydrofuran. Reaction time varies from 30 min to 15 days.

4.6 Solvolytic extraction with alkalis

Extraction with an alkaline solution was used to extract RDX from a propellant made with a polyurethane matrix-based PBX. As the energetic substances used in this propellant (GAP and RDX) show autoignition temperatures between 200° and 220°C, the solvolysis temperatures had therefore to be lower, and a range between 130° and 170°C was chosen [123]. Characteristics of the ideal solvolysis agent should be: i) able to split the urethane groups rapidly, ii) should leave the chain lengths of the polyols unchanged, iii) should not attack the energetic components, iv) should be easily removable from the recovered substances. Moreover, the process should be safe and inexpensive. Pure and alkaline water were chosen and the solvolysis was carried out in a pressure cell. Tests were conducted using a gun propellant KHP with medium grain size (2 mm in diameter, 4 mm long), which contains about 86 % by mass fine-grained RDX bonded in 14% by mass GAP-N100 binder. A mass of 1g of shredded sample was mixed with 20 to 25 g of solvolytic agent in the pressure cell.

The gun propellant KHP was solvolyzed with pure water and 0.05 M NaOH at 130°, 150° and 170°C, with solvolysis times of 10, 30 and 60 min at each temperature and with each solvolysis medium. With increasing alkalinity, increasing time and increasing temperature of solvolysis, the yield of hexogen decreases. Ten minutes of hydrolysis at 130°C resulted in the recovery of over 95% of the hexogen in this KHP formulation. The purity of the recovered RDX was high, as the equality of its melting point with that of the hexogen used in manufacturing the KHP showed. The recovery of the GAP was not possible because there is a splitting-off of nitrogen from the N₃-group, and the highly reactive nitrene thus formed produces C-N- bonds, which are solvolytically not scissionable [123].

4.7 Recovery of components from ETPE

As presented in subsection 2.2.1, research has been carried out recently at DRDC Valcartier to develop a melt-cast explosive containing an energetic thermoplastic elastomer. This explosive is composed of the ETPE (based on glycidyl azide polymer), TNT and HMX. Preliminary recycling studies [12, 15, 125] demonstrated that it was possible to separate nitramines, TNT and ETPEs in a mixture. The process started with nitramine decantation, and was followed by separation of TNT and ETPE by solid-liquid extraction.

The recycling procedure described for a PBX ETPE 2000-Octol (PBX containing 20% copolyurethane and 80% Octol) in [15] uses chloroform to precipitate the nitramines, which are then filtered and quantitatively recovered. The filtrate, which contains a mixture of the copolyurethane and TNT, was evaporated to dryness and extracted in a soxhlet with ethanol. After 5 days of continuous extraction, the ethanol solution containing TNT was evaporated and pure TNT was recovered. The residue contained in the soxhlet thimble was dissolved with ethyl acetate and spectroscopic analyses revealed quantitative separation and recovery of the pure components of the PBXs. If one considers that all the solvents involved in the recycling process can be recuperated, the recuperation of starting materials becomes inexpensive and highly feasible. Likewise, it is easy to employ a one-step operation to recover only the expensive nitramines.

In [125], the recycling process was tested with two types of nitramines: RDX and HMX. The mixture was composed of 6 g nitramines, 2 g TNT and 2 g ETPE. It was put into ethyl acetate, in which RDX and HMX were insoluble. Filtration gave RDX and HMX at a yield of 99%. After evaporation of the solvent, the TNT/ETPE mixture was placed in a soxhlet apparatus for solid-liquid extraction. The separation was first made by solubilizing TNT in ethanol (or in hot methanol [12]), the ETPE being left in the thimble. The solvent was evaporated and TNT was recuperated, with no trace of ETPE. The ETPE is removed from the thimble using ethyl acetate. Analysis indicated that a small percentage of TNT was trapped in the ETPE. As all the tests were carried out on small amounts of explosives (10 g), a large-scale study is necessary before concluding that the process is efficient for munitions demilitarization.

4.8 Examples

TPL, Inc. carried out a thorough study of the potential extraction methods for recovery of HMX from a Class 1.1 propellant (composed of Al, AP, HMX, NG, urethane binder, PEG binder), namely supercritical fluid extraction, soxhlet extraction and acid solvolysis, the latter process being chosen as the most promising. It was scaled-up, tested and evaluated [102]. The final scaled-up extraction used 100 g of PBXN-3 and 1.8 L of 6M HCl. The final product was found to be more than 99% pure. In the case of the presence

of NC, it will be degraded by HCl, but not dissolved. After the addition of HCl and agitation, when the solution settles, the degraded NC would form a layer at the top of the liquid that could be removed by skimming the surface [102].

In another work [2], TPL, Inc. used common mineral acids to oxidize, degrade and dissolve the binder system, the acid having no effect on HMX. The original paper [102] describes the studies. Passive (feed stock is soaked in the acid for days) and non-passive extractions (with stirring and sometimes heating) have been developed, some of them requiring heat for the process. Solvents tested include 1.5M HCl/cyclohexanone, 6M HCl, acetone, HCl/acetone. The process for HMX extraction was scaled-up with 6M HCl, with an extraction time of 6 hours. When nitrocellulose is present, it is degraded by HCl, but not solubilized. When the solution settles, the top layer can be skimmed. The recovered HMX is separated from the acid solution by filtration and/or centrifugation (HMX is not soluble in HCl). The recovered explosive is washed with water to remove the acid residue. The acid and wash water are neutralized with ammonium hydroxide to generate dissolved salt and binder [104]. For example, dilute HCl was used to recover HMX from PBXN-3 (nylon binder) [39]. Another example is the treatment of LX-14, a PBX, with nitric acid at 70°C [126], which dissolves the binder [127] (EstaneTM), after which the solution is gravity-fed to a centrifuge. The acid solution is neutralized and the binder degraded by ammonium hydroxide [128]. Pure HMX is recovered in a filter bag (purity over 99%) and the yield is over 96%. [104] In this process, no pre-processing is required: the LX-14 explosive is received as scrap in various shapes and sizes and processed as is [128]. Purities obtained are excellent.

