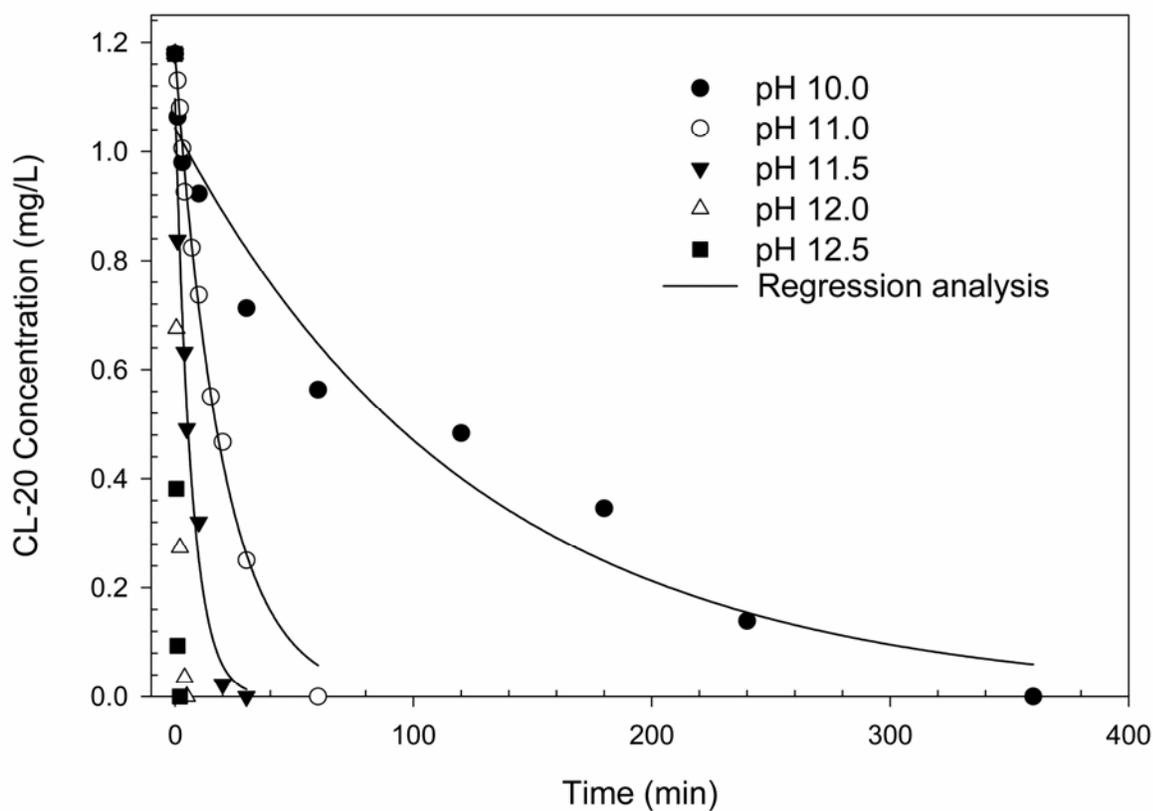Environmental Laboratory

US Army Corps
of Engineers ®
Engineer Research and
Development Center

Environmental Quality Technology Program

Chemical Remediation of an Ordnance-Related Compound: The Alkaline Hydrolysis of CL-20

Lara Santiago, Deborah R. Felt, and Jeffrey L. Davis   September 2007

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Final report

Abstract: Hexanitrohexaazaisowurtzitane (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.05,9.03,11] dodecane) or CL-20 has attracted attention as a possible replacement for, or inclusion in, military and space propellants and explosives. CL-20 is a polycyclic nitramine with a higher crystal density, a higher heat of formation, and a better oxidizer-to-fuel ratio than conventional nitramines used in propellants. The effective life cycle management of CL-20 requires development of knowledge and technologies related to the consequences and attributes of CL-20 that may be introduced into the environment. This research assessed the feasibility of using alkaline hydrolysis to treat water contaminated with CL-20. Two concentrations of the explosive were tested at pH values ranging from 10.0 to 13.0. Samples were taken from the batch reactor, quenched, and neutralized. One subsample was extracted and analyzed for explosives concentration using HPLC, and a second subsample was analyzed for anion content by IC. Alkaline hydrolysis proved to be an effective technique to degrade CL-20, as CL-20 was completely removed from aqueous solutions at all the pH levels evaluated. The reaction kinetics showed a strong dependence on the hydroxide ion concentration. Formate was indicated as an end product of the reaction.

Contents

Figures and Tables

Figures

Tables

Preface

Unit Conversion Factors

Multiply	By	To Obtain
degrees Fahrenheit	(F-32)/1.8	degrees Celsius
feet	0.3048	meters
inches	0.0254	meters
microns	1.0 E-06	meters
ounces (mass)	0.02834952	kilograms
ounces (U.S. fluid)	2.957353 E-05	cubic meters
pounds (mass)	0.45359237	kilograms
pounds (mass) per cubic foot	16.01846	kilograms per cubic meter
pounds (mass) per cubic inch	2.757990 E+04	kilograms per cubic meter
pounds (mass) per square foot	4.882428	kilograms per square meter
pounds (mass) per square yard	0.542492	kilograms per square meter
quarts (U.S. liquid)	9.463529 E-04	cubic meters
square yards	0.8361274	square meters
yards	0.9144	meters

