TECHNICAL REPORT 8309

NITROGUANIDINE WASTEWATER POLLUTION CONTROL TECHNOLOGY: PHASE III. TREATMENT WITH ULTRAVIOLET RADIATION, OZONE, AND HYDROGEN PEROXIDE

ᡧᢞᠧᠧ᠋᠋᠋ᢟᠧᡊ᠅ᡊᠧᡊᠧᡊᢏᢄᢞᠧᠺ᠕ᠺᡧᡊᡀᡊᡄᡊᠧᢤᡊᡧᡊᡶᡣᡛ᠆ᡧ᠆ᡧ᠘᠋ᡰᡱ᠈ᡘᢤᡊᡶᡊᡀᡊᡎᡊᡧᡊᡬᠺᡬᠺᡬᠺᠺᠺᠺᠺᡬᠺᢤᡘᢢ᠖ᡘ᠖ᠶ᠖ᠶᠺ᠋ᠶ

AD

CHARLES I. NOSS, Sc.D. RALPH H. CHYREK

Prepared for U.S. Army Toxac and Hazardous Materials Agency Aberdeen Proving Ground, MD 21010

US ARMY MEDICAL BIOENGINEERING RESEARCH and DEVELOPMENT LABORATORY Fort Detrick Frederick, MD 21701

JANUARY 1984

Approved for public release; distribution unlimited





84 03 23 025

ELECTE MAR 2 3 1984

B

00 က **の** က AD A 1

0

gura herzoria inversa internet incerts, united internet internet internet formal formation formation formation V

СОРУ

FILE

NOTICE

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when it is no longer needed. Do not return it to the originator.

A CARLON

REPORT DOCUMENTATION PAG	E READ INSTRUCTIONS
REPORT NUMBER 2. GO	DEFORE COMPLETING FORM
TECHNICAL DEPORT 8309	1)-A139 389
TITLE (and Substite)	5. TYPE OF REPORT & PERIOD COVERE
NITROGUANIDINE WASTEWATER POLLUTION (CONTROL Technical Report
TECHNOLOGY · PHASE III. TREATMENT W	TTH Sep 1983 - Dec 1983
ILTRAVIOLET PADIATION OZONE AND HY	DROCEN 6. PERFORMING ORG. REPORT NUMBER
DEPOYTOR	
AUTHOR(e)	8. CONTRACT OR GRANT NUMBER(.)
CHARTES T. NOSS Sc.D.	
RALPH H. CHYREK	
PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK
US Army Medical Bioengineering Reseat	rch and
Development Laboratory, ATTN: SGRD-	UBG 62720A
Fort Detrick, Frederick, MD 21701	1L162720D048
. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
US Army Medical Research and Develop	ment Command January 1984
ATTN: SGRD-RMS	13. NUMBER OF PAGES
Fort Detrick, Frederick, MD 21701	28
MONITORING AGENCY NAME & ADDRESS(11 different from	Controlling Office) 15. SECURITY CLASS. (of this report)
	SCHEDULE
Approved for public release; distribution	ution unlimited
DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribu DISTRIBUTION STATEMENT (of the ebstract entered in Big	ution unlimited ock 20, 11 different from Report)
Approved for public release; distribution statement (of the abetract entered in Big 7. Distribution statement (of the abetract entered in Big 9. SUPPLEMENTARY NOTES	ution unlimited ock 20, 11 different from Report)
Approved for public release; distribution statement (of the ebetract entered in Bid DISTRIBUTION STATEMENT (of the abstract entered in Bid SUPPLEMENTARY NOTES KEY WORDS (Continue on reverse eide if necessary and iden Chandiding	ntlfy by block number)
Approved for public release; distribution statement (of the Report) Approved for public release; distribution statement (of the obstract entered in Bid DISTRIBUTION STATEMENT (of the obstract entered in Bid SUPPLEMENTARY NOTES KEY WORDS (Continue on reverse side if necessary and iden Guanidine Ultraviolet Hydrogen peroxide Wastewater Nitroguanidine Ozone	ntily by block number) radiation
Approved for public release; distribution STATEMENT (of the obstract entered in Bid DISTRIBUTION STATEMENT (of the obstract entered in Bid DISTRIBUTION STATEMENT (of the obstract entered in Bid Distribution STATEMENT (of the obstract entered in Bid Supplementary notes Supplementary notes Networks (Continue on reverse side if necessary and iden Guanidine Ultraviolet Hydrogen peroxide Wastewater Nitroguanidine Ozone ABSTRACT (Continue on reverse did N messenty and iden Nitroguanidine in aqueous solution tion. Neither hydrogen peroxide nor guanidine. The use of hydrogen perox ultraviolet light did not increase the the apparent distribution of identify throughout all tests using ozone, hydrogen and the second solution.	ution unlimited ock 20, 11 different from Report) nilly by block number) radiation with by block number) on was degraded by ultraviolet radia- ozone was capable of degrading nitro- xide or ozone in conjunction with he rate of nitroguanidine destruction or iable products. Guanidine was stable drogen peroxide, and ultraviolet