5 Characterization techniques for energetic materials extracted from demilitarized munitions

The extracted products have to be characterized to assess their purity. Methods should complement each other and provide a broad spectrum of information on the material. Techniques used include melting point determination, Fourier transform infrared spectroscopy, nuclear magnetic resonance spectroscopy and scanning electron microscopy [102]. These are reported as useful techniques for reclaimed explosives characterization.

It is well known that parameters such as mean size, shape, purity and crystallographic structure of solid particles generally affect their physicochemical properties [129]. This is true also for explosives. The characterization of these parameters will have to be determined in the recycling process.

For example, PBX 9502 is composed of 95% by weight triaminotrinitrobenzene (TATB) and 5% Kel-F 800 binder. Recycled lots are composed of a 50-50 mix of virgin and reclaimed lots of explosives. Although the basic constituents do not differ, various studies have shown differences in mechanical properties and performance between virgin and recycled PBX 9502 [130]. These differences were thought to be caused by differences in the distribution of TATB within the microstructure of PBX 9502. The microstructure was evaluated with polarized light microscopy and scanning electron microscopy. Results showed that TATB was distributed in a less homogeneous way in the virgin material than in the recycled one. These techniques could be used for our own experiments.

In the case of LX-14, the HMX was recycled and many tests were performed to determine its properties [128]. These include purity, melting point (even though HMX does not actually melt, the melting point is read as the first movement of crystals as the HMX sublimates), number of insoluble particles, total acetone insolubles, inorganic insolubles, acidity, impact sensitivity, granulation by class, particle characterization, morphology, thermal analysis by differential scanning calorimetry, and other tests for the US qualification requirements for main charge explosives (e.g., cap test, ignition and unconfined burn, detonation velocity, etc.). Overall, testing of the recovered HMX shows qualitatively very little difference from the virgin HMX.

6 Conclusion

As a result of new laws on waste reduction and material reprocessing, disposal processes facilitating recovery and reuse are very much in demand [123]. A simple schematic illustration of the intent of the new regulations and laws is presented in Figure 7. It indicates that the material cycle for a product should transition to a “closed-loop economy” with a view to sustainable development. Also according to Bohn [123], one can define a degree of sustainability R_A for the recovery or recycling of a material according to Equation 1.

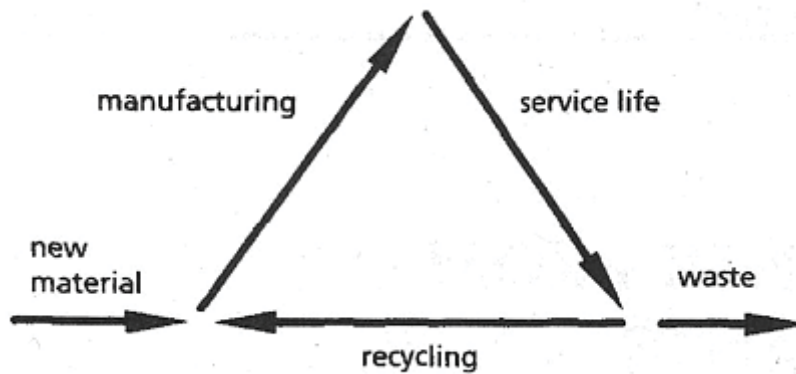


Figure 7: Schematic illustration of the intent of the new regulations and acts dealing with recycling and waste disposal (from [123])

$$R_A = \frac{\text{cost of new material} + \text{cost of non-recycling disposal method}}{\text{cost of dismantling} + \text{cost of processing} + \text{cost of logistics}} \quad (1)$$

If R_A is greater than 1, recovery is economical. The automotive industry already uses this indicator for some applications.

This report concludes with the table below, showing the various disposal methods for explosives. It presents a qualitative evaluation of the different processes (according to [63]).

Table 4: Evaluation of different processes for the disposal of explosives ([63])

Material	Recycling	Chemical conversion	Biological degradation	Burning
<i>High explosives</i>				
TNT	# Ø	# O	# Ø	# O
RDX	# Ø	+ Ø	+ Ø	# O
HMX	# O	+ Ø	–	# Ø
TNT/RDX	# Ø	# Ø	+ Ø	# O
TNT/HMX	# O	# O	–	# O
<i>Propellants</i>				
NC	–	+ Ø	# Ø	# O
NG	# Ø	+ Ø	+ Ø	# O
AP	# O	+ Ø	–	# O
Single base	+ Ø	+ Ø	+ Ø	# O
Double base	–	+ Ø	–	# O
Composite	# Ø	+ Ø	–	# O
<i>Key to symbols</i> # = large scale production possible + = feasible – = not feasible O = commercially viable Ø = not commercially viable				

