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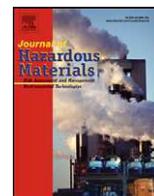
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## Dissolution of a new explosive formulation containing TNT and HMX: Comparison with octol

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### ABSTRACT

GIM (Greener Insensitive Material) is a new explosive formulation made of HMX (51.5%), TNT (40.7%), and a binder, ETPE (7.8%), which is currently investigated by the Canadian Department of National Defense for a wider use by the Army. In the present study, dissolution of GIM in water was measured and compared to the dissolution of octol (HMX/TNT: 70/30). Although the presence of ETPE did not prevent completely TNT and HMX from dissolving, GIM appeared to dissolve more slowly than octol. The ETPE was shown to prevent the formulation particles from collapsing and to retard the dissolution of both TNT and HMX by limiting their exposure to water. In both octol and GIM, the dissolution rate of the particles was governed by the compound(s) that are slower to dissolve, *i.e.* HMX in octol, and HMX and ETPE in GIM. A model based on Fick's diffusion law allowed fitting well the dissolution data of octol but was less appropriate to fit the data of GIM likely due to a physical rearrangement of the solid upon dissolution. The present findings demonstrate that ETPE in GIM decreases the risks of explosives leakage from particles of the new formulation and should facilitate the collecting of non-exploded GIM particles in training sites.

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### 1. Introduction

Melt cast explosive compositions are usually prepared by melting and casting the compositions (composition B, octol, ...) into artillery shells, rockets or bombs where they are allowed to cool down and solidify [1]. The resulting melt cast explosives have poor mechanical properties and often exhibit cracks, exudation, voids, and brittleness. Introducing a rubbery binder in high-energy compositions was shown to both improve the mechanical properties of the formulations and give them a desired insensitive character [2–5].

In this context, new high-energy melt cast plastic bonded explosives have been synthesized by researchers at Defence Research and Development Canada (DRDC, Valcartier, QC [1]). 2,4,6-Trinitrotoluene (TNT) was used as a solvent to dissolve new energetic copolyurethane thermoplastic elastomers containing a glycidyl azide polymer (GAP) and isolate the resulting explosive compositions. Conversely to the usual plastic bonded explosives which result from a curing reaction and are therefore chemically crosslinked, the formulations involving the energetic thermoplas-

tic elastomer (ETPE) (Fig. 1) are based on physical blending only and are fully recyclable. One of these new explosive formulations, named GIM for “Greener Insensitive Material”, is composed of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) (51.5%), TNT (40.7%), and ETPE (7.8%) serving as binder.

Several cases of groundwater contamination by TNT, RDX or HMX have been reported in recent years at various US and Canadian Army sites after incidental dispersion of unexploded residues on the soil surface [6,7]. Prior to its use by the Canadian Army, the new GIM formulation should therefore be tested for its potential impact on the environment. Dissolution of explosives by precipitation is the departure point and one of the controlling factors for the transport, fate, and impact of explosives [8,9]. Moreover, few studies suggested that the dissolution rate of individual explosives was decreased when present in formulations compared to the pure explosives [10–13]. The primary goal of the present study was therefore to study the dissolution of GIM particles in aqueous media and compare results with the pure explosives, HMX and TNT, as well as octol (HMX/TNT: 70/30) in order to understand the effect of the binder and the interdependence of both explosives on their dissolution rates. A second objective was to test the applicability of a dissolution model developed for solids containing *n* components dissolving at variable rates to the dissolution of GIM. Indeed, with two relatively well-known explosives, TNT and HMX, and an inert binder, ETPE, GIM appeared as an ideal model to improve our understanding of dissolution of multi-component formulations.

**Abbreviations:** ETPE, energetic thermoplastic elastomer; GIM, greener insensitive material; HMX, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine; TNT, 2,4,6-trinitrotoluene.

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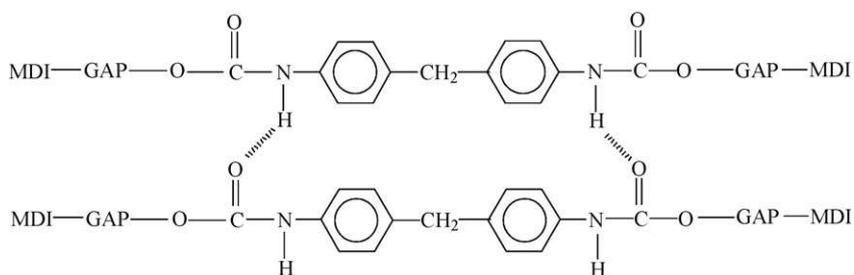


Fig. 1. Chemical structure of the energetic thermoplastic elastomer (ETPE) (MDI = Methylene bis-para phenylisocyanate; GAP = Glycidyl azide polymer).

## 2. Materials and methods

### 2.1. Materials

TNT flakes (0.1–0.4 cm, 0.06 cm thickness), HMX crystals (<0.1 cm), and octol chunks were obtained from Holston Army Ammunition Plant, Kingsport, TN. TNT and HMX were used as received while octol was mechanically ground into powder (<0.1 cm). GIM was synthesized according to the patented procedure [1] and its composition measured in triplicate using HPLC after dissolution in acetonitrile was found to be: TNT ( $40.7 \pm 2.4\%$ ), HMX ( $51.5 \pm 3.5\%$ ), ETPE ( $7.8 \pm 1.6\%$ ), RDX ( $0.0029 \pm 0.0004\%$ ). GIM chunks were cautiously cut with a scalpel into smaller parallelepipedic pieces of 0.3–0.5 cm sides and 70–100 mg each. Average density of GIM measured on 21 different pieces was found equal to  $1.15 \pm 0.29 \text{ g cm}^{-3}$ . Acetonitrile ( $\text{CH}_3\text{CN}$ , HPLC grade) was from Fisher (Nepean, ON) and deionized water was obtained with a Milli-Q<sup>UV</sup> plus (Millipore) system.

