

## POTASSIUM FERRATE: A NOVEL CHEMICAL WARFARE AGENT DECONTAMINANT

*Russell Greene [greener@battelle.org](mailto:greener@battelle.org) (Battelle Memorial Institute, West Jefferson, OH)*

*F. Michael von Fahnestock (Battelle Memorial Institute, West Jefferson, OH)*

*Bruce Monzyk (Battelle Memorial Institute, Columbus, OH)*

**ABSTRACT:** Chemical warfare agents (CWAs) present a potential threat to military and civilian populations. Current decontamination formulations for CWAs, however, have several shortfalls, including environmental hazards, health hazards, practical use limitations, logistical management difficulties, and/or unsatisfactory CWA destruction efficiencies. Potassium ferrate ( $K_2FeO_4$ ) addresses all of these issues through its high oxidation potential, stable shelf life, and benign reduced state, namely iron oxide. A series of bench-scale trials on surrogate and actual CWAs demonstrated the potential efficacy of  $K_2FeO_4$  as a viable decontamination agent. Destruction efficiencies using paste and aqueous  $K_2FeO_4$  formulations exceeded 99% for 2,2-dichloroethyl ether, Sarin, Soman, mustard and V-nerve agents. The reaction times were as good as or better than commonly accepted decontaminants, such as bleach and sodium hydroxide.

### INTRODUCTION

Chemical warfare agents (CWAs), when used militarily or in terrorist situations, leave a film of active agents on surfaces. These surfaces may include clothing, building structures, vehicles, equipment and many others. There are many conventional decontaminants currently being used for these toxic agents, however many of them have shortfalls. While most are able to effectively destroy the CWAs, many are corrosive to both the skin and the surfaces to which they are applied. For example, chlorine bleach and sodium hydroxide are very effective decontaminants, however, both are corrosive and possess other environmental hazards. In addition, many decontaminants, both actively used and proposed, are unstable (with respect to loss of activity) and/or difficult to prepare, store and transport. Potassium ferrate ( $K_2FeO_4$ ) has been proven not only to effectively destroy a broad range of CWAs, but also addresses the shortfalls of the currently used CWA decontaminants. Ferrate has many attributes that make it ideal for use as a CWA decontaminant including the following: 1) It is non-toxic on its own. 2) It is an extremely strong oxidant (oxidation potential up to 2.2 volts). 3) It possesses a broad spectrum of uses while it is able to not only decompose organics, but toxic metal ions as well. 4) Its presence can easily be visually monitored as it undergoes a noticeable color change from intense violet to orange as it reacts and is depleted. 5) It is harmless to most surfaces and can be deployed in a number of manners (i.e. paste, powder, spray, and solution).

# Report Documentation Page

*Form Approved*  
*OMB No. 0704-0188*

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

1. REPORT DATE <b>16 NOV 2004</b>	2. REPORT TYPE <b>N/A</b>	3. DATES COVERED <b>-</b>	
4. TITLE AND SUBTITLE <b>Potassium Ferrate: A Novel Chemical Warfare Agent Decontaminant</b>		5a. CONTRACT NUMBER	
		5b. GRANT NUMBER	
		5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)		5d. PROJECT NUMBER	
		5e. TASK NUMBER	
		5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Battelle Memorial Institute, West Jefferson, OH</b>		8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSOR/MONITOR'S ACRONYM(S)	
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release, distribution unlimited</b>			
13. SUPPLEMENTARY NOTES <b>See also ADM001849, 2004 Scientific Conference on Chemical and Biological Defense Research. Held in Hunt Valley, Maryland on 15-17 November 2004., The original document contains color images.</b>			
14. ABSTRACT			
15. SUBJECT TERMS			
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>	<b>UU</b>
			18. NUMBER OF PAGES <b>7</b>
			19a. NAME OF RESPONSIBLE PERSON



and VX was hindered by mass transfer in the presence of large amounts of water. The insoluble characteristics of these agents, causes a high level of partitioning and in many cases, droplets of agent are visibly present in the solutions. A unique product was formed by combining a quat and ferrate. Specifically, Aliquat 336  $[(\text{CH}_3(\text{CH}_2)_8\text{N}^+\text{X}^-)]$  was utilized where the two quaternary ammonium ions are separate molecules. Other PTCs, along with emulsifiers and wetting agents were screened in bench-scale tests involving ferrate and CWA surrogate 2,2-dichloroethyl ether (HD surrogate). The results of these tests are not discussed in this paper, other than to state that Aliquat 336 was selected for use in the subsequent trials.

