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CLEANING OF RESIDUES FROM EQUIPMENT SURFACES AFTER DEMILITARIZATION OF ARSENICAL-BASED MUNITIONS AND FILL MATERIELS

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14. ABSTRACT This report summarizes efforts to select and validate a cleaning reagent to be used in demilitarization operations. In demilitarization operations involving the chemical neutralization of arsenic-containing chemical warfare agents with sodium permanganate, the equipment becomes coated with deposits which are primarily manganese dioxide. These deposits must be removed from the equipment on a regular basis to prevent leaks and maintain operational tempo. An oxidative aqueous-based reagent identified as HPO ₂ TM reagent (U.S. Patent Number 6,960,701; all rights reserved) was found to be the best cleaning reagent in these demilitarization operations.					
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HPO ₂ TM Reagent		Arsinol		Neutralization	
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EXECUTIVE SUMMARY

This report summarizes efforts to select and demonstrate a reagent for cleaning permanganate-based residues on equipment used to demilitarize arsenical-based munitions and fill materials. The data generated from the present study will be used to support an operation of a non-stockpile demilitarization process for the destruction of recovered arsenical-based munitions. Presently, this includes the use of PMNSCM's Explosive Destruction System (EDS), a transportable stainless steel vessel used for the enclosed detonation and chemical neutralization of RCWM. The findings of this study will also support demilitarization of munitions with similar fills that may be recovered during remedial activities at various locations.

Twenty reagent candidates were evaluated and HPO_2^{TM} Reagent (U.S. Patent Number 6,960,701; all rights reserved) was selected for this application. The selected reagent was found to be effective in dissolving reagent grade manganese dioxide and solids collected during actual demilitarization operations to neutralize arsenic-based Chemical weapons.

The selected cleaning reagent was found to be compatible with a variety of materials commonly used to construct equipment used in demilitarization activities. The selected reagent was compatible with HS316, 316L and 317L stainless steels. The selected reagent was also compatible with Viton, PTFE, PFA and HDPE. The selected reagent was found not to be compatible with nylon-66.

The components to prepare the cleaning reagent are commercially available in bulk and are stable in storage. The reagent is aqueous based and non-flammable. However, the reagent is a strong oxidizer, and appropriate procedures must be followed when working with it.

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PREFACE

The work described in this report was authorized under Contract No. DAAD13-03-D-0017. This work was started in August 2005 and completed in December 2006.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of endorsement.

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CLEANING OF RESIDUES FROM EQUIPMENT SURFACES AFTER DEMILITARIZATION OF ARSENICAL-BASED MUNITIONS AND FILL MATERIELS

1. INTRODUCTION

1.1 Background.

The U.S. Army has the mission to provide centralized management and direction to the Department of Defense (DoD) for the safe destruction of all U.S. non-stockpile chemical materiel (NSCM) as defined in Public Law 102-484, 23 October 1992. Destruction of NSCM, including recovered chemical warfare materiel (RCWM), will be in accordance with federal laws, policies, regulations, and directives, as well as applicable state and local laws and regulations. The Army is the DoD focal point for the coordination of all matters relating to NSCM destruction. This is accomplished by developing, constructing, fielding, and supporting the necessary capabilities and materiel used to characterize, contain, transport, store, treat, and dispose of NSCM, for routine and emergency response scenarios.

RCWM consist of older chemical munitions that have been recovered outside the controlled chemical stockpile. Historically, upon discovery of chemical warfare materiel (CWM), explosive ordnance disposal technicians would identify and assess the condition of the munition and determine whether the ordnance was filled with toxic chemicals and if it was safe for transportation and storage. Chemical munitions that were determined to be safe were overpacked (placed into a container with packing material as appropriate) and stored onsite or transported by the U.S. Army Technical Escort Unit (now known as the 22nd Chemical Battalion) to an appropriate chemical storage facility. Those RCWM items that could not be transported or stored due to unacceptable risks were destroyed onsite using emergency destruction procedures.

The U.S. Army Product Manager for Non-Stockpile Chemical Materiel (PMNSCM) is responsible for the destruction of several categories of chemical warfare materiel in a safe, cost effective, environmentally sound manner and in compliance with the Chemical Weapons Convention. A variety of chemical warfare agents (CWAs) and other chemicals have been identified as possible fills in recovered munitions,^{1,2} but the focus of this effort was on the demilitarization of arsenical-based munitions and fill materiel. In recent full-scale testing of the Explosive Destruction System (EDS) with actual munitions and DOT bottles containing arsenic-based chemical warfare agents, sodium permanganate was found to be an effective reagent for neutralizing these materiel.^{3,4} In practice, residues of manganese dioxide were found to deposit on various surfaces in contact with the sodium permanganate reagent. This build up of residues on surfaces was not acceptable, as the surfaces must be clean in order to achieve a good seal to prevent leaks during operations. A field-useable process for removing the residues was required to maintain operational tempo during demilitarization operations.

1.2 Study Objectives.

The primary purpose of this effort was to select and demonstrate a reagent for cleaning permanganate-based residues on equipment used to demilitarize arsenical-based munitions and fill materials. The data generated from the present study will be used to support operation of a non-stockpile demilitarization process for the destruction of recovered arsenical-based munitions. Presently, this includes the use of PMNSCM's EDS, a transportable stainless steel vessel used for the enclosed detonation and chemical neutralization of RCWM. The findings of this study will also support demilitarization of munitions with similar fills that may be recovered during remedial activities at various locations.

2. EXPERIMENTAL PROCEDURES

This section describes the in-house experimental procedures and analytical methods utilized during this project. Described are incremental cleaning studies and related experimental activities used to select and evaluate candidates for cleaning equipment surfaces after demilitarization of arsenical-based munitions and fill materials.

2.1 Micro-Scale Reaction Studies.

The approach of screening reaction chemistries and reaction conditions on a micro-scale was used to quickly eliminate chemistries from consideration, and obtain information on the most efficacious reaction conditions. Additionally, the use of this micro-scale approach drastically reduced the use of hazardous chemicals, minimizing the danger to personnel performing the reactions. The volume of waste was also drastically reduced by using this micro-scale approach. While conditions were varied depending on the experiment, the basic procedure was the same throughout this study. In a typical experiment, 2 to 10 mL of reagent was added to a 15 mL glass vial, a Teflon® (TFE) coated stir flea (8 X 1.5 mm) was added, then an aliquot of the agent feedstock was added. The vial was then capped, and placed on a hot plate with magnetic stirring capabilities. In most cases, the contents of the vial were vigorously stirred during the reaction. At an appropriate time, the vials were removed from the hot plate, and analyzed.

2.2 Small-Scale Lab Reaction Studies.

The small-scale reactions were carried out in a four neck, 250 mL round bottom glass flask, equipped with an air-cooled condenser and TFE coated thermocouple. Stirring was accomplished by use of a TFE coated stir bar, and a magnetic stir plate, with the reaction stirred at moderate speed throughout the reaction. Heating was accomplished by the use of an electric heating mantle, with temperature control maintained by using a J-KEM temperature controller. Throughout all steps of the reaction, N₂ gas was purged through the reactor headspace at a rate of 1-2 mL/min, and was vented through the condenser. In selected runs the N₂ gas was then passed through two acid-filled impingers, connected in series to the condenser. Each impinger contained 3 mL of 0.1N HNO₃(aq).

In a typical run, 100 mL of cleaning reagent was added to the reactor, stirring and

N₂ purge started, and the temperature adjusted to 30 °C. Once the temperature stabilized, the feedstock was added over the course of 5-10 min, and the reaction was allowed to proceed. Samples were removed from the reactor periodically after the addition of the feedstock was completed. A total of 2 mL was removed for each time point, and the samples were analyzed for pH, oxidizing capacity (if appropriate) and total dissolved metals. In addition, observations were recorded throughout the reaction. The samples were removed from the reactor using a plastic pipet, with the pipet tip maintained approximately ¾ of an inch below the liquid surface. Stirring was stopped 1 min prior to sampling to minimize removal of undissolved solids from the reactor. If utilized, impinger samples were only collected after the run was terminated.

2.3 Reagents.

All chemicals utilized in this effort were typically of ACS reagent grade, and were used as received from the manufacturer. L-ascorbic acid (C₆H₈O₆, 99+%, CAS No. 50-81-7), ethylenediaminetetraacetic acid, tetrasodium salt hydrate (EDTA, 98%, CAS No. 64-02-8), hydrogen peroxide (H₂O₂, 50%, CAS No. 7722-84-1), manganese dioxide (MnO₂, 99+%, -60 to +230 mesh, CAS No. 1313-13-9), potassium peroxymonosulfate (Oxone®, CAS No. 76093-62-8), sodium bisulfite (NaHSO₃, 99+%, CAS No. 7631-90-5), sodium chloride (NaCl, 99+%, CAS No. 7647-14-5), sodium permanganate (NaMnO₄, 40%, CAS No. 10101-50-5) and nitric acid (HNO₃, 69.5+%, CAS No. 7697-37-2) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). The acetic acid (C₂H₄O₂, glacial, CAS No. 64-19-7) and sodium bicarbonate (NaHCO₃, U.S.P, CAS No. 144-55-8) were purchased from JT Baker (Phillipsburg, NJ, USA). The As, Fe and Mn standards were purchased from Ultra Scientific (Kingstown, RI, USA). The vinegar (white, distilled) and hydrogen peroxide (topical solution, 3%) used to prepare the peracetic acid solution was purchased from Food Lion (Salisbury, NC, USA).

The ASTM Type I water was obtained from an in-house system (18 MS, Nanopure, Barnstead, Dubuque, IA, USA).

2.4 Sample Matrices.

In addition to the reagent grade MnO₂ used to evaluate reagent efficacy, solids collected during full-scale testing of the EDS against arsinol-based fills were also utilized.³ The EDS is a trailer-mounted system designed to safely neutralize a variety of chemical munitions.^{5,6} It employs explosive-shaped charges to breach the munition's wall, exposing the chemical fill, while containing the chemical fill at the same time. Once the fill is exposed, chemical reagents are added, and the vessel is agitated and heated. After neutralization, waste materials are removed from the reaction vessel and transported to a treatment, storage, and disposal facility (TSDF) for final disposal. In a previous study,³ solids were separated from two types of waste streams: waste and sludge. The waste is a mixture of neutralent drained from the EDS and water used to rinse out the EDS. The sludge is the solids remaining in the EDS after the final rinse, and contains larger pieces of metal and other debris. The solids were isolated by vacuum filtration through a 0.8 µm cellulose nitrate filter, after which ice-cold deionized water was used to wash the solids. After air drying overnight in a hood, the solids were stored in a desiccator. Composite samples of each sample type were prepared to provide enough material for this study, and are referred to as "Arsinol Waste" and "Arsinol Sludge".

The composited solids were analyzed for total metals using the digestion procedure specified in SW846, Method 3010A,⁷ and all digestions were performed in duplicate. Approximately 50 mg of sample (exact weight recorded) was digested, and the final digest volume brought to 0.1 L. The digests were analyzed using EPA Method 200.8 for arsenic, iron, and manganese.⁸ In addition to the isolated solids, concurrent digests of a Standard Analytical Reference Material (SARM) soil (NIST 2710, Montana Soil) were also performed. The reference values were 626 mg/kg As, 33,800 mg/kg Fe, and 10,100 mg/kg Mn. The average recoveries (n=2) for the SARM soil were 96.1% for arsenic, 72.1% for iron, and 84.7% for manganese. The concurrently run laboratory QC samples, such as the laboratory control and sample matrix spikes, were all within acceptable quality limits. There were no deviations or anomalies reported during the digestion or analysis of the samples during the total metal testing. The results are summarized in Table 1.

Table 1. Total Metal Content of the Composited Solids. Results are reported in the original sample, and are averages of duplicate digestions.

Total Metal	Concentration (mg/kg) ^a	
	Arsinol Waste	Arsinol Sludge
Arsenic	32,200	60,100
Iron	12,900	48,300
Manganese	281,000	234,000

a. Average of duplicate digestions

The solution used to contaminate the coupons (Section 3.3) was prepared from neutralent generated during actual EDS operations.⁴ The permanganate had completely decomposed in this neutralent sample, so it was necessary to reconstitute to 20 wt% NaMnO₄. The EDS neutralent sample was vacuum filtered (0.45 μm Nylon membrane filter) and 720 mL of the filtrate was combined with 720 mL of 40 wt% NaMnO₄ reagent. In addition NaCl and NaHAsO₄ was added to bring the concentration of Cl⁻ and HAsO₄⁻² to near actual concentrations measured in the original neutralent.⁴ This contaminating solution was prepared three days before the coupon testing started.

2.5 Residual Oxidizing Capacity.

Residual oxidizing capacity was determined using starch-iodide paper (VWR Scientific). The starch-iodide paper is a semi-quantitative technique, relying on operator interpretation of a color change. In the presence of an oxidizer, the paper changes from white to purple. The darker the color, the higher the concentration of an oxidizer. In this study observations on color changes were recorded as follows: dark purple-black (DPB), dark purple (DP), light purple (LP), and no color change (NCC). In a previous effort, a linearity study was performed on Oxone[®] (potassium peroxydisulfate, CAS No. 37222-66-5) solutions in conjunction with testing the solutions using starch-iodide paper. The linearity study involved performing a standard titration procedure and concurrently testing with starch-iodide paper. The starch iodide paper was capable of detection down to 18 mg/L Oxone[®]. The response using starch-iodide paper became saturated (color was DPB) at 120 mg/L Oxone[®].

2.6 Total Dissolved Metals.

The filtered liquid samples were analyzed for total dissolved metals by first diluting 1 mL of sample to 100 mL with 0.01% HNO₃ (aq), with some samples prepared in duplicate. The acidified samples were analyzed using EPA Method 200.8 for arsenic, iron, and manganese.⁸ In addition to the diluted samples, analysis of liquid reference standards (Ultra Scientific) were also performed. The reference values were 1,000 mg/L arsenic, 940 mg/L iron, and 980 mg/L manganese. The average recoveries (n=2) for the reference solutions were 97.5% for arsenic, 95.1% for iron, and 93.9% for manganese. The concurrently run laboratory QC samples, such as the laboratory control and sample matrix spikes, were all within acceptable quality limits. There were no deviations or anomalies reported during the dilution or analysis of the samples during the total dissolved metals testing.

2.7 Determination of Arsenic Species.

Capillary electrophoresis (CE) with direct and indirect photometric detection was used to further characterize select samples generated during this study. Specifically, capillary zone electrophoresis (CZE) and micellar electrokinetic chromatography (MEKC), two particular disciplines of CE, were coupled with ultraviolet (UV) detection to determine arsinol degradation products. The technique of arsenic speciation by CE with direct UV detection for organoarsenicals and inorganic arsenic-containing compounds was first reported at the 1997 ERDEC Scientific Conference on Chemical and Biological Defense Research.⁹ Prior to that, CE methods were established in the literature for a number of chemical weapons agents' degradation products to include the detection of 2-chlorovinyl arsonic acid (CVAOA) by CE in 1995,¹⁰ the characterization of sulfur mustard and lewisite degradation products,^{11,12} and the characterization of phenyl-arsenical reaction products and impurities.³

The target analytes investigated by CE include the more polar, non-volatile chemicals resulting from degradation of starting feedstock or impurities in the starting feedstock or reagent. Arsinol degradation products analyzed for by CE with direct UV detection include phenylarsine oxide (PAO), triphenylarsine oxide (TPAO), phenylarsonic acid (PAOA) and diphenylarsinic acid (DPAOA). Other arsenic-containing degradation products analyzed for by

CE include the inorganic components, arsenate (AsO_4) and m-arsenite (AsO_2). These were analyzed by indirect UV detection. A summary of the targeted analytes is provided in Table 2 and the structures of the targeted organo-arsenicals are illustrated in Figure 1. Interested readers can find detailed descriptions of the CE methods in other ECBC technical reports.^{3,4}

Table 2. Summary of Targeted Analytes Determined by the CE Methods.