To allow comparisons of dissolution rates between the individual or mixed compounds and formulations, rates were normalized relative to their exposed surface. While the surface of GIM particles used in this study was deduced from their measured dimensions, specific surface areas were determined for solid TNT, HMX, and octol and the exposed surface was deduced from the weighted amount of each chemical.

The specific surface area of TNT was determined by measuring the surface areas and masses of 10 flakes, respectively. For each TNT flake, the surface area was established using a digital sliding caliper after dividing the surface into several simple geometrical shapes. The average specific surface area resulting from 10 measurements was found to be equal to  $34.4 \pm 7.5 \text{ cm}^2 \text{ g}^{-1}$ .

The specific surface areas for HMX crystals and octol powder estimated by laser diffraction using a particle size analyzer Mastersizer 2000 (Malvern Instruments Ltd., Worcestershire, UK) and assuming spherical particles were 119.7 and  $160.5 \text{ cm}^2 \text{ g}^{-1}$ , respectively.

### 2.2. Solubility measurements

The solubility of GIM was determined in water at  $10 \pm 1$ ,  $22.5 \pm 1$ , and  $29.3 \pm 1$  °C. Two pre-cut measured and weighted pieces ( $2.2\text{--}2.3 \text{ cm}^2$ , 140–160 mg in each flask) were added to 100 mL of pre-equilibrated deionized water (pH 5.5) in a glass bottle. The samples were shaken at 150 rpm and at the required temperature in a thermostated incubator, away from light. Aliquots of suspension (2 mL) were withdrawn over the course of the experiment, filtered and the filtrates diluted in acetonitrile (1:1, v:v). The resulting solutions were analyzed for TNT and HMX by HPLC-UV as described previously [14]. HPLC/MS was also used to detect and identify any degradation products of ETPE in the aqueous phase. Once the dissolved amounts of TNT and HMX reached equilibrium, the solid pieces were isolated and stirred again with a fresh batch of deion-

ized water (100 mL) in order to determine the degree of availability of each explosive.

### 2.3. Dissolution rates in batch experiments

Dissolution rates measurements were carried out in a beaker using a stainless steel propeller mounted on an overhead digital laboratory stirrer (Model BDC 3030, Caframo, Warton, ON). Deionized water (500 mL) at  $22.5 \pm 1$  °C was used as medium. The propeller was centered and lowered into the beaker halfway between the water surface and the bottom of the beaker, and adjusted to the desired stirring rate (300 rpm). A given amount of dry explosive compound was then introduced with the aid of a spatula, which corresponded to the initial time ( $t_0$ ). Samples (2 mL) were periodically withdrawn, filtered through a  $0.45 \mu\text{m}$  filter, diluted in acetonitrile (1:1, v:v) and analyzed by HPLC-UV for TNT and HMX. Dissolution rates corresponded to the change in aqueous concentration of explosive over time while keeping the concentration in bulk liquid below 10% of the solubility.

Normalized dissolution rates (in  $\text{mg min}^{-1} \text{ cm}^{-2}$ ) were measured for GIM (small cubes), octol (powder), TNT (flakes), HMX (crystals), and unbound mixtures of TNT (flakes) and HMX (crystals) using the conditions described above. For each compound four to six different amounts were introduced producing sample surface areas ranging from 1.4 to  $6.9 \text{ cm}^2$ , 1.6 to  $5.8 \text{ cm}^2$ , 1.6 to  $2.7 \text{ cm}^2$ , or 2.4 to  $9.5 \text{ cm}^2$  for TNT, HMX, octol, and GIM, respectively.

At the end of the measurement made with  $5.6 \text{ cm}^2$  of GIM, the particles were kept in the solution, stirred at 300 rpm for 24 h, filtered and introduced in 500 mL of fresh water to measure the new dissolution rate. This operation was repeated nine times. Each filtrate collected at the end of the 24 h stirring was analyzed for TNT and HMX to determine the amount of explosives remaining in the solid.

### 2.4. Long term dripping experiments

A parallelepipedic piece of GIM ( $0.45 \times 0.40 \times 0.49 \text{ cm}^3$ , 115 mg) was deposited on the top of the neck of a glass funnel (0.5 cm internal diameter) and exposed to a continuous water flow maintained with a peristaltic pump at a rate of  $0.5 \text{ mL min}^{-1}$  ( $\sim 19 \text{ drops min}^{-1}$ ) corresponding to a rainfall rate of  $60 \text{ cm h}^{-1}$ . Although higher than the rainfall rates commonly observed, this flow was selected to ensure sufficient dissolution of the particle within duration of the entire experiment (1 year). Outflow samples were collected in glass flasks covered with aluminum foil and flasks were changed every 24 h (720 mL) for 3 weeks and then every 7 days (5040 mL) for 49 weeks. Each water fraction was analyzed for TNT and HMX as described previously [14].

