ALTERATION OF THE DRINKING WATER QUALITY BY DIFFERENT METALLIC MATERIALS USED IN DISTRIBUTION SYSTEMS.

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- ✓ La selección y arbitraje de los trabajos que aparecen en este suplemento fue responsabilidad del Comité Organizador del *X IBEROMET*, quien nombró una comisión *ad-hoc* para este fin (véase editorial de este suplemento).
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Resumen

La variación de los principales parámetros fisicoquímicos que presenta el agua potable cuando está en contacto con diferentes materiales usados en las redes de distribución secundarias, fue estudiada mediante la exposición de tuberías nuevas de acero al carbono, acero galvanizado y cobre, usando sistemas piloto de tubería para cada material y uno adicional de PVC que sirve como referencia. El agua que alimenta los sistemas piloto es agua suministrada por la empresa municipal de acueducto. Estos sistemas piloto están ubicados en la Universidad de Antioquia y han sido evaluados durante un período de seis meses. Para tal fin se analizaron semanalmente parámetros fisicoquímicos y microbiológicos en muestras de agua tomadas a la entrada y salida de cada línea, luego de que el agua había tenido un tiempo de retención de 24 horas. Finalmente, se estudió la formación de biopelícula en las paredes de los tubos y la velocidad de corrosión que estos poseen con el tiempo. La velocidad de corrosión para el acero al carbono fue más alta que en el cobre y que en el acero galvanizado. La corrosión promueve la disolución de algunas especies, lo que puede incrementar la turbiedad y conductividad del agua, y en algunos casos, los contenidos de sólidos suspendidos que generan cambios de color en el agua**.** A partir de los conteos de heterótrofos totales realizados a la biopelícula formada sobre los diferentes materiales, se encontró que sobre el sistema de acero al carbono se presenta el mayor crecimiento de estas bacterias mientras que para el cobre fue el menor. En el acero galvanizado se presenta una tendencia creciente en la cantidad de bacterias durante el periodo de estudio.

Palabras Claves: *Biopelícula, Agua Potable, Corrosión en agua fresca, Calidad del agua*

Abstract

Changes in the main physical-chemical parameters of drinking water in contact with different pipe materials used in secondary distribution systems, were evaluated by exposure of new pipes of carbon steel, galvanized steel and copper. The research was done in four pilot loops located at the headquarters of the University of Antioquia, one for each metallic material, and an additional one made of PVC as reference. The water that feed each system was drinking water supplied by the municipal water company. The systems were evaluated during six months. Water physical-chemical and microbiological parameters were weekly analyzed at the entry and exit of each loop, after the water had a retention time of 24 hours.. Finally, it was studied the formation of biofilm on the pipe walls and the corrosion rate of the pipe materials. The corrosion rate for carbon steel was higher than for copper and galvanized steel. The corrosion process promoted the dissolution of some species, which might increase water turbidity and conductivity and in some cases, the suspended solid contents which generate water color changes. From the total heterotrophic counts made in the biofilm formed on the different materials, it was found that the carbon steel system has the highest growth rate of these types of bacteria whereas the copper system has the lowest. The galvanized steel system shows a tendency to increase with time during the period studied.

Keywords*: Biofilm, Drinking water, corrosion in fresh water, Water quality*

1. INTRODUCTION

When water left the water treatment plant and goes through the distribution system it can change its quality by its interaction with the pipe walls in the distribution system or by interrupted water supply, cross connections, by pipe joins with leaks, residual disinfectant loss and reactions of the disinfectant with other organic and inorganic composites. These factors can cause bad flavor and smell problems, increase of suspended particle contents causing rise of turbidity, formation and growth of biofilm that allow the presence of pathogen bacteria, deposits in the inner surface and pipeline material deterioration (Mays [1]).

Pipeline deterioration in drinking water systems can also be caused by factors as flow rate, temperature, pH, low alkalinity, dissolved oxygen, biofilm and low hardness. These factors promote the dissolution of the metal and as consequence unwanted flavor and color in the water. In addition, the deterioration of the pipe can produce tubercles that offer protection to bacteria, promoting their attachment to the wall (Bremen *et al.* [2]).

