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Are Your Stainless Steel Surfaces Being Corroded by Repeated Bleach Use?

Bleach is known to be corrosive to metals commonly found in pharmaceutical work environments. Two commonly used types of stainless steel coupons were exposed to household bleach and sodium dichloroisocyanurate solutions—the rate and degree of corrosion were compared.

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Household bleach (sodium hypochlorite solution) is used as a disinfectant in pharmaceutical, bioprocessing, and medical device facilities commonly at a 1:10 dilution (one part bleach combined with nine parts water). However, bleach is known to be corrosive to metals and can cause damage to some plastics. Even with these drawbacks, bleach is commonly used because it kills a large spectrum of microbes, is widely available, and is easy to use. Sodium dichloroisocyanurate (NaDCC) is a bleach alternative available in solid tablet form. It also kills a large spectrum of microbes, is widely available, and is easy to use.

Objective

The objective of this study is to compare the corrosion caused by bleach and NaDCC solutions at use concentrations on two common types of stainless steel surfaces and to demonstrate the advantages of using NaDCC over bleach as part of a disinfection program.

Procedure

For this study, 18 stainless steel 316 (316) and 18 stainless steel 304L (304L) 2" x 2" x 1/8" coupons were obtained from GlobePharma. Six solutions were prepared daily with deionized water (18 MΩ RODI) using commercially available Clorox® bleach and commercially available tablets containing NaDCC. The solution concentrations, formulations, and appearance are compiled in Table 1.

Three coupons were submerged in 400-mL beakers containing 250 milliliters of one solution listed above ensuring complete coverage of the coupons. The beakers were then covered with plastic wrap. The coupons were removed from the beakers daily and wiped dry for visual inspection. Any differences were documented and photographed, as noted in Figures 1-3. Noted differences include changes in color, rust and corrosion, pitting, gas evolution observed while submerged in solution, and metal deposition on the glass surface of the beaker.

After inspection, fresh solutions were prepared for each coupon-solution combination, and the coupons were placed back in their original beakers. The beakers were maintained in an ISO Class 7 environment. The study was conducted over eight weeks. However, the undiluted bleach samples were maintained an additional four weeks until metal was deposited on the glass beakers.

Table 1. Test solution formulations used in the corrosion study.

Solution	Formulation	Appearance
Deionized water	Undiluted	Clear
Household bleach	Undiluted	Slight yellow
Household bleach diluted 1:10	25 mL bleach, 225 mL water	Faint yellow
Household bleach diluted 1:50	5 mL bleach, 245 mL water	Clear
NaDCC 937 ppm (nominal 1,000 ppm)	1 tablet diluted in 1 gal water	Clear
NaDCC 187 ppm (nominal 200 ppm)	50 mL 1000 ppm solution, 200 mL water	Clear

Results

After four days, the 304L coupons in the 1:10 bleach solution exhibited definite corrosion as shown in Figure 1. The 316 coupons in the 1:10 bleach solution also exhibited corrosion, but to a lesser extent. Pitting began in the first week for both 304L and 316 coupons in the same solution. After one week, the 1:10 bleach solution containing the 304L coupon was brown from rust floating in the solution. The 1:10 bleach solution containing the 316 coupons was gray. In contrast, the 1,000-ppm NaDCC solutions containing the 316 and 304L coupons remained clear.

By eleven days, the glass beaker sides containing the 304L coupon in the 1:10 bleach solution were contaminated with rust. At two weeks, there was pitting, corrosion, and staining of both 304L and 316 1:10 bleach solutions and full-strength bleach solutions. The 304L and 316 coupons were clean in the water, 200 ppm, and 1,000 ppm NaDCC solutions (Figure 2).

At three weeks, the 1:10 bleach solution containing the 304L coupons was colored black. Corrosion began to appear on one 304L coupon in the 1:50 bleach solution. By four weeks, the 304L coupons in undiluted bleach were evolving a gas as evidenced by bubbles rising in the solution from the coupon edges and faces, and, between observations (one time), rust was splattered on the plastic wrap beaker cover. At six weeks, metal deposition began on the glass beaker wall for the 1:10 bleach solutions containing the 304L and 316 coupons. An example of metal deposition is shown in Figure 3. By eight weeks, gas was evolving from the 316 coupons in addition to the 304L coupons in the undiluted bleach solutions.

The observations summarized by week are compiled in Table 2.

In Figure 4, the photograph contrasts the impact of the bleach and NaDCC solutions to the stainless steel coupons when the solutions are at the commonly used concentrations. The 304L and 316 1:10 bleach solution coupons are discolored and corroded.