For comparison, a similar experiment was conducted with an octol particle but using a nylon mesh to hold the whole fragile solid in the funnel. Although not regular in shape, the octol particle was assumed to be spherical with a diameter of 0.44 cm

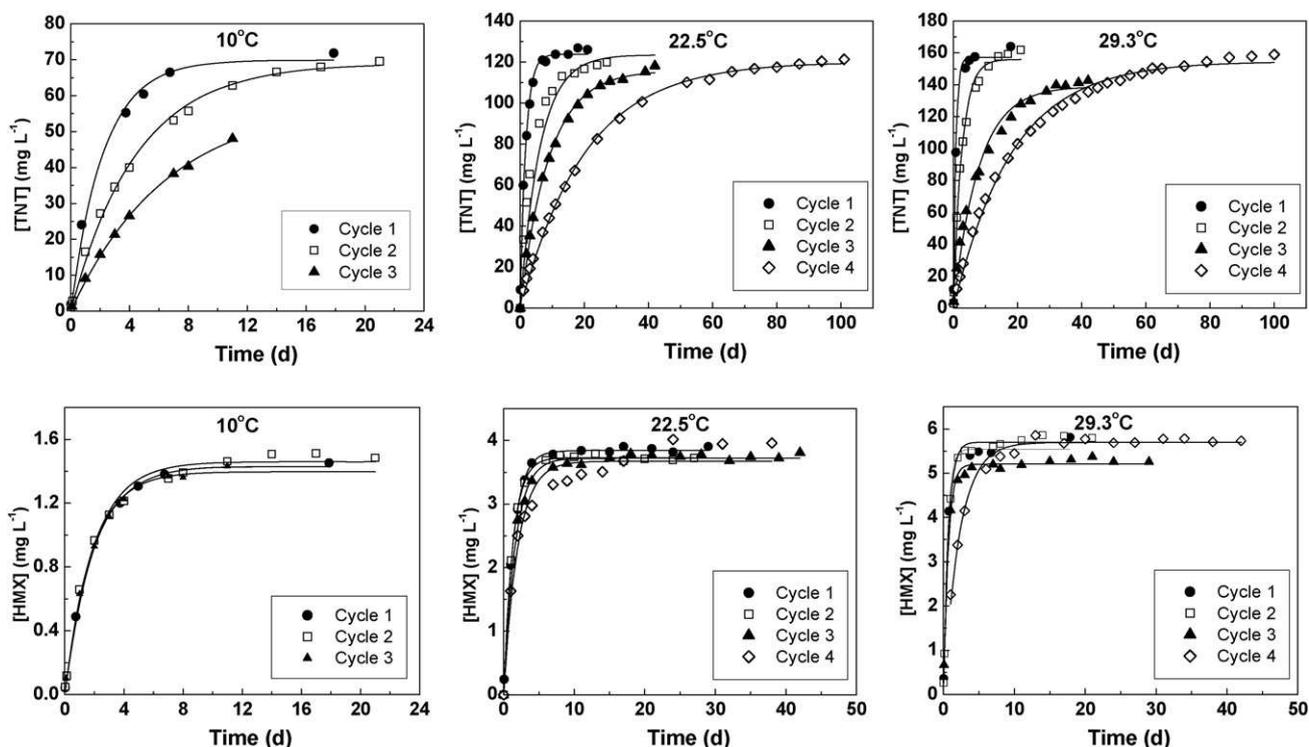


Fig. 2. Aqueous dissolution of TNT (up) and HMX (down) from GIM pieces as a function of temperature and number of contacts with fresh water.

estimated from its weight ( $70.0\text{ mg}$ ) and density ( $1.6\text{ g cm}^{-3}$ ). In the same way a continuous and constant water flow ( $0.5\text{ mL min}^{-1}$ ) was applied and outflow samples were collected and analyzed by HPLC-UV every 1–2 days for 3 weeks and then every 7 days for 34 weeks.

### 3. Results and discussion

#### 3.1. Solubility measurements

When first stirring two small pieces of GIM ( $\sim 150\text{ mg}$  in total) in water at  $10$ ,  $22.5$ , or  $29.3^\circ\text{C}$ , both TNT and HMX were released in water until an equilibrium was reached after approximately 1 week (cycle 1 in Fig. 2). The concentrations of TNT and HMX measured at equilibrium agreed well with the solubility values calculated for each component using the correlations previously established to relate aqueous solubilities of HMX and TNT with temperatures [15] (Table 1). When exposing the same pieces of GIM for a second time to fresh deionized water, TNT was released into water at a slower rate compared to the first experiments, and when repeating the same dissolution experiment with fresh deionized water

TNT dissolution continued to slow down in each dissolution cycle (Fig. 2). In contrast the dissolution rate of HMX remained more or less constant throughout the successive dissolution cycles. TNT dissolution rate thus decreased with the amount of TNT remaining in the formulation while HMX continued to dissolve at the same rate. A similar phenomenon was previously observed by Lever et al. who reported that the slow dissolution of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) controlled the dissolution of composition B (RDX/TNT/wax, 60/39/1) particles by limiting the exposed area of TNT [12].

The total amount of TNT released during the four dissolution cycles conducted at  $29.3^\circ\text{C}$  represented 98.4% of the TNT initially introduced, thus suggesting that the total amount of TNT was available for dissolution. In contrast, the total amount of HMX released under the same conditions corresponded to 2.8% of the HMX initially present, due to the lower solubility of the nitramine in water. Attempts to detect any ETPE degradation products in the aqueous filtrate obtained at  $22.5^\circ\text{C}$  using LC-MS did not show any significant peaks when scanning from 200 to 3000 Da and using both positive and negative ionization modes, thus suggesting that ETPE does not dissolve in aqueous solutions.

Table 1

Maximum TNT and HMX released from GIM pieces ( $\sim 150\text{ mg}$ ) into water (100 mL) after sequential stirring at the indicated temperatures.