References

1. CANOSCOM, ADM (IE), ADM (Mat) and DCC/NOG Ottawa, “CF ammunition demilitarization capability: Options analysis. Project No. 00001101”, Canada 2009, 312 pages.
2. Burch, D., Johnson, M. and Sims, K., “Value added products from reclamation of military munitions”, *Waste management*, 17(2-3), 1997, p.159-163.
3. US Army Research, development and engineering command, “Technology Development Program for the Demilitarization of Conventional Ammunition - Solving Global Munitions Demilitarization Problems Through the Development of Innovative Technologies”, pamphlet given at the US Army ARDEC booth at the 17th Annual Global Demilitarization Symposium and Exhibition, San Diego, CA, May 2009.
4. US Department of Defense, “Instruction Number 5000.02”, 2008, available from: <http://www.dtic.mil/whs/directives/corres/pdf/500002p.pdf>.
5. Grymonpré, D., “Design for demil efforts at GD-OTS” 44th Annual Gun & Missile Systems Conference & Exhibition, Kansas City, MO, 6-9 April 2009.
6. Government of Canada, Treasury Board of Canada, “Controlled Goods Directive”, 2006, available from: <http://www.tbs-sct.gc.ca/pol/doc-eng.aspx?id=12063§ion=text>.
7. Mescavage, G., “Demilitarization as a systems engineering requirement”, 44th Annual Gun & Missile Systems Conference & Exhibition, Kansas City, MO, 6-9 April 2009.
8. NATO Standardization agency (NSA), “NATO Standardization agreement: Safe disposal of munitions, design principles and requirements, and safety assessment”, STANAG 4518, 2001.
9. Wilkinson, J. and Watt, D., “Review of demilitarisation and disposal techniques for munitions and related materials”, MSIAC/NATO/PfP Editor, Report L-118, 2006, 102 p.
10. Government of Canada, Department of National Defence, “Ammunition and explosives procedural manual: Destruction of duds and misfired ammunition on CF ranges and training areas”, C-09-008-002/FP-000, 1993.

11. Provatas, A., "Energetic polymers and plasticisers for explosive formulations: a review of recent advances", DSTO Aeronautical and Maritime Research Laboratory, Report DSTO-TR-0966, 2000, 42 p.
12. Diaz, E., "Synthèse et caractérisation de thermoplastiques élastomères énergétiques", Ph.D. thesis, Département de chimie, Université Laval, Québec, 2006, 187 p.
13. Sanghavi, R.R., Asthana, S.N. and Singh, H., "Thermoplastics elastomers (TPEs) as binders for futuristic propellants and explosives: a review", Journal of Polymer Materials, 17(3), 2000, p. 221-232.
14. Ampleman, G., Brochu, S. and Desjardins, M., "Synthesis of energetic polyester thermoplastic homopolymers and energetic thermoplastic elastomers formed therefrom", Defence Research Establishment Valcartier, DREV TR 2001-175, 2001, 30 p.
15. Ampleman, G., Brousseau, P., Thiboutot, S., Dubois, C. and Diaz, E., "Insensitive melt cast explosive compositions containing energetic thermoplastic elastomers", US Patent 6562159, 2003.
16. Noyes, R., Chemical weapons destruction and explosive waste / unexploded ordnance remediation", Noyes Publications, Westwood, 1996, 235 p.
17. E-Mine: Electronic Mine Information Network: Stockpile destruction, 2004, available from: <http://www.mineaction.org/overview.asp?o=19>.
18. van Ham, N.H.A., "Munitions disposal as a total concept", NATO Advances Research Workshop on Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems, NATO ASI Series, Kluwer Academic Publishers, Moscow, Russia, 1994 p.47-54.
19. van Ham, N.H.A., "Recycling and disposal of munitions and explosives", Waste Management, 17(2-3), 1997, p. 147-150.
20. Getty, H.L., Miller, P.L., Cypher, M.S., Lamon, J.H., Hatz, D.P., Garrison, M.M., Hill, L.D., Martinson, D.A., Reynolds, R.E. and Munoz, J.P., "High pressure washout of explosives agents", US Patent 5737709, 1996.
21. Miller, P.L., Stignani, M.D. and Wittmer, G.G., "Abrasive fluid jet cutting composition and method", US Patent 5363603, 1992.
22. Arcuri, K.B., Goetsch, D.A., Smith, R.M., Schmit, S.J. and Miller, P.L., "Reclaiming RDX and TNT from composition B and composition B containing military shells", US Patent 6777586, 1993.

23. Galecki, G., Nambiath, P., Tyler, L.J., Fossey, R., Summers, D., Johnson, M.E., Ochs, B. and Dilozenzo, C., "Steps in the evolution of a 60-mm cutting system", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
24. Miller, P.L., "Using waterjets to safely process MPPEH", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
25. Gradient Technology, "Gradient Technology's Waterjet Systems", 2009, available from: <http://www.gradtech.com/Demil.html>.
26. Elie-Delacruz, F. and Follin, J.F., "Cryofracture demilitarization program update", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
27. Follin, J.F. "The cryofracture demilitarization process: an evolving technology", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2009.
28. Mayemura, M. and Follin, J.F., "Cryofracture demilitarization program update", 16th Global Demilitarization Symposium & Exhibition, Salt Lake City, Utah, May 5-9, 2008.
29. Sullivan, F., "Development of a transportable system that integrates cryofracture and plasma demilitarization technology", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
30. General Atomics, "General Atomics - Products and Technologies", 2009, available from: <http://www.ga.com/technology.php>.
31. Follin, J.F., "Transportable cryofracture technology for the destruction of obsolete munitions", International Chemical Weapons Demilitarization Conference, Interlaken, Switzerland, May 19-22, 2008.
32. Hashish, M. and Miller, P.L., "Cutting with high-pressure ammonia jets for demilitarization of chemical weapons", Journal of Pressure Vessel Technology, 124(4), 2002, p. 487-492.
33. Roeske, F., Benterou, J., Lee, R. and Roos, E., "Cutting and machining energetic materials with a femtosecond laser", Propellants, explosives and pyrotechnics, 28(2), 2003, p. 53-57.
34. Wynne, D., "Unserviceable ammunition demilitarization via chemical dissolution", 16th Global Demilitarization Symposium & Exhibition, Salt Lake City, Utah, May 5-9, 2008.

