Disinfection Alternatives to Control Corrosion on Water Systems.

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Abstract — *Disinfection is one of the most common processes in the world since the human understood that the water contained pathogens that can be lethal. Since this, new methods and techniques of disinfection had been developed and studied. An effective disinfection method should be one that besides eliminating the pathogens present in water, does not affect the water system or human health in other manners. The most common disinfectant for water is hypochlorite, since is an economic solution for most pathogens that may be present in potable water, but it presents a problem since it is a very corrosive solution and most water systems are built from mild steel and copper. Oxidation of metals can become a problem for water systems. The deterioration of metals can cause iron and copper molecules to be added to water, which are known to have a direct impact on human health. Chlorine dioxide may be a solution for this common problem since it is a selective biocide with less impact on the metals and health.*

Key Terms — *Chlorine, Chlorine Dioxide, Corrosion, Disinfection.*

INTRODUCTION

One of the most known problems of hypochlorite disinfection is the high corrosivity of this product. Corrosion is defined as a naturally occurring phenomenon commonly defined as the deterioration of a metal, substance or its properties because of a reaction with the environment. Most metals tend to corrode for its exposure to the environment, even more if they are in direct contact the oxidizers. Since chlorine is an oxidizing biocide it will have a direct impact on the oxidizing potential of the water, which will result on corrosion of the metals present in the water system. A solution for systems that are currently being impacted by the corrosivity of hypochlorite can be chlorine dioxide, which as chlorine is an oxidizing biocide, but works at less concentration of product, and is known for being a selective product. Chlorine dioxide is described as a selective product since it will attack pathogens and microorganisms before affecting the metal surfaces. Current federal regulations specify that the maximum concentration for residual chlorine in potable water plants is 4 milligrams per liter (mg/L) or parts per million (ppm), while for chlorine dioxide is 0.80 mg/L. Based on the microbial charge of the systems, chlorine dioxide residual can be decreased to even 0.40 milligrams per liter and still achieve acceptable microbial counts. This different in residual is vital for preventing excessive corrosion in metal systems, lowering the corrosion rate under the recommended parameters for water systems. Typically, corrosion rates in the systems are measured by coupons with the same metals that are present on the system. Corrosion coupons are rectangular pieces of metal that are installed on recirculating water from the system emulating system conditions to represent the corrosion type and rate (weight loss of the material) in a period. Other quantifiable method had been emerging to measure corrosion rates on the system, but these are limited to the corrosion rate at a specific moment in a specific area of the system. Corrosion Coupon are installed on the water system in a rack, and typically analyzed three months later. Periods longer that one month are required since the first month is an attemperator month for the metal.

This method was used to compare the corrosion rates on a system that was treated with chlorine and then changed to chlorine dioxide. Total iron tests were also performed to understand and quantify corrosion rates in a water distribution system. Values up to 0.55 milligrams per liter were detected when the system was being treated with chlorine. These values were reduced to 0.02 milligrams per liter after chlorine dioxide was introduced as a disinfectant on the system.

Other Studies

Chlorine dioxide usage began in the early 1800's that has been known for the high solubility and effectiveness in water pathogens. Typically, chlorine dioxide is generated on site in gas or aqueous form, by combining sodium chlorate ad sodium chlorite. This solution is used as a biocide and as a disinfectant for industry use. One of the most important characteristics of this oxidant is that is a more selective agent than chlorine, meaning that the product will work more effectively on heavily polluted environments and will impact less the metals of a system. In comparison with hypochlorite, it has been proven that chlorine dioxide is more effective at lower dosages and that it is not as reactive as ozone. On other hand, hypochlorite tends to degrade at higher water alkalinity and temperature, while chlorine dioxide remains stable at a wider variety of pH [1].

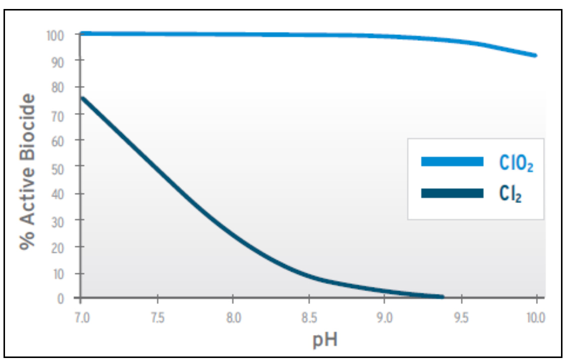

Figure 1
Water pH versus Biocide Effectiveness of Chlorine and Chlorine Dioxide

Reference [2] concluded that the use of chlorine dioxide as a disinfectant and biocide for a hospital water system worked effectively at dosages below the Environmental Protection Agency recommendations and maintained the copper corrosion rate very low in comparison with the control samples. Chlorine dioxide kills bacteria via the disruption of cellular processes, and it is very effective for potable and process water. Mild Steel and Copper Corrosion coupons were used to monitor corrosion rates on the system, which were evaluated 9 months after the beginning of the use of the treatment. Other coupons were installed on a non-treated part of the water system to monitor corrosion rates and for comparison. Control samples for the copper coupon was measured at 0.4 mills per year, while the copper corrosion coupon that was on the system measured 0.3 mills per year.