Cycle	TNT from GIM pieces ( $\text{mg L}^{-1}$ )			HMX from GIM pieces ( $\text{mg L}^{-1}$ )		
	$10^\circ\text{C}$	$22.5^\circ\text{C}$	$29.3^\circ\text{C}$	$10^\circ\text{C}$	$22.5^\circ\text{C}$	$29.3^\circ\text{C}$
1	71.8	126.1	163.9	1.45	3.91	5.81
2	69.5	119.8	161.8	1.48	3.79	5.86
3	–	118.1	142.7	–	3.81	5.38
4	–	121.3	159.1	–	3.96	5.78
	Aqueous solubility of TNT calculated using $\ln S = 17.263 - 3691.3/T(K)$ [15]			Aqueous solubility of HMX calculated using $\ln S = 22.399 - 6230/T(K)$ [15]		
	$10^\circ\text{C}$	$22.5^\circ\text{C}$	$29.3^\circ\text{C}$	$10^\circ\text{C}$	$22.5^\circ\text{C}$	$29.3^\circ\text{C}$
	68.0	118.1	156.4	1.47	3.73	5.99

\* Reaction was stopped after 11 days of the run # 3 due to incubator failure.

**Table 2**  
Normalized dissolution rates,  $r$ , of TNT and HMX measured individually, in unbound mixtures, in octol or in GIM, at 300 rpm and 22.5 °C.

Constituent	Surface (cm <sup>2</sup> )	$r$ (TNT) (10 <sup>-3</sup> mg.min <sup>-1</sup> .cm <sup>-2</sup> )	Surface (cm <sup>2</sup> )	$r$ (HMX) (10 <sup>-3</sup> mg.min <sup>-1</sup> .cm <sup>-2</sup> )
TNT	1.4	17.3		
TNT	2.8	14.2		
TNT	4.3	19.2		
TNT	5.2	17.8		
TNT	6.0	17.5		
TNT	6.9	16.4		
Average	–	17.1 ± 1.7		
HMX			1.6	0.88
HMX			1.6	1.46
HMX			2.2	1.14
HMX			2.2	1.25
HMX			2.8	0.73
HMX			2.8	1.04
Average			–	1.1 ± 0.3
Unbound mix	4.4	17.8	1.7	1.73
Unbound mix	5.3	19.3	2.2	2.15
Unbound mix	6.2	16.5	2.8	1.31
Unbound mix	1.4	15.8	5.8	1.21
Average	–	17.4 ± 1.5	–	1.6 ± 0.5
Octol	1.6	12.5	1.6	1.32
Octol	1.8	12.8	1.8	1.39
Octol	2.0	8.0	2.0	1.00
Octol	2.4	9.6	2.4	0.67
Octol	2.7	11.6	2.7	1.00
Average	–	10.9 ± 2.1	–	1.1 ± 0.3
GIM cubes	2.4	9.7	2.4	0.33
GIM cubes	3.9	9.1	3.9	0.27
GIM cubes	4.1	9.9	4.1	0.43
GIM cubes	5.6	8.9	5.6	0.39
GIM cubes	7.1	10.8	7.1	0.37
GIM cubes	9.5	10.1	9.5	0.37
Average	–	9.8 ± 0.7	–	0.4 ± 0.1

HMX which is the major component of GIM dissolved less rapidly than TNT and had its dissolution limited by its low solubility in water. As a result, the nitramine was left at the periphery of GIM pieces as the only explosive to dissolve while TNT got concentrated at the center of GIM pieces. The dissolution rate of TNT was thus hampered by its limited exposure to water but one needed to determine whether the decreasing exposed area was due to the remaining HMX, ETPE, or both.

### 3.2. Dissolution kinetics in batch experiments

Dissolution kinetics may vary with the type of stirring, the stirring rate, and the type of aqueous environment used for measurements. For this reason it is difficult to compare the measured dissolution rates to data reported in the literature. In order to determine whether the presence of ETPE in GIM had an effect on the dissolution of TNT and HMX, dissolution rates were measured at room temperature in water for TNT alone, HMX alone, mixtures of unbound TNT and HMX, octol, and GIM. A stirring rate of 300 rpm was selected that allowed the maximum immersion and motion of solids in the beaker without generating a vortex.

TNT and HMX dissolution curves measured over the first 30 min for each experiment were adequately described by linear regressions thus indicating that the selected conditions allowed applying Fick's first law (Eq. (1)) with a concentration in the bulk liquid negligible with respect to the solubilities of each explosive. The resulting

normalized dissolution rates of TNT and HMX measured at room temperature are summarized in Table 2.

$$\frac{dm}{dt} = -\frac{D}{h}a(C^s - C^b) \quad (1)$$

where  $dm/dt$  is the change in solid mass over time (mg s<sup>-1</sup>),  $D$  is the diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>),  $a$  is the surface area (cm<sup>2</sup>),  $C^s$  is the solubility (mg cm<sup>-3</sup>),  $C^b$  is the concentration in bulk liquid (mg cm<sup>-3</sup>), and  $h$  is the boundary layer thickness (cm).

The dissolution rate of pure HMX was around 15 times lower than the dissolution rate of pure TNT measured under the same conditions (Table 2), which differs from the ratio of approximately two previously determined by Lynch et al. [10,16]. Normalized TNT dissolution rates measured in the present study (17 × 10<sup>-3</sup> mg min<sup>-1</sup> cm<sup>-2</sup>) were close to those previously reported for pure TNT (11–16 × 10<sup>-3</sup> mg min<sup>-1</sup> cm<sup>-2</sup> at 20 °C [10,16]). On the contrary the dissolution rates for HMX (1 × 10<sup>-3</sup> mg min<sup>-1</sup> cm<sup>-2</sup>) were found to be approximately 10 times lower than the reported values (8–13 × 10<sup>-3</sup> mg min<sup>-1</sup> cm<sup>-2</sup> at 20 °C [10,16]). No significant difference was observed between the dissolution rates determined individually or in unbound mixtures of TNT and HMX, using various ratios of TNT to HMX (Table 2), thus suggesting very little physical interactions between the two chemicals.

