



Effect of chlorine-based sanitizers properties on corrosion of metals commonly found in food processing environment



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ABSTRACT

In order to gauge the effect of pH and chloride concentration on the corrosion of metal surfaces commonly found in a food processing environment, different metal samples (stainless steel, carbon steel, aluminum, and copper) were exposed to chlorinated and electrolyzed oxidizing (EO) water. The samples were suspended in the chlorinated and EO solutions in a way to observe corrosion on the metals completely submerged in the solution as well as above the solution's surface. The pH and chloride concentrations of the chlorinated and EO water samples played a significant role in mass loss for all the metal samples. Increases in surface roughness were linked to pH and chloride concentrations. Metal surfaces left suspended above the solution surfaces showed greater increases in surface roughness compared to the metal surfaces completely submerged in the solutions. This data demonstrates the need for care when selecting and using a chlorine-based sanitizer in food processing environments.

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1. Introduction

Electrolyzed-oxidizing (EO) water is a low (~ 2.5) pH, high oxidation–reduction potential (ORP, ~ 1100 mV) chlorine-based sanitizer that contains hypochlorous acid as its primary antimicrobial compound (Kim et al., 2000; Venkitanarayanan et al., 1999). Additionally, EO water can be modified by mixing electrolyzed-reducing (primarily a sodium hydroxide solution) water with the EO water to produce slightly acidic EO water, which usually has a pH of 6.0 and an ORP of 900 mV (Cao et al., 2009). Despite the effectiveness of EO water in killing many types of foodborne pathogens, it is well known that chlorine-based sanitizers such as EO water cause corrosion in susceptible materials.

Corrosion is defined as the process between a material and its environment that results in the degradation of the material. As such, corrosion is not so much a material's property as it is a response to the environment. The rate of corrosion depends on several environmental variables, such as pH and the concentration, as well as the identity, of chemical species within the material's environment (Fontana and Green, 1986).

The pH of a solution plays a rather complex role in the corrosion process. For example, pH's role in corrosion appears to be much more dominant when the $\text{pH} < 5$ as opposed to $5 < \text{pH} < 9$. However, some metals (namely aluminum and zinc) experience a large increase in corrosion rate when $\text{pH} > 9$ (Tomashov, 1966; Vujicic and Lovrecek, 1985). One of the reasons why there is

complexity surrounding the role of pH in corrosion is because of counter ions. A counter ion (sometimes referred to as a conjugate base), can either slow down (i.e. SO_4^{2-} from sulfuric acid) or speed up (Cl^- from hydrochloric acid) corrosion at certain pH levels (Chin and Nobe, 1972; Ellison and Schmeel, 1978).

In terms of EO water in previous works (Ayebeh and Hung, 2005; Dong et al., 2003), pH was discovered to play a large role in corrosion rate. All the metals (stainless steel, carbon steel, aluminum, copper) and dental alloys (Au–Ag–Pd and silver) tested in the 2 studies above showed a higher rate of corrosion (as measured by mass loss and surfaces roughness changes) in EO water samples that had a low (< 3.0) pH.

Solution components such as chloride ions are also large factors that determine corrosion rates in chlorine-based sanitizers. Many studies have explored the role of chloride in the corrosion of various metals, especially stainless steel, and all seem to agree that increased chloride concentrations lead to higher rates of corrosion (Fang et al., 2011; Prawoto et al., 2009). It must be noted however, that these studies occurred in solutions other than chlorine-based sanitizers, so the role of chloride in EO water on corrosion still needs clarification.

The rate of corrosion of metals in the presence of chlorine-based sanitizers including EO water is a product of several closely-associated variables discussed above. Therefore, any attempt at corrosion research must account for all of these variables. The purpose of this study is to evaluate the corrosive effect of chlorine-based sanitizers with different properties on several metal surfaces commonly found in food processing environments.

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Nomenclature

Acronyms

Al	3003-H14 aluminum
Cu	110 copper
CS	ASTM A-36 medium carbon steel
CW1	chlorinated water at pH 2.5
CW2	chlorinated water at pH 6.0
CW3	chlorinated water at pH 9.3
EO1	EO water produced from generator #1 at pH 2.5 with a free chlorine concentration of 40 mg/L
EO2	EO water produced from generator #1 at pH 6.0 with a free chlorine concentration of 40 mg/L
EO3	EO water produced from generator #2 at pH 2.5 with a free chlorine concentration of 40 mg/L
EO4	EO water produced from generator #3 at pH 3.0 with a free chlorine concentration of 40 mg/L

EO5	EO water produced from generator #3 at pH 7.2 with a free chlorine concentration of 40 mg/L
ORP	oxidation–reduction potential
ppm	parts per million
R	surface roughness (μm)
SS	316 stainless steel