Chemical Name	CAS Number	Chemical Formula	Analyte Formula	CE Reporting Limit (mg/L) ^a
Sodium arsenite	1327-53-3	NaAsO_2	AsO_2^-	3.3
Potassium arsenate	7784-41-0	KH_2AsO_4	HAsO_4^-	1.6
Phenylarsonic acid	98-05-5	$\text{C}_6\text{H}_7\text{AsO}_3$	$\text{C}_6\text{H}_5\text{AsO}_3^{-2}$	0.5
Diphenylarsinic acid	4656-80-8	$\text{C}_{12}\text{H}_{11}\text{AsO}_2$	$\text{C}_{12}\text{H}_{10}\text{AsO}_2^-$	0.5
Phenylarsine oxide	637-03-6	$\text{C}_6\text{H}_5\text{AsO}$	$\text{C}_6\text{H}_5\text{AsO}$	1.0
Triphenylarsine oxide	1153-05-5	$\text{C}_{18}\text{H}_{15}\text{AsO}$	$\text{C}_{18}\text{H}_{15}\text{AsO}$	0.5

a. Reporting limit at the instrument; does not include dilution factor of the sample.

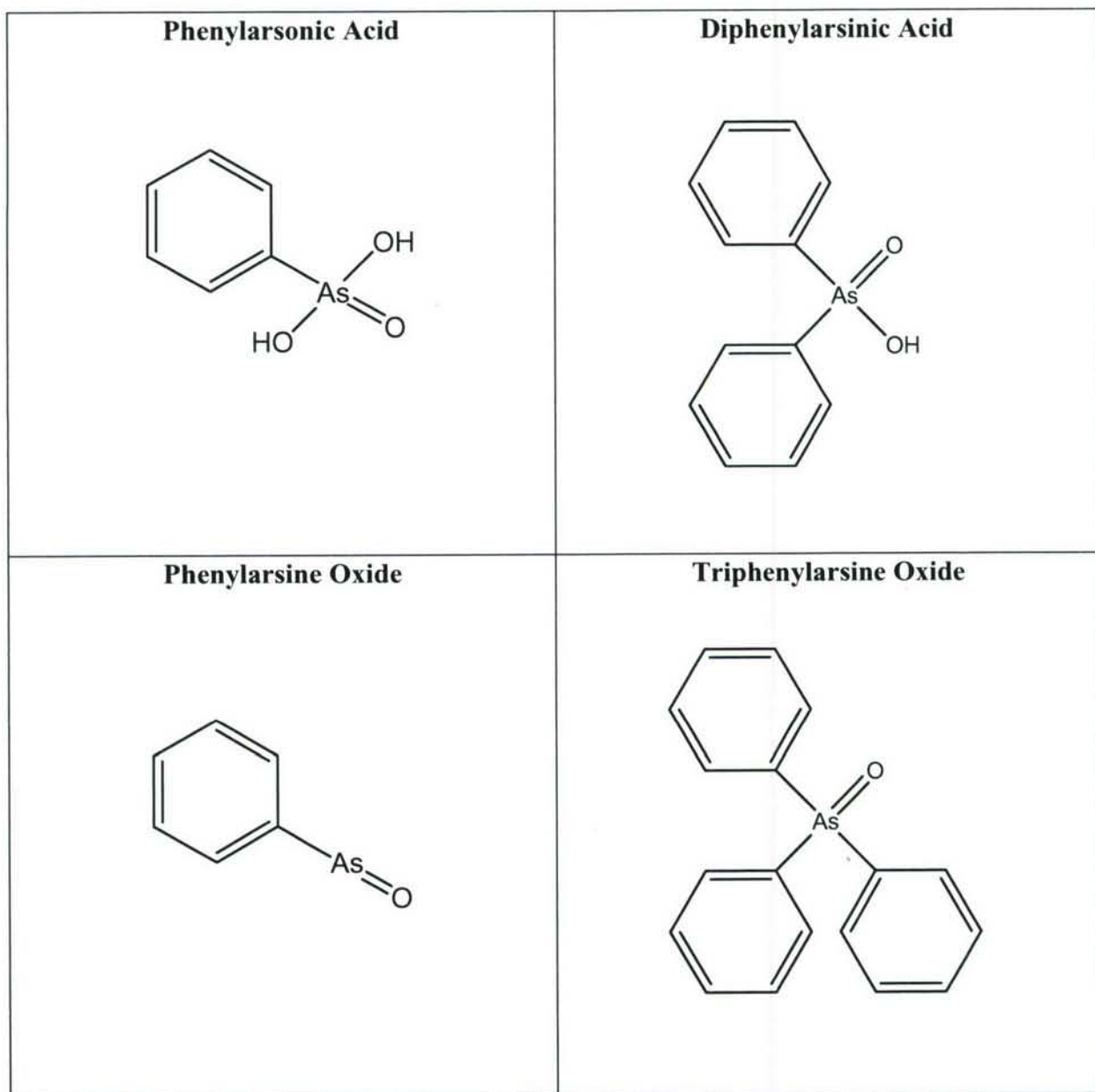


Figure 1. Structures of Select Organo-Arsenicals Determined by the CE Methods.

3. RESULTS AND DISCUSSION

3.1 Selection of Cleaning Reagent.

Initial work examined the micro-scale performance of 16 cleaning reagent candidates, including one recommended by the manufacturer of permanganate. This was followed by small-scale screenings of five reagents selected for further evaluation, and then force-to fail experiments utilizing the best candidate. Finally, a lab-scale demonstration of cleaning scenarios was conducted.

3.1.1 Micro-Scale Screening of Reagent Candidates.

In initial experiments, 16 candidate cleaning solutions were evaluated for efficacy in dissolving manganese dioxide, which is a primary component of the films being deposited on equipment subjected to permanganate reagent.^{3,4} These solutions included a cleaning solution recommended by the manufacturer of NaMnO_4 ,¹³ five concentrations of nitric acid ranging from 2.2 to 35%, six concentrations of HPO_2^{TM} reagent ranging from 50% to 100% full-strength, 50 wt% aqueous sodium hydroxide, and three commercially available cleaning solutions. The cleaning solution recommended by Carus is an aqueous peracetic acid solution prepared by mixing dilute acetic acid with dilute hydrogen peroxide. The HPO_2^{TM} reagent was originally developed for the neutralization of HD, HL and other organo-arsenicals.^{14,15} These solutions were evaluated at room temperature ($\sim 22\text{-}24\text{ }^\circ\text{C}$), at a loading of 50 mg manganese dioxide to 2 mL of cleaning solution. Visual estimates of percent manganese dioxide dissolved were made at 2 and 18 hr after the candidate cleaning solution was added to the manganese dioxide.

The results are summarized in Table 3. The only two candidates to visibly dissolve any of the manganese dioxide were the peracetic acid solution, and the six concentrations of the HPO_2^{TM} reagent. Surprisingly, the nitric acid solutions (including the 35%) did not (by visual observation) dissolve any of the manganese dioxide. The nitric acid treatments were repeated, and the same results were obtained. The peracetic acid solution recommended by Carus only dissolved 10% of the manganese dioxide, even after 18 hr of contact. The 100% HPO_2^{TM} reagent dissolved 50% after 2 hr, and 80% after 18 hr. These results are illustrated in Figure 2. It should be noted, even prior to this preliminary study, the 100% HPO_2^{TM} reagent was used to clean glassware contaminated with permanganate residues during lab-scale evaluations of the permanganate chemistry.^{3,4}

Table 3. Dissolution of Manganese Dioxide by Candidate Cleaning Solutions.

Cleaning Solution	Observations		
	Initial	After 2 Hr	After 18 Hr
Peracetic Acid	Bubbled; warm to touch	No longer bubbling; ~10% of MnO ₂ dissolved	No longer bubbling; ~10% of MnO ₂ dissolved
35% HNO ₃	No apparent reaction	No apparent reaction	No apparent reaction
17.5% HNO ₃	No apparent reaction	No apparent reaction	No apparent reaction
8.8% HNO ₃	No apparent reaction	No apparent reaction	No apparent reaction
4.4% HNO ₃	No apparent reaction	No apparent reaction	No apparent reaction
2.2% HNO ₃	No apparent reaction	No apparent reaction	No apparent reaction
100% HPO ₂ TM Reagent	Bubbled; hot to touch	Still bubbling; ~50% of MnO ₂ dissolved	No longer bubbling; ~80% of MnO ₂ dissolved
83% HPO ₂ TM Reagent	Bubbled; warm to touch	Still bubbling; ~30% of MnO ₂ dissolved	No longer bubbling; ~30% of MnO ₂ dissolved
80% HPO ₂ TM Reagent	Bubbled; warm to touch	Still bubbling; ~30% of MnO ₂ dissolved	No longer bubbling; ~30% of MnO ₂ dissolved
75% HPO ₂ TM Reagent	Bubbled; warm to touch	Still bubbling; ~30% of MnO ₂ dissolved	No longer bubbling; ~30% of MnO ₂ dissolved
67% HPO ₂ TM Reagent	Bubbled; warm to touch	Still bubbling; ~15% of MnO ₂ dissolved	No longer bubbling; ~15% of MnO ₂ dissolved
50% HPO ₂ TM Reagent	Bubbled; warm to touch	Still bubbling; ~15% of MnO ₂ dissolved	No longer bubbling; ~15% of MnO ₂ dissolved
50% NaOH	No apparent reaction	No apparent reaction	No apparent reaction
Easy Off® Oven Cleaner ^a	No apparent reaction	No apparent reaction	No apparent reaction
CLR Cleaner ^b	No apparent reaction	No apparent reaction	No apparent reaction
Easy Off BAM Cleaner ^c	No apparent reaction	No apparent reaction	No apparent reaction

a). Easy Off® Heavy Duty Original Oven Cleaner; contains NaOH; pH = 13.
b). Calcium, Lime, Rust Remover; contains lactic acid, gluconic acid, and surfactants; pH = 3-4.
c). Easy Off® BAM Grime and Lime Remover; contains sulfamic acid; pH = 0-1.

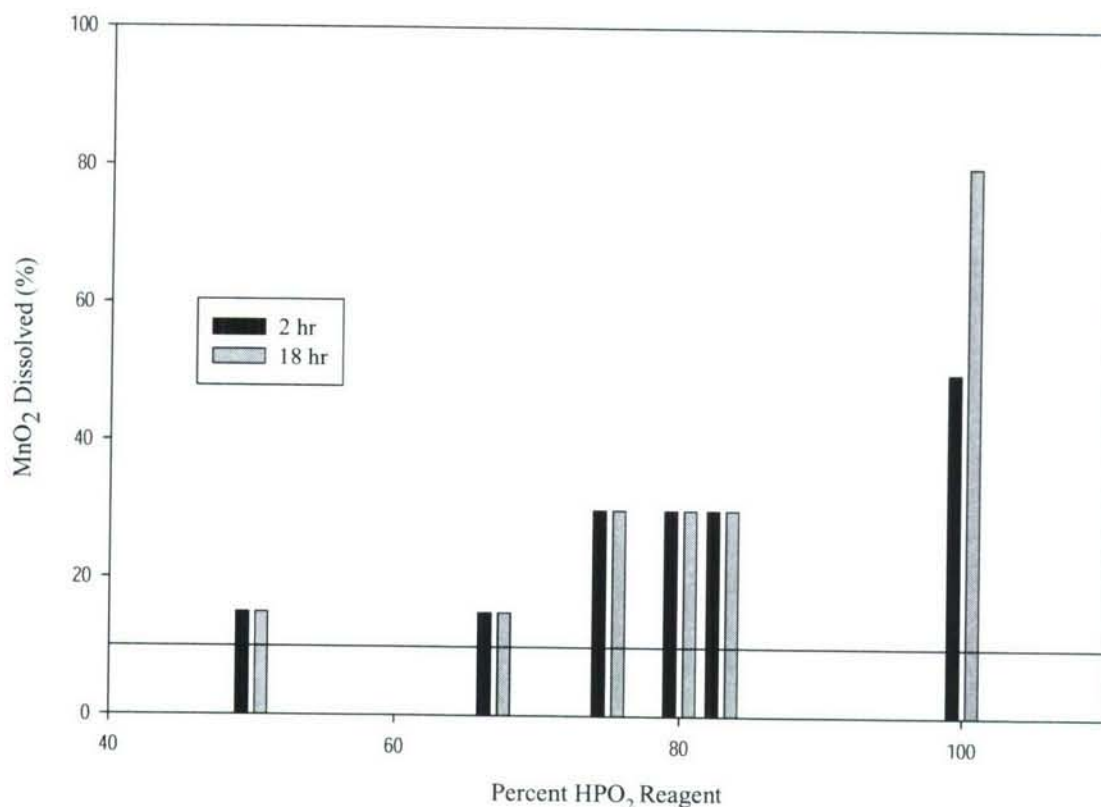


Figure 2. Efficacy of HPO₂TM Reagent for Dissolving Manganese Dioxide. The solid horizontal line is the dissolution of manganese dioxide by a peracetic acid solution after 18 hr reaction.

3.1.2 Small-Scale Screening of Reagent Candidates.

Results from the micro-scale screening (Section 3.1.1) and discussions with the working group, resulted in five reagents being chosen for evaluation during the initial small-scale screening. The reagents evaluated were: HPO₂TM reagent, HPO₂TM reagent modified with 5% (wt/v) sodium bicarbonate, a 1:1 (v:v) mixture of white vinegar and 3% hydrogen peroxide, 5% (wt/v) sodium bisulfite in 0.01% acetic acid, and 5% (wt/v) ascorbic acid in 0.01% acetic acid. The HPO₂TM reagent was modified with sodium bicarbonate because sodium bicarbonate has been demonstrated to be activated to peroxydicarbonate in the presence of peroxide.¹⁶ In addition, the modification of HPO₂TM reagent with bicarbonate has been demonstrated to enhance the effectiveness against arsenic-based CWAs.¹⁷ The acidic ascorbic acid was selected because acidic reducing conditions have been demonstrated to be effective in dissolving manganese dioxide.¹⁸ In addition, deionized water was also evaluated as a control. The reactions were conducted in a completely randomized order, with each reaction conducted in duplicate. A total of 12 small-scale reactions were conducted during this small-scale screening effort.

The small-scale reactions were carried out in a four neck, 250 mL round bottom glass flask, equipped with an air-cooled condenser and TFE coated thermocouple. Stirring was

accomplished by use of a TFE coated stir bar, and a magnetic stir plate, with the reaction stirred at moderate speed throughout the reaction. Heating was accomplished by the use of an electric heating mantle, with temperature control maintained by using a J-KEM temperature controller. Throughout all steps of the reaction, N₂ gas was purged through the reactor headspace at a rate of 0.5-1 mL/min, and was vented through the condenser. During the bisulfite runs only, the N₂ gas was then passed through two acid-filled impingers, connected in series to the condenser. Each impinger contained 3 mL of 0.01% HNO_{3(aq)}.