The dissolution rates of pure TNT and HMX exceeded of a factor 1.8 and 2.7 the respective dissolution rates measured for TNT and HMX in small cubes of GIM, thus demonstrating a slightly slower dissolution of components when present in GIM formulation com-

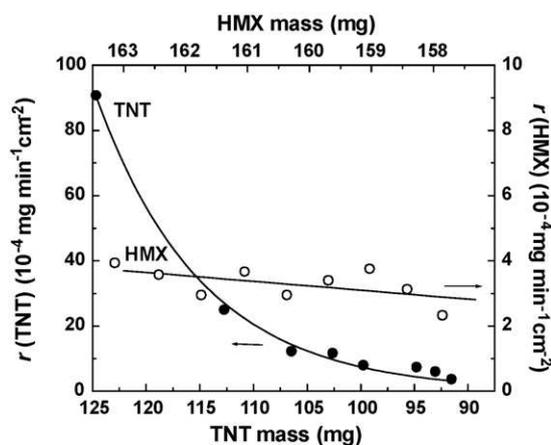


Fig. 3. TNT and HMX normalized dissolution rates from GIM pieces re-used as a function of their respective mass remaining in the solid (300 rpm and 22.5 °C).

pared to the pure compounds. Dissolution of TNT from octol was slower than that of pure TNT while HMX dissolution was the same in octol as it was in pure HMX. Therefore, while in octol, the dissolution rate of TNT was most likely slowed down by the presence of HMX, in GIM both TNT and HMX dissolved more slowly probably due to the presence of the third component present, namely ETPE.

In one of the experiments, dissolutions rates were measured nine times by contacting the same pieces of GIM with new volumes of fresh water. Normalized dissolution rates for TNT and HMX were plotted as a function of the amount of TNT or HMX present in the solid pieces at the beginning of each rate measurement (Fig. 3). TNT dissolution rate decreased exponentially with the amount of TNT remaining in the solid so that a 10 fold slower dissolution was measured after the 4th dissolution cycle. The dissolution rate of HMX also decreased but much more slowly. After nine cycles both TNT and HMX dissolved at the same rate ( $\sim 30 \times 10^{-3} \text{ mg min}^{-1} \text{ cm}^{-2}$ ).

### 3.3. Long term dissolution in dripping experiments

To understand the dissolution of GIM over long periods of time and to be able to predict its behavior when GIM particles dispersed on the soil surface are subjected to rainfall events, a long term dissolution experiment was conducted using a GIM particle. A piece of GIM was deposited in a funnel and subjected to a continuous and constant flow of dripping water for 47 weeks. The free flowing of water under the particle mimicked a rain flow falling on a particle lying on a porous soil where the water would disappear quickly into the ground.

When the particle of GIM was subjected to water dripping, it immediately began to dissolve. Concentration of TNT in the eluate collected during the first 24 h was high ( $6 \text{ mg L}^{-1}$ ) but dropped relatively fast to less than  $1 \text{ mg L}^{-1}$  during the following 10 days (Fig. 4a) and continued to decrease slowly to reach  $0.02 \text{ mg L}^{-1}$  after 47 weeks. HMX concentration in the eluates decreased very slowly from an initial value of  $0.25 \text{ mg L}^{-1}$  to a value of  $0.05 \text{ mg L}^{-1}$  after 47 weeks. During a period extending from 60 to 120 days, HMX and TNT were liberated in water at almost the same rate, in accord with the results obtained in the mechanically stirred system (see Fig. 3).

After 63 days, the water flow was stopped for few minutes to allow the slightly shrunken piece of GIM ( $0.28 \times 0.37 \times 0.43 \text{ cm}^3$ ) to be photographed using a microscope. The surface of the water-exposed piece showed a rough ETPE framework with cavities of up to  $0.04 \text{ cm}$  average diameter generated by the dissolution of the explosives at the surface (Fig. 5). The GIM piece was then placed back under the water dripping flow to continue the experiment. After 330 days the experiment was stopped and the remaining