One of the greatest concerns in drinking water production is the risk of contamination with pathogenic microorganisms. Ingress of pathogens into the distribution system can rapidly lead to an infection of thousands of people. When pathogenic bacteria has entered a distribution network, the bacteria will remain in the biofilm for a prolonged period (Fass *et al.* [3]); biofilm may act as a safe haven for pathogenic bacteria where they are able to survive or maybe even grow (Keevil *et al* [4], Armon *et al.* [5]).

The aim of this work is to evaluate the alteration of the drinking water quality caused by pipeline deterioration and biofilm growth. For this study were chosen materials currently used in urban water distributions systems in Medellín city. The exposure time was six months. The changes in physical-chemical and microbiological parameters commonly used to evaluate water quality are analyzed for each pipe system.

2. MATERIALS AND METHODS

2.1 Pipe loop system

Pipes loops were designed and constructed for three materials (carbon steel, copper, galvanized) with an additional pipe loop of PVC to serve as reference. These systems helped to determine the variation of water quality, biofilm growth, formation of deposits on the pipe surface and pipe corrosion rate. Also, these loops allowed obtaining similar conditions to a water distribution system. Each system consisted of a 3 m long and 0.0254 m nominal diameter pipeline, which was connected at both ends with PVC pipeline to form a closed pipe loop. Each loop system operated at two different conditions; at flow-through during 6 days in order to provide real operation condition of a distribution system and at recirculation-flow during one day in order to provide a longer retention time and to increase water-pipe wall interaction; the latter flow condition will allow a more clear evaluation of variations in water parameters. The flow velocity used in loop systems was 0.3 $m.s^{-1}$ .The adequacy of the system to operate in any configuration was accomplished through a series of valves. Each system had a pump, flow meter, sampling valve and a set of valves to adjust the operation of the system. A complete outline of the pipe loop system is presented in Figure 1.

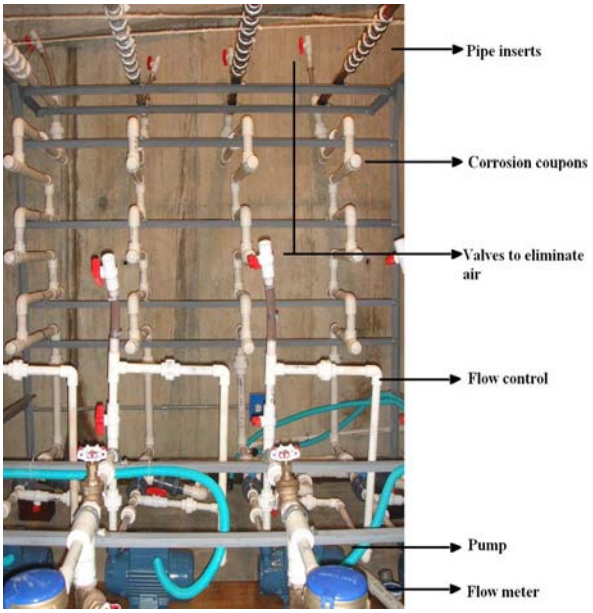


Figure 1. Pipe loop systems employed.

The pilot-scale arrangement was located at the University of Antioquia and it was fed with

drinking water from the municipal distribution system. This water has low hardness and low alkalinity; some parameters of the water used in this study are presented in Table 1.

Table 1. Physical-chemical parameters of the feeding water during a period of 6 months.

Parameter	*Method**	*Value / Units*
Temperature	2550 B	20.3 °C
pH	4500H +B	6.95
Conductivity	2510 B	67.5 µS/cm
Dissolved oxygen	4500 -OG	6.1 mg/L
Residual Chlorine	4500-Cl	0.91 mg/L
Turbidity	2130 B	1.19 NTU
Alkalinity, as CaCO3	2320 B	15.0 mg/L
Total Hardness, CaCO3	2340 C	32.4 mg/L
Total solids	2540 B	59 mg/L
Total dissolved solids	2540 E	50 mg/L
Heterotrophic bacteria	9215 D	10 CFU/100mL
Total Coliforms	9222 B	0 CFU/100mL

* Standard Methods (1995)

2.2 Measuring corrosion rate.

Coupons of each material were made and installed following the ASTM standard D-2688 [6] to evaluate the corrosion rate by weight loss method. Metal coupons of carbon steel, copper, galvanized steel were used in the corresponding pipe loop. Stainless steel coupons were installed in the control system (PVC loop). Three coupons of each metal were used at each time and the average of the mass loss was used to calculate the corrosion rate. Corrosion rate is determined at 1, 3 and 6 months of exposure.