INCLASSIFIED SECURITY CLASSIFICATION OF THIS PAGE (When Date Entered

20. Abstract - Continued

Nitroguanidine (100 mg/L) was undetectable after 100 minutes of exposure to ultraviolet radiation. When the initial nitroguanidine concentration was 20 mg/L, only 30 minutes were required to reduce the nitroguanidine to less than 0.10 mg/L. Nitroguanidine degradation by ultraviolet light was independent of pH between the values of 3 and 11. Guanidine formation during the photolysis of nitroguanidine was pH dependent. Guanidine formation increased as the pH decreased. \mathcal{A}

PREFACE

The research reported herein was performed at the request of the US Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, MD, under Project Pll - Treatment of Munition Production Wastes, which is part of the DARCOM Pollution Abatement and Environmental Control Technology Program. Subtask Pll1.04.04, Nitroguanidine Wastewater Treatment Criteria, Charles Denzler, Project Engineer, calls for characterization of Sunflower Army Ammunition Plant (SFAAP) wastewaters (through document review and sample analysis) and bench scale treatability studies for control, primarily, of nitroguanidine and guanidine nitrate. Four treatment technologies have been identified for testing by the US Army Medical Bioengineering Research and Development Laboratory (USAMBRDL) under Phase III of this subtask;¹ these are photolysis by ultraviolet radiation, ozone and hydrogen peroxide oxidation unpromoted or promoted by ultraviolet radiation, activated carbon adsorption, and ion exchange. Studies on the latter two processes are described in an accompanying report.²

High performance liquid chromatography (HPLC) analyses were performed at USAMBRDL by Mr. Ernst E. Brueggemann, and ion chromatography analyses were performed by Ms. Louanna J. Baxter.

Purification of nitroguanidine and synthesis of nitrosoguanidine was performed by Mr. Alan B. Rosencrance.

Access	sion F	or			
NTIS	GRA&I				
DTIC ?	ГАВ				
Unann	ounced				
Justi	ficati	on			
By Distribution/					
Avai	labili	ty C	odes		
	Avail	and	/or		
Dist	Spec	ial			
A·1		;	2. 神社		

TABLE OF CONTENTS

1

· · · ·

X

¥.

5

ŀ

 $\mathbf{x} \in \mathcal{A}$

 ~ 100

с.

 (\cdot, \cdot)

51.54

PREFACE
INTRODUCTION
RESULTS AND DISCUSSION
Degradation Rates
SUMMARY AND CONCLUSIONS
EXPERIMENTAL PROCEDURES14
Materials
REFERENCES
DISTRIBUTION LIST

APPENDIX

A.	Data	Tablesl	7
----	------	---------	---

FIGURES

1.	Destruction of Nitroguanidine by 0.1% Hydrogen Peroxide, Ozone Saturated Reactor Solutions, and Ultraviolet Radiation at pH 7 and Ambient Temperature
2.	Destruction of Nitroguanidine by Ulraviolet Radiation and Ultraviolet Radiation Coupled with 0.01% Hydrogen Peroxide or Ozone Saturated Reactor Solutions at pH 7 and Ambient Temperature
3.	Effect on Guanidine by 0.1% Hydrogen Peroxide, Ozone Saturated Reactor Solutions, and Ultraviolet Radiation at pH 7 and Ambient Temperature9
4.	Effect of Initial Nitroguanidine Concentration on the Rate of Ultraviolet Photolysis10
5.	The Formation of Guanidine is Shown to be Dependent Upon pH as Nitroguanidine is Degraded with Ultraviolet Radiation
6.	The Formation of Guanidine is Shown to be Dependent Upon pH as Nitrosoguanidine is Degraded with Ultraviolet Radiation
7.	Reactor Schematic

TABLES

2. Pseudo-first Order Rate Constants for Nitroguanidine Degradation......8

INTRODUCTION

Sunflower Army Ammunition Plant (SFAAP) is a government-owned, contractoroperated installation under the administration of the US Army Armament Munitions and Chemical Command (AMCCOM). Manufacturing capabilities at SFAAP are primarily for propellants and related materials. A 40 ton/day plant for continuous manufacture of nitroguanidine has been constructed at SFAAP. The plant utilizes technology which, though tested individually, has never been previously tested in operation. Although the production facility was originally planned to operate with no wastewater discharge, it now appears that as much as 400,000 gpd may be generated.