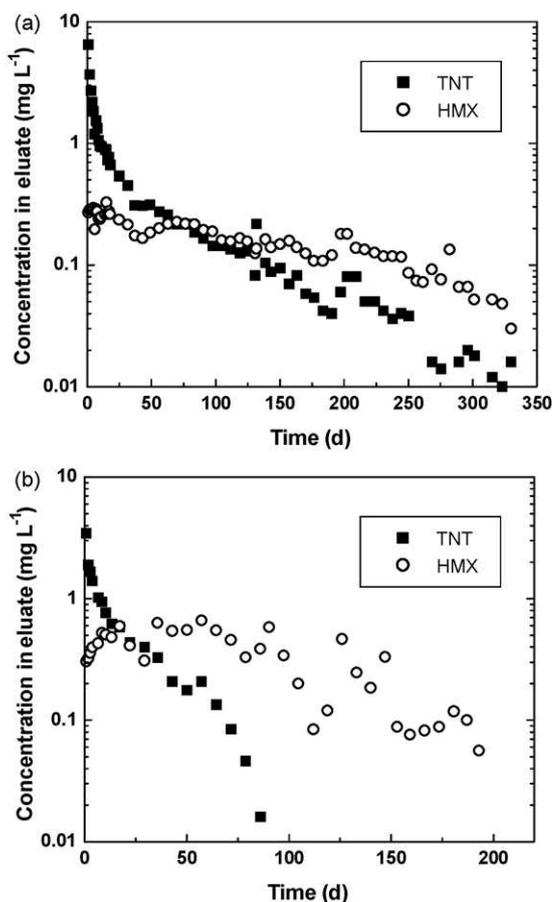


Fig. 4. TNT and HMX concentrations in the eluates obtained by dripping water on (a) a cube of GIM (115 mg) and (b) a particle of octol (70 mg) ( $T = 22.5 \text{ }^\circ\text{C}$ ; Water flow:  $0.5 \text{ mL min}^{-1}$ ).

particle ( $0.27 \times 0.30 \times 0.33 \text{ cm}^3$ ) was photographed again (Fig. 5). Deeper cavities were present at the surface of the particle and the color of GIM had changed from golden orange to reddish brown. Some insoluble products of TNT photolysis may be the cause of this change of color. The total amounts of TNT ( $46.2 \text{ mg}$ ) and HMX ( $34.8 \text{ mg}$ ) recovered in the eluates at the end of the experiment represented 99% and 59% of the respective amounts of explosives initially present in the solid which confirmed the potential leakage of the whole TNT contained in GIM into the environment.

The effect of ETPE on the dissolution of TNT and HMX was estimated by comparing the results obtained with GIM with those obtained with octol. An octol particle was therefore subjected to the same constant water flow. The octol piece started to dissolve in a way very similar to GIM with a dissolution rate for TNT that decreased fast during the first ten days of exposure and a dissolution rate for HMX that oscillated around an average value (Fig. 4b). However, after 35 days the fragile octol particle disintegrated in small pieces, which resulted in a higher surface area and an increased dissolution of both TNT and HMX. Similar disintegration of octol particles into smaller pieces under water flow has been recently observed by other researchers [13]. TNT was entirely dissolved after 80 days and only 5.5% of HMX remained to be dissolved after 238 days.

Dissolution of TNT and HMX was slower in GIM than in octol. Moreover, dissolution of TNT and HMX occurred in a much more regular manner in GIM than in octol, as supported by the smooth dissolution curves measured from GIM against the uneven ones obtained with octol (Fig. 4). The binder present in GIM thus gave a mechanical stability to the formulation which avoided its