1   Introduction

Chemical and physical properties of CL-20

Several new nitramine compounds have attracted attention as possible replacements for, or inclusion in, military and space propellants and explosives. CL-20, hexanitrohexaazaisowurtzitane (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.05,9.03,11] dodecane), is one of these compounds. A common synonym for CL-20 is hexanitrohexaazaisowurtzitane (HNIW). The chemical structure of CL-20 and the related nitramines RDX and HMX is shown in Figure 1.
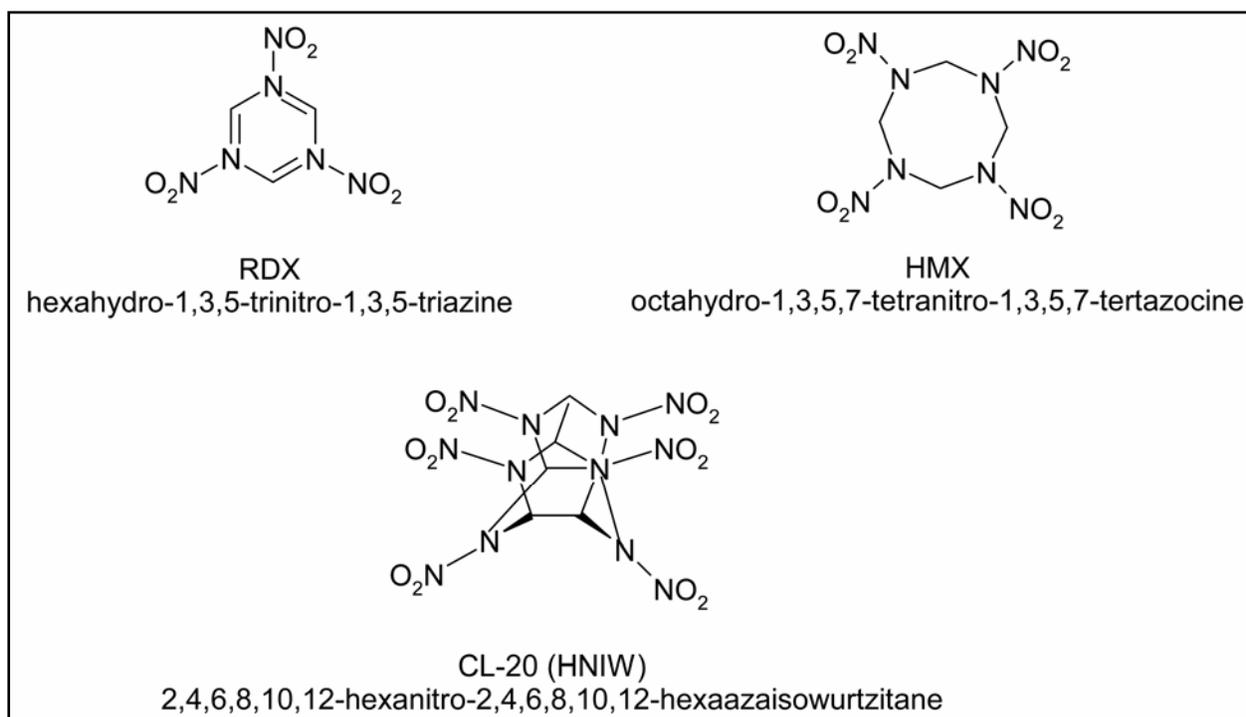
Figure 1. Structure of CL-20 and related nitramines, RDX and HMX.

The synthesis of CL-20 was reported in 1986 and patented by A. Neilsen in 1990 (Chung et al. 2000). CL-20 is referred to as a cage compound because it resembles two RDX rings joined at several carbon atoms (Larson et al. 2001). CL-20 is a polycyclic nitramine with a higher crystal density, a higher heat of formation, and a better oxidizer-to-fuel ratio than conventional HMX or RDX solids used in propellants. Because of CL-20's high chemical energy and its moderate sensitivity, propellants and explosives using CL-20 deliver superior performance over conventional

high-energy propellants and explosives. Potential applications for CL-20 include boost propulsion for military or space vehicles and as minimum signature propellants (Oehrle 1994). Propellants and explosives formulations using CL-20 are expected to have better performance in terms of specific impulse, burn rate, ballistics, and improved detonation velocity compared to RDX and HMX.

In addition to improved performance, CL-20 meets stringent munitions sensitivity requirements. The new CL-20 propellant exhaust is free of lead, acid, and aluminum oxide emissions (Chan and Boggs 2004). Because CL-20 contains no halogens, its combustion products are more environmentally friendly than those derived from the combustion of propellants made with ammonium perchlorate.

The physical and chemical properties of CL-20 have been studied by several research teams and compared to those of RDX and HMX (Karakaya et al. 2005; Monteil-Rivera et al. 2004; Stevens Institute of Technology 2003). The aqueous solubility of CL-20 is very low but increases with increasing temperature. At 25 °C, the solubility has been reported as 3.6 mg/L (Monteil-Rivera et al. 2004), 4.8 mg/L (Stevens Institute of Technology 2003), and 4.3 mg/L (Karakaya et al. 2005). The octanol-water partitioning coefficient, K_{ow} has been reported as 1.92, which implies a greater binding to organic matter than is seen with RDX and HMX. The observed decomposition products included nitrite (NO_2^-), nitrous oxide (N_2O), and formate ($HCOO^-$). Monteil-Rivera et al. (2004) concluded from these measurements that CL-20 would be less persistent in the environment than either RDX or HMX.

Environmental impacts

The production of CL-20 at the industrial level has increased significantly because of the extensive interest in the compound. Studies on the environmental impact of CL-20 are scarce. Trott et al. (2003) and Bhushan et al. (2003) examined the potential for biodegradation of CL-20 in soil. They both reported the existence of aerobic and anaerobic decomposition pathways. Trott et al. (2003) used laboratory-scale unamended soil microcosms and determined that CL-20 degraded in all active soils but was not completely removed; they also reported the existence of a transient metabolite. Bhushan et al. (2003) alternated cycles of aerobic and anaerobic growth conditions to achieve complete removal of

the CL-20; they isolated a bacterial strain that was able to degrade CL-20 using it as the sole nitrogen source with the observed end products of degradation being nitrite, nitrous oxide, and formate. Bhushan et al. (2003) postulated a decomposition pathway that involved an initial denitration reaction which, in RDX and HMX, leads to ring cleavage and breakdown of the rings into smaller compounds. Hawari et al. (2004) studied the possible photodegradation of CL-20 in solution and reported final products of nitrite, nitrate, formate, nitrogen, and nitrous oxide. The authors suggested the following two pathways of decomposition: a sequential breakage of the N-NO$_2$ bonds and an initial denitration followed by hydrolytic ring cleavage and spontaneous decomposition to the final products as suggested by Bhushan et al. (2003).