Because nitroguanidine has never been manufactured on an industrial scale in this country, little information is available on the environmental impact of nitroguanidine and production wastewaters discharge. Kaplan et al.,¹ have reported that nitroguanidine was sensitive to ultraviolet light, and preliminary work at USAMBRDL has indicated that aqueous nitroguanidine degrades in bright sunlight with a half-life of about 20 hours.² Degradation products included guanidine, nitrite, and two cations. Since SFAAP wastewaters are presently stored in open basins and photolysis appears to be a feasible pathway for degrading aqueous nitroguanidine, it is essential that the product(s) be determined.

Butler³ has indicated that 98 percent of an aqueous solution containing 1,100 mg/L of nitroguanidine was degraded by a photolytic process. The process consisted of treatment with 40 percent hydrogen peroxide and ultraviolet light with an iron catalyst. The reaction temperature was 190°F, the pH of the solution was 2, and the exposure time ranged from 4 to 5 hours. Using similar treatment conditions, guanidine nitrate was not degraded.⁴ Studies by Noss and Chyrek⁵ have shown that photolytic destruction of nitramine munitions were inhibited by hydrogen peroxide when concentrations exceeded 0.1 percent. Initial hydrogen peroxide concentrations of about 0.01 percent have little effect on ultraviolet light intensity, but should enhance radical formation and photolytic activity.

RESULTS AND DISCUSSION

DEGRADATION RATES

Nitroguanidine was degraded by ultraviolet radiation, but was unaffected by hydrogen peroxide or ozone treatments. Figure 1 shows that 0.1 percent hydrogen peroxide or ozone-saturated reactor solutions did not decrease nitroguanidine concentrations. However, a 60 percent loss of nitroguanidine was observed after 1 hour when a 100 mg/L nitroguanidine solution was irradiated with ultraviolet light. Figure 2 shows that the use of ozone or hydrogen peroxide in conjunction with ultraviolet light did not enhance nitroguanidine destruction. Calculated pseudo-first order reaction rate constants (Table 1) show that ozone application actually decreased the rate of nitroguanidine destruction. Table 2 demonstrates that the rate of degradation of nitroguanidine was not dependent upon pH.





¢



 \sim

UV	uv + 0 ₃	UV + H ₂ 0 ₂ ^a		
0.017	0.010	0.015		
(-0.991)	(-0.997)	(-0.953) ^b		

TABLE 1. PSEUDO-FIRST ORDER RATE CONSTANTS FOR NITROGUANIDINE DEGRADATION Pseudo-First Order Rate Constants, -kmin-1

Initial H_2O_2 concentration was a. 0.01 percent.

60000000 1 x V

b. Numbers in parentheses are correlation coefficients.

TABLE	2.	PSE	UDO-FI	RST (ORDER	RATE	CONSTANTS
	FOR	NI	roguai	NIDIN	E DEG	RADAT	ION
Pseud	o-Fi	rst	Order	Rate	Cons	tants	, $-k_{\min}-1$

UV	UV + H ₂ 0 ₂
0.017 (-0.991)	0.015 (-0.953)*
	UV 0.017 (-0.991)

11 0.016 0.016

(-0.990)

(-0.989)

Numbers in parentheses are correlation 8. coefficients.

Guanidine was decidedly refractory with respect to treatments by ozone, hydrogen peroxide, and ultraviolet light. The stability of guanidine is demonstrated in Figure 3. Further studies on guanidine degradation were discontinued.

Data from initial studies on nitroguanidine degradation by ultraviolet light produced a half-life of approximately 50 minutes. Continuing experiments conducted over 4 to 5 half-lives showed a dramatic disappearance of nitroguanidine when the reactor solution concentration reached 20 mg/L. A straight-line plot on semi-log paper no longer existed, indicating that the destruction of nitroguanidine was not pseudo-first order over the entire concentration range. Figure 4 shows the apparent zero order degradation of nitroguanidine when initial concentrations equaled 100 mg/L and 20 mg/L. Each line had a correlation coefficient equal to -0.998. The slopes were -0.979 mg liter⁻¹ min⁻¹ and -4.460 mg liter⁻¹ min⁻¹ for initial nitroguanidine concentrations of 100 mg/L and 20 mg/L, respectively.









and analysis analysis because analysis analysis

Figure 4. Effect of Initial Nitroguanidine Concentration on the Rate of Ultraviolet Photolysis.