In these runs, 100 mL of reagent was added to the reactor, stirring and N₂ purge started, and the temperature adjusted to 30 °C (86 °F). Once the temperature stabilized, MnO₂ (0.95-1.00 g, exact mass recorded) was quickly added as a single bolus, and the reaction was allowed to proceed. Time point samples were removed from the reactor 15, 30, 45, 60, 90, 120, 180, 240, 300, and 360 min after the MnO₂ was added to the reactor. A total of 2 mL was removed for each time point sample, and immediately filtered through a 0.2 µm PTFE Acrodisc® filter. The samples were then analyzed for pH (pH strips), oxidizing capacity (if applicable; Section 2.5), and total dissolved manganese (Section 2.6). In addition, observations were recorded throughout the reaction. The time point samples were removed from the reactor using a plastic pipet, with the pipet tip maintained approximately ¾ of an inch below the liquid surface. Stirring was stopped one minute prior to sampling, to minimize removal of undissolved solids from the reactor. Impinger samples were only collected after the run was terminated at 360 min and were only utilized for the bisulfite runs.

A summary of results is found in Table 4 and the dissolved manganese results are illustrated in Figures 3 through 5. The HPO₂TM reagent was the only reagent which completely dissolved the MnO₂. In the case of the HPO₂TM reagent, there were no visible solids remaining 15 min after the MnO₂ was added to the reagent. In the bisulfite runs, the appearance of the remaining solids changed significantly and the dissolved manganese initially increased, then decreased over time. It is suspected manganese carbonate (MnCO₃, CAS No. 598-62-9) was being formed in the bisulfite runs.¹⁸ On average, in the bisulfite runs, the first impinger trapped 0.71 mg of SO₄⁻², and the second impinger trapped 0.65 mg of SO₄⁻². In total, assuming all the SO₄⁻² is from SO₂, this translates into 0.91 mg of SO₂ being trapped by the impingers. This is less than 0.03% of the total theoretical amount of possible SO₂.¹⁹ It appears the nitric acid solution was not an effective trapping agent for SO₂.

Table 4. Summary of Results from the Small-Scale Screening Reactor Runs.

Candidate Solution	Exotherm		pH ^a		KIS ^b		Solids Remaining?
	(°C)	(°C/min)	Initial ^c	Final ^d	Initial ^c	Final ^d	
DIW	0	NA	5.0 – 5.3	5.0 – 5.3	NA	NA	Yes
HPO ₂ TM	16.7	2.2	1.0	1.3 – 1.6	DPB	DPB	No ^e
Modified HPO ₂ TM	30.1	1.1	7.0 – 7.5	5.0 – 5.5	DPB	DPB	Yes
Vinegar: Peroxide	1.9	0.2	2.0 – 2.5	4.5	DP	NCC ^f	Yes
Bisulfite	0	NA	4.0	5.0 – 5.3	NA	NA	Yes
Ascorbic Acid	0	NA	2.0	4.5 – 5.0	NA	NA	Yes

a. Determined using narrow range pH strips.

b. Residual oxidizing capacity determined using starch iodide paper; darker color indicates stronger oxidizer.

c. Reagent before MnO₂ added.

d. Determined on 360 min time point sample.

e. No visible solids at the 15 min sampling point.

f. No reaction; oxidizing capacity of reagent exhausted. Reagent exhausted at 240 min time point.

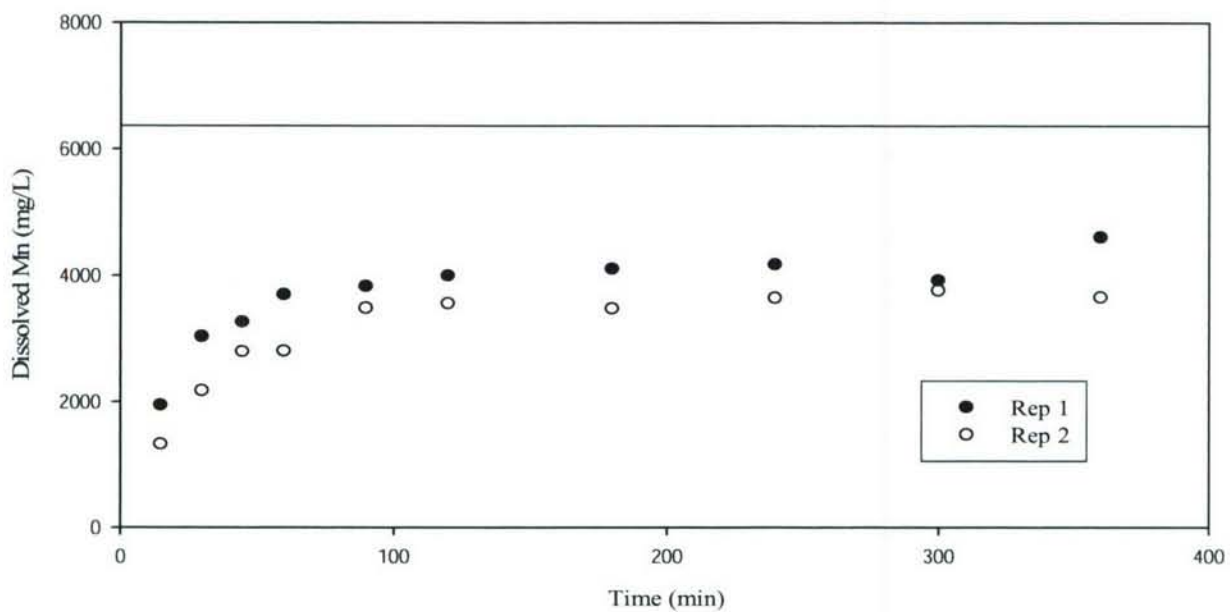
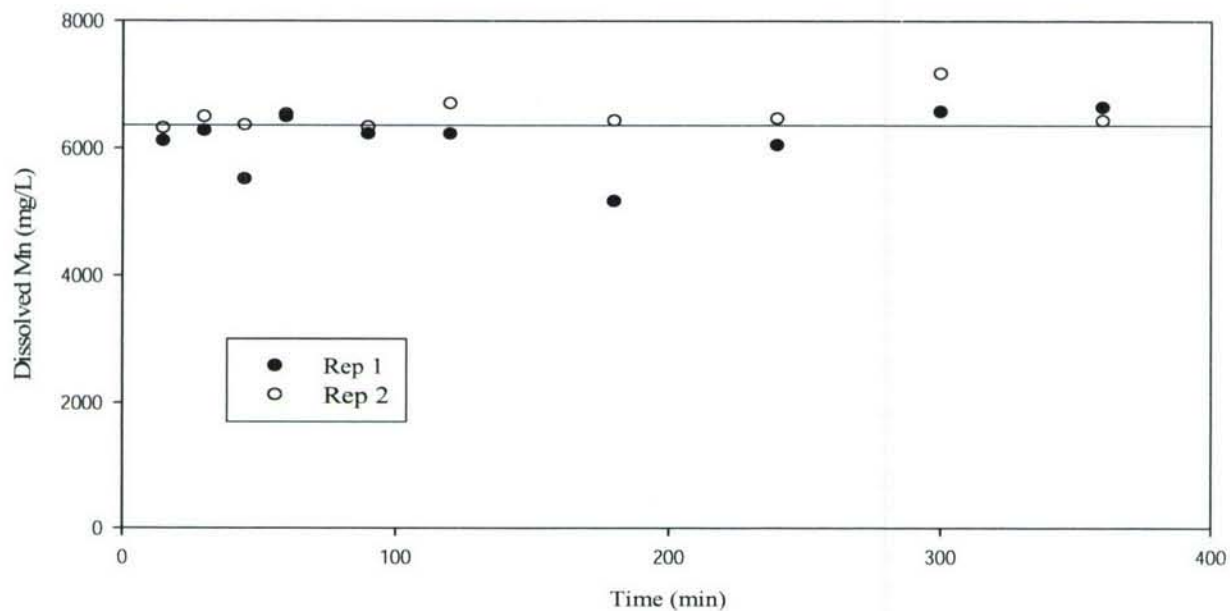


Figure 3. Dissolved Manganese as a Function of Time when Manganese Dioxide is Exposed to HPO₂TM-Based Cleaning Reagent Candidates. The upper panel is the HPO₂TM reagent, and the bottom panel is the modified HPO₂TM reagent. The horizontal black lines represent the theoretical amount of dissolved manganese if all the manganese dioxide is dissolved in 0.1 L.

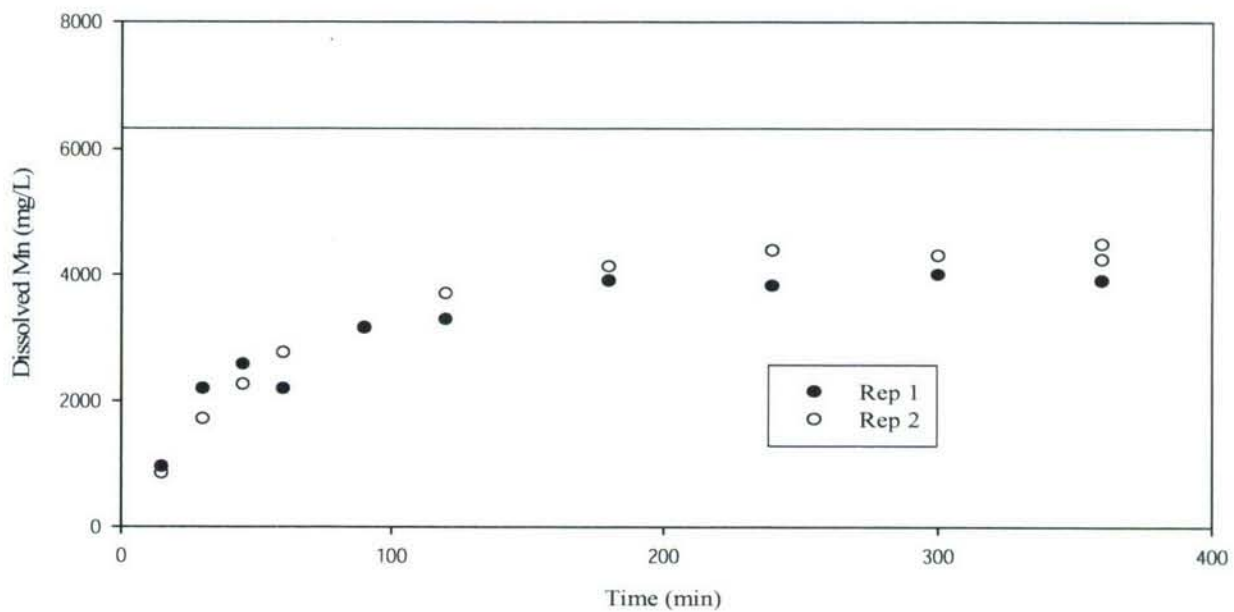
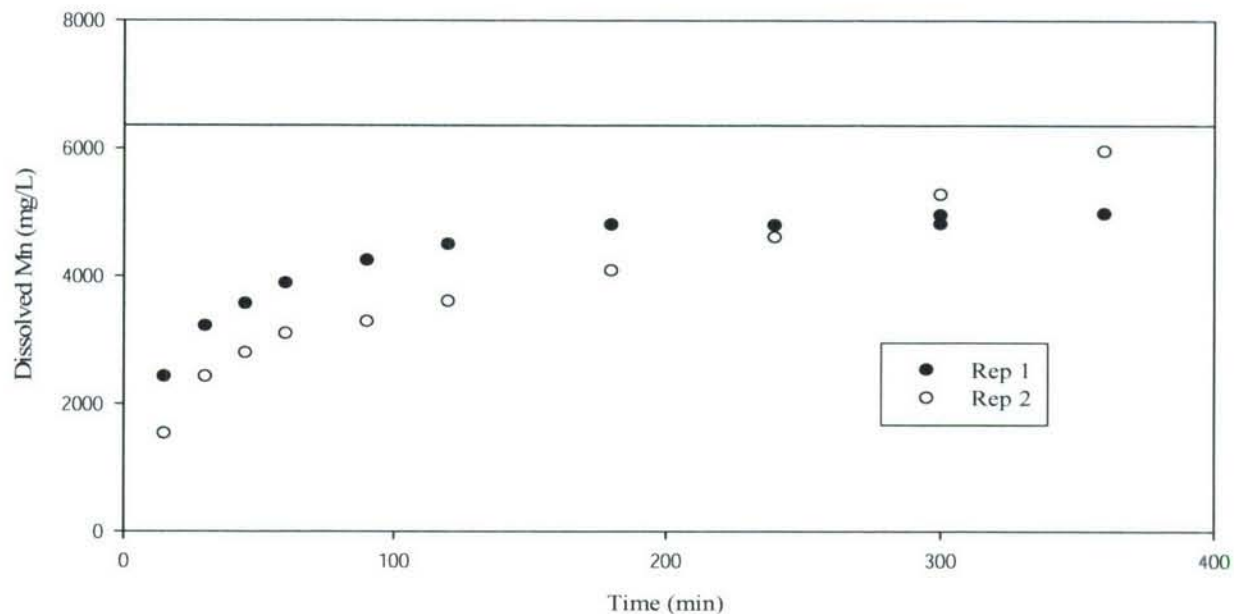


Figure 4. Dissolved Manganese as a Function of Time when Manganese Dioxide is Exposed to Cleaning Reagent Candidate. The upper panel is the ascorbic acid reagent, and the bottom panel is the peracetic acid reagent. The horizontal black lines represent the theoretical amount of dissolved manganese if all the manganese dioxide is dissolved in 0.1 L.

