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Temporal Stability of Solid Oxidizers at High Temperature and Humidity

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19. ABSTRACT (Continue on reverse if necessary and identify by block number) (CW/BW) decontamination operations may rely on aqueous solutions prepared from stored solid oxidizers. Needed are data defining the shipboard storage stability of candidate oxidizers. Therefore, the stability of a series of potential decontaminants has been examined at high temperature (90+ °C) and humidity (95+% R.H.). The loss of oxidizing capacity in aliquots of the oxidizers was followed with time by iodometric titration. Calcium hypochlorite lost over 99% of its oxidizing capacity in less than two days, whereas lithium hypochlorite retained one-third oxidizing capacity for approximately twenty days. Sodium perborate, and sodium persulfate were very hygroscopic and unstable with time. H-48 (see text) decomposed in approximately two days, while sodium isocyanurate lost about 80% of its oxidizing capacity in two weeks. The data presented document severe stability problems of one sort or another with all the materials tested, although overall the sodium isocyanurate appeared to be the more stable candidate under extreme conditions. In any case, packaging and storage considerations are shown to be important for any potential decontaminant to be stored under environmentally severe conditions.				
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Temporal Stability of Solid Oxidizers at High Temperature and Humidity

I. INTRODUCTION

Decontamination (decon) of impacted Naval elements may prove necessary in times of conflict. Operations can be compromised by the presence of Chemical Warfare/Biological Warfare (CW/BW) agents, which must be neutralized to maintain mission capability. The decon process could require washdown of the impacted surfaces, washdown with water, fresh or sea, with or without chemicals which assist in neutralizing the agents/toxins. The majority of toxic organic materials, and CW/BW agents, will succumb to a decon based on oxidation/hydrolysis.

Historically, aqueous solutions of hypochlorite have been a decon fluid of choice. Aqueous hypochlorite oxidizes organic matter, hydrolyzes G-agents (Block and Davis, 1978), and, as a function of pH, can counter BW materials such as spores (Hoffman and Spiner, 1962; Fielding, et al., 1967, 1968; Pellenbarg, 1983). Overall, decon with aqueous hypochlorite, especially from solid calcium hypochlorite, has the potential to be broad spectrum, can be effective against both CW and BW toxics, and is rapid.

However, solid calcium hypochlorite exhibits characteristics which can compromise its overall utility in decon operations. Calcium hypochlorite disperses slowly to give a corrosive solution/slurry, the solid tends to decompose in storage, and as a bulk solid, exhibits logistics problems. It would be advantageous to seek replacements/supplements for calcium hypochlorite. Ideally, such candidate decon materials should be stable in storage, disperse rapidly to give easily dispensed true solutions, possess a demonstrated effectiveness against CW/BW materials, and, if possible, lend themselves to on-site generation.

This report addresses in detail the question of storage stability of candidate decon materials. Candidate solids were exposed to extremes of temperature (90+ °C) and humidity (95+%
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RH) to assess relative stability of the materials. Those materials which were most stable with time under extreme conditions are worth further consideration when addressing other screening criteria in selection for possible decon use. By design, no candidates were exposed to cool, or ambient wet or dry conditions: stability data at the environmental extremes should prove most useful for initial screening.

II. EXPERIMENTAL

Candidate decon materials (see Table 1) were weighed out in replicate and placed in separate uncovered 6 cm diameter Pyrex petri dishes. All reagents were used as received from the suppliers. The solid aliquots were put into a Blue M Model environmental chamber, set to maintain a temperature of 90°C and a relative humidity of 98%. One set of aliquots was taken at the start of the experiment, and titrated iodometrically to assess oxidant content at that time. (see Pierce and Haenisch, 1948, for a thorough discussion of iodometry). All of the test reagents oxidize iodide quantitatively, and the liberated iodine can be titrated quantitatively with standardized thiosulfate to assess oxidant capacity. The relevant reactions using hypochlorite (as from calcium hypochlorite) as the example oxidizer are given in (1) and (2) below:



Periodically during the month long test, sets of the oxidizers in petri dishes were removed from the test chamber. The contents of the petri dishes were transferred to separate 100 mL volumetric flasks, using distilled water to bring the solution to volume. For all test oxidizer, 2.0 mL aliquots of the resulting solution, measured in replicate with a fixed volume dispensing syringe, were combined with 100 mL distilled water in separate 200 mL beakers. The pH of these solutions was adjusted to 4.5 ± 0.5 with 2N sulfuric acid in distilled water, and 4.0 mL of 10% wt/wt potassium iodide (Fisher) in distilled water were added to the reaction beaker with stirring. The resulting solution was titrated to a pale straw (yellow) color with 0.1 N sodium thiosulfate solution (Fisher), then 2-3 drops of starch indicator (1g soluble starch [mix starch to a paste with cold water] mixed slowly into 100 mL boiling water containing 1 g boric acid [Fisher] as a preservative, cooled prior to use) were added to give a dark blue solution which was titrated to clear, colorless with additional thiosulfate. The total volume of thiosulfate needed to attain this endpoint was recorded. These data, when normalized against the actual weight of oxidizer present in a given aliquot of solid, are reported in Table 2 as a monitor of oxidizer content in the oxidizer samples as a function

of time. Blanks, consisting of 100 mL of house distilled water plus necessary reagents, consumed no thiosulfate, consistently indicating low- to zero- background oxidants.