In Figure 5, the photograph contrasts the impact of the bleach and NaDCC solutions to the stainless steel coupons when the solutions are at similar active chlorine levels. The bleach solution, though diluted at 1:50, still affects the more corrosion resistant 316 stainless steel through discoloration.

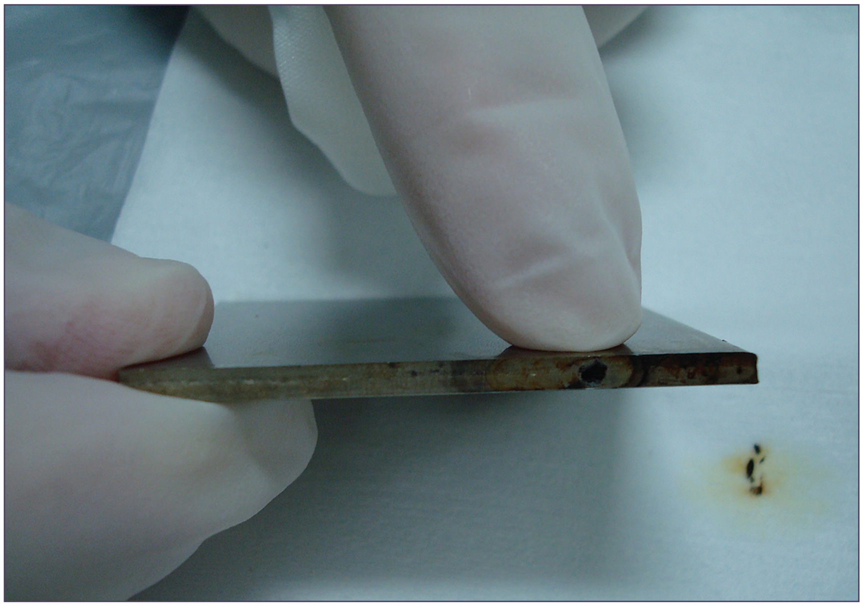

Figure 1. The photograph shows corrosion and pitting beginning on the edge of a 304L coupon exposed to the 1:10 bleach solution within the first week. Note the rust spot transferred to the work surface.

Solution	Coupon	Time (weeks)	
		1	8
Water	304L		
	316		
Bleach 50,000 ppm	304L	CC	CC,C,P,R,G
	316	CC	CC,C,P,G
Bleach 1:10 5,000 ppm	304L	CC,C,P	CC,C,P,R,M
	316	CC,C,P	CC,C,P,M
Bleach 1:50 1,000 ppm	304L		C
	316		C
NaDCC 1,000 ppm	304L		
	316		
NaDCC 200 ppm	304L		
	316		

Table 2. Physical changes observed summarized by week.
Key:
C = Corrosion, the beginning of observation of corrosion;
CC = Color change, the silver metal changes to a slight orange or darker color;
G = Gas evolution, bubbles of gas evolving from the metal are visible in the solution;
M = Metal deposition, dark and also shiny deposition on the beaker wall;
P = Pitting, divots in the metal surface;
R = Rust, a red, flaky material on the coupon face or edge or a deposit on the bottom of the beaker.

Discussion

Stainless steel

There are different types of stainless steel. The addition of differing levels of other elements, molybdenum, nickel, manganese, and chromium, to iron gives steel various properties—in this case, corrosion resistance. The 304L and 316 stainless steel grades used in this experiment are designed to be more corrosion resistant, but not corrosion-proof. The difference in the metals' content gives 316-grade stainless steel its higher corrosion resistance when compared to the 304L-grade.

Many pieces of equipment found in pharmaceutical, bioprocessing, and medical device facilities are constructed of 304L and 316 grades of stainless steel. This equipment is easy to clean and is resistant to corrosion by common chemicals and cleaners. However, continual use of bleach solutions as part of a disinfection program promotes corrosion of the equipment requiring the equipment to be replaced periodically.