2.3 Measurement of water parameters.

Prior to the pipe loops operation, these were washed and disinfected following the AWWA Standard [7] for disinfecting water mains and using sodium hypochlorite (NaOCl) with a chlorine concentration of 300 mg/L for 15 minutes. The process consisted in a preliminary flushing, disinfection and final flushing. Disinfection was made to ensure that the inner wall of the pipes were free of microorganisms.

Loops operated mostly at flow-through condition, except once a week when water quality was evaluated; in this case loops were operated at recirculation flow for 24 hours. Water samples were taken before (influent water) and after (effluent water in each pipe loop) the 24 hours of recirculation. The influent sample was the same for all pipe loops because these systems have a common entry. The variation of water quality was determined comparing the effluent water parameters with the influent ones.

Conductivity was measured with a conductimeter WTW series inolab cond720. Dissolved oxygen was measured using a WTW model oxy 320 portable D.O. meter. Turbidity was measured using a Turbiquant model 1100 IR turbidimeter. Residual chlorine was measured using the DPD (N, N diethyl-p-phenylenediamine) colorimetric method.

Water total heterotrophic bacteria were determined using agar plate count (HPC) with incubation at 37°C for 2 days. Count of heterotrophic bacteria is reported as Colony Forming Units per square centimeter (CFU/cm^2). Total coliforms were determined using M-Coli Blue agar with incubation at 37°C for 1 day; both measures were done by the membrane filter procedure.

2.4 Measuring biofilm growth

Each pipe loop has a permanent pipe section and seven pipe inserts to be removed at different times. Each pipe insert was a 0.05 m long. Inserts were removed at 0.5, 1, 3 and 6 months of exposure. After the removal of the pipe section from the system, the biofilm were scraped with a citobrush from the inner pipe wall surface, subsequently it was sonicated, homogenized and then analyzed for total heterotrophic bacteria in a similar manner as water.

3. RESULTS AND DISCUSSION

3.1 Corrosion

Corrosion is an electrochemical process in which metal is oxidized and an electron acceptor (usually oxygen or hydronium ion) is reduced. Corrosion processes sometimes lead to the deposition of an oxidized film on the surface of the corroding metal. In the cases of iron, zinc and copper, some oxides, hydroxides, carbonates and hydroxicarbonates of the corroding metals can be deposited. These films can promote slow corrosion by protecting the underlying layers from contact with the corroding medium (Stone *et al* [8]). In the case of iron, the compounds usually found on corrosion scales include goethite, lepidocrocite, magnetite, siderite,

ferrous hydroxide, ferric hydroxide, ferrihydrite and calcium carbonate (Stone *et al.* [8]). These corrosion deposits reduce the hydraulic capacity of pipes and more energy is required to deliver water at a desired flow rate. In addition, corrosion compounds can adversely affect water quality during distribution (Sarin *et al.* [9]), Larson and Sollo [10]). Some additional consequences are: (a) red water or colored water when iron is released from corrosion deposits, (b) high demand for chlorine and dissolved oxygen (Lu *et al.* [11]), (c) biofilm growth, and (d) adsorption and accumulation of substances such as arsenic and radium, which can be released on modification of water quality (Sarin *et al.* [9]).

When metal surfaces are covered with corrosion compounds, iron may be released by (a) direct corrosion of the iron pipe, (b) dissolution of ferrous components, and (c) hydraulic scouring of particles from iron compounds. In corroded pipes iron release often bears no simple relationship to iron corrosion rate. The interactions of corroded iron surfaces with water quality are not completely understood. However, it is recognized that water quality parameters can influence iron release from corroded iron/steel pipes in distribution systems. Some of these factors include dissolved oxygen, pH, alkalinity, water flow conditions, temperature, water treatment practices and fluctuations in water quality (Sarin *et al.* [9]).