The iodine liberating reaction between iodide and the hypochlorite and iodide and the monoperoxyphthalate was complete once the reagents had been mixed. However, the other iodide-peroxygen reaction rates were noticeably slower, so that the peroxygen-iodide reactions were allowed to proceed for 20 minutes prior to titration. A more detailed investigation of the kinetics of these peroxygen-iodide interactions is needed.

III. RESULTS AND DISCUSSION

The titers of thiosulfate solution (0.1N) required to reduce the liberated iodine by a given test aliquot of 2.0 mL oxidizer solution are listed in Table 2. At the high temperature and humidity of the test, only sodium isocyanurate and sodium persulfate exhibited any appreciable residual oxidizer capacity after 21 days. This fact is significant. If any of the tested materials prove as efficacious for decon as hypochlorite, extreme care and attention will need be given their packaging and storage. No candidate solid oxidizer will long retain its efficacy in a warm, moist storage situation. Needed now are data which address solid stability in a warm, dry environment, as will be studied in a follow-on effort.

Note from Table 2 that the benchmark decon solid, calcium hypochlorite, exhibited very poor long-term stability in this study. The solid calcium hypochlorite lost 99% of its oxidizer capacity in only two days at high temperature and humidity. Furthermore, as time passed, the solid developed an increasing proportion of hard, insoluble residue, first seen in quantity after eight days. Such a residue would make dissolution/dispersion of fluid made from aged calcium hypochlorite difficult at best: application equipment could be clogged by the high proportion of insoluble material in such a "solution."

Lithium hypochlorite, like calcium hypochlorite, exhibited poor stability during this test. However, over-all deterioration of the lithium salt was not as rapid: after 21 days, the solid LiOCl retained approximately one-third of its initial oxidizing capacity. However, both hypochlorites proved to be hygroscopic, and picked up enough water from the humid test environment to form a solution. This result likely gives rise to a corrosive fluid which could damage storage containers, storage areas, and handling equipment. It is vital to study the corrosivity of both fresh and aged hygroscopically formed solutions of both calcium and lithium hypochlorite to assist in the proper design of storage containers and procedures.

Several other tested materials proved to be as hygroscopic as were the hypochlorites. The sodium percarbonate, and sodium persulfate dissolved after two days, and the sodium perborate became damp within one week of exposure to a high humidity environment. Accompanying this sample dissolution was a rapid deterioration in oxidizer capacity. Any of these materials could exhibit severe degradation of decon capacity if improperly stored. Thus, the perborate lost over half its oxidizer capacity in 2 weeks at high temperature and humidity, and the persulfate and perborate similarly lost half.

In contrast to the marked hygroscopicity exhibited by the majority of the materials tested, the magnesium monoperoxybenzoic acid (H-48) and the sodium dichloroisocyanurate did not sorb much water. The H-48 only discolored with time, and after three weeks, the isocyanurate began to cake. More significantly, the H-48 lost its oxidizer capacity after only 2 days exposure to temperature and humidity extremes, while the isocyanurate retained approximately 20% of its capacity over the three week test period. Based on stability of solid starting material, one could offer the sodium isocyanurate as a potentially useful decon candidate. However, this potential must be examined by testing the efficacy of isocyanurate solution in actual decon applications. Indeed, the potential decon efficacy of all the materials tested, save the calcium hypochlorite, remains to be demonstrated.

IV. CONCLUSIONS

The study described in this report examined the stability in storage at high temperature and humidity of seven candidate decon materials. Of those studied, only sodium dichloroisocyanurate and sodium persulfate retained significant oxidizer capacity over the duration of the test. The majority of the test materials proved to be hygroscopic, and rapidly formed aqueous solutions, in which decomposition reactions were likely enhanced. The hygroscopic nature of the majority of the tested materials, however, appears to offer a new approach to decon. If one were to formulate a dry powder decon which had a combination of a hygroscopic substance and an oxidizer (ideally a hygroscopic one such as the lithium hypochlorite or the sodium percarbonate), this dry powder material could be dispersed onto a contaminated surface. Once on the surface, the powder would sorb atmospheric water, and form a chemically active, aqueous film capable of both oxidizing and hydrolyzing material on the contaminated surface. The key point in this approach is the total lack of need for an external water source. Decon operations could rely on atmospheric humidity, which for the U.S. Navy is usually high. This new approach to decon should be investigated.