35. Brogle, R., Rys, P., Rochat, E. and Heller, W.E., "Recycling of explosives from obsolete medium caliber ammunition", 3rd International Autumn Seminar on Propellants, Explosives and Pyrotechnics: Theory and Practice of Energetic Materials, Chengdu, China, proceedings published by Sichuan Kexue Jishu Chubanshe, p. 45-59.
36. Giltner, S.G., Meschberger, J. and Worsey, P.N., "Overview of the demilitarization program for Class 1.1 warheads and rocket motors using high pressure waterjets at the University of Missouri-Rolla", 24th International annual conference of ICT: Energetic materials - insensitivity and environmental awareness, Karlsruhe, Federal Republic of Germany, proceedings published by Fraunhofer - Institut für Chemische Technologie, 1993, p. 34-1 – 34-6.
37. US Department of Defense, "Joint Demilitarization Technology Program - A report to Congress", 2003, 18 p., available from:
http://www.js.pentagon.mil/biosys/org/demil_rept2003_final.pdf
38. Milewski, E., Miszczak, M. and Szymanowski, J., "Utilization methods for explosives withdrawal from military stocks: desining, carrying out and practical implementation", NATO Advances Research Workshop on Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems, Moscow, Russia, proceedings published by Kluwer Academic Publishers, Disarmament Technologies – vol. 14, 1994, p. 25-32.
39. Burch, D., "Reformulation/reuse of explosives, propellants and pyrotechnics for commercial applications", NATO Advances Research Workshop on Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems, Moscow, Russia, proceedings published by Kluwer Academic Publishers, Disarmament Technologies – vol. 14, 1994, p.113-120.
40. Summers, D. and Worsey P.N., "Programmed extraction of explosive and propellant from military casings", 24th International annual conference of ICT: Energetic materials - insensitivity and environmental awareness, Karlsruhe, Federal Republic of Germany, proceedings published by Fraunhofer - Institut für Chemische Technologie, 1993, p. 50-1 – 50-13.
41. Giltner, S.G., Sitton, O. and Worsey, P.N., "The reaction of Class 1.1 propellants and explosives to water jet impact", 24th International annual conference of ICT: Energetic materials - insensitivity and environmental awareness, Karlsruhe, Federal Republic of Germany, proceedings published by Fraunhofer - Institut für Chemische Technologie, 1993, p. 41-1 – 41-13.
42. Creedon, W.P. and Spritzer, M.H., "Cryogenic size reduction of solid propellant", General Atomics, report AFRL-ML-TY-TR-1998-4541, 117 p.

43. Emery, D.F., Johnson, R. and Malins, C., “Ultrasonic fragmentation and separation of cast energetic materials”, 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
44. SITIS (DoD Small Business Innovation Research Interactive Topic Information System), “Separation of Fragmented Energetic Materials via Directed Ultrasonic Energy”, A05-198 (Army), available from:
http://www.dodsbir.net/sitis/archives_display_topic.asp?Bookmark=27979.
45. Malins, C., “Ultrasonic fragmentation of energetic materials for removal and recovery”, 17th Global Demilitarization Symposium & Exhibition, San Diego, California, May 11-14, 2009.
46. TPL, inc., “Defense Systems Division”, 2007, available from:
<http://www.tplinc.com/DefSysDiv.html#Anchor-61801>.
47. Seitzinger, A., “CO₂ blast 5x decon system (CO₂ blast): Demonstration & validation testing”, International Chemical Weapons Demilitarization Conference, Scotland, UK, 2005.
48. Automation Technologies Ltd, “Automatic cryogenic cleaning dry ice CO₂”, 2009, available from: <http://www.p-h-s.co.uk/automation/cryogenic.htm>.
49. General Atomics, “Cryocycle”, 2009, available from:
<http://www.ga.com/atg/APS/cryocycle/index.php>.
50. Federal Remediation Technologies Roundtable, Remediation technologies screening matrix and reference guide, version 4.0: “Thermal treatment technologies for explosives”, 2009, available from: http://www.frtr.gov/matrix2/section2/2_10_2_2.html.
51. Thompson, G., “OB/OD is a safe demil process”, 17th Global Demilitarization Symposium & Exhibition, San Diego, California, May 11-14, 2009.
52. Morris, J.B., McNesby, K.L., Resce-Rodriguez, R.A., Schroeder and M.A., Fifer, “Extraction of nitramine propellants using supercritical fluids”, . 24th International annual conference of ICT: Energetic materials - insensitivity and environmental awareness, Karlsruhe, Federal Republic of Germany, proceedings published by Fraunhofer - Institut für Chemische Technologie, 1993, p. 36-1 – 36-14.
53. Maranda, A., Nowaczewski, J. and Mischczak, M., “Application of the explosives withdrawn from military stocks in the coal-mining industry”, 24th International annual conference of ICT: Energetic materials - insensitivity and environmental awareness, Karlsruhe, Federal Republic of Germany, proceedings published by Fraunhofer - Institut für Chemische Technologie, 1993, p. 72-1 – 72-13.