Other uses for chlorine dioxide is for disinfection of fresh-cut food. This industry in inclined in the usage of chlorine dioxide as a disinfectant agent since it is more stable and works at a wide range of pH, produces less carcinogenic byproducts, and is less corrosive than chlorine and ozone [1].

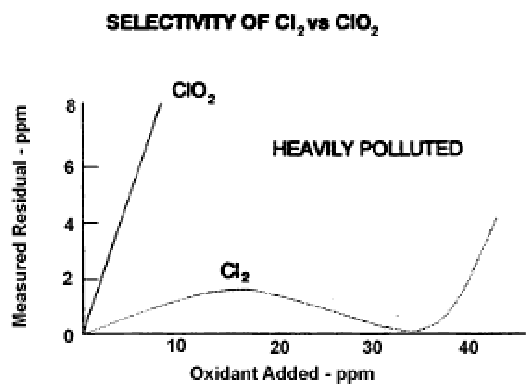

Figure 2
Chlorine Dioxide Selectivity Compared to Chlorine

Water Systems Corrosion

The most common way to quantify and observe corrosion on water systems is with corrosion coupons. Corrosion coupons are rectangular pieces of metal, typically with measurements of 3" x 0.5" x 1/16". The coupons used are placed on a coupon rack that will hold the coupon in a parallel position to the flow of the water, without touching the rack. The material for the corrosion coupons needs to be from the same metallurgy as the system analyzed. Most water systems are made from metal alloys, mild steel, copper, bronze and stainless steel. If more than one coupon is installed, they should follow the galvanic series to prevent the plating of other steel to interfere with the corrosion of another metal. Coupons are precisely weighted and coated to have a smooth surface. The importance of the exact weight of the coupon is to compare after a period the mass loss of the material [3].

Figure 2
Corrosion Coupon Example

Between two (2) and six (6) months are allowed for coupons examination on systems. Lectures are measures in mills per year (mpy), which implies 1/1000 of an inch per year of corrosion. Average corrosion rate is calculated by (1), where K is a constant of 3.65 x 10^4, W is the mass loss of the coupon in grams, T is the total time of exposure in days, A is the area of the coupon in square centimeters and D is the density of the coupon material in grams by cubic centimeters [4].

$$\textit{Corrosion Rate (mm/y)} = (K \times W)/(A \times T \times D) \qquad (1)$$

Coupons not only provide a quantifiable way to measure corrosion trend, but also allow to perform visual inspection to determine corrosion types.

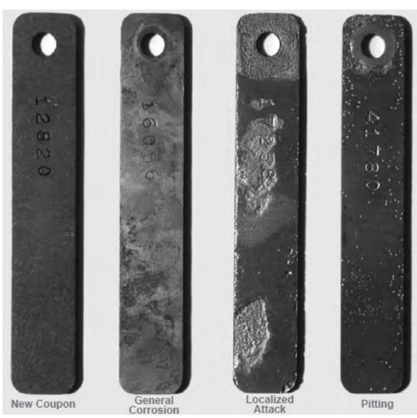

Figure 4
Types of Corrosion that can affect a Water System

Most corrosion reactions are electrochemical, in which the metal element return to its native state. For oxidation to occur, transfer of electrons must take place between to areas with dissimilar electrical potential. The corrodible surface will be to one that has electrons to lose, which is why metals corrode. Many forms of corrosion are known, including general, localized, pitting and crevice corrosion. General corrosion is the most common type of corrosion in water systems treated with oxidant biocides. For a coupon to have generalized corrosion equal deterioration of the material surface area. This type of corrosion is a result of alternations between anodic and cathodic conditions at a specific location of the system, which results at an even corrosion across the coupon surface. This can happen by the metal loss in which a given area is alternately a cathode and an anode [5].