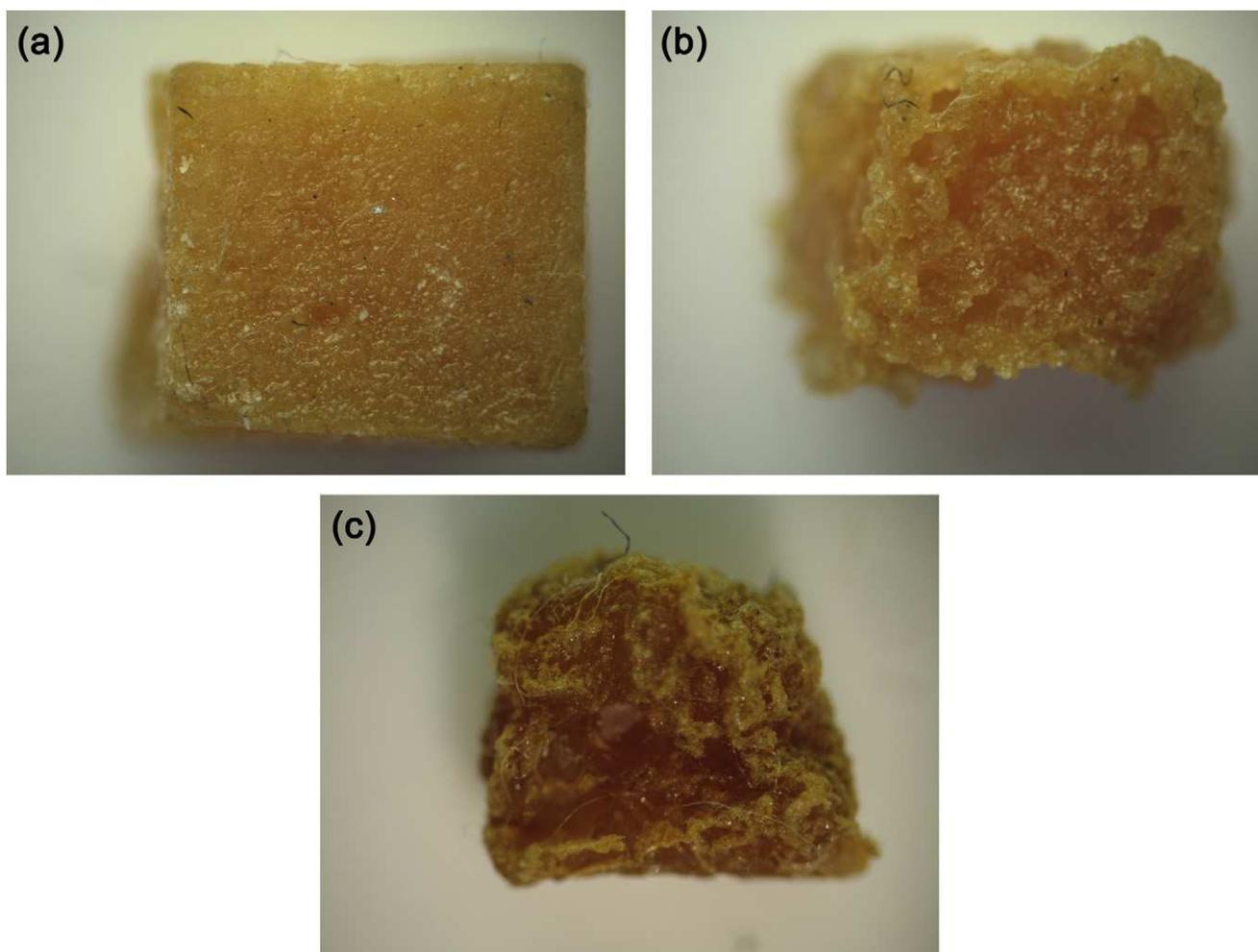


Fig. 5. Microscopic photographs of a piece of GIM non-exposed (a) and exposed for 9 weeks (b) or 47 weeks (c) to a water dripping flow.

breakdown into smaller pieces and hence limited the accelerated dissolution that would result from disintegration of the particle. The present findings show that GIM would be more prone than octol to remain integral in the environment therefore facilitating its physical removal from contaminated sites.

### 3.4. Dissolution modeling

#### 3.4.1. Brief description of the model

Data obtained with GIM and octol were fitted using a model based on Fick's first law of diffusion previously reported by Lynch et al. to predict dissolution of HMX and TNT from octol particles [17]. Given the observations above reported, *i.e.* rapid decrease of TNT dissolution rate and quasi constant HMX dissolution rate upon exposure to water, model 3 was selected among the three models presented because it was the only one assuming a decreasing dissolution rate for the explosive that dissolves faster. Model 3 was an adaptation of a general theory put forward by Carmichael et al. [18] to determine dissolution rates of a multi-drug non-disintegrating sphere the components of which had different solubilities, different diffusion coefficients and varying boundary layer thicknesses.

In model 3 as described by Lynch et al. for octol [17], TNT and HMX are assumed to be homogeneously distributed in a sphere. As the explosive compounds dissolve, TNT regresses into the solid particle and leaves outside a layer of HMX. By using spherical coordinates and assuming the concentration in the bulk solu-

tion negligible compared to solubility, Eq. (1) was re-written as Eq. (2).

$$\frac{dr_i}{dt} = -\frac{D_i}{h_i X_i \rho} C^s \quad (2)$$

where  $r$  is the radius of the sphere in cm,  $\rho$  is the density of the solid in  $\text{mg cm}^{-3}$ ,  $X$  is the mass fraction and the suffix  $i$  refers to the component  $i$ .

Assuming a constant mass fraction for each explosive compound and adding the layer of HMX to the boundary layer of TNT, integration of Eq. (2) gave rise to distinct expressions for  $r_{\text{HMX}}$  and  $r_{\text{TNT}}$  (see Ref. [17] for more details).

#### 3.4.2. Application of model 3 to dissolution of octol and GIM

Dissolution of octol was modeled using the equations presented in Ref [17].

GIM is also a formulation containing TNT and HMX, although in a different ratio from octol and combined to a significant amount of binder (ETPE). No sign of ETPE disappearance or dissolution was observed during the time frame of the reported experiments. Hence GIM can be described as a three-component formulation with TNT being the fastest dissolving compound, HMX being a slowly dissolving compound and ETPE being an insoluble material. When considering a GIM particle that is being dissolved, one would expect to encounter from outside to inside an external layer of GIM, an intermediate layer of HMX plus GIM, and a core containing the three components. Two different hypotheses were formulated in

**Table 3**  
Modeling parameters estimated at 22.5 °C.

Parameters	Octol		GIM	
	TNT	HMX	TNT	HMX
$C^s$ (g cm <sup>-3</sup> )	$1.181 \times 10^{-4}$	$3.729 \times 10^{-6}$	$1.181 \times 10^{-4}$	$3.729 \times 10^{-6}$
$D$ (cm <sup>2</sup> s <sup>-1</sup> ) [19]	$6.28 \times 10^{-6}$	$5.63 \times 10^{-6}$	$6.28 \times 10^{-6}$	$5.63 \times 10^{-6}$
$h$ (cm)	$1.62 \times 10^{-2}$	$3.87 \times 10^{-3}$	$1.43 \times 10^{-2}$	$9.62 \times 10^{-3}$
$J$ at $t_0$ (mg min <sup>-1</sup> cm <sup>-2</sup> )	$2.75 \times 10^{-3}$	$3.30 \times 10^{-4}$	$3.10 \times 10^{-3}$	$1.31 \times 10^{-4}$
$\rho$ (g cm <sup>-3</sup> )		1.6		1.2
$\mu_{\text{water}}$ (N s m <sup>-2</sup> )		$9.469 \times 10^{-4}$		$9.469 \times 10^{-4}$
$m_0$ (mg)		70.0		115.0
$r^0$ (cm)		0.219		0.284

the present study to describe the dissolution of the GIM particle: Either the ETPE was considered to have no effect on the dissolution rates of TNT or HMX (hypothesis 1) or the ETPE was considered to retard the dissolution of both compounds by limiting the access of water to the explosives (hypothesis 2). Hypothesis 1 led to equations similar to those described in model 3 [17] except that the input parameters should be the ones specific to GIM instead of octol (see Table 3 for the definition of these parameters). According to hypothesis 2, the boundary layer film thicknesses for HMX and TNT should be reexpressed as follows:

$$h_{\text{HMX}} = h_{\text{HMX}} + r_{\text{ETPE}} - r_{\text{HMX}} = h_{\text{HMX}} + r_{\text{ETPE}}^0 - r_{\text{HMX}} \quad (3)$$

$$h_{\text{TNT}} = h_{\text{TNT}} + r_{\text{ETPE}} - r_{\text{TNT}} = h_{\text{TNT}} + r_{\text{ETPE}}^0 - r_{\text{TNT}} \quad (4)$$