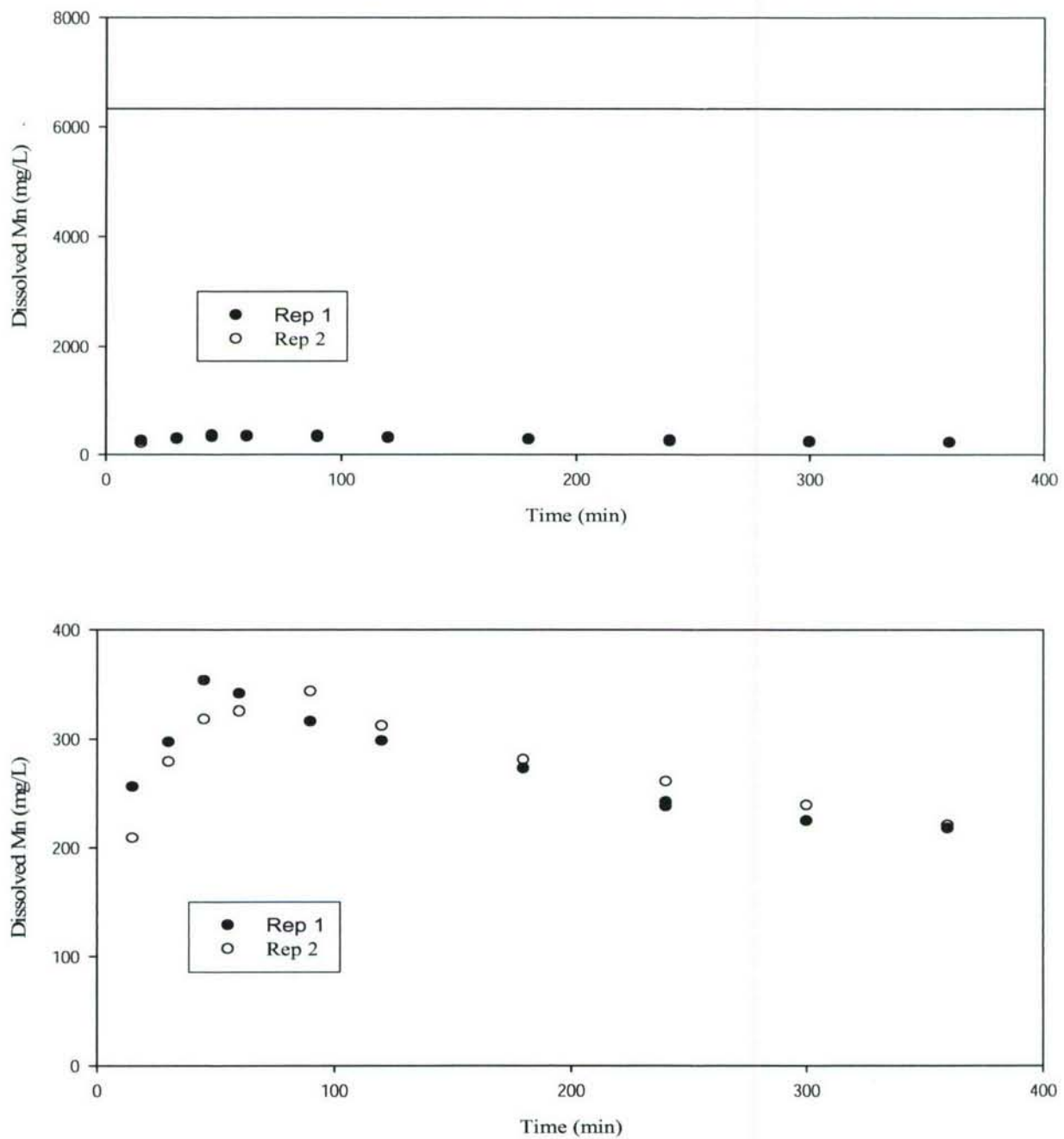


Figure 5. Dissolved Manganese as a Function of Time when Manganese Dioxide is Exposed to a Bisulfite-Based Cleaning Reagent. The upper panel is full-scale, and the bottom panel is zoomed in. The horizontal black lines represent the theoretical amount of dissolved manganese if all the manganese dioxide is dissolved in 0.1 L.

3.1.3 Micro-Scale Force to Failure Experiments.

The small-scale reactions described in Section 3.1.2 were performed at a loading of MnO₂ to reagent of 10 mg/mL. Micro-scale experiments were conducted to examine the efficacy of reagents, under a variety of loadings. In these micro-scale experiments, various amounts of MnO₂ (ranging from 100 to 2,000 mg; exact weight recorded) were weighed into 40 mL glass vials, a stir bar added, then 10 mL of reagent was added. A total of seven loadings were evaluated in duplicate, for a total of 14 samples per reagent. The vials were placed on a stir plate, stirred at a moderate speed for 60 min, and maintained at 30 °C. At the end of 60 min, the entire sample was filtered (0.45 µm Acrodisc™), and the undissolved MnO₂ washed with deionized water to remove excess reagent. The pH and residual oxidizing capacity (if appropriate) were determined on the filtrate, and the amount of MnO₂ remaining was determined after drying overnight in a desiccator.

The dissolved Mn and pH data are illustrated in Figures 6 through 8. Across all loadings, the average amounts of dissolved Mn for each of the reagents were: 34.7 mg/mL for HPO₂™ reagent, 11.0 mg/mL for ascorbic acid reagent, 7.20 mg/mL for peracetic acid reagent, 5.79 mg/mL for modified HPO₂™ reagent, and -0.923 mg/mL for bisulfite reagent. Overall, the HPO₂™ was the most efficacious in dissolving MnO₂, being three times better than the next best candidate. In addition, HPO₂™ reagent was the only reagent candidate to completely dissolve the MnO₂ at any of the loadings.

The negative dissolution for the bisulfite reagent is indicative of the formation of a solid suspected to be MnCO₃. The formation of MnCO₃ has been reported to occur during the reaction of manganese compounds with sulfite and bisulfite salts.¹⁸ The solids recovered during the bisulfite runs were digested and analyzed for total Mn using established procedures.^{7,8} The average (n=4) weight percent Mn in the solids recovered from the bisulfite runs was 54.7 wt%. This value falls within the theoretical limits for MnCO₃ (47.8 wt%) and MnO₂ (63.2 wt%), suggesting the presence of a mixture of the two chemicals. The apparent negative dissolution is therefore from formation of MnCO₃, with the extra weight coming from carbonate, not Mn. The formation of SO₂ (Section 3.1.2) and the formation of a solid should preclude the use of sulfite/bisulfite reagents in the demilitarization of CWAs with permanganate based reagents. In addition to the generation of a toxic gas,²⁰ the generation of MnCO₃ might encapsulate CWAs, preventing effective neutralization.

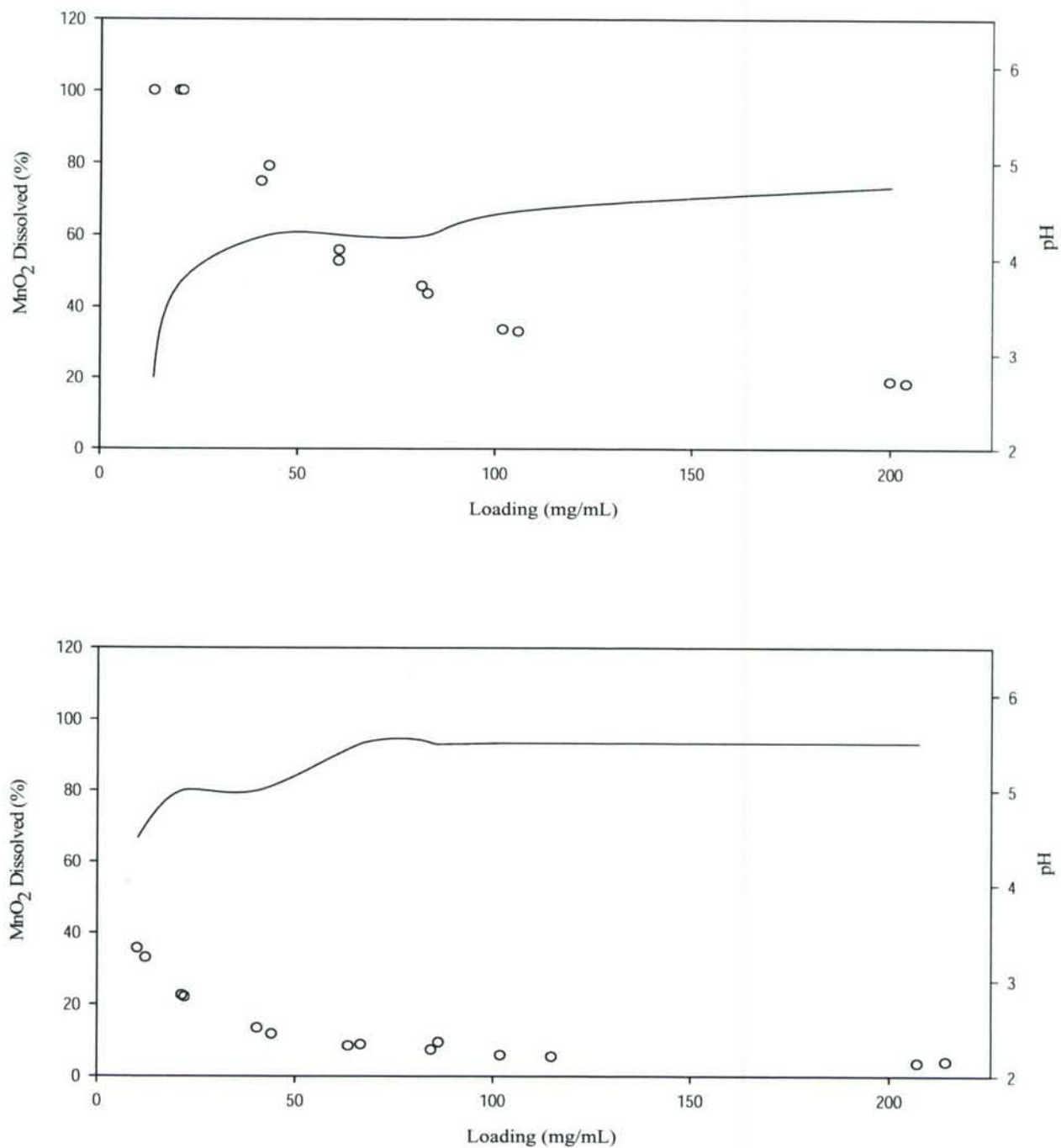


Figure 6. Percent Dissolution as a Function of Loading when Manganese Dioxide is Exposed to HPO₂TM-Based Cleaning Reagent Candidates. The upper panel is the HPO₂TM reagent, and the bottom panel is the modified HPO₂TM reagent. The open circles are percent manganese dioxide dissolved and the solid line is the pH of the filtrate.

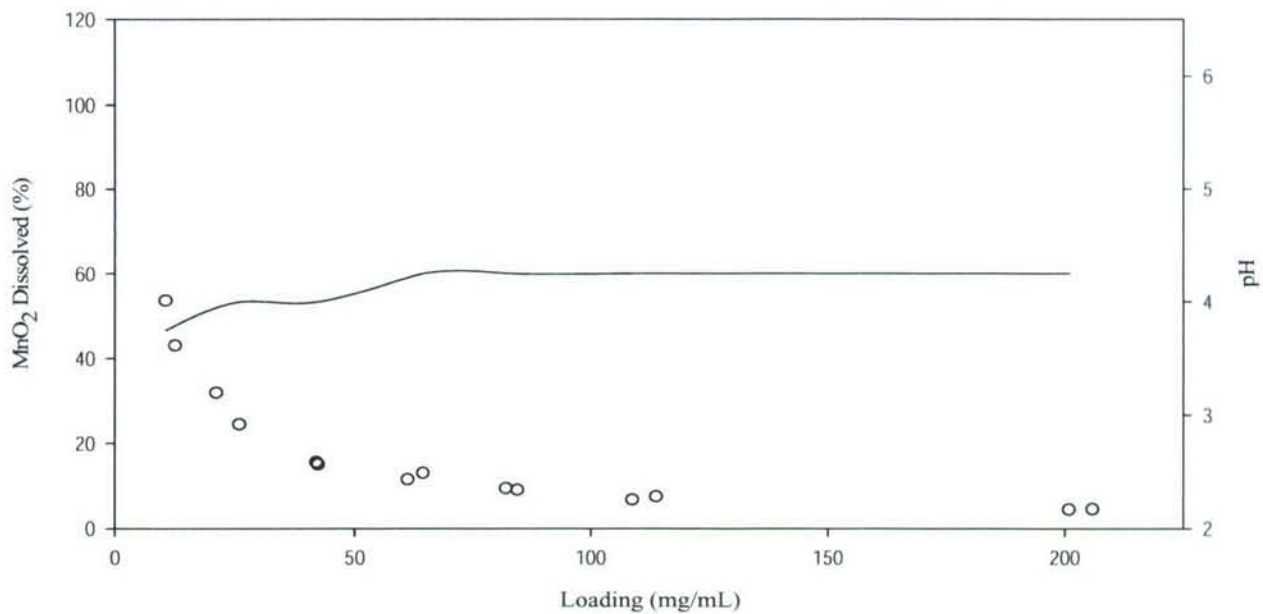
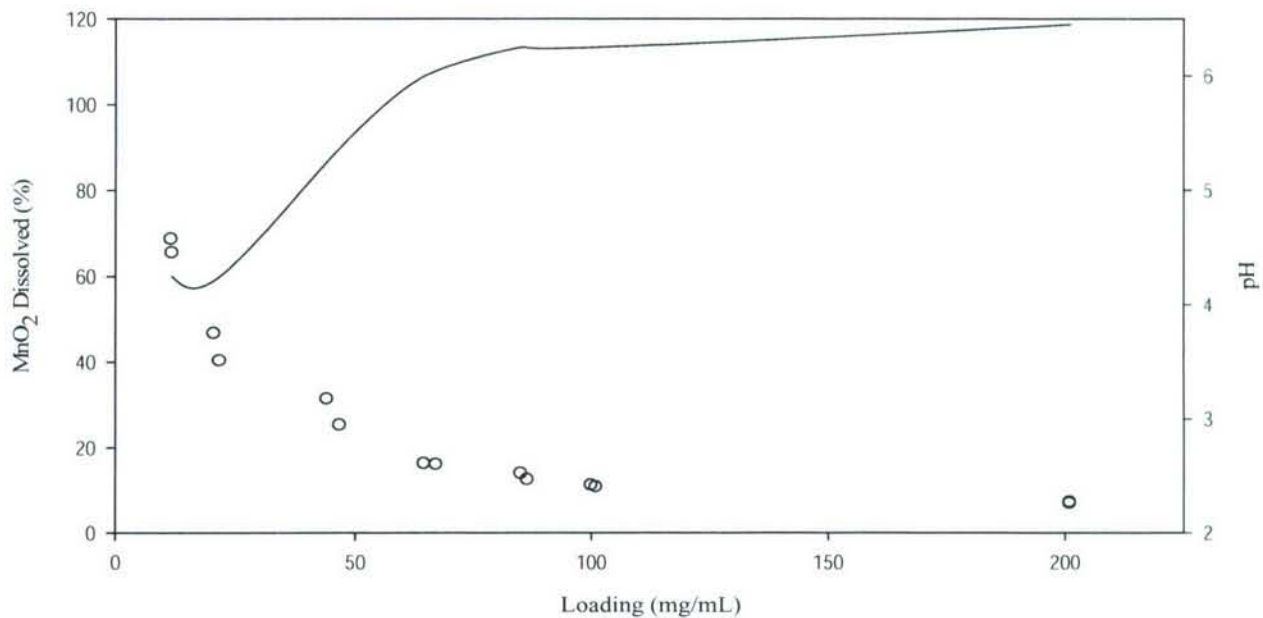


Figure 7. Percent Dissolution as a Function of Loading when Manganese Dioxide is Exposed to Cleaning Reagent Candidates. The upper panel is the ascorbic acid reagent, and the bottom panel is the peracetic acid reagent. The open circles are percent manganese dioxide dissolved and the solid line is the pH of the filtrate.