PRODUCTS

Figure 5 shows that little difference in nitroguanidine destruction by ultraviolet light was observed at pH 5 compared to trials conducted at pH 11. However, guanidine was produced at neutrol and acidic pH values, while none was produced in highly alkaline solutions. Furthermore, only 2 to 12 mg/L of nitrite-nitrogen and nitrate-nitrogen were found under any given set of conditions. This means that at least 50 percent of nitroguanidine-nitrogen was not recovered during ultraviolet treatment at neutral or acidic pH values. Nonrecoverable nitrogen was as high as 80 to 85 percent when nitroguanidine solutions were treated at pH 11.

The production and subsequent destruction of nitrosoguanidine was observed during nitroguanidine treatment with ultraviolet light. Nitrosoguanidine was therefore considered to be a possible intermediate formed as nitroguanidine degraded. Figure 6 shows the results of nitrosoguanidine destruction by ultraviolet light at pH 5 and 11. At pH 11, the degradation of nitrosoguanidine yielded little guanidine. However, at pH 5, 80 mg/L of nitrosoguanidine yielded 58 mg/L of guanidine. Essentially 100 percent of the nitrosoguanidine-nitrogen was recovered as guanidine-nitrogen, nitritenitrogen, and nitrate-nitrogen at pH 5, while only 25 percent of the total nitrogen was recovered after treatment with ultraviolet light at pH 11. These data indicate that nitrosoguanidine is a likely intermediate in guanidine formation during ultraviolet irradiation of nitroguanidine, but other products and pathways exist which have yet to be determined.

Analyses of degraded samples for cyanoguanidine, cyanamide, urea, melamine, ammeline, and ammonia have demonstrated trace concentrations of each. Urea was considered to be a likely product, but only 2 to 3 mg/L could be recovered after the photolysis of 100 mg/L of nitroguanidine. Biguanidine was also considered as a possible product, but its presence has not yet been demonstrated.

Further work on the identification of nitroguanidine degradation products is recommended. It is important to demonstrate that photolytic products can be varied by altering reaction conditions, but the identity of these compounds must also be elucidated.

SUMMARY AND CONCLUSIONS

Nitroguanidine was degraded with ultraviolet radiation. The end products of ultraviolet photolysis are dependent upon the wastewater pH. At pH values ranging between 3 and 10, guanidine and nitrate-nitrogen were produced, accounting for approximately 40 percent of the total nitrogen content. An additional 10 percent of the total nitrogen was recovered as identifiable compounds at low concentrations. The remaining 50 percent of nitroguanidinenitrogen was not recovered.

At pH values greater than 11, no guanidine was formed during photolysis of nitroguanidine. Under these conditions, greater than 80 percent of the initial nitroguanidine-nitrogen content was not recovered. The difference in the amount of recoverable total nitrogen at acidic and alkaline pH values was associated with the production of guanidine. In summation, the rate of





in a contraint

 \cdot

ultraviolet photolysis of nitroguanidine was independent of pH, but the production of guanidine occurred only below pH 11.

Neither hydrogen peroxide nor ozone was capable of degrading nitroguanidine or guanidine. The use of hydrogen peroxide or ozone in conjunction with ultraviolet light did not increase the rate of nitroguanidine destruction or the apparent distribution of identifiable products. Guanidine persisted throughout all tests. Therefore, guanidine formation from photolysis of nitroguanidine must be considered when effluent limits are set for both nitroguanidine and guanidine.

EXPERIMENTAL PROCEDURES

MATERIALS

THE PRODUCT PRODUCT PROCESS AND THE PRODUCT PRODUCT PRODUCT PRODUCT PRODUCT

Nitroguanidine was obtained commercially, recrystallized from water, and dried to a constant weight. Guanidine was purchased from J.T. Baker Chemical Co. and used without further purification. Hydrogen peroxide was purchased from Fisher Scientific as a 30 percent solution, then diluted to desired concentrations immediately prior to use. Ozone was produced on-site with a W.R. Grace and Co. Ozone Generator, Model LG-2-L2, operated at 250 watts and 10 SCFH.

SOURCE OF NITROSOGUANIDINE

The reactor column is shown in Figure 7. The column consists of a stainless steel cylinder, 78 inches high and 6.6 inches in diameter. It contains a sintered stainless steel gas sparger with a mean pore size of 5 micrometers, which is located approximately 2 inches above the base of the reactor. An 80watt lamp encased in a 1-inch quartz sleeve runs vertically through the center of the column. The lamp emits ultraviolet light at a wavelength of 253.7 nm. Mixing of reactor contents was achieved by recirculating wastewater at a flow rate of 2 gpm.