Superscripts and subscripts

a	average of the absolute value of all peaks and pits
Z	absolute value of the highest peak or deepest pit
Max	average of the absolute value of the largest 5 peak and pit measurements
S	with salt addition

2. Materials and methods

2.1. Metal sample preparation and cleaning

Four different metals cut into strips (coupons) were used: 316 stainless steel (SS), ASTM A-36 medium carbon steel (CS), 3003-H14 aluminum (Al) and 110 copper (Cu) (Instrument Design and Fabrication Shop, Athens, GA, USA). All coupons were cut and polished (120 grit) in the same place they were purchased from so that they had a food grade finish. The coupons for each material were cut to be $\frac{1}{16}$ " thick, $\frac{1}{2}$ " wide, and 3" long. Additionally, all coupons had a $\frac{1}{4}$ " hole drilled in the center, $\frac{1}{4}$ " away from one end. Prior to use, the specimens were degreased by scrubbing each coupon with a bleach-free detergent powder (Alconox®, Alconox Inc., White Plains, NY, USA) using a brush with soft nylon bristles. After being rinsed in deionized water, the specimens were soaked in acetone and kept in a desiccator before use. The degreasing method is described in American Society of Testing and Materials (ASTM) standard G31-72 (ASTM, 2004).

2.2. Solutions used for corrosion testing

Six types of chlorinated water were used in this study: pH 2.5 with and without 600 mg/L chloride added (CW1 and CW1_s), pH 6.0 with and without 600 mg/L chloride added (CW2 and CW2_s), and pH 9.3 with and without 600 mg/L chloride added (CW3 and CW3_s). The chlorinated water samples were made by diluting 5% NaOCl in deionized water to yield a 40 mg/L free chlorine concentration. The pH for each chlorinated water sample was adjusted by the addition of 1 N HCl. Chloride concentrations were adjusted by the addition of NaCl.

In addition to the 6 types of chlorinated water in this study, EO water from 3 different generators were also used as treatment solutions in this study. The properties of the 5 different EO water solutions produced from the 3 different generators are described in Table 1. Samples "EO1" and "EO2" were produced from the first EO water generator (generator #1) and diluted with deionized water to yield a free chlorine concentration of 40 mg/L (from about 60 mg/L). "EO3" was produced from a second EO water generator and was used as is. "EO4" and "EO5" were produced from the third EO water generator (generator #3) and diluted from about 160 mg/L free chlorine with deionized water to yield a free chlorine concentration of 40 mg/L.

Table 1

Properties of CW and EO water samples.

Sample	Salt addition	[Free Cl] (mg/L)	pH	ORP	[Cl ⁻] (mg/L)
CW1	N	40	2.5	1150	357
CW1 _s	Y	40	2.5	1150	871
CW2	N	40	6.0	940	51.5
CW2 _s	Y	40	6.0	940	400
CW3	N	40	9.3	690	26.7
CW3 _s	Y	40	9.3	690	458
EO1	N	60, diluted to 40	2.5	1150	90
EO2	N	60, diluted to 40	6.0	950	77.5
EO3	N	40	2.5	1160	912
EO4	N	250, diluted to 40	3.0	1160	280
EO5	N	250, diluted to 40	7.2	690	500

Data presented in this table are representative values of samples used throughout the experiment and is not an average value.

CW = chlorinated water.

EO1&2 are EO water prepared from EO generator #1 at pH 2.5 and 6.0, respectively.

EO3 is EO water prepared from EO generator #2 at pH 2.5.

EO4&5 are EO water prepared from EO generator #3 at pH 2.5 and 6.0, respectively.

2.3. Measurement of solution properties

Solution pH was measured using a digital pH/ORP meter (Accumet AR50, Fisher Scientific Co., Fair Lawn, NJ). Free chlorine was determined by the DPD-FEAS titrimetric method (Hach Scientific, Loveland, CO). Chloride ions were measured by a chloride ion probe (These properties were measured and recorded after each solution was made).

2.4. Immersion tests

A total of 77 coupons (11 treatment solutions for 7 weeks) for each metal per rep were used for the experiment. The coupons were immersed individually in Mason jars containing 400 mL of each test solution so that 25% of the surface area of each coupon is above the solution surface, leaving 75% submerged. The coupons were suspended by means of fluorocarbon string tied through the hole in each coupon. The ends of the string were anchored on the outsides of the jar.

After recording solution and coupon properties (weight and surface roughness), the experiment was started by suspending each coupon in test solution as described previously. Test solutions were replaced with freshly prepared solutions every 72 h. After each week of exposure (and every week thereafter until no

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