In Figure 2 it is observed the behavior of the corrosion rate of the four materials for a period of six months where carbon steel has the highest corrosion rate and stainless steel has the lowest. The higher corrosion rate in carbon steel system is because its corrosion products did not form a protective layer during this time, whereas in galvanized steel pipe, zinc forms a protective layer consisting of zinc oxide, hydroxides and various basic salts. Copper presents a lower corrosion rate which could be caused by the formation of copper oxide products, which are stable and little soluble in water helping to the decay of corrosion rate with the exposure time (Shim *et al.* [12]).

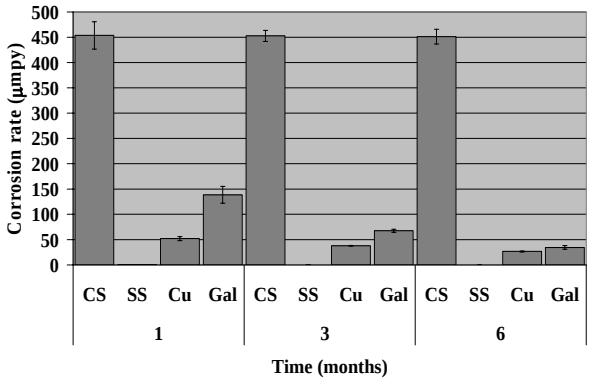


Figure 2. Corrosion rates for the materials during the period of study. CS: Carbon Steel, SS: Stainless Steel, Cu: Copper and Gal: Galvanized Steel.

3.2 Variation of the water parameters

Water physical-chemical parameters such as dissolved oxygen, pH, conductivity and redox potential play an important role in the corrosion process. When drinking water has high values of dissolved oxygen and pH is neutral (Figure 2 and 3) oxygen participates in the cathodic reaction (Pisigan and Singley [13]) :

$$O_2 + H_2O + 4e\text{-} = 4OH^- \quad (1)$$

$$2\,H_2O + 2e\text{-} = H_2 + 2OH^- \quad (2)$$

The cathodic reactions produce some pH rising, depending of extend of the reaction. The anodic reaction is the metal dissolution:

$$Me = Me^{n+} + ne^- \quad (3)$$

In the case of iron, when drinking water has low hardness and alkalinity, the anodic reaction is:

$$Fe = Fe^{2+} + 2e^- \quad (4)$$

$$2Fe^{2+} + 1/2O_2 + 4HCO_3^- + 5H_2O = 2Fe(OH)_3 + 4H_2CO_3 \quad (5)$$

Iron in anodic regions is oxidized to ferrous ions (Fe^{2+}), which is in turn further oxidized by dissolved oxygen to form ferric hydroxide [$Fe(OH)_3$].

As it can be seen in Figure 3, all systems present a consumption of dissolved oxygen after recirculation, 70 percent approximately for carbon

steel and galvanized pipes, and 30 percent for copper pipe loop. Taking into account that water has low alkalinity and low hardness and there was dissolved oxygen consumption, this can indicate that a corrosion process has occurred. There is more decay of dissolved oxygen in metallic materials than in polymeric materials like PVC and this decay can be explained by the corrosion processes of active material, also a little increment of the water temperature (3-5 ºC) observed in all loops during the recirculation period can contribute to the decrease of dissolved oxygen.

Dissolved Oxygen is a good oxidizer but when a system like drinking water is chlorinated the corrosivity in copper and iron is enhanced and chlorine is more powerful cathodic depolarizer than Dissolved Oxygen (Stone *et al.* [8], Pisigan and Singley [13]).

When water is chlorinated, the following spontaneous reaction occurs:

$$Cl_2 + H_2O = HOCl^- + H^+ + Cl^- \quad (6)$$

Then $HOCl^-$ ionizes:

$$HOCl^- = H^+ + OCl^- \quad (7)$$

At the pH values commonly encountered in drinking water both species OCl^- and $HOCl^-$ coexist as free residual chlorine. At neutral pH (Figure 4), significant amounts of $HOCl^-$ can be present to serve as reactant in the cathodic reduction (Stone *et al.* [8]).

In the case of the copper the anodic reaction is:

$$4Cu^0 = 4Cu^+ + 4e^- \quad (8)$$

And the possible cathodic reaction in chlorinated water with a slightly basic pH is:

$$HOCl^- + H^+ + 2e^- = Cl^- + H_2O \quad (9)$$

In this study both cathodic reactions occurred: reduction of hypochlorous acid from residual free chlorine (disinfectant) and reduction of oxygen in corrosion processes.