Active ingredient

The sodium hypochlorite found in bleach and NaDCC is the active antimicrobial ingredient belonging to the oxidizing group of disinfectants. They form hypochlorous acid (HOCl) in water which interacts with biomolecules found in microbes resulting in cell death.[1–7]

Household bleach: Bleach is composed of sodium hypochlorite (NaOCl), sodium hydroxide (NaOH), and sodium chloride

(NaCl). It is produced by passing chlorine gas through a dilute sodium hydroxide solution or by electrolysis of salt water. Sodium hypochlorite is reactive and may chlorinate organic compounds.[8] This solution contains HOCl in equilibrium with the hypochlorite ion as shown by the equations below.

$$NaOCl \rightarrow Na^+ + OCl^-$$
$$OCl^- + H^+ \rightleftharpoons HOCl \text{ (hypochlorous acid)}$$

Sodium Dichloroisocyanurate: NaDCC is formed through the pyrolysis of urea which forms cyanuric acid. The cyanuric acid is reacted with chlorine and sodium hydroxide to form NaDCC.[9] In water, the NaDCC forms HOCl in equilibrium with a complex mixture of various chlorinated cyanurate chemical species.[10]

$$NaCl_2(NCO)_3 + H_2O \rightleftharpoons 2HOCl + NaH_2(NCO)_3$$

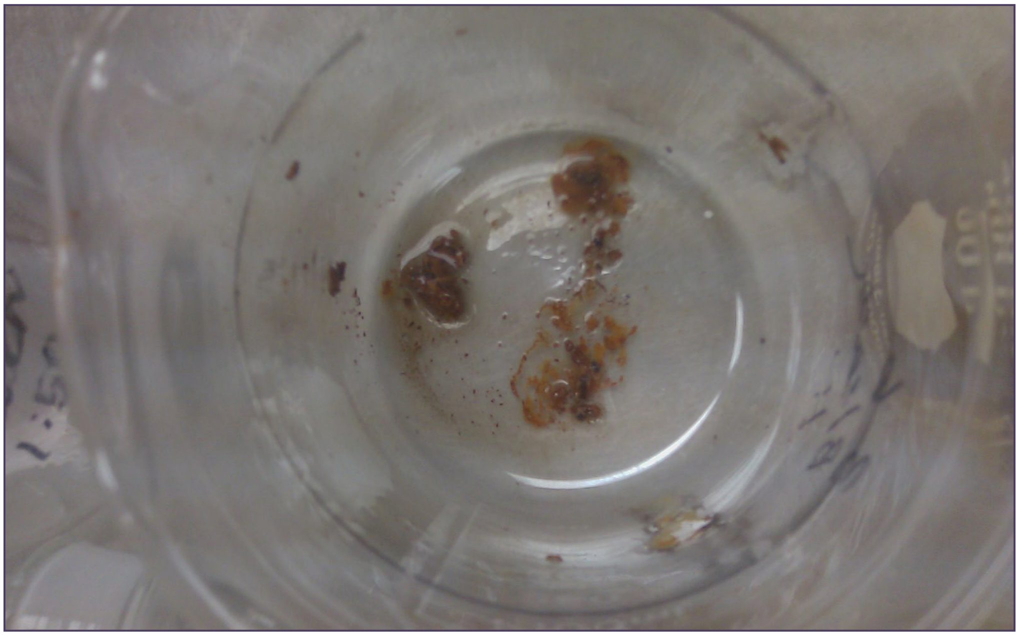

Figure 3. The photograph shows rust remaining at the bottom of the beaker that contained the more corrosion resistant 316 coupons exposed to the more commonly used 1:10 bleach solution. Even though the experiment finished at eight weeks, the 316 coupons were soaked for an additional month until metal deposits were showing in the beaker.

The NaDCC used in this experiment was supplied by Brulin & Company, Inc. (EPA Registration Number 71847-2-106).[11] On the label, the use instructions indicate adding one tablet per gallon for 937 ppm active chlorine.

Product use

To make a 1:10 bleach solution (5,000-ppm active chlorine), 1¾ cup bleach is added to one gallon of water with mixing as described by the bleach EPA label. For the 1,000-ppm NaDCC solution, one tablet is added to one gallon of water and allowed to dissolve through the effervescence, a process that takes less than two minutes. Each product is to be used per EPA registration label guidelines on hard, nonporous, inanimate surfaces that have been pre-cleaned. The products are applied to the pre-cleaned surface. The surface must remain wet for the prescribed contact time of ten minutes. If the surface dries before ten minutes, the reapplication of more solution is required. After ten minutes, the product may be allowed to dry on the surface or be removed.