Once the surrogate screening process was completed, a test was conducted using HD. The CWA was again added directly to a 25 mL decontamination solution, this time containing ferrate and the PTC. Samples were taken at the completion of a two-hour test time, and samples taken for analysis via GC-FPD/FID.

**Small Flask Reactions.** A third series of tests were performed with the CWAs VX and HD. The objective of these experiments was to further examine the effectiveness of the ferrate/PTC formulation. The agents VX and HD were specifically examined due to their hydrophobic characteristics. The determination was made, that these two agents represented the worst-case scenario. The small flask reactions were divided into two types: “wet” and “dry.” The “wet” experiments consisted of a 5 mL decontamination solution of different combinations of ferrate, PTC and the pH buffer  $\text{KH}_2\text{PO}_4$ . An approximate decontaminant:CWA molar ratio of 14:1 was used. The specific test matrices are outlined in following sections of this paper. The tests were conducted in 20 mL scintillation vials and stirred with a magnetic stir bar for 2 hours. The “dry” experiments were the same as the “wet” tests, with the exception of the water. There was no water added to the decontamination formulation, resulting in a paste-like decontaminating agent. In both the “wet” and “dry” tests, the entire matrix was extracted in chloroform at the completion of the test run and an aliquot of the extraction analyzed with a GC for residual CWAs.

## RESULTS AND DISCUSSION

As stated earlier, the testing discussed in this paper was conducted in three phases. The summary and discussion of the results will be separated by the three test phases.

**Large Volume/High Water Content Results.** Promising destruction results for the nerve agent GD were accomplished in this first phase of testing. Figure 1 illustrates the concentration of GD ( $\mu\text{g}/\text{mL}$ ) in the solution over time. There was a ferrate:GD molar ratio of approximately 7.1 in these tests. All tests lasted 2 hours with specific sampling times throughout the length of the test, which were run in triplicate. A “positive” control sample was included in the test, which consisted of a 25 mL solution of solvent that the GD was spiked into. The purpose of the “positive” control was to validate the agent application, sampling and extraction process. All “positive” controls remained within an acceptable range of the theoretical concentrations. As shown in Figure 1, greater than 99% of the GD was destroyed within 15 minutes of reaction time. The results however, were less promising for the nerve agent VX. As shown in Figure 2, there was an initial spike in

Figure 1

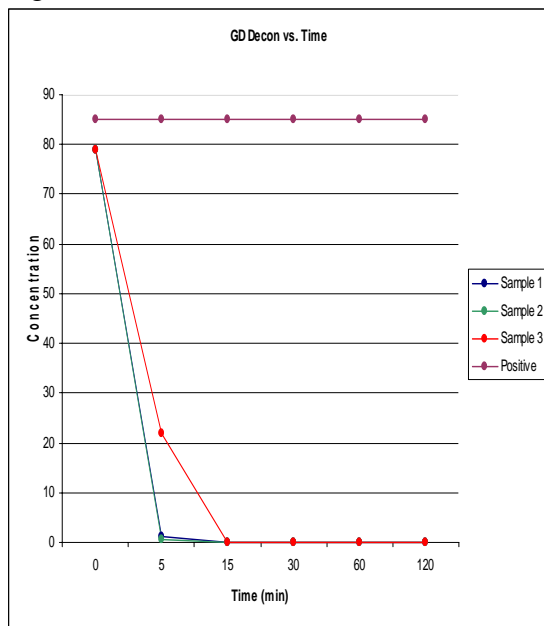
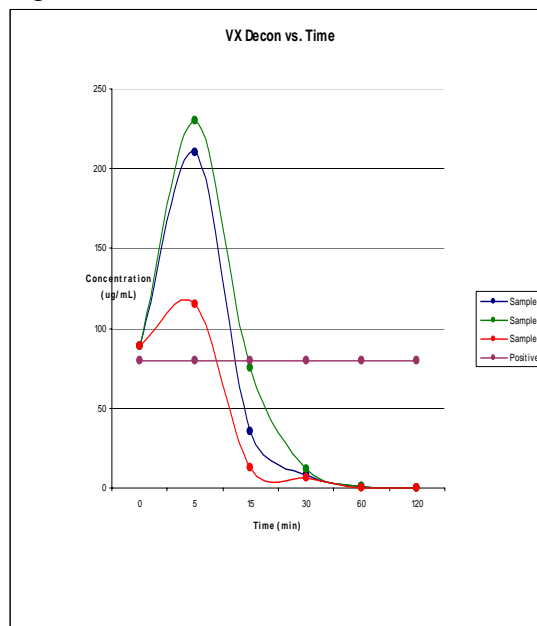


Figure 2



concentration at the first sampling time. In fact, the concentration was higher than the theoretical concentration as well as the “positive” control. It was hypothesized that the erratic concentrations were a result of a non-homogeneous solution. Because of the insolubility of VX in water, pockets of agent were forming in the solution. It was this fact, as well as similar results with HD, that led the test team to investigate the use of PTCs.