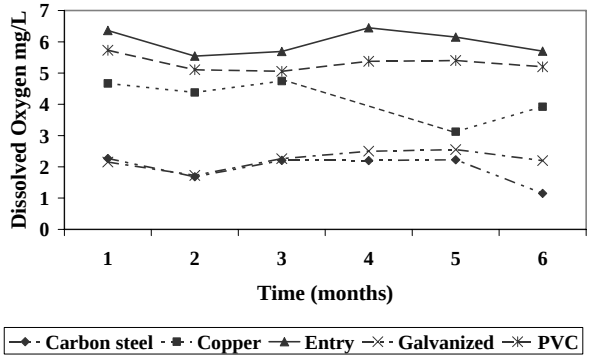


Figure 3. Dissolved Oxygen changes for a period of 6 months.

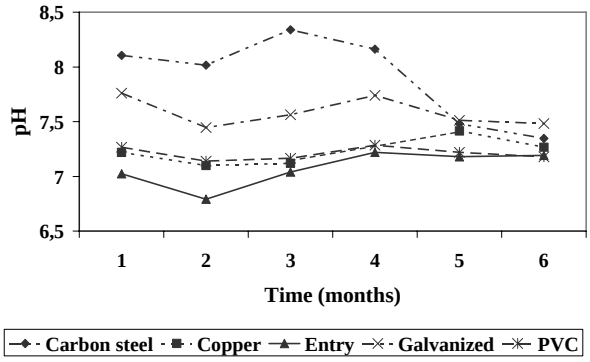


Figure 4. pH changes for a period of 6 months.

Changes in turbidity and conductivity in all systems after recirculation (Figures 5 and 6) are caused by dissolution of active metals; in this study carbon steel pipe is the main participant in these changes. Probably it promoted iron ions flow and releasing of iron oxides and hydroxides formed on the pipe wall during recirculation. Additionally, these species could cause an increase in soluble ionic species when they go into the water, which is consistent with an increase in conductivity. The carbon steel system has the highest values for turbidity and conductivity whilst PVC has the lowest ones. After recirculation, water from the carbon steel system presented red color which is attributed to suspended solids and these solids promote an increase in turbidity.

The increase in pH in all systems after recirculation can be associated with metal corrosion (see equations (1)-(2)), since according to the general mechanism of corrosion, when influent water pH is

neutral and has low alkalinity and low hardness, hydroxyl ions and metallic hydroxides are generated (Pisigan and Singley [13]). Consequently, more active metals such as steel could present increase of pH.

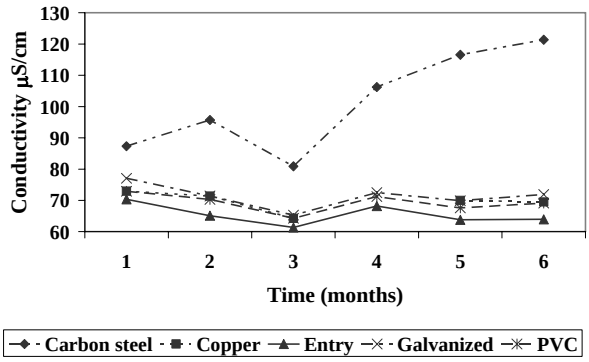


Figure 5. Conductivity changes for a period of 6 months.

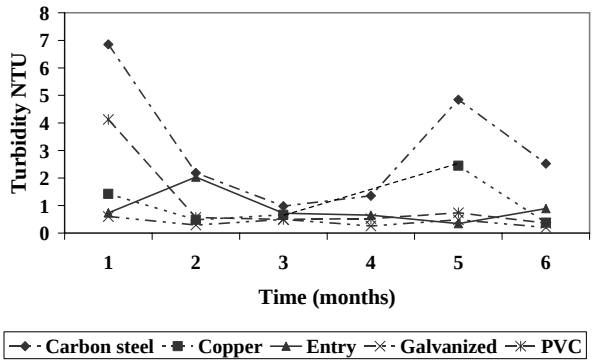


Figure 6. Turbidity changes for a period of 6 months.