54. Bingham, J., "Sensitivity and environmental considerations in the life cycle of CDB propellants and rocket motors", 24th International annual conference of ICT: Energetic materials - insensitivity and environmental awareness, Karlsruhe, Federal Republic of Germany, proceedings published by Fraunhofer - Institut für Chemische Technologie, 1993, p. 36-1 – 36-14.
55. UXB International, inc., "Dynasafe SDC Static Detonation Chamber", 2009, available from: <http://www.uxb.com/products/munitions/dynasafe/sdc.cfm>.
56. Dynasafe, 2008, available from: <http://www.dynasafe.com>.
57. Heaton, H., "Design of a mobile demilitarization plant", 16th Global Demilitarization Symposium & Exhibition, Salt Lake City, Utah, May 5-9, 2008.
58. CH2MHill, "CH2M Hill: Solutions without boundaries", 2009, available from: <http://www.ch2m.com/corporate/>.
59. Imakita, T., Kitamura, R., Ueda, M. and Kiyoshi Asahina, J., "Destruction test for M55 nerve agent rocket mortar using surrogate chemicals by DaVinch", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
60. Inada, Y., Kurose, K. and Washida, T., "Destruction of old chemical bombs using DaVinch at Kanada, Japan", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
61. Krause, H.H. "Advanced disposal and recycling technologies of energetic materials", NATO Advances Research Workshop on Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems, Moscow, Russia, proceedings published by Kluwer Academic Publishers, Disarmament Technologies – vol. 14, 1994, p. 91-97.
62. Lauritzen, E.K., "Post-war ammunition stockpile recovery", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
63. Wanninger, P., "Conversion of high explosives", International Symposium on Special Topics in Chemical Propulsion Challenges, Propellants and Combustion: 100 Years after Nobel, Stockholm, symposium proceedings published by Begell House, New York, 1996, p. 155-166.
64. Mitchell, A.R., Coburn, M.D., Schmidt, R.D., Pagoria, P.F. and Lee, G.S., "Advances in the chemical conversion of surplus energetic materials to higher value products", Thermochemica Acta, 384(1-2, Special Issue: Sp. Iss. SI), 2002, p. 205-217.

65. Encyclopaedia Britannica, 2008, available from: <http://www.britannica.com>.
66. Center for public environmental oversight, "Plasma Arc Technology", 2002, available from: <http://www.cpeo.org/techtree/ttdescript/plarctech.htm>.
67. Flynn, D., "Installation, Optimization and Testing of a Mobile Plasma Treatment System", 17th Global Demilitarization Symposium & Exhibition, San Diego, California, May 11-14, 2009.
68. Mescavage, G., "Development of a Plasma Ordnance Demilitarization System for Pyrotechnic Ordnance", 17th Global Demilitarization Symposium & Exhibition, San Diego, California, May 11-14, 2009.
69. Hayes, R.W., Clayson, J., Lasson, C., Heald, C., Crist, B., Johnson, G. and Hoggard, S., "Decontamination of Test Range Metal Debris Using a Transportable Flashing Furnace", El Dorado Engineering, inc., ESTCP project MM-2004-12, 2005, 80 p.
70. Bunte, G. and Krause, H.H., "Disposal of energetic materials by alkaline pressure hydrolysis and combined techniques", NATO Advances Research Workshop on Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems, Moscow, Russia, proceedings published by Kluwer Academic Publishers, Disarmament Technologies – vol. 14, 1994, p. 259-269.
71. Dahn, A., "Chemical and biological processes for decomposition of nitrocellulose-based propellants", NATO Advances Research Workshop on Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems, Moscow, Russia, proceedings published by Kluwer Academic Publishers, Disarmament Technologies – vol. 14, 1994, p. 191-212.
72. Flesner, R., Dell'Orco, P.C., Spontarelli, T., Bishop, R.L., Skidmore, C.B., Uher, K. and Kramer, J.F., "Pilot-scale base hydrolysis processing of HMX-based plastic-bonded explosives". NATO Science Series, Partnership sub-series 1, vol. 22, 1998, p. 35-45.
73. Wikipedia, 2008, available from: <http://en.wikipedia.org/wiki>.
74. "Supercritical water oxidation (SCWO)", Jane's Nuclear, Biological and Chemical Defence, January 2007.
75. Krause, H.H., "Recycling and disposal techniques for energetic materials". NATO ASi Series. Partnership sub-series 1, vol. 16 Demilitarisation of munitions, 1997, p. 73-80.