On the basis of evidence of RDX and HMX toxicity and possible carcinogenicity, and the structural similarity of these compounds to CL-20, it was early postulated that CL-20 has similar effects (Trott et al. 2003). The preliminary research presented by the Stevens Institute of Technology (2003) suggested that there was no short-term toxicity to soil microorganisms and this was supported by the soil microcosm evaluations of Bhushan et al. (2003) and Trott et al. (2003) and the study of Monteil-Rivera et al. (2004). However, this evaluation is contradicted by Robidoux et al. (2004) and Gong et al. (2004). Robidoux et al. (2004) established that CL-20 is toxic to earthworms. Gong et al. (2004) performed an ecotoxicological screening and found that CL-20 was toxic in various environmental situations. Strigul et al. (2006) reported evidence of plant uptake, which would provide a means for CL-20 to enter the food chain. The carcinogenicity of CL-20 has not been established nor have exposure guidelines been set. The effective life-cycle management of CL-20 requires development of knowledge and technologies related to the consequences and attributes of CL-20 that may be introduced into the environment.

Alkaline hydrolysis

Alkaline hydrolysis uses E2-elimination as a destruction mechanism. E2-elimination follows a second-order rate law. Alkaline hydrolysis is known to degrade nitroaromatics and nitramines in solution (Balakrishnan et al. 2003). Nitroaromatics are subject to nucleophilic attack by hydroxide ions. Hydrolysis of compounds containing nitro groups leads to the formation of nitrite and nitrate ions. Nitro groups are electron withdrawing and, therefore, extract the electron-rich oxygen atom in the hydroxide ion. This typically results in substitution of the remaining

hydrogen atom (from the hydroxide ion) onto the original contaminant molecule thus replacing the nitro group (Garg et al. 1991).

From previous studies of the alkaline hydrolysis of HMX and RDX, it was suggested that alkaline hydrolysis of these two explosives follows the E2-mechanism (Heilmann et al. 1996). Research performed on RDX indicates that its degradation in alkaline media was initiated by a single denitration step, which then hydrolyzed further, leading to rapid ring cleavage and decomposition (Hoffsommer et al. 1977). Studies in alkaline hydrolysis of RDX and HMX indicated that both compounds are susceptible to degradation by alkaline attack (Heilmann et al. 1996). If the base also shows nucleophilic character, it is accompanied by a nucleophilic substitution at an electron-poor carbon atom, which occurs in RDX's heterocyclic system when it is destroyed by alkaline hydrolysis (Wu 2001).

Balakrishnan et al. (2003) examined the degradation intermediates and end products produced by base hydrolysis of RDX and HMX. They confirmed that the initial step in alkaline hydrolysis is denitration of the ring, causing ring cleavage and subsequently decomposition. Both compounds formed nitrite, nitrous oxide, nitrogen, ammonia, formaldehyde, formic acid, and carbon dioxide. Balakrishnan et al. (2004) in a study of the effect of zero-valent iron on the decomposition of CL-20 found the same breakdown pathways being used. The conclusion is that the end products of the decomposition of CL-20 are the same (nitrite, nitrate, and formate) regardless of whether the means of that decomposition is biological or chemical.

Karakaya et al. (2005) examined the kinetics of the alkaline hydroxide reaction over a range of CL-20 concentrations that bracketed its upper and lower solubility limits. The NaOH concentration ranged from 0.25 to 300 mM. Two concentrations of CL-20 were used in this study, 3 mg/L and 500 mg/L. The concentration-time profiles suggest temperature-dependent, second-order reaction kinetics. The rate is reported to be significantly faster than that of RDX.

2   Objectives and Experimental Design

Objectives

The objectives of this research are as follows:

- Assess the feasibility of using alkaline hydrolysis to treat water contaminated with the explosive chemical CL-20.
- Study the kinetics of the alkaline hydrolysis reaction.
- Characterize possible by-products of the alkaline degradation reaction.

Experimental design

The kinetics of the alkaline hydrolysis opf CL-20 was examined using batch reactors. Two concentrations of the explosive were tested at pH values ranging from 10.0 to 13.0. Samples were taken from the batch reactor, quenched and neutralized, and divided. One portion of the sample was extracted using SW 846, Method 8330 (U.S. Environmental Protection Agency (USEPA) 1994) and analyzed by high-performance liquid chromatography (HPLC). The second portion of the sample was analyzed for anion content by ion chromatography (IC).

The first experiment examined CL-20 degradation at pH 12.0, 12.5, and 13.0. Samples were taken at 1, 5, 10, 20 and 30 min and 1, 2, 4, 8, and 24 hr until degradation was complete. The second experiment examined CL-20 degradation at pH 10.0, 10.5, 11.0, 11.5, 12.0, 12.3, and 12.5. Samples were taken at 30 seconds, 1, 2, 3, 4, 5, and 6 min until degradation was complete.

3 Material and Methods

Chemicals

Hexanitrohexaazaisowurtzitane (CL-20) was obtained from China Lake Weapons Division. The calibration standards for CL-20 were prepared by dissolving CL-20 crystals in distilled, deionized water (DDI) followed by filtration. Each batch of stock solution was analyzed prior to use. Unused stock was stored in the dark at 4 °C. The two initial CL-20 stock solutions had concentrations of 1.18 and 1.69 mg/L.

Alkaline solutions were prepared dissolving a few drops of 10 M sodium hydroxide (NaOH) in 50 mL of DDI water until the desired pH value was reached. Reagent grade NaOH, hydrochloric acid (HCl), and sulfuric acid (H_2SO_4) were purchased from Fisher Scientific. Acetonitrile (HPLC grade) was obtained from Sigma-Aldrich. DDI (> 18.1 mΩ) was prepared with a Barnstead-Thermolyne still.