3.3 Biofilm growth

Figure 7 shows the count of total heterotrophic bacteria present in the effluent water for different pipe material and exposure times. The biofilm growth on the inner surface of the pipe for each material and different exposure times can be observed in Figure 8.

It can be seen that heterotrophic bacteria counts found in water sampled from the less active materials loops (i.e. PVC and copper) were superior respect those found in carbon and galvanized steels (see Figure 7). However, this behaviour is inversed when the heterotrophic bacteria present in the biofilm are considered (see Figure 8). This situation can be explained because PVC and copper pipes have smooth inner walls and this does not facilitate biofilm attachment, whereas carbon and galvanized steel pipes have a bigger roughness, facilitating biofilm growth. On the other hand, tubercles formed by corrosion in the active materials assist the attachment of bacteria. Additionally, tubercles can offer protection to bacteria against disinfectants.

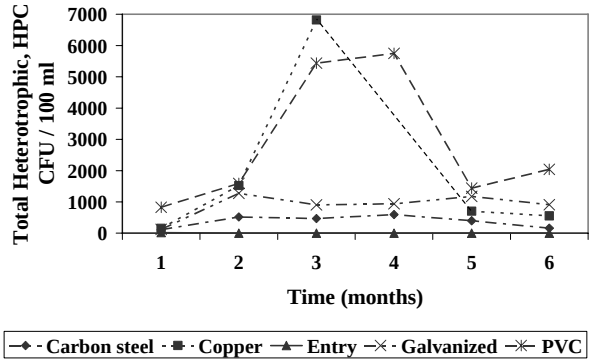


Figure 7. Total Heterotrophic bacteria in the water.

A particular situation could take place with PVC pipe, when PVC are in contact with drinking water some carbonated species can migrate from the PVC wall to the water bulk and promote bacteria growth (Skjevrak *et al.* [14]).

Loss of residual chlorine (disinfectant) and temperature increase were observed in the effluent water after recirculation; these facts can contribute to biofilm growth. Detachment of biofilm formed on the pipelines of the city distribution system can release bacteria into the water feeding the experimental loops.

In all systems occurred a decay of the disinfectant element, this fact can be attributed to different causes such as the reduction reaction of corrosion processes, consumption by tubercles and reaction of the disinfectant element with some species such as iron and manganese into the water bulk. (Lu *et al.* [11]).

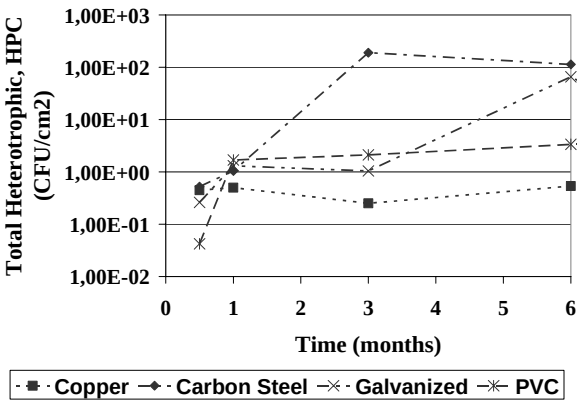


Figure 8. Total Heterotrophic bacteria on the inner surface of the pipe.

4. CONCLUSIONS

Carbon steel was the material that suffered the biggest deterioration when it was in contact with drinking water; this was because low alkalinity and high dissolved oxygen content in the water. Also, carbon steel had the biggest biofilm growth; this was because the tubercles formed in the pipe wall after corrosion process offered protection to the biofilm against the disinfectant and promoted bacteria attachment. Copper was the system that had the lowest biofilm growth because it is a smooth material and it has some corrosion products that are known to be toxic to the bacteria.

The corrosion process of carbon steel promoted dissolution of some products that increased turbidity and conductivity in the water and in some cases produced suspended solids that increased water color. The PVC system had the lowest values in turbidity and conductivity.

According to the results of this study carbon steel causes the most alteration of water quality whereas PVC and copper induced fewer changes.

Pilot systems are a good option to make this sort of studies because they could offer similar conditions to water distribution systems and the operational parameters can be closely controlled, mainly water retention time and water volume/pipe surface area ratio.

5. ACKNOWLEDGEMENTS

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