76. Rising, S. and Elliott, J., "Update on demil technology programs at General Atomics", 16th Global Demilitarization Symposium & Exhibition, Salt Lake City, Utah, May 5-9, 2008.
77. General Atomics, "Supercritical Water Oxidation", 2009, available from: <http://www.ga.com/atg/APS/scwo/index.php>.
78. Turbosystems Engineering, "Supercritical Water Oxidation Technology", 2002, available from: <http://www.turbosynthesis.com/summitresearch/sumhome.htm>.
79. Sullivan, F., "The advanced supercritical water oxidation for liquid waste disposal", 16th Global Demilitarization Symposium & Exhibition, Salt Lake City, Utah, May 5-9, 2008.
80. Faylor, B., "Molten Salt Takes the Bang out of High Explosives", Science & Technology Review, 1996, p. 16-17.
81. Upadhye, R.S., Watkins, B.E., Pruneda, C.O. and Brummond, W.A., "Molten salt destruction as an alternative to open burning of energetic material wastes", Submittal to the I&EC Special Symposium American Chemical Society, Laurence Livermore National Laboratory, document no UCRL-JC117575, 1994.
82. "Evaluation of Demonstration Test Results of Alternative Technologies for Demilitarization of Assembled Chemical Weapons: A Supplemental Review for Demonstration II". Committee on Review and Evaluation of Alternative Technologies for Demilitarization of Assembled Chemical Weapons: Phase II, Board on Army Science and Technology, National Academy Press, 2001, 66 p.
83. Vijgen, J., "Solvated electron technology (SET) - Pesticides treatment technology fact sheet", 2008, available from: http://www.ihpa.info/docs/nato/NATO_SETFactSh&Annex9.pdf.
84. Orbey, N., "Recovery and reuse of core ingredients from decommissioned/obsolete gun propellant", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
85. Naval Sea System Command (NAVSEA), "Reclaimed Formulation HMX", NAVSEA Indian Head, Surface Warfare Center Division. 2009.
86. Cumming, A.S., "Demilitarisation and disposal - United Kingdom studies and applications", NATO Advances Research Workshop on Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems, Moscow, Russia, proceedings published by Kluwer Academic Publishers, Disarmament Technologies – vol. 14, 1994, p. 41-46.

87. Department of the Navy - Research, Development & Acquisition, 2009, available from:
http://acquisition.navy.mil/rda/home/acquisition_one_source/program_assistance_and_to_ols/best_practices_and_lessons_learned/innovative_partnering_approach_to_reclamation_of_explosives.
88. Wulfman, D.S., Sitton, O., Worsey, G., Beistel, D.W., Podzimek, M., Worsey, G. Nixon, F.T. and Burch, D., "Management of recovered polymer bonded explosives by means of reformulation", 24th International annual conference of ICT: Energetic materials - insensitivity and environmental awareness, Karlsruhe, Federal Republic of Germany, proceedings published by Fraunhofer - Institut für Chemische Technologie, 1993, p. 40-1 – 40-17.
89. Prundea, C. and Humphrey, J., "Strategies for the disposition of high explosives resulting from dismantlement of nuclear weapons", 24th International annual conference of ICT: Energetic materials - insensitivity and environmental awareness, Karlsruhe, Federal Republic of Germany, proceedings published by Fraunhofer - Institut für Chemische Technologie, 1993, p. 33-1 – 33-8.
90. Kimmell, T., Folga, S., Frey, G., Molberg, J., Kier, P., Templin, B. and Goldberg, M., "Technology Resource Document for the Assembled Chemical Weapons Assessment Environmental Impact Statement", Environmental Assessment Division, vol. 4: Assembled Systems for Weapons Destruction at Pueblo Chemical Depot, Argonne National Laboratory, ANL/EAD/TM-101, 2001, 130 p.
91. Tri-rinse, "Industrial Shredding and Shearing", 2009, available from:
http://www.tri-rinse.com/index.php?option=com_content&view=article&id=90&Itemid=111.
92. HVF West, inc., "HVF West LLC" Contract Number: GS-10F-0088U, 2009, available from:
https://www.gsaadvantage.gov/ref_text/GS10F0088U/0D91QJ.1LRFCK_GS-10F-0088U_HVFPRICELIST.PDF.
93. Wulfman, D.S., Sitton, O., Nixon, F.T., Podzimek, M., Worsey, G., Beistel, D., Worsey, P., Burch, D. and Johnson, M., "Reformulation of solid propellants and high explosives: An environmentally benign means of demilitarizing explosive ordnance", The Canadian Journal of Chemical Engineering, 75(5), 1997, p. 899-912.
94. Burch, D., Johnson, M. and Sims, K., "Value added products from reclamation of military munitions", Twenty-second International Pyrotechnics Seminar, Fort Collins, Colorado, 1996.