Alkaline hydrolysis batch reactors

The reactor assembly is shown in Figure 2. The controller for the titration reactor was purchased from Systematics, Inc. (Bristol, RI), model 960-0150. The acid/base pumps (model DL-PK) are from the Barnant Company (Barrington, IL).

Previously prepared alkaline solution, half of the required total volume, was added to each reaction vessel, set on a magnetic stir plate, and a pH electrode immersed in the solution. A pH controller connected to the electrode was set to the desired reaction pH level and upper and lower pH limits were set within ± 0.2 pH unit of that level. Pumps connected to the controller maintained the desired reaction pH by adding an acidic solution (0.2 N H_2SO_4) when the upper pH limit was exceeded or a basic solution (5.0 N NaOH) when the reaction mixture measured less than the lower pH limit. An equal volume of the CL-20, prepared in distilled, deionized water, was added when the pH was stable. During an actual experiment, the beaker with the explosive was wrapped in aluminum foil to inhibit photodegradation of the CL-20. The reactions were run at room temperature (25 ± 1 °C).
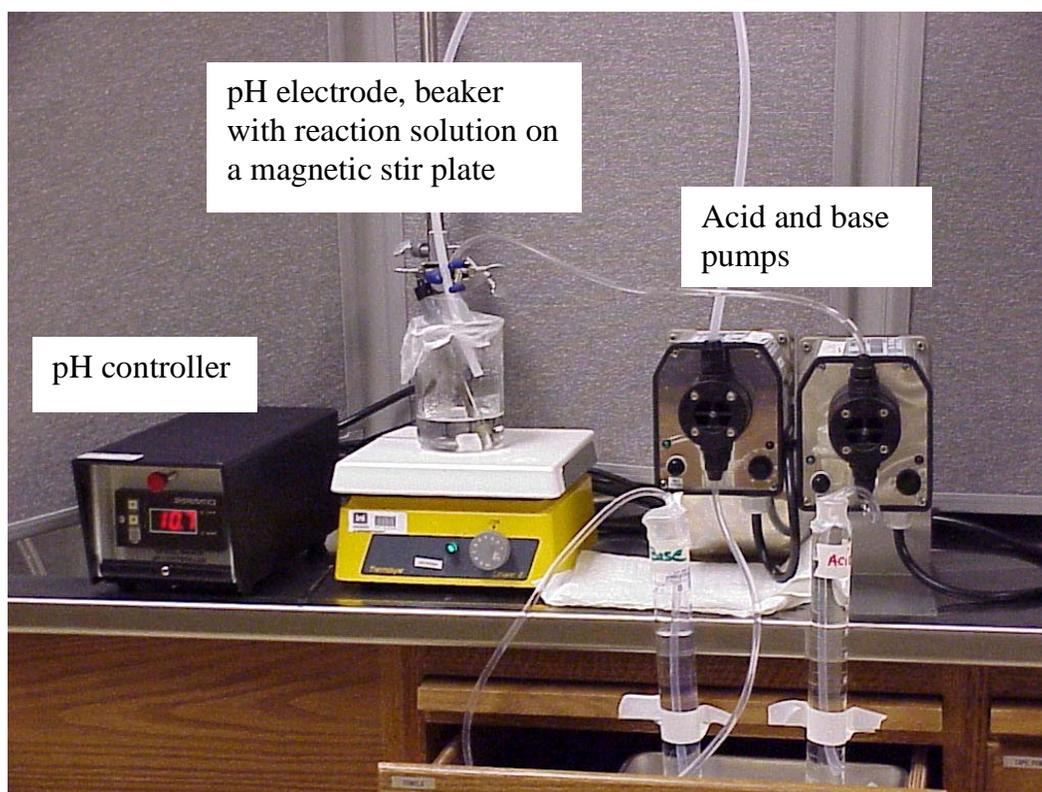
Figure 2. The batch reactor assembly used to track the alkaline hydrolysis of CL-20.

For the initial runs at pH 12.0, 12.5, and 13.0, reaction mixtures were monitored by taking 1-mL aliquots out of the batch reactor at the predetermined times and placing each sample in a 20-mL scintillation vial. These samples were quenched immediately with 1 mL of 0.02 N H_2SO_4 to halt the reaction. The samples were neutralized to pH 6-8 using 0.2 N H_2SO_4 and 1.0 N NaOH. The second set of experiments required that the samples be taken at very short time intervals. Consequently they were quenched using 1 mL of 0.2 N H_2SO_4, instead of 0.02 N H_2SO_4 as before.

Representative, duplicate subsamples of 670 µL were transferred to ion chromatography vials. The remainder of the sample in the scintillation vial was extracted with acetonitrile (1:1) according to SW846 US EPA Method 8330 (1994) for HPLC analysis.

Explosive analysis

HPLC was used to evaluate CL-20 degradation over time at the selected pH values using a DIONEX Summit HPLC. The HPLC consists of a DIONEX P580 pump, a DIONEX ASI-100 auto-sampler injector and a

DIONEX UVD 340U UV/VIS detector monitored at 254 nm. Chemical separation was achieved using a C-18 column at 24 °C. The mobile phase was a mixture of 50% methanol - 50% water (v/v) at a flow rate of 1.0 mL/min. Chromeleon 6.40 chromatography software was used for data analysis.

The pH values analyzed in the first set of experiments were 12.0, 12.5, and 13.0. After the alkaline hydrolysis reaction started, 1-mL aliquots were taken at 1 min, 5 min, 10 min, 20 min, 30 min, 1 hr, 2 hr, 4 hr, 8 hr, 1 day, 2 days, 3 days, and so on until the HPLC measurements confirmed that the explosive was completely degraded. These monitoring times were chosen arbitrarily because the expectation was that the reaction would take more than 1 day to be completed. The decomposition rate of the CL-20 was much faster than expected, necessitating a second alkaline hydrolysis experiment using shorter time intervals. This second experiment was performed at pH values of 10.0, 10.5, 11.0, 11.5, 12.0, 12.3, and 12.5. After the alkaline hydrolysis reaction started, 1-mL aliquots were withdrawn at 30 sec, 1 min, 2 min, 3 min, 4 min, 5 min, 6 min, and so on until the HPLC measurements confirmed that the explosive was completely removed. Because it is a very fast reaction the use of metering pumps was not necessary to maintain the desired pH.