**Large Volume/High Water Content with Phase Transfer Catalyst Results.** A small amount of testing was conducted utilizing the ferrate/PTC formulation in the larger volume/high water content reaction tests. CWAs GB and HD were tested in this phase, with the GB exhibiting similar destruction rates as the GD from the first phase of testing. In fact greater than 99% of the GB was destroyed within 5 minutes of reaction time. This is not surprising, considering the high water solubility of GB. The GB test was identical to the previous tests described above, but included the PTC Aliquat 336.

A similar test was conducted with HD, however, rather than sampling at specific times throughout the length of the test, samples were only taken at the conclusion of the test. The tests were run in 250 mL round-bottom flasks with overhead stirring. The tests were run for 2 hours and triplicate samples taken from each flask at the completion of the test run. Table 1 shows the test matrix and the results of the test. As illustrated in the table, all samples exhibited greater than 90% destruction of the HD. In retrospect, sample 2 two should have been without the PTC. Because sample number 2 exhibited greater than 90% destruction of HD, the results are not completely conclusive that the ferrate was responsible for the destruction of the HD. In fact, it could be that with the PTC present in sample 2, it allowed the HD to be hydrolyzed in the water. The third phase of testing addresses this issue through control samples which narrow down the effect of the individual components.

Table 1.

RUN #	AMOUNT OF AGENT (mg)	PTC AMOUNT (g) (Aliquat 336)	PURIFIED K <sub>2</sub> FeO <sub>4</sub> AMOUNT	DI WATER/ BLEACH AMOUNT	.pH Buffer (g)	Results (µg/mL)
1.A	637 mg	1.0 g	7.0 g	25 mL DI Water	13 g	<0.5
1.B	“	“	“	“	“	<0.5
1.C	“	“	“	“	“	<0.5
2.A	637 mg	1.0 g	0	25 mL DI Water	13 g	16.75
2.B	“	“	“	“	“	5.71
2.C	“	“	“	“	“	24.1
3.A	637 mg	1.0 g	0	25 mL Bleach	13 g	<0.5
3.B	“	“	“	“	“	<0.5
3.C	“	“	“	“	“	<0.5

**Small Flask Reactions Results.** From the first two phases of testing, it was determined that HD and VX presented the greatest challenge for destruction. To address this challenge, additional testing was conducted utilizing the ferrate/PTC formulation. However, in this phase, the reactions took place on a smaller scale with lower amounts of both decontaminant and CWA. Table 2 and Table 3 illustrate the test matrices for two of the test runs, as well as the results.

Table 2.

Sample ID	AMOUNT OF VX (mg)	PTC AMOUNT (mg) (Purified Aliquat 336)	PURIFIED K <sub>2</sub> FeO <sub>4</sub> AMOUNT (mg)	DI WATER	.pH Buffer KH <sub>2</sub> PO <sub>4</sub> (mg)	Total Remaining VX (mg)	% Destruction
49788-50-1	10.1 mg	40 mg	260 mg	0	140 mg	1.65	83.7
49788-50-2	10.1 mg	40 mg	260 mg	0	140 mg	0.776	92.3
49788-50-3	10.1 mg	40 mg	260 mg	0	140 mg	0.657	93.5
49788-50-4	10.1 mg	0	0	0	140 mg	7.87	22.1
49788-50-5	10.1 mg	0	260 mg	0	140 mg	3.71	63.3
49788-50-6	10.1 mg	40 mg	260 mg	5 mL	140 mg	BDL	>99
49788-50-7	10.1 mg	40 mg	260 mg	5 mL	140 mg	BDL	>99
49788-50-8	10.1 mg	40 mg	260 mg	5 mL	140 mg	BDL	>99
49788-50-9	10.1 mg	0	0	5 mL	140 mg	3.69	63.5
49788-50-10	10.1 mg	0	260 mg	5 mL	140 mg	0.005	>99

Table 3.