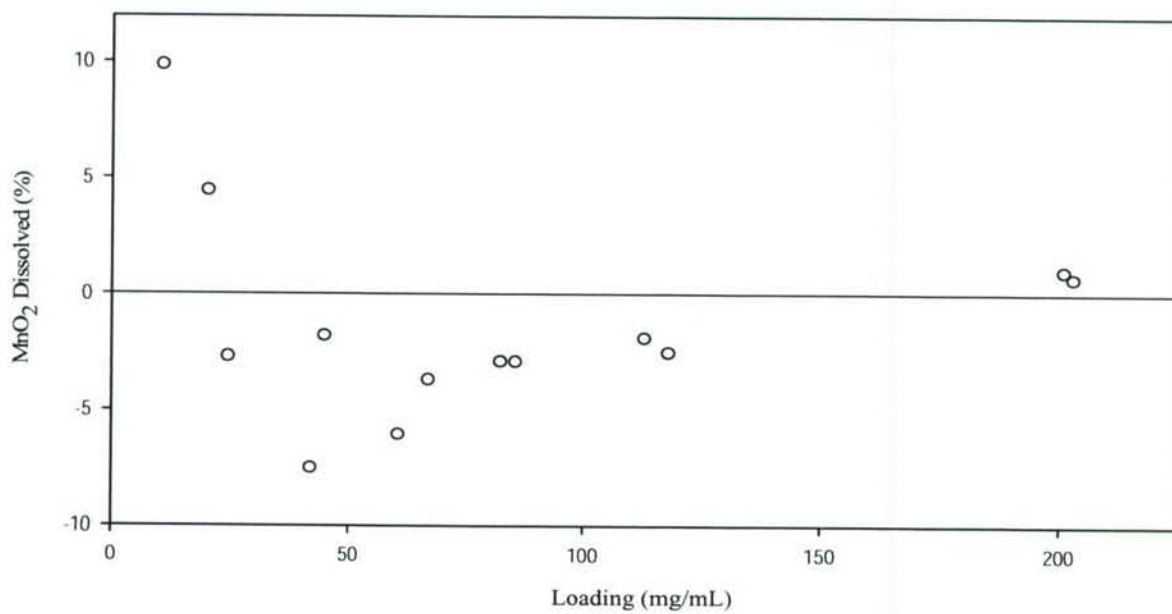
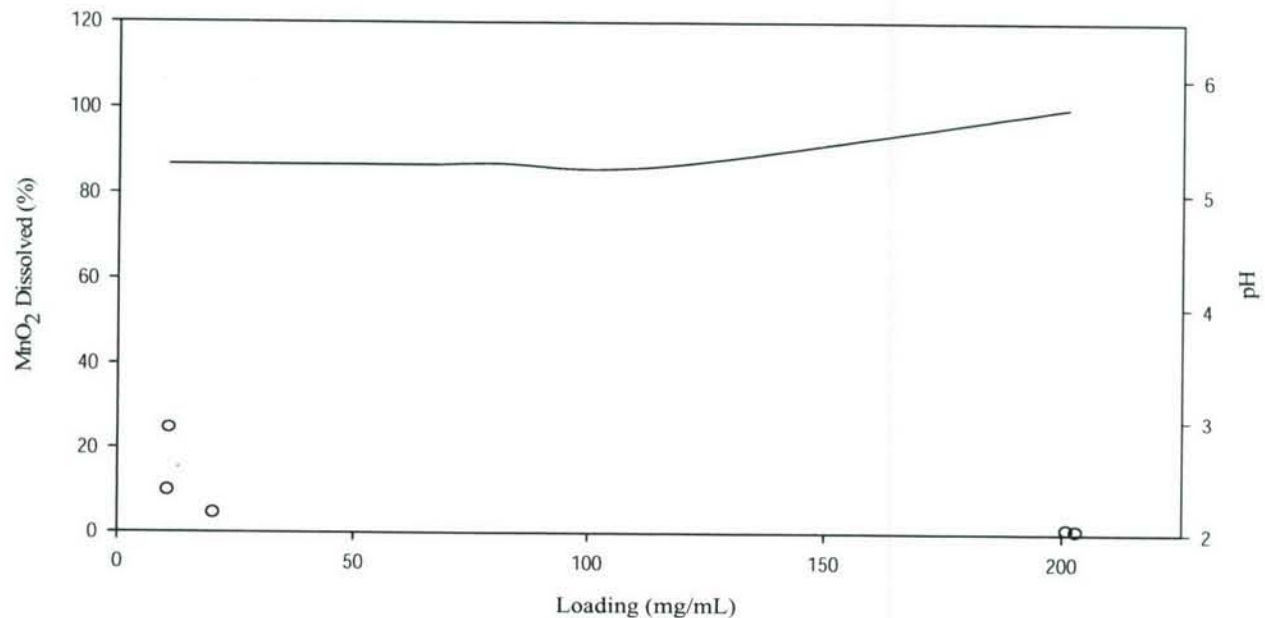


Figure 8. Percent Dissolution as a Function of Loading when Manganese Dioxide is Exposed to a Bisulfite-Based Cleaning Reagent Candidate. The upper panel is full scale and the lower panel is zoomed in to show the dissolution data. The open circles are percent manganese dioxide dissolved and the solid line in the upper panel is the pH of the filtrate.

3.1.4 Small-Scale Force to Failure Experiments.

In consultation with the working group and based on previous results (Section 3.1.3), HPO₂TM reagent (U.S. Patent Number 6,960,701; all rights reserved) was chosen for further evaluation during the small-scale force to failure experiments. In addition, deionized water was also evaluated as a control. The feedstocks evaluated during this effort were reagent grade MnO₂, isolated solids from arsinol/EDS sludge samples and isolated solids from arsinol/EDS waste samples.³ The reactions were conducted in a completely randomized order, with the reactions conducted in duplicate. A total of 10 small-scale reactions were conducted during this small-scale force to failure effort.

The small-scale reactions were carried out in a four neck, 250 mL round bottom glass flask, equipped with an air-cooled condenser and TFE coated thermocouple. Stirring was accomplished by use of a TFE coated stir bar, and a magnetic stir plate, with the reaction stirred at moderate speed throughout the reaction. Heating was accomplished by the use of an electric heating mantle, with temperature control maintained by using a J-KEM temperature controller. Throughout all steps of the reaction, N₂ gas was purged through the reactor headspace at a rate of 0.5-1 mL/min, and was vented through the condenser.

In these runs, 100 mL of reagent was added to the reactor, stirring and N₂ purge started, and the temperature adjusted to 30 °C (86 °F). Once the temperature stabilized, the feedstock (approximately 10 g, exact mass recorded) was added over 15-25 min (2-5 min for water reactions), and the reaction was allowed to proceed. Time point samples were removed from the reactor 5, 10, 15, 20, 25, 30, 60, 120, 180, 360, 1440 and 1,800 min after the feedstock was added to the reactor. A total of 2 mL was removed for each time point sample, and the samples were analyzed for pH, oxidizing capacity, and total dissolved metals (Mn for MnO₂; Mn, Fe, As for EDS solids). In addition, observations were recorded throughout the reaction and select samples were analyzed by CE (Section 2.7) for arsenic-species. The time point samples were removed from the reactor using a plastic pipet, with the pipet tip maintained approximately ¾ of an inch below the liquid surface. Stirring was stopped one minute prior to sampling, to minimize removal of undissolved solids from the reactor. At the end of the run, the entire sample was filtered (0.45 µm AcrodiscTM) while still warm, and the retained solids washed with deionized water to remove excess reagent. The washed solids were allowed to dry in a desiccator overnight before obtaining the weight of undissolved solid remaining after the reaction.

The exotherm, pH, oxidizing capacity and total percent of solids dissolved are summarized in Table 5. The dissolution rates for each metal over the first hour of reaction are summarized in Table 6. Note the dissolution rate of MnO₂ by HPO₂TM reagent was calculated using only the five minute time point. The dissolution of MnO₂ by HPO₂TM reagent was extremely fast, with total dissolved Mn reaching a maximum at the five minute sampling point. Total dissolved metals as a function of reaction time are illustrated in Figures 9 and 10. The HPO₂TM reagent was effective in dissolving significant quantities of the arsinol waste and arsinol sludge feedstocks. On average, the HPO₂TM reagent dissolved 42.6% of the arsinol waste and 26.2% of the arsinol sludge. This is 1.4 and 2.75 times more than the corresponding deionized water controls. The HPO₂TM reagent was also effective in dissolving MnO₂, with 31.9% of the

MnO₂ being dissolved. Overall, the HPO₂TM had the capacity to dissolve 31.9 mg/mL of MnO₂, 42.6 mg/mL of arsinol waste, and 26.2 mg/mL of arsinol sludge. The dissolution rates for Mn and Fe were significantly higher for the HPO₂TM reagent as compared to the deionized water controls. There was no detectable Fe in any of the deionized water samples, and only trace (1-3 mg/L) levels of Mn. Interestingly, the dissolution rates for As were significantly higher in the deionized water controls, with the HPO₂TM reagent exhibiting apparent negative dissolution rates. The decrease in dissolved As over time in the HPO₂TM runs is believed to be related to the reaction of dissolved As with the dissolved Mn and Fe, with remaining solids, or a combination of the two processes. The complexation of As with Mn and Fe to form solids is well documented.^{3,4} There was a significant excess of Mn and Fe in the starting solids relative to As, with average molar ratios of 8.6 and 2.73, respectively. Additionally, there were also large excesses of dissolved Mn and Fe in the samples relative to As, with average molar ratios of 40.5 and 9.98, respectively. The elevated concentrations of dissolved Mn and Fe in samples generated with HPO₂TM reagent would accelerate the complexation process with As.

The initial observation of negative dissolution rates for dissolved As led to additional experiments being performed to investigate whether EDTA would maintain the As in solution. Two reactions of HPO₂TM reagent with arsinol waste were repeated, with either 5,000 or 10,000 mg/L EDTA added to the starting reagent. Overall, there were no significant differences in overall dissolution, with an average of 48.9% of the arsinol waste being dissolved. There were slight increases in the amounts of dissolved As, but the levels did not come close to those obtained during the deionized water runs. The dissolved As results are illustrated in Figure 11. EDTA, at the levels investigated, was not effective in maintaining the dissolved As concentrations.

Time point samples from one of the arsinol sludge runs with deionized water were also analyzed by CE (Section 2.7) to determine arsenic-containing species. There were three arsenic-containing species determined to be in the samples and the results are illustrated in Figure 12. If all the As in the arsinol sludge was dissolved, the concentration would be 6,010 mg/L. Using the average of last two time points, the total dissolved As was determined to be 1,150 mg/L. This is an approximately 19% recovery of the As from the sludge. This recovery is comparable to recoveries previously obtained on these types of materials.^{3,4} Using dimensional analysis the CE results were converted to total As; the concentration was calculated to be 1,260 mg/L As. This calculated concentration is not significantly different from the measured concentration, suggesting all the arsenic-species have been detected.

Table 5. Summary of Results from the Small-Scale Force to Failure Experiments. The reported results are the averages of duplicate reactor runs.

Solid Feedstock	Exotherm		pH ^a		KIS ^b		Solids Dissolved (%)
	(°C)	(°C/min)	Initial ^c	Final ^d	Initial ^c	Final ^d	
Deionized Water Control							
Waste	0	NA	4.5-5.0	8.5-9.0	NA	NA	29.5
Sludge	0	NA	4.5-5.0	7.0-7.5	NA	NA	9.51
HPO ₂ TM Reagent							
MnO ₂	58.6	5.33	1.0	6.0-6.5	DPB	White	31.9
Waste	60.7	5.38	1.0	1.9-2.0	DPB	LP	42.6
Sludge	63.4	4.24	1.0	1.9-2.0	DPB	LP	26.2

a. Determined using narrow range pH strips.

b. Residual oxidizing capacity determined using starch iodide paper; darker color indicates stronger oxidizer.

c. Reagent before MnO₂ added.

d. Determined on 1,800 min time point sample.

Table 6. Summary of Dissolution Rates in the First Hour of Reaction. The reported results are the averages of duplicate reactor runs.

Reagent Type	Solid Type	Dissolution Rate (mg/L/min)		
		Mn	As	Fe
DIW	Waste	0.00163	5.80	0
DIW	Sludge	0.0612	5.70	0
HPO ₂ TM	MnO ₂	3,700 ^a	NA	NA
HPO ₂ TM	Waste	10.1	-0.792	1.22
HPO ₂ TM	Sludge	12.4	-1.51	9.74

a. Estimated value. Dissolved Mn was at maximum value at 5 min time point.

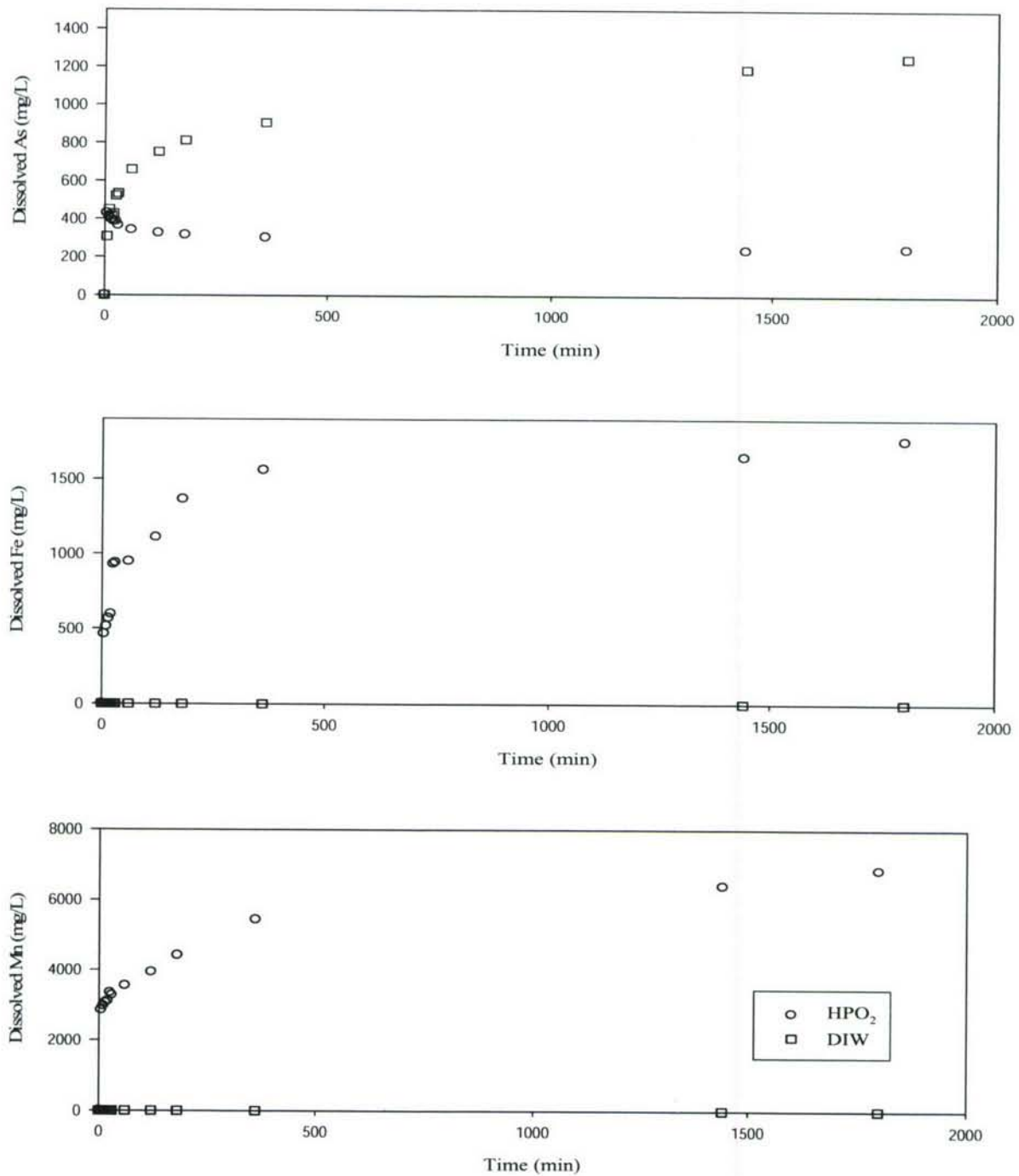


Figure 9. Total Dissolved Metals as a Function of Time when Arsinol Sludge is Exposed to Two Different Solutions. The plotted data are averages of duplicate reactor runs.