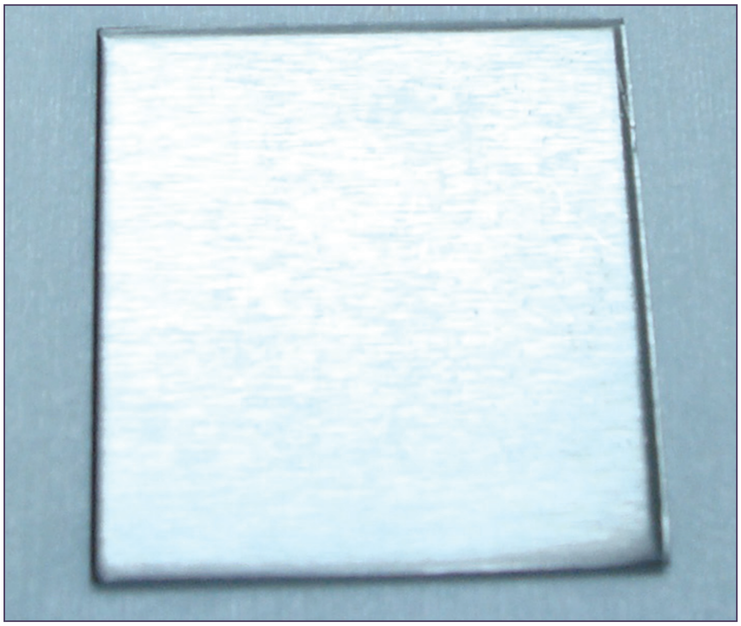

Figure 2. The photograph shows the clean face of a 316 coupon exposed to 1,000-ppm NaDCC solution for three weeks.

While bleach is used to disinfect hard, nonporous, inanimate surfaces, as found on the Clorox® Bleach label,[12] it also includes the following instructions, not found in the NaDCC product label:

- "Do not use this product on steel, aluminum, silver, or chipped enamel.
- If used on metal, a solution of this product should be allowed to stand for no more than five minutes, and then rinsed off thoroughly with clean water; otherwise, it may slightly discolor and eventually corrode the metal."

It is interesting to note that the second instruction for limiting exposure to five minutes is less than the prescribed contact time.

Conclusion

This study shows the corrosive effects of bleach solutions on 304L and 316 coupons at use levels typically employed for equipment disinfection in the pharmaceutical, bioprocessing, and medical device industries as part of their standard operating procedures. The NaDCC solutions did not show corrosive effects to the stainless steel coupons as shown in Figures 4 and 5.

Users of diluted bleach solutions on stainless steel must replace carts,

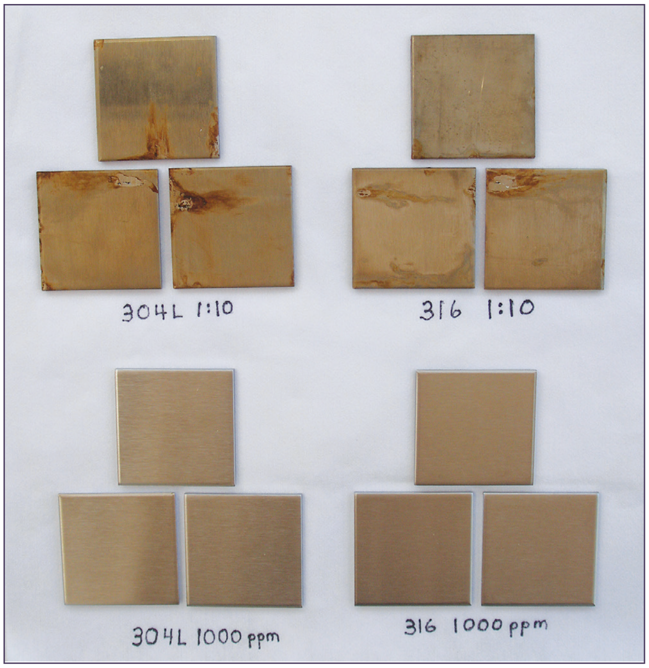

Figure 4. **The photograph above shows the coupons exposed to typical use concentrations of 1:10 bleach and 1,000-ppm NaDCC solutions at the end of the study. Note the discoloration and corrosion of the 304L and 316 1:10 bleach solution coupons.**