Ion chromatography

Ion chromatography was used for analysis of the alkaline hydrolysis transformation products. Anion analysis was performed using a Dionex ICS-2500 ion chromatograph equipped with a DIONEX ASRS-ULTRA 4 mm column. Chemical separation and detection was achieved using an IONPAC AS11 guard column (4 mm X 50 mm), an AS11 analytical column (4 mm X 250 mm), and DIONEX CD20 conductivity detector (1.25 µL internal volume). The gradient elution was conducted with 100 mM NaOH, water and 5 mM NaOH at 1.5 mL/min by a DIONEX GP40 gradient pump. Samples (670 µL) were automatically injected by a DIONEX automated sampler. The instrument was calibrated using standard anionic solutions. Each sample was analyzed for nitrite (NO_2^-), nitrate (NO_3^-), formate ($HCOO^-$), acetate (CH_3COO^-), citrate ($C_6H_5O_7^{-3}$), and oxalate ($C_2O_4^{-2}$) ions from the active treatment, and sulfate (SO_4^{-2}) ion from the controls.

4 Results and Discussion

Kinetics

CL-20 concentration 1.18 mg/L

Figure 3 presents the concentration profiles obtained at the different pH values for the runs with an initial CL-20 concentration of 1.18 mg/L. The average HPLC measurements of the duplicate samples were used. Table 1 presents the CL-20 pseudo-first-order rate constant (k) values and the correlation coefficients for the runs presented on Figure 3. The decomposition of CL-20 at pH 12.0 and 12.5 proceeded so quickly that regression analysis could not be performed on the data. The experiment was repeated at these higher pH values, sampling the batch reactors at more frequent time intervals.
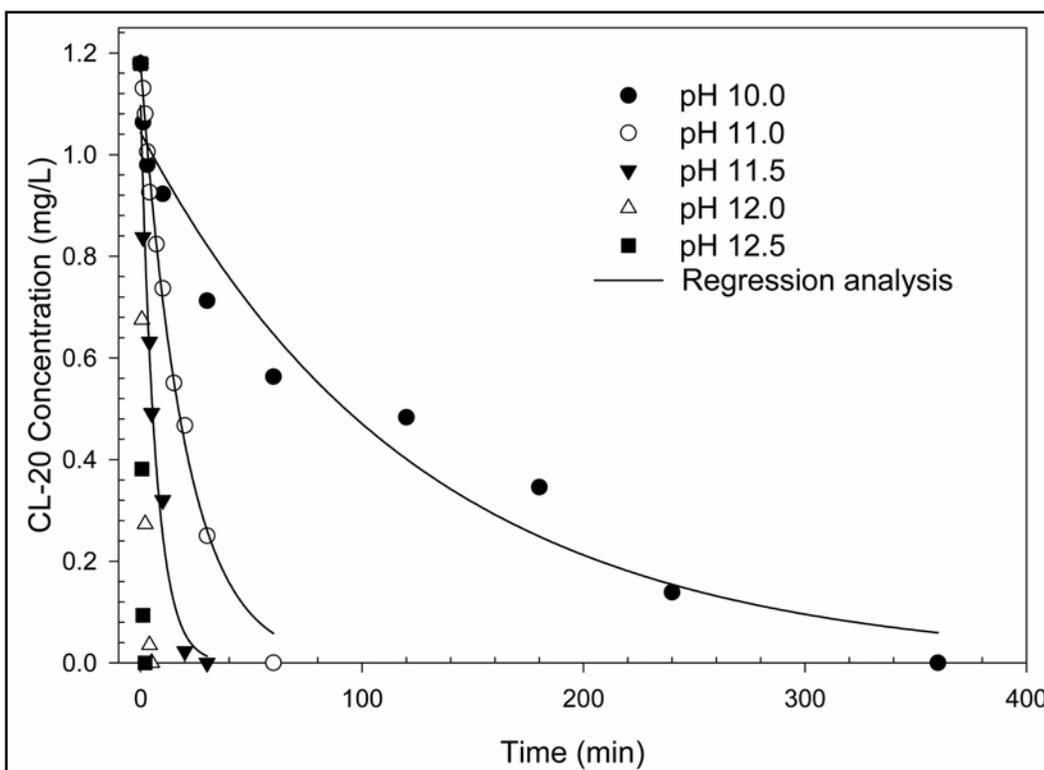
Figure 3. CL-20 concentration profiles at different pH values at an initial concentration of 1.18 mg/L.

Table 1. CL-20 reaction rate constant (*k*) at different pH values at an initial CL-20 concentration of 1.18 mg/L.

pH	*k* (min^{-1})	R^2
10.0	0.00797	0.958
11.0	0.0503	0.995
11.5	0.1477	0.976
12.0	0.8580	0.989
12.5	2.338	0.999