METHODS

Nitroguanidine and guanidine solutions were prepared within an hour before use. The pH was adjusted with hydrochloric acid or sodium hydroxide. In indicated experiments, test solutions were buffered with 0.001 M sodium phosphate or sodium borate to maintain pH values of 7 and 11, respectively. Samples were removed from the reactor column at timed intervals. Each sample bottle contained sodium thiosulfate to quench oxidants which may have been present in the sample. Nitroguanidine, guanidine, cyanoguanidine, melamine, ammeline, and nitrosoguanidine concentrations were determined according to the methods described by Burrows, et al.⁶ Nitrite-nitrogen and nitrate-nitrogen concentrations were determined by the EPA Automated Cadmium Reduction Method, number 353.2.



REFERENCES

- Kaplan, D.L., J.H. Cornell, and A.M. Kaplan. 1981. Microbial and Chemical Transformation of Nitroguanidine. TR-81/019, US Army Natick Research and Development Laboratories, Natick, MA.
- Dennis, W.H. Jr. 19 September 1982. Memorandum Report, SGRD-UBG-R. Subject: Photolysis of Nitroguanidine. US Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD.
- Butler, J. 31 May 1983. Subject: Process Treatment Development for Destruction of Nitroguanidine. Project No. 83-9541, DeSoto, KS.
- Rohr, J. 21 July 1983. Subject: Decomposition of Guanidine Nitrate and Nitroguanidine. Project No. 83-9541, Desoto, KS.
- 5. Noss, C.I. and R.H. Chyrek. 1983. Tertiary Treatment of Effluent from Holston Army Ammunition Plant Industrial Liquid Waste Treatment Facility. IV. Ultraviolet Radiation and Hydrogen Peroxide Studies: TNT, RDX, HMX, TAX, and SEX. Technical Report 8308, US Army Medical Bioengineering Research and Development Laboratory, Ft. Detrick, Frederick, MD.
- Burrows, E.P., E.E. Brueggemann, E.H. McNamee, L.J. Baxter, and S.H. Hoke. Nitroguanidine Wastewater Pollution Control Technology: Phase II. Characterization and Analytical Methods Development. Technical Report 8311. US Army Medical Bioengineering Research and Development Laboratry, Fort Detrick, Frederick, MD. Draft.

APPENDIX A

DATA TABLES

Time (min)	рН	Nitroguanidine (mg/L)	Cyanoguanidine (mg/L)	Guanidine (mg/L)	Nitrite + Nitrate-N (mg/L)
0	3	106.00	<0.25	<1.0	0.6
10	NDa	95.10	<0.25	1.3	2.3
20	ND	82.53	<0.25	3.7	3.6
30	ND	71.97	0.29	7.5	5.9
40	ND	61.20	0.47	11.2	7.9
50	ND	50.51	0.63	13.9	8.8
60	ND	44.35	0.70	16.5	10.5
0	7	102.50	<0.25	<1.0	0.6
10	ND	91.38	<0.25	<1.0	2.9
20	ND	77.25	<0.25	<1.0	4.5
30	ND	67.95	0.84	2.4	6.4
40	ND	56.65	1.20	4.6	8.1
50	ND	44.52	1.64	8.4	10.7
60	ND	39.12	1.93	9.6	11.6
0	11	100.17	<0.25	<1.0	0.6
10	ND	87.90	<0.25	<1.0	2.7
20	ND	77.91	<0.25	<1.0	4.4
30	ND	66.25	<0.25	<1.0	6.2
40	ND	56.57	<0.25	<1.0	7.6
50	ND	47.40	<0.25	<1.0	9.0
60	ND	37.75	<0.25	<1.0	13.0

TABLE A-1. DESTRUCTION OF NITROGUANIDINE WITH ULTRAVIOLET RADIATION

a. ND = not determined.