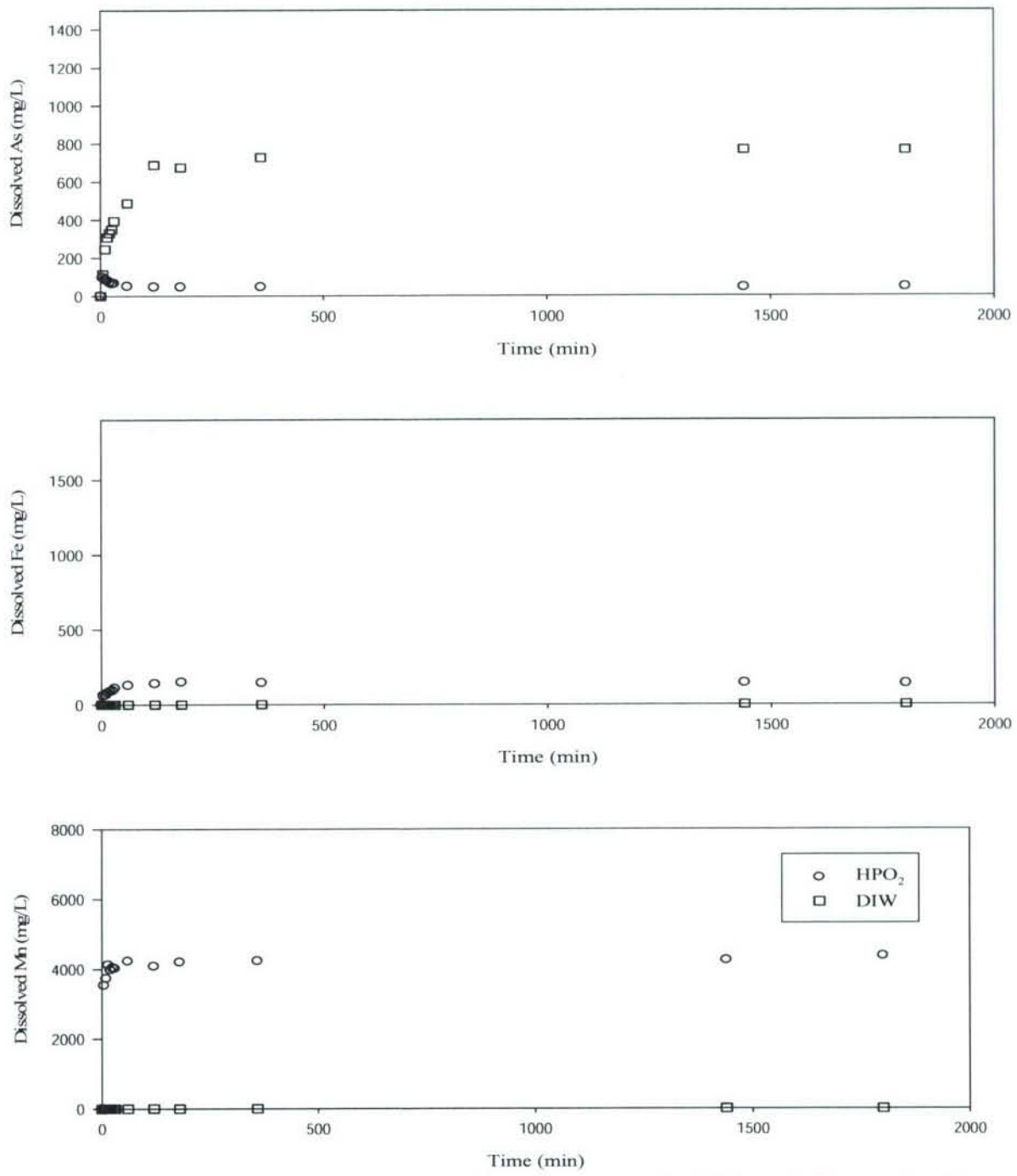


Figure 10. Dissolved Metals as a Function of Time when Arsinol Waste is Exposed to Two Different Solutions. The plotted data are averages of duplicate reactor runs.

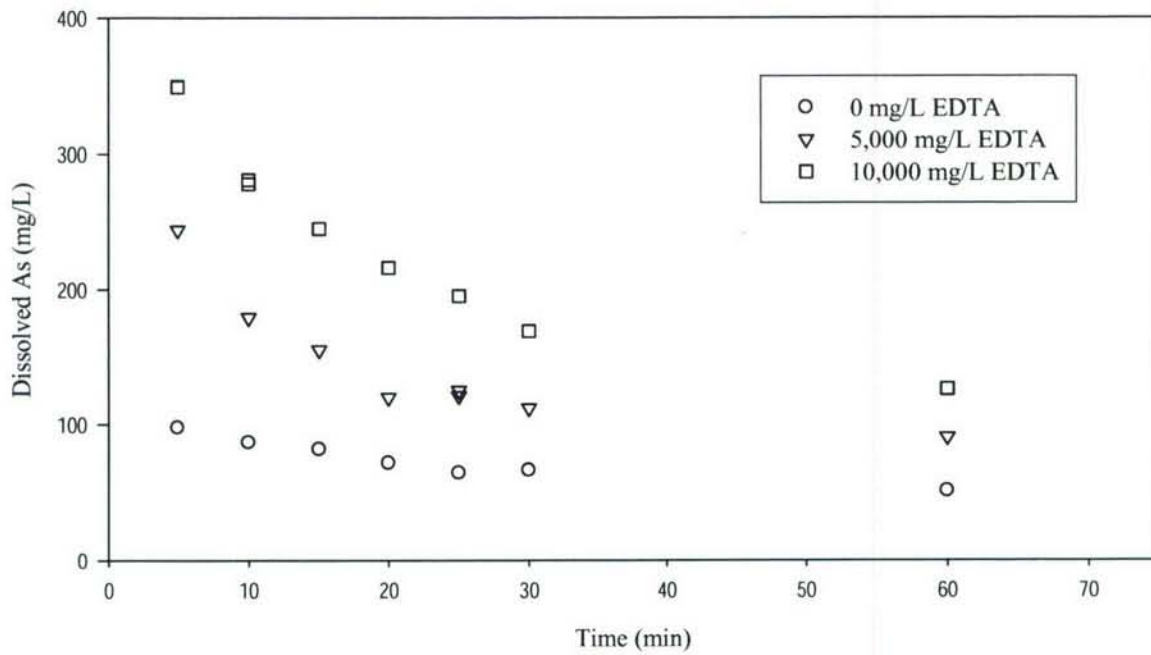
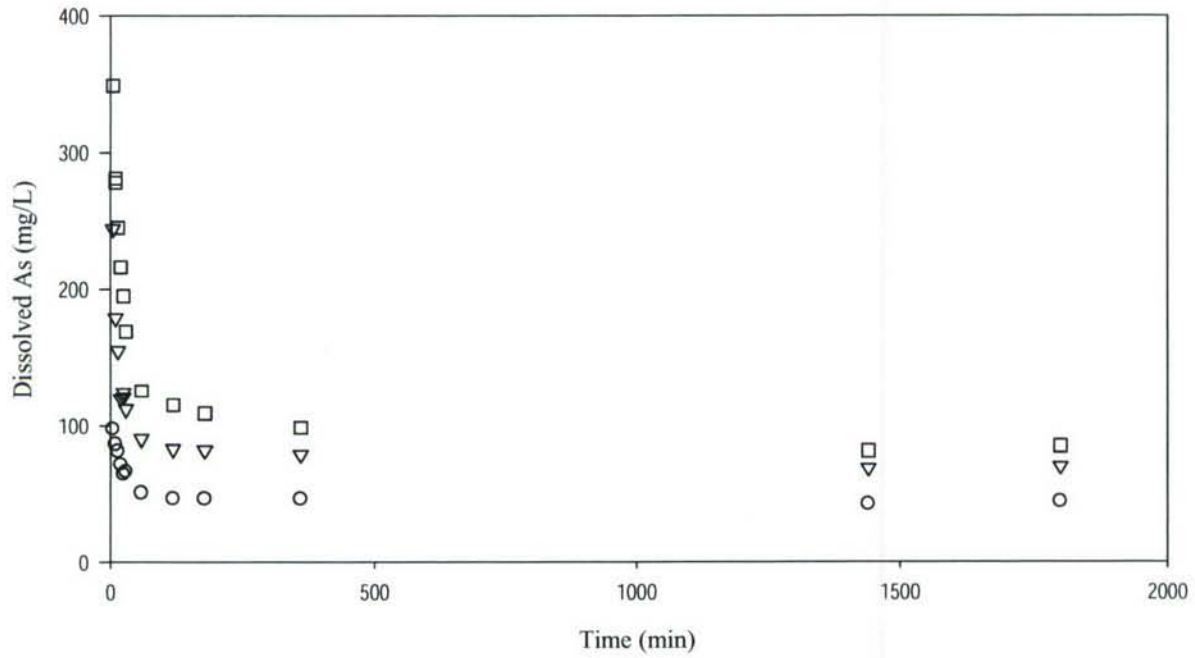


Figure 11. Total Dissolved Arsenic as a Function of Time when Arsinol Waste is Exposed to HPO_2^{TM} Reagent with EDTA.

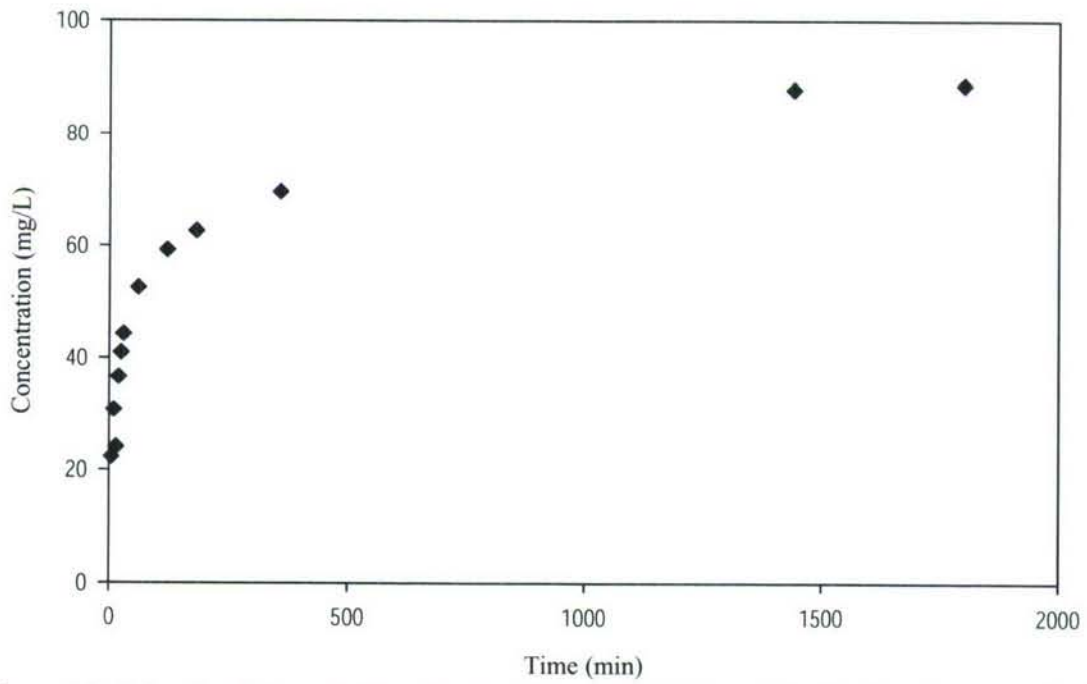
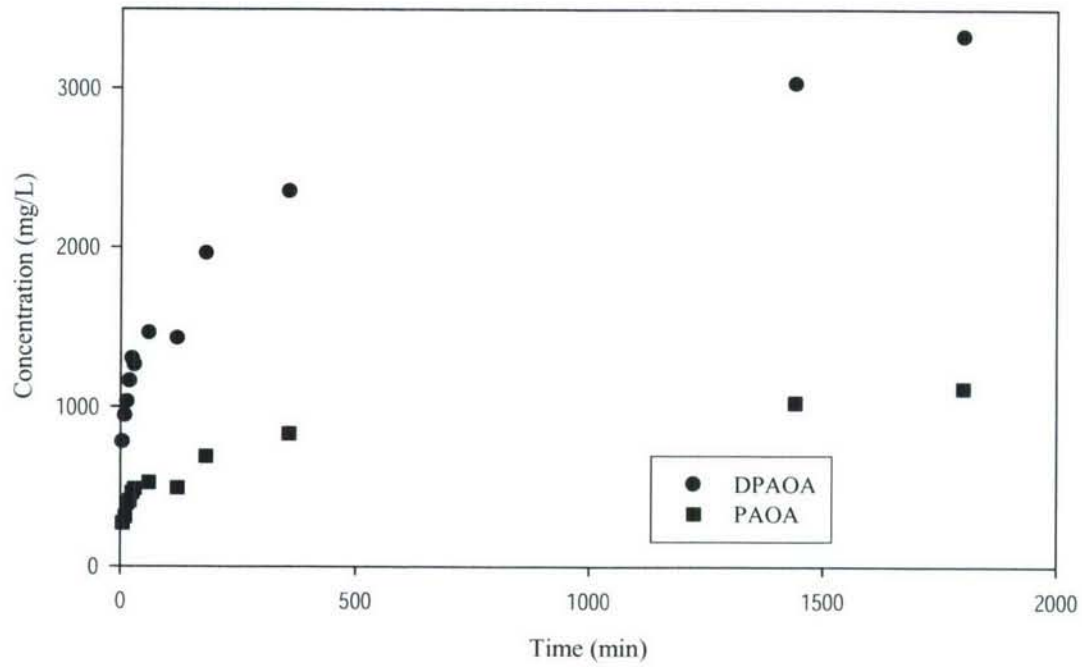


Figure 12. Dissolved Arsenic Species as a Function of Time. The feedstock was arsinol sludge and the reagent was deionized water. The bottom panel is arsenate.

3.2 Preparation and Characterization of HPO₂TM Reagent.

The HPO₂TM reagent (U.S. Patent Number 6,960,701; all rights reserved) was originally developed for the chemical neutralization of HD, L, and HL mixtures.^{14,15} In studies investigating the neutralization of arsenic-based CWAs,^{3,4} HPO₂TM reagent was not only found to be efficacious against the CWAs, but also useful in cleaning laboratory glassware contaminated with permanganate residues. This section summarizes the preparation and characteristics of the HPO₂TM reagent.

3.2.1 Preparation of HPO₂TM Reagent.

Concentrated H₂O₂ solutions are strong oxidizers, and need to be handled with appropriate precautions. The OXONE® solutions are acidic, and should be handled as corrosives. Two scenarios for the preparation of HPO₂TM reagent are presented. The first is lab-scale preparation and the second is a field-scale preparation. A summary of properties is included as Table 7. **Read and understand the MSDS of each component before preparing and using this reagent.**

On a lab-scale, HPO₂TM reagent is prepared by weighing 25±0.05 g of OXONE® into a 250 mL Erlenmeyer flask, then adding 100±1 mL of deionized water (18MS) and 50±1 mL of 50% H₂O₂. The solution is then stirred until all solids are dissolved. The solution is typically clear and colorless, though some solids (K₂SO₄) may settle out over time. It is preferred to prepare only as much reagent will be needed for a day of operations.