CL-20 concentration 1.69 mg/L

Figure 4 presents the concentration profiles with the initial CL-20 concentration of 1.69 mg/L. Table 2 shows the pseudo-first-order rate values and the correlation coefficients for the runs presented on Figure 4. The results presented on Tables 1 and 2 suggest that as the pH increases, the rate constant also increases.
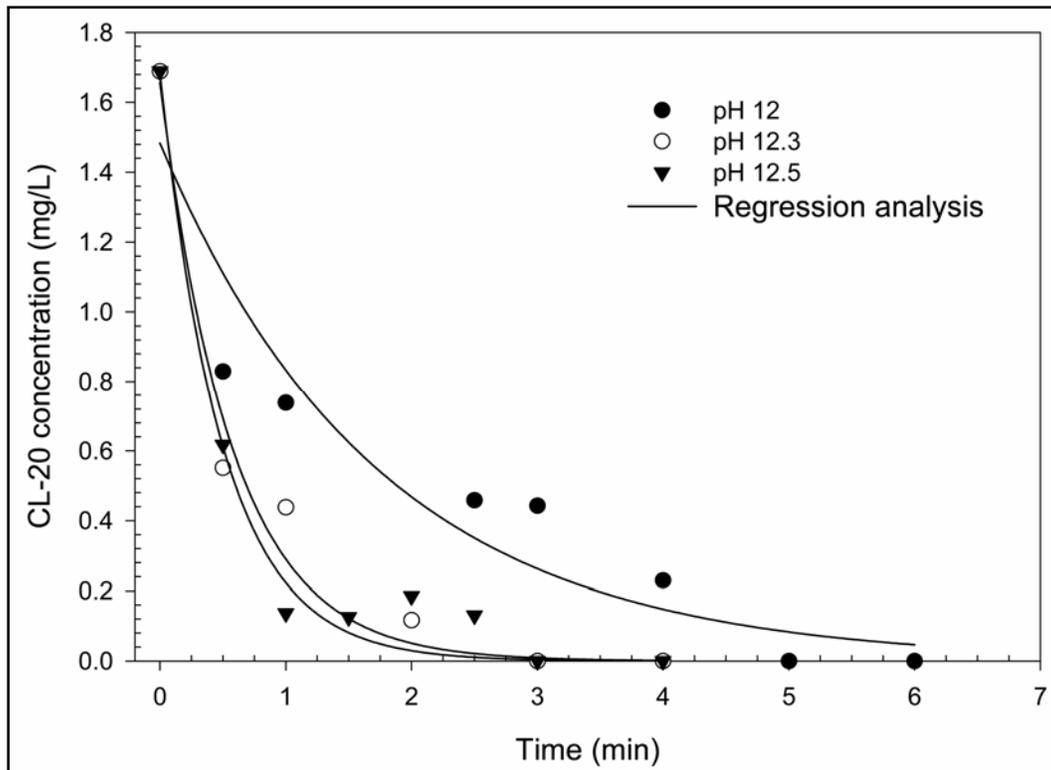
Figure 4. CL-20 concentration profiles at different pH valuesat an initial concentration of 1.69 mg/L.

Table 2. CL-20 reaction rate constant (k) at different pH values at an initial CL-20 concentration of 1.69 mg/L.

pH	k (min⁻¹)	R²
12.0	0.5768	0.911
12.3	1.7426	0.977
12.5	2.0222	0.979

As mentioned previously, the pseudo-first order rate constant (k) apparently is a function of the pH and, therefore, of the hydroxyl ion concentration, [OH⁻]. The hydroxyl ion concentration was calculated using the following formula:

$$[OH^-] = 10^{pH-14} \qquad (1)$$

Figure 5 illustrates the relationship between k and [OH-] using the data from Tables 1 and 2 and performing a linear regression analysis.
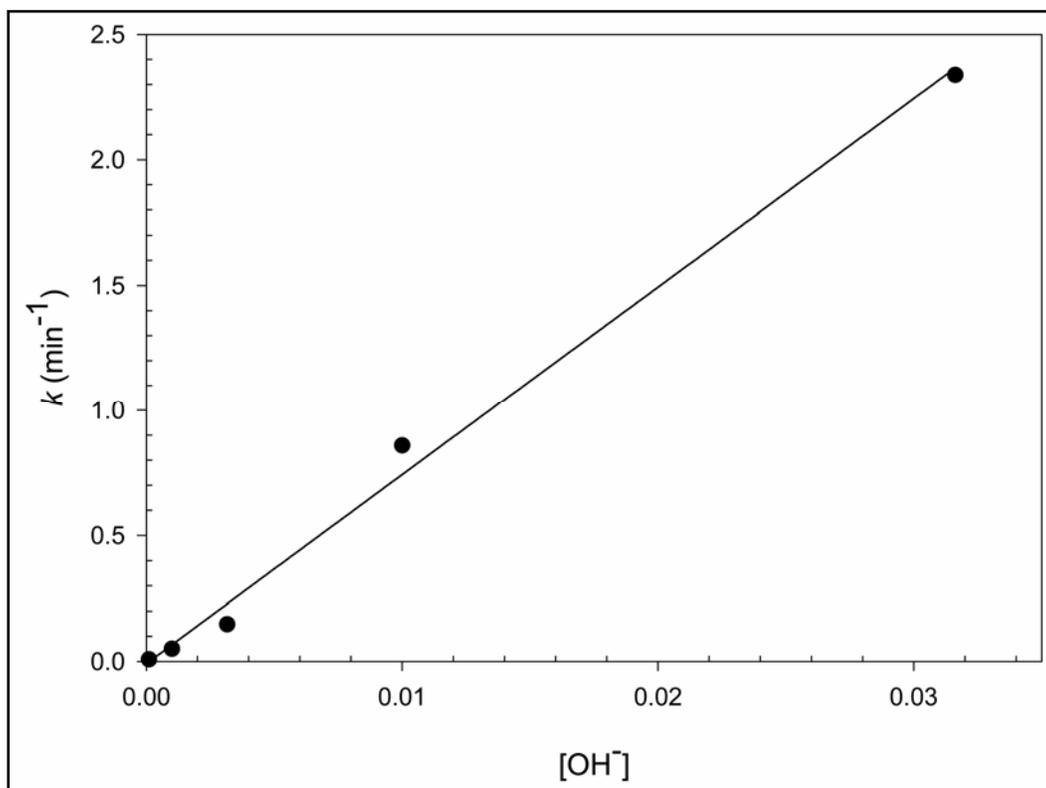
Figure 5. Linear regression of reaction rate, k, versus hydroxyl ion concentration, [OH-].

A hyperbolic equation to describe how the values of rate constant (k) increase with the increase of the reaction [OH⁻] was suggested.

$$k = \frac{k_{max}[OH^-]}{K_{OH^-} + [OH^-]}$$
$$k\,max = 20.65\,min^{-1} \tag{2}$$
$$K_{OH^-} = 0.2471[M]$$
$$R^2 = 0.9957$$

A slight increase of the R^2 value was observed; however, the difference is not significant enough to justify the hyperbolic model.