Figure 5
General Corrosion Example (A small amount of metal is taken evenly throughout the system or coupon)

Localized corrosion tends to occur on high stress areas of the system like welds, ruptures of coating and uneven surfaces. Also, dissimilar metals on conductive water will result on localized corrosion (galvanic type). This type of corrosion affects a metal surface that is confined to a small area and take the form of a cavity. One of the most dangerous localized corrosion type is pitting, which indents the metal wall creating pinholes that can affect the structure.

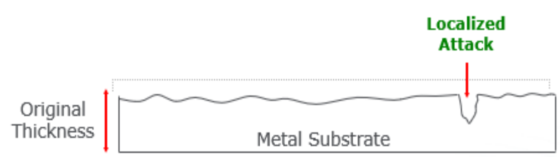

Figure 6
Localized Corrosion Example

Another type of corrosion is crevice corrosion, which results from a small area that is isolated. This also can be a result from water being different from the system at this isolated area. This differential created a potential difference that created conditions favorable for current flow, a corrosion cell. Crevice corrosion tend to occur in holes, gaskets, joints and under deposits on the system.

Microbiologically influenced corrosion is a type of corrosion that is enhanced by microorganism on the water that can convert iron ions and create oxidation reaction in the system. Heavily microbially influenced system can experience this type of corrosion, especially if scale or deposits are present.

Chlorine is among the most corrosive substances used to disinfect water for potable and industrial use. This solution is typically used for economic reasons, but it has been proved that it affects metals by pitting/crevice corrosion. This results on reduction of the utility life and higher maintenance costs. Before 1970 most water systems were built with lead piping for its corrosion resistance. Due to lead related illnesses, lead piping were replaced with copper and mild steel for distribution systems. For its ease of installation, copper has become one of the most common material used for piping and tubing. One of the most affected materials from chlorine is mild steel. Mild steel is one of the most used materials for water pipes and systems. Mild steel is a type of carbon steel, with no more than 2% carbon. This material is widely used on industries for its ease of use, machinability, weldability and wide availability. The lack of alloying metals implies that this material is susceptible to oxidation if it is not coated properly [5].

Figure 7
Mild Steel Corrosion Coupon after 60 Days Exposed to Chlorinated Water

It is known that chlorine has negative effects in water distribution systems for its corrosiveness [4]. The corrosion of mild steel on water system results on aesthetic concerns regarding water quality. Taste, color and odor of the water are a product of oxidation, known as red waters. Red water events occur when iron corrosion particles are released into the water system and mixed with the water. There is also a phenomenon known as black water, which is caused by ferrous species from iron on oxygen depleted water.

Figure 7 is an example of a mild steel corrosion coupon that was being used to monitor an industrial water tank treated with chlorine. On this application, no more than 2.0 milligrams per liter were used to maintain bacterial control. No stagnant water was present since recirculation pumps are present in the system. The corrosive appearance in the coupon was developed in sixty days after installing the coupons. Localized corrosion can be observed in the sample. Water systems that receive results on corrosion coupons like the example would most likely run into high costs replacing water tanks, pipes and pumps. At this level of corrosion, components of the system can get more than 10 mills per year of corrosion. Because of these observations, chlorine dioxide treatment can be used to replace the current treatment.

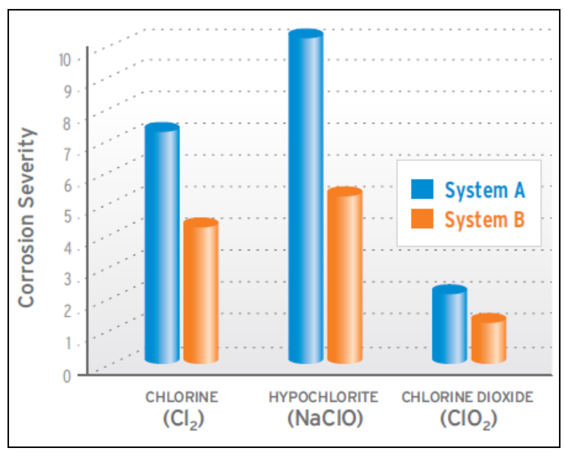

Figure 8
Comparison of Corrosion Severity with the Usage of Biocides

Example's corrosion coupons were analyzed by a certified lab following ASTM G1-03:2011 and ASTM G4-01:2014 procedures. Figure 6 corrosion rate was determined to be 12.2 mpy, while the maximum recommended parameter for water systems of this type is 4 mpy. This resulted on a high importance matter because of the implications that the replacement of the piping and water system parts could have. The deterioration of metal parts on the system due to the corrosion rate can foul the system in years of operation. As a solution for this problem ozone, peroxide, ultraviolet lamps, bromine and chlorine dioxide were considered as a replacement for chlorine disinfection.