53351 3333

Time (min)	рН	Nitroguanidine (mg/L)	Cyanoguanidine (mg/L)	Guanidine (mg/L)	Nitrite + Nitrate-N (mg/L)	Ozone ^a
0	3.01	110.55	<0.25	<1.0	0.1	-
10	3.01	109.07	<0.25	<1.0	<0.1	+
20	3.07	108.82	<0.25	<1.0	<0.1	+
30	3.04	110.05	<0.25	<1.0	<0.1	-
40	3.03	106.77	<0.25	<1.0	<0.1	-
50	3.00	106.64	<0.25	<1.0	0.5	-
60	3.00	104.86	<0.25	<1.0	0.5	+
0	6.68	108.78	<0.25	<1.0	<0.1	_
10	6.87	109.44	<0.25	<1.0	<0.1	+
20	6.77	110.31	<0.25	<1.0	0.1	+
30	6.68	109.20	<0.25	<1.0	<0.1	+
40	6.58	108.88	<0.25	<1.0	<0.1	+
50	7.01	109.57	<0.25	<1.0	<0.1	+
60	6.65	109.39	<0.25	<1.0	0.1	+
0	10.86	98.70	<0.25	<1.0	0.1	-
10	10.90	97.02	<0.25	<1.0	<0.1	· —
20	10.84	94.54	<0.25	<1.0	<0.1	-
30	10.83	90.95	<0.25	<1.0	<0.1	-
40	10.86	88.88	<0.25	<1.0	<0.1	-
50	10.65	87.22	<0.25	<1.0	<0.1	-
60	10.80	84.94	<0.25	<1.0	0.1	-

TABLE A-2. DESTRUCTION OF NITROGUANIDINE WITH OZONE

AND THE CONTRACTOR STATEMENT

oooo areeeeee haareest heeeeeee hooreeee gestersot b

Received a contraction of the second

a. Ozone was always present in off-gases from the reactor, but in solution as measured with syringaldazine was reported as present or absent.

Time (min)	pН	Nitroguanidine (mg/L)	Cyanoguanidine (mg/L)	Guanidine (mg/L)	Nitrite + Nitrate-N (mg/L)
0	3.02	117.10	<0.54	<1.0	0.1
10	NDa	117.70	<0.54	<1.0	0.2
20	ND	117.32	<0.54	<1.0	0.2
30	3.00	116.74	<0.54	<1.0	0.1
40	ND	116.78	<0.54	<1.0	0.1
50	ND	117.15	<0.54	<1.0	0.2
60	2.46	117.49	<0.54	<1.0	0.2
0	6.79	117.06	<0.54	<1.0	<0.1
10	ND	116.60	<0.54	<1.0	0.1
20	ND	116.72	<0.54	<1.0	0.1
30	7.02	117.14	<0.54	<1.0	0.1
40	ND	116.34	<0.54	<1.0	0.1
50	ND	117.13	<0.54	<1.0	0.2
60	6.88	118.59	<0.54	<1.0	0.3
0	11.02	111.30	<0.54	<1.0	<0.1
10	ND	115.82	<0.54	<1.0	0.1
20	ND	114.36	(0.54	<1.0	<0.1
30	11.03	116.18	<0.54	<1.0	0.1
40	ND	115.02	<0.54	<1.0	<0.1
50	ND	115.99	<0.54	<1.0	0.1
60	10.91	115.83	<0.54	<1.0	0.3

TABLE A-3. DESTRUCTION OF NITROGUANIDINE WITH 0.1% HYDROGEN PEROXIDE

9

a she a s

a. ND = not determined.

-0

Time (min)	рН	Nitroguanidine (mg/L)	Guanidine (mg/L)	Nitrite + Nitrate-N (mg/L)	н ₂ 02 (%)	03 ^a
0	8.45	117.63	<1.0	0.3	NA	
10	4.18	103.62	3.3	0.2	NA	+
20	6.75	95.14	3.7	0.2	NA	+
30	9.98	86.15	4.2	0.3	NA	+
40	6.28	79.22	4.1	0.2	NA	+
50	4.05	72.22	4.2	0.1	NA	+
60	3.59	64.00	4.9	0.1	NA	+
0	6.76	114.59	<1.0	0.5	0.01	NAB
10	4.40	102.10	4.8	1.0	NDC	NA
20	4.63	90.20	8.6	0.5	ND	NA
30	4.23	83.14	11.2	1.0	ND	NA
40	3.91	70.99	14.9	5.3	ND	NA
50	3.96	59.79	19.0	8.3	ND	NA
60	3.65	43.40	21.6	4.5	ND	NA
0	10.71	106.17	<1.0	0.5	0.01	NA
10	10.79	95.47	3.8	2.1	ND	NA
20	10.76	83.73	7.6	3.9	ND	NA
30	10.75	73.03	9.0	5.2	ND	NA
40	10.75	61.13	10.9	6.6	ND	NA
50	10.74	50.65	13.4	8.2	ND	NA
60	10.72	41.69	14.5	8.6	ND	NA

TABLE A-4. DESTRUCTION OF NITROGUANIDINE WITH ULTRAVIOLET RADIATION COUPLED WITH OZONE OR HYDROGEN PEROXIDE

a. Ozone was always present in off-gases from the reactor, but in solution as measured with syringaldazine was reported as present or absent.

b. NA = Not applicable.