Reaction by-products

Ion chromatography was performed on the samples in order to detect possible by-products of the CL-20 alkaline hydrolysis (Tables 3 to 9). The analyzed ions were acetate (CH_3COO^-), formate ($HCOO^-$), chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), carbonate (CO_3^{-2}), and sulfate (SO_4^{-2}). Sulfate ion is not a possible by-product of the alkaline hydrolysis, but it was included because sulfuric acid (H_2SO_4) was used to quench the samples. Although the chloride ion was not present in the water or CL-20, the chloride ion was included in the analysis because some samples were quenched with HCl.

A qualitative analysis of the IC results of alkaline hydrolysis at pH 11.0 (Table 5) suggested that possible by-products of the CL-20 degradation included acetate, formate, nitrite, nitrate, and carbonate. The CL-20 had completely degraded after 1 hr at pH 11.0. As seen in Table 5, the product concentrations did not remain constant throughout the reaction. This result suggests that although the parent compound, CL-20, transforms quickly, the overall reaction takes some time to go to completion.

Table 3. IC analysis (mg/L) of products of alkaline hydrolysis of CL-20 at pH 10.0.

Sample Time	Acetate	Formate	Nitrite	Nitrate	Carbonate
24 hr	19.71	1.72	nd	0.27	74.05
48 hr	5.78	0.80	nd	0.36	69.15
72 hr	14.10	0.99	nd	0.37	69.40
nd = non-detect.					

Table 4. IC analysis (mg/L) of products of alkaline hydrolysis of CL-20 at pH 10.5.

Sample Time	Acetate	Formate	Nitrite	Nitrate	Carbonate
3 hr	32.43	4.32	2.27	2.32	100.26
4 hr	4.73	0.51	nd	0.37	76.80
6 hr	5.43	0.67	nd	0.35	81.35
8 hr	8.27	1.35	nd.	0.25	72.08
24 hr	10.30	1.65	nd	0.40	72.53
48 hr	4.09	0.65	0.33	0.33	78.10
72 hr	7.47	1.17	0.49	0.44	72.09
nd = non-detect					

Table 5. IC analysis (mg/L) of products of alkaline hydrolysis of CL-20 at pH 11.0.

Sample Time	Acetate	Formate	Nitrite	Nitrate	Carbonate
1 hr	21.69	2.81	1.09	1.18	72.29
2 hr	6.32	0.63	nd	0.37	77.30
3 hr	8.99	1.10	nd.	0.37	66.92
4 hr	9.55	1.19	nd	0.28	66.89
6 hr	4.88	0.66	nd.	0.54	72.91
8 hr	5.25	0.77	nd	0.38	72.54
24 hr	5.11	0.74	nd	0.31	68.76
48 hr	5.95	0.86	nd	0.44	68.28
72 hr	5.93	0.94	nd	0.38	67.89
nd = non-detect					

Table 6. IC analysis (mg/L) of products of alkaline hydrolysis of CL-20 at pH 11.5.

Sample Time	Acetate	Formate	Nitrite	Nitrate	Carbonate
1 hr	12.35	2.02	nd	0.45	246.25
2 hr	18.26	2.84	0.97	0.80	72.97
3 hr	8.84	1.26	nd	0.35	72.75
4 hr	13.19	3.00	nd	0.48	77.18
6 hr	11.93	1.52	nd	0.37	71.44
8 hr	11.90	2.07	nd	0.39	71.84
24 hr	13.15	2.33	0.25	0.94	70.39
48 hr	16.28	2.72	0.19	1.01	70.32
72 hr	22.61	2.06	nd	1.39	80.11
96 hr	14.82	2.41	nd	1.77	71.53
nd = non-detect					

Table 7. IC analysis (mg/L) of products of alkaline hydrolysis of CL-20 at pH 12.0.

Sample time	Acetate	Formate	Nitrite	Nitrate	Carbonate
0.5 hr	13.24	2.86	nd	0.37	80.50
1 hr	11.24	1.05	nd	0.33	70.28
2 hr	21.68	3.37	0.93	1.33	80.10
3 hr	13.33	2.13	nd	0.38	71.71
4 hr	14.13	1.68	nd	0.34	73.81
6 hr	10.45	2.23	nd	0.44	68.40
8 hr	12.88	1.62	nd	0.29	70.23
25 hr	17.17	1.54	nd	0.57	64.73
48 hr	21.53	3.70	nd	0.47	63.14
72 hr	18.66	1.61	nd.	0.50	62.21
96 hr	nd	3.89	0.76	0.34	54.99
120 hr	12.07	2.95	4.40	0.32	nd
144 hr	34.79	5.27	1.99	0.77	nd
nd = non-detect					

Table 8. IC analysis (mg/L) of products of alkaline hydrolysis of CL-20 at pH 12.5.

Sample Time	Acetate	Formate	Nitrite	Nitrate	Carbonate
0.5 min	9.32	0.47	nd	0.23	173.15
1 min	14.31	0.78	nd	0.29	86.86
2 min	16.19	1.20	nd	0.31	89.32
3 min	13.03	0.78	nd	0.24	90.20
4 min	12.68	0.77	nd	0.30	80.74
5 min	32.30	4.31	7.54	2.46	83.45
6 min	n.a.	0.78	nd	0.35	76.94
7 min	4.35	0.89	nd	0.34	76.63
8 min	nd.	0.82	nd	0.31	76.23
9 min	14.24	0.63	nd	0.61	74.50
10 min	14.40	0.61	nd	0.19	70.62
20 min	10.83	0.47	nd	0.24	65.20
30 min	13.74	1.86	0.49	0.78	75.15
1 hr	15.54	2.59	nd	0.41	70.40
2 hr	12.68	1.63	nd	0.52	73.16
3 hr	10.02	1.50	0.19	0.86	67.87
4 hr	16.47	1.75	5.27	0.84	71.56
6 hr	16.42	1.70	nd	0.41	71.50
8 hr	8.53	2.22	nd	0.47	73.73
24 hr	14.27	1.62	0.73	0.29	63.22
48 hr	15.99	3.65	2.11	0.69	63.73

Sample Time	Acetate	Formate	Nitrite	Nitrate	Carbonate
72 hr	19.40	3.65	2.11	0.94	nd
96 hr	27.75	5.23	3.88	0.97	nd
120 hr	2.59	3.50	2.83	1.17	nd
144 hr	3.90	2.17	4.58	1.87	Nd
nd = non-detect					

Table 9. IC analysis (mg/L) of products of alkaline hydrolysis of CL-20 at pH 13.0.