<b>R U N #</b>	<b>AMOUNT OF HD (mg)</b>	<b>PTC AMOUNT (mg)  (Purified Aliquat 336)</b>	<b>PURIFIED K<sub>2</sub>FeO<sub>4</sub> AMOUNT (mg)</b>	<b>DI WATER AMOUNT</b>	<b>.pH Buffer KH<sub>2</sub>PO<sub>4</sub> (mg)</b>	<b>Results Total Mass Remaining (mg)</b>	<b>% Destruction</b>
3. A	12.5 mg	40 mg	260 mg	0	140 mg	<b>1.22 mg</b>	<b>90%</b>
3. B	12.5 mg	40 mg	260 mg	0	140 mg	<b>1.60 mg</b>	<b>87%</b>
3. C	12.5 mg	40 mg	260 mg	0	140 mg	<b>2.69 mg</b>	<b>79%</b>
3. D	12.5 mg	40 mg	0	0	140 mg	<b>11.15 mg</b>	<b>11%</b>
3. E	12.5 mg	0	260 mg	0	140 mg	<b>9.96 mg</b>	<b>20%</b>
4. A	12.5 mg	40 mg	260 mg	5 mL	140 mg	<b>1.10 mg</b>	<b>91%</b>
4. B	12.5 mg	40 mg	260 mg	5 mL	140 mg	<b>1.50 mg</b>	<b>88%</b>
4. C	12.5 mg	40 mg	260 mg	5 mL	140 mg	<b>1.38 mg</b>	<b>89%</b>
4. D	12.5 mg	0	0	5 mL	140 mg	<b>1.68 mg</b>	<b>87%</b>
4. E	12.5 mg	0	260 mg	5 mL	140 mg	<b>&lt; 0.5 mg</b>	<b>+ 99%</b>

As shown in the above tables, results for both HD and VX exhibit similar properties. In each of the tables, note that the first five samples are the “dry” tests (no water added) and the second five are the “wet” tests (5 mL of water added). It is apparent from the results of the “dry” samples, that removal of the phase transfer catalyst from the decontamination formulation significantly inhibits the destruction of the CWA. This does not seem to be the case in the “wet” samples. More testing will need to be conducted to effectively determine the mechanisms effecting the reactions. However, the percent destruction of the CWA by the decontamination solution remains promising. It should be noted that visual observations made during laboratory tests, indicated a concern that during mixing, some of the CWA may have “splattered” onto the upper walls of the reaction flask, thus not allowing it to come in contact with the decontaminant. With the entire contents of the flask being extracted at the completion of the test, all CWA would have been detected, whether it had been in contact with the decontaminant or not.

### **FURTHER TESTING**

While results from the initial proof-of-principal testing are promising, it is certainly necessary to conduct further testing. Further testing would determine the full extent of the ability of potassium ferrate to act as a viable CWA decontaminating agent. In addition, it would allow refinement of ideal use conditions, examination of deployment methods, determination of regulatory compliance ability and increased efficacy of ferrate in the presence of larger volumes of water. Specific testing may include: 1) Defining decontamination use procedures, refine formulation. 2) Identify and evaluate ferrate

formulated and physical product forms. 3) Verify complete detoxification by assaying for problem CWA intermediates, etc. 4) Perform contaminated-surface decontamination testing (coupon testing). 5) Perform side by side comparison studies with currently accepted decontaminants.

## **CONCLUSIONS**

The chemical properties of potassium ferrate represent a very attractive candidate for a CWA decontaminant. Ferrate is able to address the shortfalls of the currently used and proposed decontaminants, while efficiently destroying the toxic agents. The testing discussed in this paper by no means proves the extent to which ferrate can be used in this role, however it certainly proves the basic chemical principals are accurate and that further testing regarding this topic is worthwhile. The unique formulation of the potassium ferrate combined with a PTC could very well prove to be a significant breakthrough. It is also important to note that preliminary data generated from other studies indicate that potassium ferrate is a viable biological warfare agent decontaminant as well. Other studies conducted at Battelle yield promising data for the destruction of Highly Energetic Materials, namely munitions. This, combined with the data produced in the study detailed in this paper, are evidence that potassium ferrate has the potential of fulfilling the role of a universal decontaminant. Again, not only are the destruction efficiencies attractive, but the benign nature of the compound and its reaction products as well. The applications could be significant in both a civilian and military sense.