95. Maranda, A., Nowaczewski, J. and Paplinski, A., "Dismantling of conventional munitions and reuse of energetic materials for industrial purposes", Defense Industries: Science and Technology Related to Security: Impact of Conventional Munitions on Environment and Population, NATO Science Series vol. 44, Kluwer Academic Publishers, 2004, P. 361-372.
96. Snow, R., Hansen, K., Geary, J. and Ochs, B., "Manufacturing blasting agent & flashless powder for small arms from large grain gun propellants", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
97. Machacek, O., Eck, G. and Tallent, K., "Development of new high energy blasting products using demilitarized and excess propellant grains from conventional ammunition rounds", Conference Information: 2nd International Autumn Seminar on Propellants, Explosives and Pyrotechnics - Theory and Practice of Energetic Materials. Shenzhen, People's Republic of China, Publishing House of Ordnance Industry, 1997.
98. Khomeriki, S., Mikhelson, R. and Tudeschi, H., "Development of a technology and industrial explosives based on utilized ammunition", World of mining - Surface & underground, 57(4), 2005, p. 264-269.
99. Morgan, M.E. and Miller, P.L., "Recycling propellants and explosives into the commercial explosive industry", International Symposium on Special Topics in Chemical Propulsion Challenges, Propellants and Combustion: 100 Years after Nobel, Stockholm, symposium proceedings published by Begell House, New York, 1996, p. 199-204.
100. Carton, E.P. and Stuivinga, M., "Future for explosive materials processing", Impact engineering and applications: Proceedings of the 4th international symposium on impact engineering, Kumamoto, Japan, 2001, p. 495-502.
101. Stoller, H.M., Perry, M.L. and Schilling, T.J., "A preliminary evaluation of Comp A-3 and LX-14 explosives as blasting agents for the explosive bonding of dissimilar metals, Final Report, Contract No. N00164-91-C-0028/Mod.1", TPL, inc., TPL-FR-1000.2. 1995, 20 p.
102. Stoller, H.M., Schilling, T.J., Hardcastle, F.D. and Perry, M., "The extraction and reuse of HMX from solid rocket motor propellants for commercial applications", TPL inc, TPL-FR-2042, 1993, 54 p.
103. Mitchell, A.R. and Sanner, R.D., "Chemical conversion of energetic materials to higher value products", 24th International annual conference of ICT: Energetic materials - insensitivity and environmental awareness, Karlsruhe, Federal Republic of Germany, proceedings published by Fraunhofer - Institut für Chemische Technologie, 1993, p. 34-1 – 34-6.

104. Burch, D., Griggs, J., Johnson, M. and Sims, K., "Recovery / reuse of energetics from military munitions", Twenty-four International Pyrotechnics Seminar, Monterey, California, 1998, p. 101-112.
105. Courtney-Green, P., "Demilitarization developments in NATO", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
106. Arctech USA., 2008, available from: <http://www.arctech.com/>.
107. Kaushik, N., "Actodemil technology for recycling of propellants and energetic wastes - an overview of various applications", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
108. "Actodemil technology (United States)", Jane's Nuclear, Biological and Chemical Defence, January 2007.
109. Siniscalchi, K. and Kaushik, N., "Actodemil technology for recycling of propellants and energetic wastes at Tooele Army Depot, Tooele, Utah", 16th Global Demilitarization Symposium & Exhibition, Salt Lake City, Utah, May 5-9, 2008.
110. Kim, B.J., Hsieh, H. and Tai, F., "Method and system for treating waste nitrocellulose", US Patent 5849984, 1998.
111. Mitchell, A.R., Sanner, R.D. and Pagoria, P.F., "Chemical conversion of energetic materials to higher value products", The Second International Conference on Combustion: Conversion and Environmental Problems of Energetic Materials, Workshop on Peaceful Utilization of Energetic Materials", St.Petersburg, Russia, June 3-6, 1996.
112. Sigma-Aldrich, 2008, available from: www.sigmaaldrich.com/
113. Mitchell, R.A., Coburn, M.D., Schmidt, R.D. and Pagoria, P.F., "Chemical conversion of energetic materials to higher value products (paper submitted)", 1998 Global Demilitarization Symposium, Coeur d'Alene, Idaho, 1998.
114. Cannizzo, L. and Huntsmann, L., "Extraction and recovery of nitramines from propellants, explosives, and pyrotechnics", US Patent 6414143, 2002.
115. Gerber, P., Bunte, G., Niehaus, M., Teipel, U. and Krause, H., "Processing of energetic materials with supercritical CO₂". NATO Advances Research Workshop on Conversion Concepts for Commercial Applications and Disposal Technologies of Energetic Systems, Moscow, Russia, proceedings published by Kluwer Academic Publishers, Disarmament Technologies – vol. 14, 1994, p. 91-97.

116. Morris, J.B., "Separation of RDX from Composition B via a supercritical fluid extraction process", US Army Research Laboratory, Army Research Lab Aberdeen Proving Ground, MD, Report A452363, 9 p.
117. Morris, J.B., "Extraction & recycling of LOVA propellants using supercritical fluids", SERDP interim report, PP-660 FY98 Annual report, Army Research Laboratory, 10 p.
118. Vande Kieft, L.J. and Hillstrom, W.W., "Preliminary hazard analysis of supercritical fluid separation of energetic materials", Army Research Laboratory, Aberdeen Proving Ground, MD, ARL-TR-1420, 1997, 22 p.
119. Morris, J.B., "Extraction of nitroguanidine (NQ) from triple-base gun propellant", Army Research Laboratory, ARL-TR-2669, 2002, 36 p.
120. Reed, R., Ciaramitaro, D.A. and Brady, V.L., "Binders facilitating ordnance demilitarization", Twenty-four International Pyrotechnics Seminar, Monterey, California, 1998, p. 457-467.
121. Melvin, W.S. and Starling, J.P., "Recovery and reuse of rocket propellants", Second aerospace environmental technology conference, Huntsville, AL, 6-8 August 1996.
122. Brogle, R., Rys, P. and Rochat, E., "Environmentally friendly recycling of hexal in medium caliber ammunition in industrial scale", Propellants, explosives and pyrotechnics, 25, 2000, p. 153-157.
123. Bohn, M.A., Schweppe, R. and Weisweiler, W., "Recovering of components from plastic bonded propellants", Waste management, 17(2-3), 1997, p. 175-185.
124. Tompa, A.S., French, D.M., Butler, G.B. and Kaufman, M. S., "Solvolytic degradation of pyrotechnic materials containing crosslinked polymers", US Patent 4098627, 1978.
125. Diaz, E., Brousseau, P., Ampleman, G. and Thiboutot, S., "Less sensitive melt-cast explosives containing energetic thermoplastic elastomers", Defence R&D Canada, Technical report DREV TR 2001-185, 2002, 52 p.
126. Burch, D., Clark, K., McGregor, T. and Johnson, R., "Requalification of demilitarized HMX for DOD/DOE applications", 15th Global Demilitarization Symposium & Exhibition, Reno, Nevada, May 14-17, 2007.
127. McGregor, T., "Qualification of reclaimed HMX for military applications", 16th Global Demilitarization Symposium & Exhibition, Salt Lake City, Utah, May 5-9, 2008.