Sameri

Ę.

c. ND = not determined.

Time (min)	рH	Nitroguanidine (mg/L)	Cyanoguanidine (mg/L)	Guanidine (mg/L)	Nitrite + Nitrate-N (mg/L)	^н 2 ⁰ 2 (х)	Ozone ^a
0	5.07	<0.10	<0.20	109	0.1	ND ^b	_
10	5.26	5 <0.10	<0.20	110	0.3	ND	-
20	5.03	3 <0.10	<0.20	99	0.3	ND	-
30	5.03	3 <0.10	<0.20	107	0.4	ND	-
40	5.10) <0.10	<0.20	119	0.3	ND	-
50	5.27	7 <0.10	<0.20	105	0.3	ND	-
6 0	4.97	7 <0.10	<0.20	104	0.3	ND	-
0	4.90) <0.10	<0.20	95	0.1	0.01	NAC
10	4.91	L <0.10	<0.20	104	0.3	ND	NA
20	4.85	5 <0.10	<0.20	115	0.3	ND	NA
30	4.79	<0. 10	<0.20	107	0.2	ND	NA
40	4.77	<0.10	<0.20	98	0.2	ND	NA
50	4.77	/ <0.10	<0.20	92	0.7	ND	NA
60	3.50	0 <0.10	<0.20	100	0.3	ND	NA
0	5.44	<0.10	<0.20	100	0.1	NA	-
10	4.04	€ <0.10	<0.20	106	0.1	NA	+
20	3.86	5 <0.10	<0.20	106	0.3	NA	+
30	3.62	2 <0.10	<0.20	97	0.2	NA	+
40	3.50	0 <0.10	<0.20	101	0.4	NA	-
50	3.40	0.10	<0.20	125	0.3	NA	+
60	3.38	8 <0.10	<0.20	104	0.3	NA	-
0	5.27	7 <0.10	<0.20	126	0.1	NA	-
10	4.59	3 <0.10	<0.20	129	0.3	NA	+
20	4.64	4 <0.10	<0.20	132	0.2	NA	+
30	4.44	4 <0.10	<0.20	121	0.2	NA	+
40	4.18	3 <0.10	<0.20	121	0.4	NA	+
50	3.96	6 <0.10	<0.20	126	0.4	NA	+
60	3.79	<0.10	<0.20	124	0.2	NA	+

TABLE A-5. DESTRUCTION OF GUANIDINE WITH ULTRAVIOLET RADIATION COUPLED WITH OZONE OR HYDROGEN PEROXIDE AND OZONE ALONE

a. Ozone was always present in off-gases from the reactor, but in solution as measured with syringaldazine was reported as present or absent.

b. ND = not determined.

RESEARCH REPORTED AND A REPORT OF A

c. NA = not applicable.

 TABLE A-6.
 DESTRUCTION OF NITROGUANIDINE AND GUANIDINE IN BUFFERED SOLUTIONS

 AT
 PH
 7
 AND 11
 WITH ULTRAVIOLET RADIATION

Buffer	Time (min)	Hq	Nitroguanidine (mg/L)	Cyanoguandine (mg/L)	Guanidine (mg/L)	Nitrite + Nitrate-N (mg/L)	Nitrosoguanidine mg/L
1×10 ⁻³ M	0	10.80	99.92	<0.20	1	0.9	<0.10
Borate	10	10.70	96.66	<0.20	. ₽	2.3	0.48
	20	10.71	80.84	<0.20	₽	3.5	0.83
	8	10.63	70.70	<0.20	₽	4.9	0.92
	40	10.55	62.52	<0.20	₽	5.8	0.93
	50	10.47	53.45	<0.20	1>	7.1	0.92
	60	10.38	45.00	0.28	<1	8.1	0.86
1-10-3 v	c		10 27	00 07	;	с с	
	> ;	0.94	103.2/	<0.20 20	.	0.3	01•10
Phosphate	10	6.90	91.72	<0.20	m	2.0	0.48
	20	6.86	80.30	0.31	9	3.4	0.86
	90	6.80	68.09	0.24	7	4.9	1.05
	40	6.75	57.19	0.37	10	6.3	1.08
	50	6.71	47.75	0.80	12	7.4	1.05
	60	6 • 56	36.97	0.97	14	8.6	16.0
Ix10 ⁻³ M	0	10.92	<0.10	<0.20	143	0.3	<0.10
Borate	10	10.64	<0.10	<0.20	142	0.3	<0.10
	20	10.62	<0.10	<0.20	122	0.3	<0.10
	30	10.64	<0.10	<0.20	121	0.3	<0.10
	40	10.70	<0.10	<0.20	133	0.3	<0.10
	20	10.71	<0.10	<0.20	134	0.3	<0.10
	60	10.74	<0.10	<0.20	143	0.3	<0.10