On a field-scale, HPO₂TM reagent can easily be prepared in 5-gallon plastic pails. The pail should be clean and free of extraneous material. The plastic pail should not have been previously used to store other chemicals. Add 8 L of water (preferably deionized) to the plastic pail, then slowly add 2 kilograms of OXONE®. The dissolution of OXONE® is slightly endothermic and it might take 1-2 hr for all the OXONE® to dissolve. Dissolution can be aided by stirring the solution with a clean plastic utensil such as a paddle or spatula. Once the salts are dissolved, slowly add 4 L of 50% H₂O₂. Once all the H₂O₂ is added, stir with the plastic utensil to make sure the reagent is mixed. The reagent is typically clear and colorless, with no visible solids, though some salt (K₂SO₄) may settle out over time. This reagent should not be stored in a tightly sealed container as pressure will build up in the container.

Table 7. Summary of Properties of HPO₂TM Reagent.

Parameter	Value
Appearance	Generally clear and colorless
pH	3-4 ^a
Viscosity @ 25 °C (cST)	1.060
Viscosity @ 35 °C (cST)	0.875
Viscosity @ 55 °C (cST)	0.680
Surface Tension @ 25 °C (dynes/cm)	69.2
Density @ 25 °C (g/mL)	1.158
Active Oxygen (%)	7.89

a. Reagent becomes more acidic (1-2) during storage as H₂SO₄ is formed.

3.2.2 Storage Stability of HPO₂TM Reagent.

The evaluation of reagent storage stability was performed using two different sources of water to prepare the OXONE® solution and HPO₂TM reagent. The first source of water was distilled, deionized water prepared using an on-demand in-house system. This water meets ASTM specifications for Type I organic-free water, and was utilized to provide a baseline of stability performance. The second source was tap water obtained from a laboratory sink located on APG-EA grounds. This second water source was evaluated to gather complementary data on how stable the reagents would be when using source water which might be typically available during field operations. These two water sources were characterized and the results are summarized in Table 8.

A temperature controlled stability study was performed on both 25 wt% OXONE® solution and HPO₂TM reagent that were prepared in deionized and tap water. A single batch of each solution was prepared, and then 200 mL aliquots were placed into 250 mL beakers. The beakers were constructed of 316 stainless steel, high density polypropylene (HDPE), and Pyrex glass. These beakers were covered with three layers of Parafilm[®], with a small opening left in the middle for a pipet. When not being sampled, the hole was covered with a watch glass. The beakers were maintained at either 30 or 50 °C in a water bath. Sample aliquots of 100 µL were periodically removed and analyzed for percent active oxygen using a standard titration method. Samples, in duplicate, were removed twice a day over a five day sampling period.

The decay of active oxygen appeared to follow first order reaction kinetics and half-lives were calculated using a first-order model. Half-lives are summarized in Table 9. Overall, short-term storage of HPO₂TM reagent in HDPE bottles appears to be the best strategy. However, long-term storage is not recommended due to material compatibility issues (Section 3.2.3). In practice, it is recommended the reagent be prepared in small quantities and used the same day it is prepared. The use of tap water to prepare the reagent reduces the

stability, with a four-fold drop in half-life when compared to using deionized water.

Table 8. Characterization of Two Source Waters Used during the Reagent Stability Study.

Analyte	Detection Limit	Deionized Water	Tap Water
pH	0.010	6.24	7.42
Specific Conductance ($\mu\text{S}/\text{cm}$)	1.0	1.6	248
Total Hardness (CaCO_3 equivalents; mg/L)	2.0	ND	50.8
Total Dissolved Solids (mg/L)	30	ND	136
Total Organic Carbon (mg/L)	2.0	ND	2.3
Acidity to pH 3.7 (CaCO_3 equivalents; mg/L)	3.0	ND	ND
Acidity to pH 8.3 (CaCO_3 equivalents; mg/L)	3.0	ND	ND
Alkalinity to pH 4.5 (CaCO_3 equivalents; mg/L)	2.0	ND	29.5
Alkalinity to pH 8.3 (CaCO_3 equivalents; mg/L)	2.0	ND	ND
Calcium (mg/L)	0.202	ND	11.9
Magnesium (mg/L)	0.101	ND	4.77
Total Copper (mg/L)	0.0040	ND	0.106
Total Iron (mg/L)	0.101	ND	0.153
Sulfate (mg/L)	4.5	ND	20.4
Chloride (mg/L)	3.8	ND	45.5
Fluoride (mg/L)	0.7	ND	0.7
Nitrite (mg/L)	4.3	ND	ND
Nitrate (mg/L)	4.9	ND	9.0
Phosphate (mg/L)	1.4	ND	ND

Table 9. Half-Lives of 25 wt% OXONE® Solution and HPO₂TM Reagent Stored under Various Conditions. The half-lives were calculated using a first order model.

Reagent Type	Water Type	Container Type	Half-Life (hours)	
			@30 °C	@50 °C
OXONE®	Deionized	Glass	6,930	248
OXONE®	Deionized	Plastic	17,300	462
OXONE®	Deionized	Stainless Steel	9,900	192
OXONE®	Tap Water	Glass	6,930	267
OXONE®	Tap Water	Plastic	13,900	301
OXONE®	Tap Water	Stainless Steel	3,470	94.6
HPO ₂ TM	Deionized	Glass	3,470	462
HPO ₂ TM	Deionized	Plastic	2,310	1,160
HPO ₂ TM	Deionized	Stainless Steel	1,730	462
HPO ₂ TM	Tap Water	Glass	495	385
HPO ₂ TM	Tap Water	Plastic	533	289
HPO ₂ TM	Tap Water	Stainless Steel	433	239

3.2.3 Compatibility of Materials with HPO₂TM Reagent.

The HPO₂TM reagent proposed for cleaning equipment utilized to neutralize arsenic-based CWAs will come into contact with various materials during the processing and handling steps, so a baseline evaluation of the materials compatibility of the HPO₂TM reagent was conducted. This baseline evaluation focused on the three types of stainless steel, and five types of polymers typically encountered in PMCD reactor systems,²¹ and on a candidate storage drum material. The materials compatibility studies were conducted in accordance with standard NACE and ASTM test methods.^{22,23}

The baseline compatibility of HPO₂TM reagent with 316, 316L, and 317L stainless steels was conducted at two temperatures, 25 and 80 °C. The 316 stainless steel coupons were heat sensitized (HS) at 1250 °F for one hour to simulate the effects of welding. The 316L and 317L stainless steel coupons were used without any pretreatment. All of the stainless steel coupons were approximately 0.75 X 2 in., and were approximately 0.04 in. thick. Each type of stainless steel was evaluated separately, though duplicate coupons were used at each location in the test chamber. In each test, a sample of each material was suspended in the vapor phase, another of each material was half immersed, and a third of each was totally immersed. Care was taken that none of the sample coupons were touching each other. The test vessel was then purged with nitrogen, and sealed. The testing was initiated within 24 hr of the HPO₂TM reagent being prepared. After 14 days, the test specimens were removed, and after cleaning all the specimens, corrosion rates were calculated based on mass loss, and assumed uniform loss of

metal. The corrosion data are summarized in Table 10. There was very little corrosion observed, with the overall average corrosion rate being <0.03 mpy. In all cases there were no signs of attack such as pitting or staining when the specimens were examined under a light microscope at 20X. Under the conditions evaluated, these three stainless steels are compatible for use with HPO_2^{TM} reagent.

The baseline compatibility of HPO_2^{TM} reagent with HDPE, nylon-66, PTFE, Viton and PFA was conducted at a single temperature of $50\text{ }^\circ\text{C}$. All of the coupons were approximately 1×2 in., and were approximately 0.06 in. thick. Each type of polymer was evaluated separately, though duplicate coupons were used. In this evaluation, all test coupons were fully immersed. Care was taken that none of the sample coupons were touching each other. The test vessel was then purged with nitrogen, and sealed. The testing was initiated within 24 hr of the HPO_2^{TM} reagent being prepared. After 30 days, the test specimens were removed, rinsed with deionized water, and air dried. The test specimens were reweighed, measured and visually inspected. The percent change in weight, dimension and volume were calculated and changes in hardness were measured. These results are summarized in Table 11. Viton, PTFE, PFA and HDPE all performed well, with little or no change as a result of immersion in HPO_2^{TM} reagent. Nylon-66 performed poorly, with crazing observed in all of the test specimens. There was chalking at the surface and loss of rigidity, suggesting that the nylon-66 was being chemically attacked. Nylon-66 is not compatible with HPO_2^{TM} reagent under the conditions evaluated.

The baseline suitability of HDPE as a storage container for HPO_2^{TM} reagent was conducted at a single temperature of $50\text{ }^\circ\text{C}$ using an environmental stress-cracking protocol. All of the coupons were 1.5×0.5 in. and were 0.125 in. thick. A controlled imperfection (0.75 in. long by 0.020 in. deep) was placed on one surface with a razor blade fitted into a nicking jig. Just prior to exposure, each test specimen ($n=10$) was bent into a U shape with the imperfection on the outside radius of the bend. The stressed specimens were placed into a restraining frame and the entire assembly was placed into the test vessel. Care was taken that none of the assemblies were touching each other. The test vessel was then purged with nitrogen and sealed. The testing was initiated within 24 hr of the HPO_2^{TM} reagent being prepared. After 30 days of continuous exposure the assemblies were removed, rinsed with deionized water and air dried. While HDPE performed well in the baseline immersion testing, six of the 10 test coupons failed during the stress-cracking protocol. The HDPE used during this study is not suitable for long-term storage of HPO_2^{TM} reagent. Additional testing with actual drum material is required to determine whether a specific manufacture's drum will be suitable for long-term storage of HPO_2^{TM} reagent.

Table 10. Corrosion of Stainless Steels by HPO₂TM Reagent at Two Different Temperatures. Coupons were exposed for 14 days. Reported values are the averages of duplicate coupons. Estimated detection limit is 0.006 mpy.

Coupon Location	Average Corrosion Rate (mpy) ^a			Remarks
	HS 316	316L	317L	
<u>Tests Conducted at 25 °C</u>				
Liquid ^b	0.0164	0.0278	0.0265	No visible signs of attack. ^c
Interface ^c	0.009	0.0138	0.0237	No visible signs of attack. ^c
Vapor ^d	0.009	0.0193	0.0112	No visible signs of attack. ^c
<u>Tests Conducted at 80 °C</u>				
Liquid ^b	0.0328	0.0411	0.0120	No visible signs of attack. ^c
Interface ^c	0.0263	0.0296	0.0180	No visible signs of attack. ^c
Vapor ^d	0.0260	0.0690	0.0238	No visible signs of attack. ^c

a). mils per year; 1 mil = 0.001 inch.
b). Coupon suspended 100% immersed in liquid.
c). Coupon suspended 50% immersed in liquid, and 50% in vapor.
d). Coupon suspended 100% in the vapor.
e). Coupons examined with a light microscope (20X) for signs of attack such as staining and pitting.

Table 11. Compatibility of Polymers with HPO₂TM Reagent. Studies were conducted at 50 °C and coupons were exposed for 30 days.

Coupon Material	Volume Change (%)	Mass Change (%)	Hardness Change (Shore D)
Viton	+0.02	+0.47	+1.5
PTFE	-0.87	+0.01	-1.3
PFA	-0.45	+0.01	-0.3
Nylon-66 ^a	+4.8	+9.1	-7.8
HDPE	+0.13	+0.08	+2.0

a. Craze cracks with loss of rigidity. One specimen cracked when flexed.

The U.S. Army Product Manager for Non-Stockpile Chemical Materiel is responsible for the destruction of several categories of chemical warfare materiel in a safe, cost effective, environmentally sound manner and in compliance with the Chemical Weapons Convention. A variety of CWAs and other chemicals have been identified as possible fills in recovered munitions,^{1,2} but the focus of this effort was on the demilitarization of arsenical-based munitions and fill materiels. In recent full-scale testing of the EDS with actual munitions and DOT bottles containing arsenic-based chemical warfare agents, sodium permanganate was found to be an effective reagent for neutralizing these materiels.^{3,4} In practice, residues of manganese dioxide were found to deposit on various surfaces in contact with the sodium permanganate reagent. This build up of residues on surfaces was not acceptable, as the surfaces must be clean in order to achieve a good seal to prevent leaks during operations. A field-useable process for removing the residues was required to maintain operational tempo during demilitarization operations.

The lab-scale evaluation of cleaning solutions was conducted using Inconel 718 and 316L stainless steel test coupons typically used in material compatibility studies. All of the test coupons were approximately 0.75 X 2 in., and were approximately 0.04 in. thick. The coupons were randomly selected for two surfaces treatments. The first treatment was a smooth polished surface, which mimics the polished surfaces found in the EDS. The second treatment was a rough finish, which mimics the interior surface of the EDS exposed to the explosive charges. The rough finish was created by vigorously rubbing the bottom half of the coupon with 60 grit sand paper (horizontal to the long axis), followed by scratching grooves into the coupon with a nail, and finally using a hammer to put divits into the coupon with a nail. All coupons were cleaned with 2-propanol, rinsed with deionized water, and air dried prior to the cleaning study.

The coupons were contaminated by suspending duplicate coupons in reconstituted neutralent from an actual EDS run (Section 2.4) for six days. The coupons were suspended such that no coupons were touching and only the bottom half of the coupon was submerged. After six days, the coupons were removed from the neutralent and allowed to air dry for 24 hr before conducting the cleaning study.

The contaminated coupons were randomly selected for one of three cleaning solution candidates using three different cleaning strategies. The cleaning solutions were deionized water, peracetic acid (Section 3.1.1), and HPO_2^{TM} reagent (Section 3.2). The first cleaning strategy was "soaking" which consisted of placing the contaminated coupon in a plastic beaker containing 40 mL of the cleaning solution for five minutes, dipping the coupon three times, gently rinsing with deionized water, and patting dry. The second cleaning strategy was "brushing", which is the same as the "soaking" strategy except the coupon was gently brushed with a toothbrush prior to the deionized water rinse. The third cleaning strategy was "spraying" which consisted of spraying the coupon three times with cleaning solution while the coupon was hanging, waiting one minute, then spraying the coupon three times with deionized water. After 15 min, the coupon was then patted dry.

The observations made during the experiment are summarized in Table 12 and

photographs of selected coupons are illustrated in Figures 13 through 17. The use of deionized water in the soak and soak/brush scenarios was not effective, with significant staining left on the coupons. There were no significant differences observed between the smooth and rough surface treatments when using deionized water. The use of deionized water in the spray scenario was also not effective, with significant staining remaining after then cleaning and drying cycle. One observation about the spray scenario (relevant to all cleaning reagents); the spray was only applied to one side of the coupon, and there was some migration of residue from the back of the coupon to the front, particularly at the bottom of the coupon.

The use of peracetic acid in the soak and soak/brush scenarios was more effective than the deionized water, with only slight staining remaining. There were no significant differences observed between the smooth and rough surface treatments when using peracetic acid. The use of peracetic acid in the spray scenario was more effective than deionized water, with only slight staining remaining on the coupons. The excessive staining remaining at the edges of the coupon is from the migration phenomenon described above.

The use of HPO₂TM reagent was the most effective reagent in all cleaning scenarios, with no differences observed between the smooth and rough surface treatments. In all cases, the surface of the coupon was visually cleaned of all permanganate-based residues, except for the residue which migrated from the back of the coupon. In some cases there was a white residue on the coupon surface after drying. This residue is believed to be K₂SO₄, which is a decomposition product of HPO₂TM reagent. This white residue was removed with an additional water rinse.

Table 12. Summary of Observations for Each Cleaning Reagent and Strategy.