128. Poehlein, S.K., Burch, D., Johnson, R., Beyard, M. and Larson, S., "Requalification of demilitarized HMX for military use", 36th International Annual Conference of ICT: Energetic Materials: Performance and Safety 2005. 36th International annual conference of ICT: Energetic materials Performance and Safety, Karlsruhe, Federal Republic of Germany, proceedings published by Fraunhofer - Institut für Chemische Technologie, 2005, p. 80/1 – 80/13.
129. van der Heijden, A.E.D.M., Bouma, R.H.B., Carton, E.P., Martinez Pacheco, M., Meuken, B., Webb, R. and Zevenbergen, J.F., "Processing, application and characterization of (ultra)fine and nanometric materials in energetic compositions", Conference of the American Physical Society - Topical Group on Shock Compression of Condensed Matter, Baltimore, MD, AIP Conference Proceedings, vol. 845, p. 1121-1126.
130. Peterson, P.D. and Idar, D.J., "Microstructural differences between virgin and recycled lots of PBX 9502", Propellants, explosives and pyrotechnics, 30(2), 2005, p. 88-94.

List of symbols/abbreviations/acronyms/initialisms

%	Percentage
°C	Degree Celcius
ADNT	4-amino-2,6-dinitrotoluene
ANFO	Ammonium nitrate and fuel oil
Atm	Atmosphere (pressure unit)
CF	Canadian Forces
CFTO	Canadian Forces Technical Orders
CO ₂	Solid carbon dioxide or dry ice (in the context of this report)
Comp B	Composition B
CTPB	Carboxy-terminated polybutadiene
DMSO	Dimethylsulfoxide
DND	Department of National Defence
DOE	Department of Energy
DPA	Diphenylamine
DRDC	Defence Research & Development Canada
DRDKIM	Director Research and Development Knowledge and Information Management
EM	Energetic materials
ETPE	Energetic thermoplastic elastomer
EPA	Environmental Protection Agency
FC	Forces canadiennes
g	Gram
GAP	Glycidyl azide polymer
HAT	1,4,5,8,9,12-hexaazatriphenylene
HCl	Hydrochloric acid
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
HTPB	Hydroxyl-terminated polybutadiene
HTPE	Hydro-terminated polyethers

ITAR	International Traffic in Arms Regulations
M	Molar
mm	Millimeter
NaOH	Sodium hydroxide
NC	Nitrocellulose
NG	Nitroglycerin
NO _x	Nitrogen oxides
NQ	Nitroguanidine
NTDI	Nitrotoluene diisocyanate
NTO	Nitrogen tetroxide
OB/OD	Open burning/Open detonation
PBX	Plastic bonded explosive
PEG	Polyethylene glycol
PETN	Pentaerythritol tetranitrate
PNA	Pentanitroaniline
Psi	Pound per square inch (pressure unit)
R&D	Research & Development
R3	Resource recovery and reuse
RDX	Cyclo-1,3,5-trimethylene-2,4,6-trinitramine
TAB	Triaminobenzene
TATB	1,3,5-triamino-2,4,6-trinitrobenzene
TDI	Toluene 2,4-diisocyanate
TNB	1,3,5-trinitrobenzene
TNBA	2,4,6-trinitrobenzoic acid
TNT	Trinitrotoluene
TPE	Thermoplastic elastomer
US	United States
UXO	Unexploded ordnance

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The Canadian Forces (CF), as well as the United States Army and other military organizations, have a large inventory of munitions to support a multitude of tasks and missions, including training to ensure operational readiness. Throughout the life cycle of the munitions, items may become deteriorated, obsolete or declared surplus to requirement, and safe disposal options are then needed. This disposal should ensure that the items are rendered unusable for their intended military or strategic purpose and should be irreversible. Disposal should be carried out in accordance with regulations and safety and environmental requirements. This technical memorandum will present a literature review of the main technologies available in the demilitarization area. The classical destruction methods, such as open burning, will be reviewed, as well as new technologies that offer a more environmentally friendly way to dispose of munitions and methods that allow the recycling of the explosive content for other applications.

The design of future weapons is currently ongoing, for example through the RIGHTTRAC project. This design requires the use of explosive and propellant formulations having characteristics such as: enhanced performance, reduced vulnerability during storage and transportation, improved mechanical properties, decreased signature, extended service life and reduced environmental impact in manufacture, use and disposal. As demilitarization is a part of the life cycle of munitions, it must be addressed early to influence the design and positively impact future demilitarization execution. The up-front design for demilitarization (“Design for Demil”) is a new trend seen not only in the RIGHTTRAC project, but also in other organizations. This report will present an overview of the technologies, either present in the market or still in the laboratory in the development process, that deal with demilitarization.

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Demilitarization; munitions; unexploded ordnances; recycling; reuse; removal; explosives; gun propellant; energetic materials; environment; destruction; disposal, literature review; extraction; combustion; contamination; disassembly.

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