Integration of Eq. (2) after replacing  $h_i$  by the respective above expressions gives the following equations:

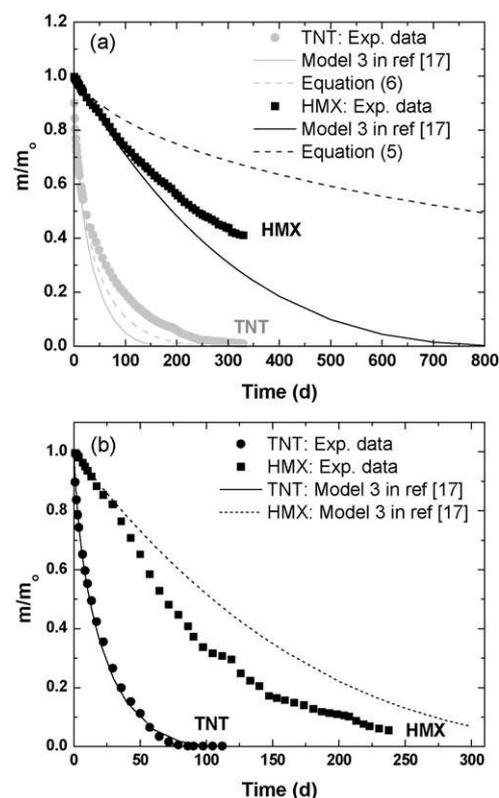
$$r_{\text{HMX}} = h_{\text{HMX}} + r_{\text{ETPE}}^0 - \sqrt{2 \left( \frac{D_{\text{HMX}} C_{\text{HMX}}^s}{X_{\text{HMX}} \rho} \right) t + h_{\text{HMX}}^2} \quad (5)$$

$$r_{\text{TNT}} = h_{\text{TNT}} + r_{\text{ETPE}}^0 - \sqrt{2 \left( \frac{D_{\text{TNT}} C_{\text{TNT}}^s}{X_{\text{TNT}} \rho} \right) t + h_{\text{TNT}}^2} \quad (6)$$

The persistence of TNT and HMX in the GIM or octol particles was modeled using the parameters summarized in Table 3.

In the GIM particle (115 mg), predictions that did not take into account retardation by ETPE led to theoretical persistence times shorter than the ones obtained experimentally (Fig. 6a). The retardation of TNT dissolution by HMX was thus not sufficient to mimic the actual dissolutions of explosives in GIM. In fact both TNT and HMX dissolution were retarded by an additional factor. Taking into account the retardation by the remaining ETPE according to Eqs. (5) and (6) led to overestimated retardation for HMX and was not sufficient to reproduce the retardation of TNT dissolution. Model 3 was thus not appropriate to fit the dissolution of GIM. A possible explanation for the poor modeling obtained with GIM is that the present model is based on the assumption that all components are initially distributed homogeneously in the spherical particle to dissolve. However, ETPE is not fully homogeneously distributed in GIM as shown by the rigid net and empty channels left after the loss of explosives (see Fig. 5c). Another source of error may result from the shrinkage of the particle. Indeed, while Eqs. (5) and (6) assume a constant radius for the insoluble ETPE, the experiment showed a reduction in particle size throughout the dissolution process. Needless to say that this shrinkage has likely led to modified mass fractions in the particle whereas those are presumed constant in the model.

In contrast, model 3 gave much more satisfying results for the prediction of octol dissolution (Fig. 6b). TNT dissolution was very well predicted using this model. As for HMX, its dissolution was well predicted during the first 30 days of the experiment but as soon as the particle broke apart dissolution occurred faster than



**Fig. 6.** Persistence of TNT and HMX from (a) a GIM particle (115 mg) subjected to a constant flow of water (0.5 mL min<sup>-1</sup>) and (b) an octol particle (70.0 mg).

what was predicted which can be easily explained by the increase of contact surface.

Finally, it is worthwhile noting that in agreement with the governance of dissolution by the slowly dissolving compounds, HMX dissolution rate had a strong effect on the predictions of dissolution of GIM and octol, whereas that of TNT had much less impact. The determination of HMX dissolution rate under environmental conditions will thus be a major step in predicting the dissolution of formulations containing significant amounts of this nitramine.

#### 4. Conclusion

The dissolution of GIM in water was measured and compared to that of octol. GIM appeared to solubilize more regularly and more slowly than octol. Indeed the presence of the energetic binder ETPE in GIM had two effects: it prevented particles from collapsing and it retarded the dissolution of both TNT and HMX by limiting their exposure to water. In GIM like in octol, the dissolution rate of solid particles was governed by the compound(s) that dissolved at a slower pace, *i.e.* HMX in octol and HMX and ETPE in GIM. A model proposed by Lynch et al. [17] based on Fick's diffusion law

and on the retardation of the faster dissolving compound by the slower dissolving one allowed predicting well the dissolution data of octol. The same model with or without an additional contribution from ETPE was less appropriate to fit the data of GIM, likely due to a physical transformation and rearrangement of the remaining solid. Despite the non-fully satisfactory predictions obtained for GIM, the present findings demonstrate that ETPE decreases the risks of explosives leakage from solid explosive particles. It should also help maintaining non-exploded particles intact in the field hence facilitating their physical removal by site managers.

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