V. RECOMMENDATIONS

This study has identified several items which impact directly on the utility of decon fluids to be prepared from solid, stored precursors. Specifically needed now are data which:

1. Compare the decon efficacy of the candidates examined in this study against appropriate CW and BW simulants, and, ultimately, live agents and toxins. Special attention should be given sodium dichloroisocyanurate, which exhibited fair long term stability in this study.
2. Investigate the corrosivity to Naval alloys associated with solutions of the candidates formed by hygroscopic uptake of atmospheric water.
3. Address the stability of the candidate materials in a hot, dry environment.
4. Study effective packaging/storage procedures for those candidates which prove effective in decon tests with simulant/agents.
5. Examine in detail the concept of a hygroscopic, dry powder decon approach which would employ sorbed atmospheric water to assist in decon operations.

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Table 1 Solid Oxidizers Tested

Oxidizer	Formula	Formula Weight	Sample Weight	Source
Calcium Hypochlorite	$\text{Ca}(\text{OCl})_2$	143.1	0.3501 ± 0.0004	Fisher
Lithium Hypochlorite	LiOCl	58.4	0.7320 ± 0.0012	Lithco
Magnesium bis(2-carboxylato monoperoxybenzoic acid) hexadryate (H-48)	$\text{MgC}_{16}\text{H}_{24}\text{O}_{16}$	496.3	1.2391 ± 0.0009	Interox
Sodium Dichloro-isocyanurate	$\text{NaCl}_2(\text{NCO})_3 \cdot 2\text{H}_2\text{O}$	220.0	0.6408 ± 0.0014	Olin
Sodium Perborate	$\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$	153.8	0.7718 ± 0.0006	Alfa
Sodium Percarbonate	Na_2CO_4	122.0	0.6126 ± 0.0018	Alfa
Sodium Persulfate	$\text{H}_2\text{S}_2\text{O}_8$	238.0	1.1929 ± 0.0016	Alfa

Sources:

Fisher Scientific Company, Fairlawn, NJ
 Lithco, Lithium Corporation of America, Bessemer City, NC
 Interox America, Houston, TX
 Olin Chemicals, Stamford, CT
 Alfa Products, Danvers, MA

Table 2
Titer Data For Oxidizers

I. CALCIUM HYPOCHLORITE (sample size = 0.3581±0.0004 g)

<u>Sample Age, days</u>	<u>Titer, mL, Thosulfate Reagent</u>	<u>Appearance of Sample</u>
0	1.28	dry opaque white granules
2	0.032	sample dissolved to frothy fluid
8	0.017	sample dry, crusty, w/insoluble residue
14	0.012	no further change
21	0.017	no further change

II. LITHIUM HYPOCHLORITE (sample size = 0.7320±0.0012 g)

<u>Sample Age, days</u>	<u>Titer, mL, Thosulfate Reagent</u>	<u>Appearance of Sample</u>
0	0.69	dry opaque white granules
2	0.023	white grains in white fluid
8	0.025	as previous
14	0.015	no further change
21	0.018	no further change

III. SODIUM DICHLOROISOCYANURATE (sample size = 0.6408±0.0004 g)

<u>Sample Age, days</u>	<u>Titer, mL, Thosulfate Reagent</u>	<u>Appearance of Sample</u>
0	1.93	dry opaque white grains
2	1.70	no change
8	1.62	no change
14	0.84	no change
21	0.38	sample grains caked together

Table 2 (continued)

IV. MAGNESIUM BIS(2-CARBOXYLATOMONOPEROXYBENZOIC ACID)

HEXAHYDRATE (H-48) (Sample Size = 1.2391 ± 0.0009 g)

<u>Sample Age, days</u>	<u>Titer, mL, Thosulfate Reagent</u>	<u>Appearance of Sample</u>
0	1.50	dry opaque white grains
2	0.010	sample has yellow tinge
8	0.18	sample light brown
14	0.015	no change from previous
21	0.015	no further change

V. SODIUM PERBORATE (Sample size = 0.7718 ± 0.0006 g)

<u>Sample Age, days</u>	<u>Titer, mL, Thosulfate Reagent</u>	<u>Appearance of Sample</u>
0	0.27	dry milky white crystals and grains
2	0.19	no change
8	0.63	sample change, milky in appearance
14	0.014	sample crystallized into clear cubes
21	0.14	crystals milky in appearance

VI. SODIUM PERCARBONATE (sample size = 0.6126 ± 0.0018 g)

<u>Sample Age, days</u>	<u>Titer, mL, Thosulfate Reagent</u>	<u>Appearance of Sample</u>
0	0.31	dry, opaque white grains
2	0.026	sample dissolved
8	0.020	sample crystallized in a film
14	0.013	damp film of needle- like crystals
21	0.02	no further change

Table 2 (continued)

VII. SODIUM PERSULFATE (Sample Size = 1.1929 ± 0.0016 g)

<u>Sample Age,</u> <u>days</u>	<u>Titer, mL,</u> <u>Thosulfate Reagent</u>	<u>Appearance of</u> <u>Sample</u>
0	0.082	dry, clear crystals
2	0.52	sample dissolved
8	0.58	sample in solution
14	0.40	no change from previous
21	0.25	no change from previous