Time (min)	рН	Nitroguanidine (mg/L)	Guanidine (mg/L)	Cyanoguanidine (mg/L)	Nitrosoguanidine (mg/L)
0	9.57	99.95	<1	<0.20	<0.10
20	6.84	78.39	2	0.37	0.88
40	6.48	55.35	5	0.80	1.16
60	4.41	34.36	10	1.82	1.30
80	4.20	14.25	17	2.52	0.82
100	4.15	0.15	21	2.80	0.12
120	4.30	<0.10	20	2.73	<0.10
140	4.37	<0.10	21	2.70	<0.10
160	4.40	<0.10	21	2.66	<0.10
180	4.31	<0.10	21	2.67	<0.10
200	4.40	<0.10	20	2.65	<0.10
220	4.38	<0.10	21	2.60	<0.10
240	4.36	<0.10	20	2.52	<0.10
0	4.71	<0.10	106	<0.20	<0.10
20	4.62	<0.10	ND ^a	<0.20	<0.10
40	4.66	<0.10	ND	<0.20	<0.10
60	4.66	<0.10	109	<0.20	<0.10
80	4.64	<0.10	ND	<0.20	<0.10
100	4.61	<0.10	ND	<0.20	<0.10
120	4.59	<0.10	114	<0.20	<0.10
140	4.57	<0.10	ND	<0.20	<0.10
160	4.54	<0.10	ND	<0.20	<0.10
180	4.51	<0.10	110	<0.20	<0.10
200	4.51	<0.10	ND	<0.20	<0.10
220	4.50	<0.10	ND	<0.20	<0.10
240	4.49	<0.10	111	<0.20	<0.10

TABLE A-7.DESTRUCTION OF NITROGUANIDINE AND GUANIDINEWITH ULTRAVIOLET RADIATION

a. ND = not determined.

Time (min)	pH	Nitrosoguanidine (mg/L)	Guanidine (mg/L)	Nitrite + Nitrate (mg/L)	Nitroguanidine (mg/L)	Cyanoguanidine (mg/L)
0	4.60	80.60	<1	1.1	28.96	<0.20
15	3.94	52.09	19	ND	26.03	<0.20
30	4.49	26.24	38	ND	13.87	0.45
45	4.23	6.46	53	ND	7.48	0.54
60	3.96	0.16	57	ND	<0.10	0.70
75	4.30	0.10	56	ND	<0.10	0.69
90	3.98	<0.10	59	16.5	<0.10	0.74
0	10.90	76.54	<1.0	<1.0	29.89	<0.20
15	10.82	58.64	1.5	ND	23.54	<0.20
30	10.56	36.92	2.5	ND	26.51	<0.20
45	10.29	20.95	3.2	ND	18.62	<0.20
60	10.27	11.24	3.4	ND	8.98	<0.20
75	10.29	3.35	3.7	ND	5.52	0.23
90	10.28	0.81	3.6	11.8	2.88	0.28

TABLE A-8. DESTRUCTION OF NITROSOGUANIDINE WITH ULTRAVIOLET RADIATION

· ·

TABLE A-9.DESTRUCTION OF NITROGUANIDINEWITH ULTRAVIOLET RADIATION

Time (min)	pH	Nitroguanidine (mg/L)	Guanidine (mg/L)
0	5.00	20.86	<1.0
5	4.53	15.75	1.1
10	4.33	10.84	2.1
15	4.15	6.17	3.3
20	4.13	2.41	4.7
30	4.07	<0.10	5.5
40	4.09	<0.10	5.7
50	4.10	<0.10	5.3
60	4.02	<0.10	5.3

DISTRIBUTION LIST

No.	of
Cop	les

5

US Army Medical Research and Development Command ATTN: SGRD-RMS Fort Detrick, Frederick, MD 21701

- 12 Defense Technical Information Center (DTIC) ATTN: DTIC-DDA Cameron Station Alexandria, VA 22314
- 1 Commandant Academy of Health Sciences, US Army ATTN: HSHA-CDB Fort Sam Houston, TX 78234

2 Library Technician US Army Medical Bioengineering Research and Development Laboratory ATTN: SGRD-UBZ-IL Fort Detrick, Frederick, MD 21701