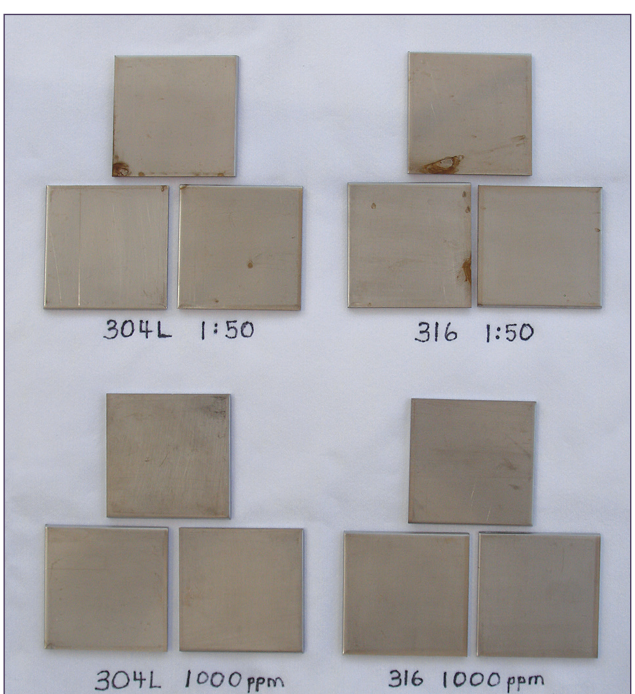

Figure 5. **The photograph above shows the coupons exposed to similar active chlorine concentrations of 1:50 bleach and 1,000-ppm NaDCC solutions at the end of the study. Note the discoloration and corrosion of the 304L and 316 1:50 bleach solution coupons.**

hoods, biological safety cabinets, filter dryers, and other equipment periodically due to corrosion following repeated exposure to bleach disinfectant solutions. Substituting NaDCC for bleach can reduce the frequency of replacement of expensive equipment incurring a cost savings while maintaining the disinfection level required for product manufacturing. This suggests using a NaDCC solution in place of bleach as part of a disinfectant rotation.

References

1. Maillard, J-Y. “Bacterial target sites for biocide action.” *J Appl Microbiol* 2002; 92(suppl): S16-S27.
2. Russell, AD. “Principles of antimicrobial activity and resistance.” In: Block, S, ed. *Disinfection, Sterilization, and Preservation*, ed. 5. Philadelphia: Lippincott Williams & Wilkins; 2001.
3. Albrich, J. M., C. A. McCarthy, and J. K. Hurst (1981). “Biological reactivity of hypochlorous acid: Implications for microbicidal mechanisms of leukocyte myeloperoxidase.” *Proc. Natl. Acad. Sci.* 78 (1): 210–214. doi:10.1073/pnas.78.1.210. PMC 319021. PMID 6264434.
4. Carr, AC; Van Den Berg, JJ; Winterbourn, CC (1996). “Chlorination of cholesterol in cell membranes by hypochlorous acid.” *Archives of Biochemistry and Biophysics* 332 (1): 63–9. doi:10.1006/abbi.1996.0317. PMID 8806710.
5. Vissers, MC; Carr, AC; Chapman, AL (1998). “Comparison of human red cell lysis by hypochlorous and hypobromous acids: insights into the mechanism of lysis.” *The Biochemical Journal* 330 (Pt 1): 131–8. PMC 1219118. PMID 9461501.
6. Fair, G. M., J. Corris, S. L. Chang, I. Weil, and R. P. Burden (1948). “The behavior of chlorine as a water disinfectant.” *J. Am. Water Works Assoc.* 40: 1051–1061.
7. Knox, WE; Stumpf, PK; Green, DE; Auerbach, VH (1948). “The Inhibition of Sulfhydryl Enzymes as the Basis of the Bactericidal Action of Chlorine.” J*ournal of Bacteriology* 55 (4): 451–8. PMC 518466. PMID 16561477.
8. Richardson, SD; Plewa, MJ; Wagner, ED; Schoeny, R; Demarini, DM (2007). “Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research.” Mutation research 636 (1–3): 178–242. doi:10.1016/j.mrrev.2007.09.001. PMID 17980649.
9. Klaus, Huthmacher, Dieter Most “Cyanuric Acid and Cyanuric Chloride.” *Ullmann’s Encyclopedia of Industrial Chemistry*, 2005, Wiley-VCH, Weinheim. ISBN 10.1002/14356007.a08 191
10. Bloomfield, S.F. and Miles, G.A. “The Antibacterial Properties of Sodium Dichloroisocyanurate and Sodium Hypochlorite Formulations.” *J. Appl. Bacteriol.*, 46, 1979, 65-73.
11. NaDCC EPA label: http://www.epa.gov/pesticides/chem_search/ppls/071847-00002-20110511.pdf
12. Bleach EPA label: http://www.epa.gov/pesticides/chem_search/ppls/005813-00001-20110913.pdf

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