Cleaning Reagent	Cleaning Strategy		
	Soaking	Brushing	Spraying
Deionized Water	No reaction when coupon put into reagent.	No reaction when coupon put into reagent.	No reaction when coupon sprayed reagent.
Peracetic Acid	Moderate foaming when coupon put into reagent.	Moderate foaming when coupon put into reagent.	Moderate foaming when coupon sprayed with reagent.
HPO ₂ TM Reagent	Heavy foaming when coupon put into reagent.	Heavy foaming when coupon put into reagent.	Heavy foaming when coupon sprayed with reagent. Foam clung to coupon.

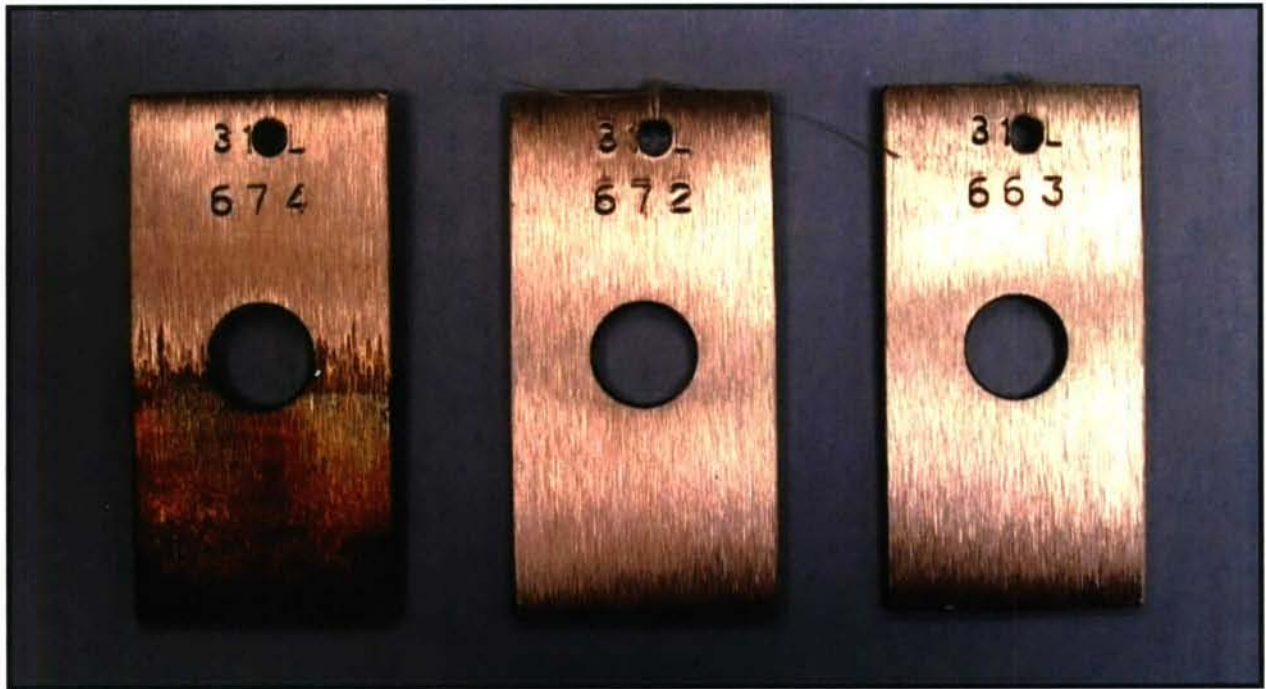


Figure 13. Example Photographs of the Soak and Soak/Brush Cleaning Scenarios for Smooth Finish Treatment. The top panel is the soak scenario and the bottom panel is the soak/brush scenario. Deionized water is on the left, peracetic acid is the middle, and HPO_2^{TM} reagent is on the right.



Figure 14. Example Photographs of the Soak and Soak/Brush Cleaning Scenarios for Rough Finish Treatment. The top panel is the soak scenario and the bottom panel is the soak/brush scenario. Deionized water is on the left, peracetic acid is the middle, and HPO_2^{TM} reagent is on the right.



Figure 15. Example Photographs of the Spray Cleaning Scenario Using Deionized Water. The top panel is the contaminated coupons, the middle panel is the coupons after reagent, and the bottom panel is the coupons after water rinse and air drying for 15 min.

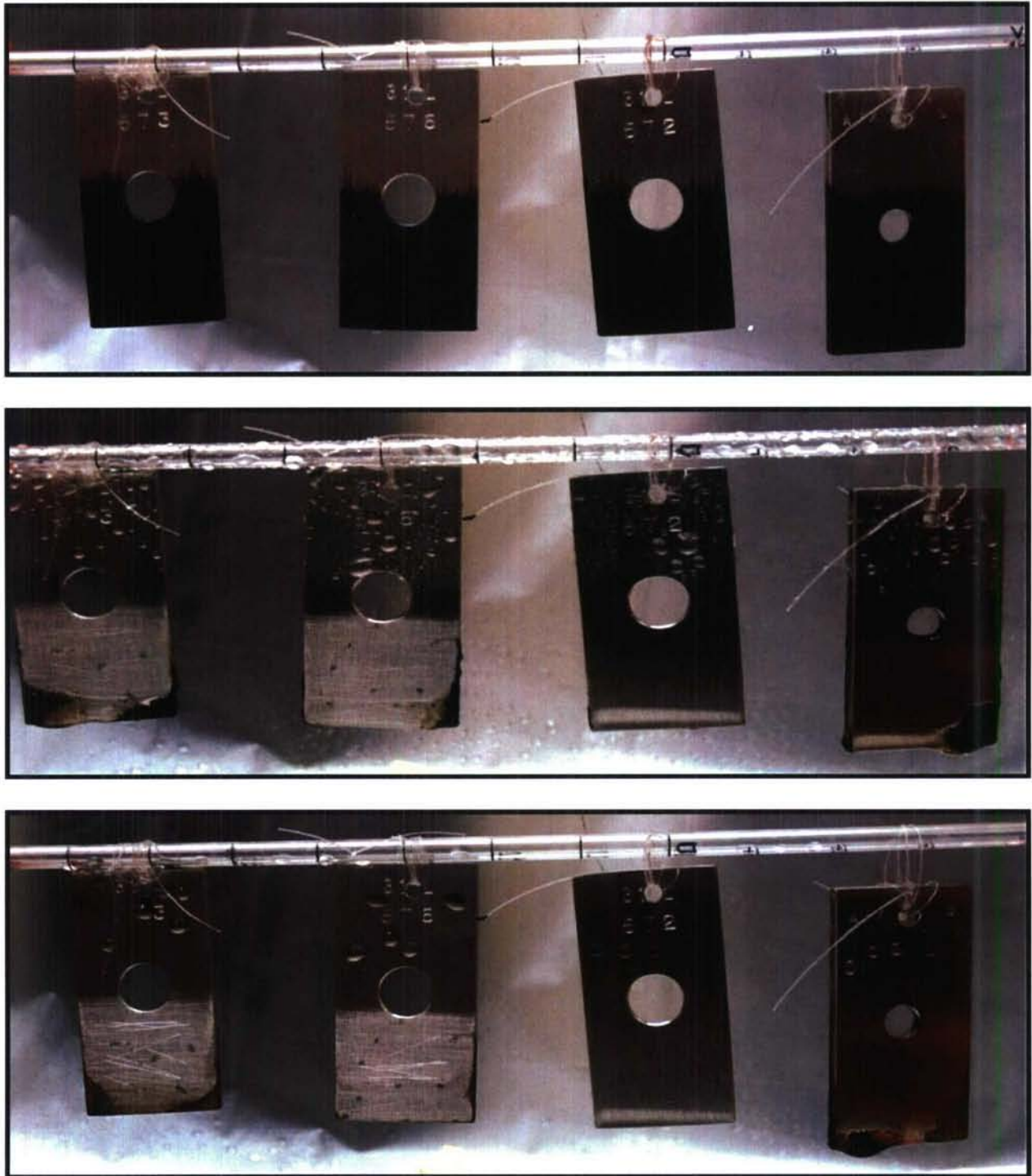


Figure 16. Example Photographs of the Spray Cleaning Scenario Using Peracetic Acid. The top panel is the contaminated coupons, the middle panel is the coupons after reagent, and the bottom panel is the coupons after water rinse and air drying for 15 min.

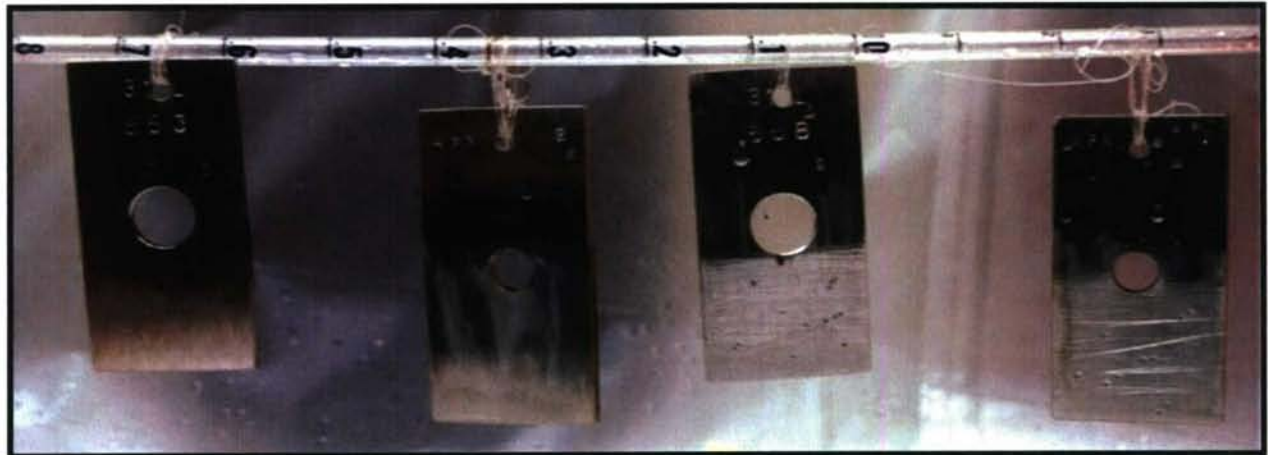
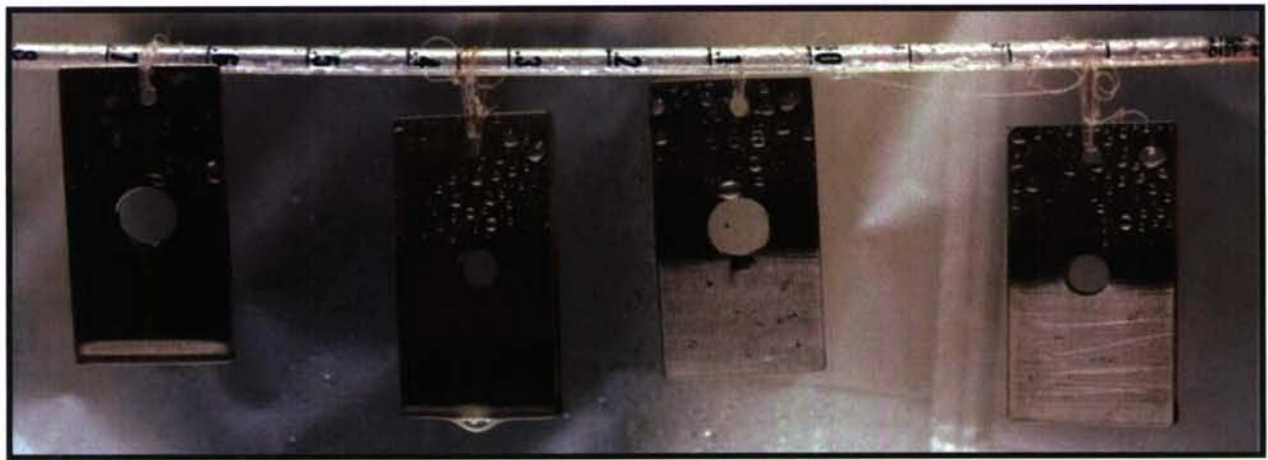
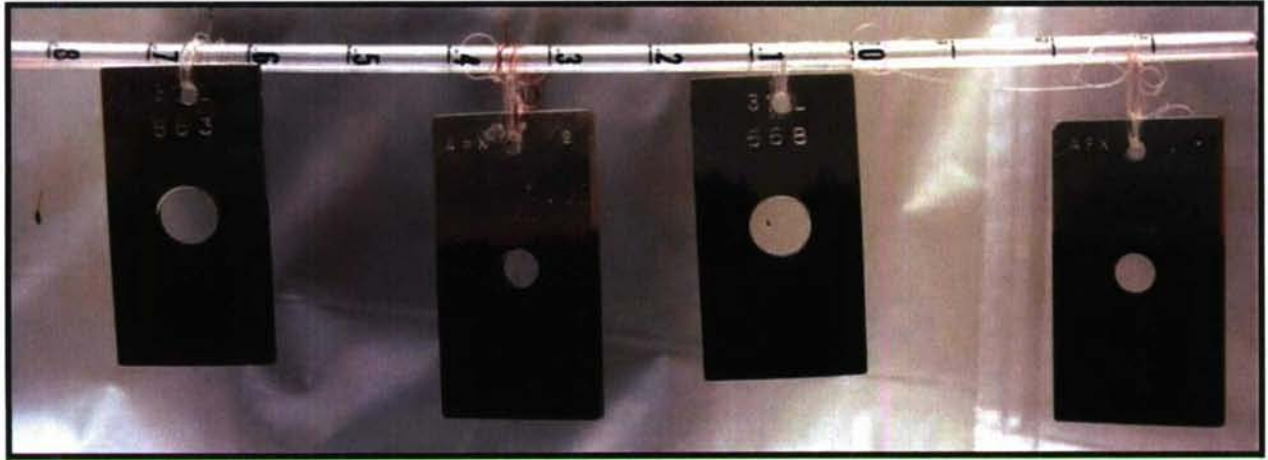


Figure 17. Example Photographs of the Spray Cleaning Scenario Using HPO₂TM Reagent. The top panel is the contaminated coupons, the middle panel is the coupons after reagent, and the bottom panel is the coupons after water rinse and air drying for 15 min.

4. CONCLUSIONS

This report summarizes efforts to select and demonstrate a reagent for cleaning permanganate-based residues on equipment used to demilitarize arsenical-based munitions and fill materials. The data generated from the present study will be used to support operation of a non-stockpile demilitarization process for the destruction of recovered arsenical-based munitions. Presently, this includes the use of PMNSCM's EDS, a transportable stainless steel vessel used for the enclosed detonation and chemical neutralization of RCWM. The findings of this study will also support demilitarization of munitions with similar fills that may be recovered during remedial activities at various locations.

Twenty reagent candidates were evaluated and HPO₂TM Reagent (U.S. Patent Number 6,960,701; all rights reserved) was selected for this application. The selected reagent was found to be effective in dissolving reagent grade manganese dioxide and solids collected during actual demilitarization operations to neutralize arsenic-based chemical weapons. In addition, the reagent was also found to be efficacious in removing residues which had adhered to surfaces commonly found in equipment used to demilitarize CWAs.

The selected cleaning reagent was found to be compatible with a variety of materials commonly used in demilitarization activities. The selected reagent was compatible with HS316, 316L and 317L stainless steels. The selected reagent was also compatible with Viton, PTFE, PFA and HDPE. The selected reagent was found not to be compatible with nylon-66.

The components to prepare the cleaning reagent are commercially available in bulk and are stable in storage. The reagent is aqueous based and non-flammable. However, the reagent is a strong oxidizer, and appropriate procedures must be followed when working with this reagent.

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