Sample Time	Acetate	Formate	Nitrite	Nitrate	Carbonate
6 min	29.60	3.53	1.64	2.14	122.97
7 min	nd	0.38	nd	0.52	105.39
8 min	nd	0.32	nd	0.44	97.10
9 min	3.51	0.33	nd	0.40	83.36
10 min	nd	0.28	nd	0.44	87.66
20 min	3.16	1.11	nd	0.61	87.55
30 min	4.15	0.44	nd	0.45	129.55
1 hr	nd	0.41	nd	0.34	82.48
2 hr	6.48	0.65	0.62	0.82	77.20
3 hr	4.28	0.33	nd	0.42	80.67
4 hr	nd	1.47	0.29	0.70	78.84
6 hr	nd	0.37	nd	0.62	73.95
8 hr	nd	0.42	0.75	0.50	76.82
24 hr	nd	0.33	nd	0.65	76.89
48 hr	nd	0.38	nd	1.04	74.77
72 hr	nd	nd	nd	0.40	70.38
96 hr	nd	nd	0.89	0.28	nd
120 hr	nd	0.45	1.85	0.84	nd
nd = non-detect					

Acetate, formate, nitrate, and carbonate were found in almost every sample. Nitrite was found in very low concentrations at 1 hr for the pH 11.0 sample, as shown in Table 5, but it was not detected at later sampling times. This suggests that nitrite could be an intermediate product, although nitrite is generally very transient under most environmental conditions. Acetate was detected in all samples as shown in Tables 3 to 9. Therefore, acetate could either be an intermediate or final product of the alkaline hydrolysis of CL-20.

Heilmann et al. (1996) found that the alkaline hydrolysis of RDX yields nitrite, formate, acetate, formaldehyde, ammonia, nitrous oxide, and nitrogen. Similar by-products are expected for CL-20 because of its structural similarity with RDX. There is strong evidence that the initial denitration of cyclic nitramines in water is sufficient to cause ring cleavage followed by spontaneous decomposition to form the final products nitrous oxide, ammonia, and formate as end products of CL-20 degradation (Balakrishnan, et al., 2003). Balakrishnan et al. (2004) reported the presence of the toxic compound glyoxal as one of the end products of CL-20 degradation by zero-valent iron, in addition to the nitrogen compounds.

5   Conclusions

Alkaline hydrolysis can be a very effective technique to degrade CL-20; CL-20 was completely removed from aqueous solutions at all the pH values evaluated. CL-20 alkaline hydrolysis kinetics showed a strong dependence on the hydroxide concentration. It can be concluded from the experimental data presented in this report that the CL-20 degradation reaction kinetics can be accurately described by a pseudo-first order rate equation. A value of 0.858 min^{-1} was determined for the rate constant at the experimental temperature of 25 ºC at pH 12.0. For comparison, Emmrich (1999) reported a value of 0.361 hr^{-1}, that is 0.006 min^{-1} for the alkaline hydrolysis of TNT at 25 ºC with a pH of 12.0. Evidently, CL-20 degrades much faster during alkaline hydrolysis than TNT. Balakrishnan et al. (2003) reported that CL-20 decomposition was faster then RDX and HMX decomposition when subjected to hydrolyzing conditions. This is probably due to the complexity of the chemical structure of CL-20, which may make the CL-20 molecule more susceptible to attack by the hydroxyl ion. RDX and HMX, by comparison, are much simpler compounds.

Balakrishnan et al. (2003) proposed nitrous oxide, ammonia, and formate as end products of CL-20 alkaline hydrolysis. Formate was also present according to the IC results of this study. More analysis needs to be performed before the alkaline hydrolysis degradation pathways of CL-20 can be postulated.

Future work in this area should include detailed analysis of the intermediates as well as the end products of the alkaline hydrolysis over a range of pH values. The intermediates and end products should also be analyzed for their environmental toxicity to ensure that the alkaline hydrolysis of CL-20 is an environmentally sound remediation treatment.

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14. ABSTRACT

Hexanitrohexaazaisowurtzitane (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo [5.5.0.05,9.03,11] dodecane) or CL-20 has attracted attention as a possible replacement for, or inclusion in, military and space propellants and explosives. CL-20 is a polycyclic nitramine with a higher crystal density, a higher heat of formation, and a better oxidizer-to-fuel ratio than conventional nitramines used in propellants. The effective life cycle management of CL-20 requires development of knowledge and technologies related to the consequences and attributes of CL-20 that may be introduced into the environment. This research assessed the feasibility of using alkaline hydrolysis to treat water contaminated with CL-20. Two concentrations of the explosive were tested at pH values ranging from 10.0 to 13.0. Samples were taken from the batch reactor, quenched, and neutralized. One subsample was extracted and analyzed for explosives concentration using HPLC, and a second subsample was analyzed for anion content by IC. Alkaline hydrolysis proved to be an effective technique to degrade CL-20, as CL-20 was completely removed from aqueous solutions at all the pH levels evaluated. The reaction kinetics showed a strong dependence on the hydroxide ion concentration. Formate was indicated as an end product of the reaction.

15. SUBJECT TERMS

Alkaline hydrolysis	Explosives	
CL-20	Remediation	
	Batch reactor	

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