As in [5], the corrosion rates for chlorine dioxide in comparison to mostly used disinfectants tend to be lower, with results at 0.14 ± 0.03 mm/year and more uniform corrosion pattern. Results up to 0.17 ± 0.03 mm/year were obtained by other disinfectants on a six months period.

COUPON INFORMATION		
Coupon Metallurgy	Mild Steel	
Coupon Type	bar-style 3 x 1/2 x 1/16 inch (76 x 12.7 x 1.6 mm)	
Serial number	CD7286	
PERIOD OF EXPOSURE		
Date inserted	03-Mar-2017	
Date removed	18-May-2017	
Total days of exposure	76	
WEIGHT LOSS		
Initial Weight	10.6139 g	
Final Weight	10.6102 g	
Weight Loss (Total)	0.0037 g	
Weight Loss (Corrected)	0.0037 g	
CORROSION RESULT		
Corrosion Type	None - the coupon is without noticeable or measural	
Corrosion Rate by Weight Loss	<0.1 Mils per year	<0.003 mm/year

COUPON INFORMATION		
Coupon Metallurgy	Copper	
Coupon Type	bar-style 3 x 1/2 x 1/16 inch (76 x 12.7 x 1.6 mm)	
Serial number	DG4687	
PERIOD OF EXPOSURE		
Date inserted	03-Mar-2017	
Date removed	18-May-2017	
Total days of exposure	76	
WEIGHT LOSS		
Initial Weight	11.8629 g	
Final Weight	11.8603 g	
Weight Loss (Total)	0.0026 g	
Weight Loss (Corrected)	0.0026 g	
CORROSION RESULT		
Corrosion Type	None - the coupon is without noticeable or measurable corrosion.	
Corrosion Rate by Weight Loss	<0.1 Mils per year	<0.003 mm/year

Figure 9
Comparison of Corrosion Severity with the Usage of Biocides

Additional to corrosion coupon monitoring and testing in this system, total iron tests were performed regularly to monitor residual iron on the system. HACH method 8635 with a DR900 equipment were used to conduct the mentioned tests. Results with a median of 0.4815 ppm were received when the water distribution system was disinfected with chlorine, with results as high as 0.55 ppm, these results are presented on Table 1.

Table 1
Total Iron Tests Performed on the Water System While Disinfected with Chlorine

Date	Total Iron (ppm)	Date	Total Iron (ppm)
6/6/2016	0.44	8/10/2016	0.55
6/8/2016	0.44	8/23/2016	0.52
6/10/2016	0.46	8/31/2016	0.50
6/14/2016	0.40	9/9/2016	0.49
6/15/2016	0.39	9/14/2016	0.48
6/20/2016	0.46	9/23/2016	0.45
6/28/2016	0.48	9/30/2016	0.48
7/11/2016	0.55	10/5/2016	0.48
7/18/2016	0.54	10/11/2016	0.49
8/5/2016	0.52	10/25/2016	0.51
Average		**0.4815**	

The residual of chlorine dioxide on the system was changed to a setpoint of 0.40 ppm, validated with microbiological samples to maintain proper control. After the disinfectant treatment was replaced with chlorine dioxide a system flush was performed to lower the concentrations of iron on the system that were caused by the chlorine corrosiveness. The consequent tests for total iron received decreased values of an average of 0.02 ppm on the system, with results as high as 0.03 ppm, these results are presented on Table 2. With these results we can conclude that the corrosion rate on the system is negligible. The high total iron concentrations of iron prior to the change to chlorine residual was one of the reason that help to make the decision of changing the disinfectant. With a corrosion rate this high, serious problems can be predicted on the system, that will lead to high replacements cost for system components. The higher costs of chlorine dioxide disinfection are one of the main reasons people still use chlorine as the preferred disinfectant for water systems, but this can be contradictive because of the high corrosiveness of the chlorine, that can lead to higher replacement costs.

Table 2
Total Iron Tests Performed on the Water System While Disinfected with Chlorine Dioxide

Date	Total Iron (ppm)	Date	Total Iron (ppm)
11/16/2016	0.00	1/30/2017	0.00
11/21/2016	0.02	2/6/2017	0.02
11/30/2016	0.03	2/13/2017	0.03
12/6/2016	0.01	2/21/2017	0.02
12/13/2016	0.00	2/27/2017	0.00
12/23/2016	0.00	3/6/2017	0.01
12/24/2016	0.01	3/13/2017	0.01
12/27/2016	0.01	3/20/2017	0.02
1/3/2017	0.02	3/29/2017	0.01
1/24/2017	0.02	4/3/2017	0.01
Average		**0.02**	

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