



The corrosive nature of manganese in drinking water

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HIGHLIGHTS

- ▶ Corrosion of distribution systems affects the quality of drinking water.
- ▶ Corrosion in water distribution systems is related to acidity and carbon dioxide.
- ▶ Pipes are corroded and manganese is deposited on pipes and dissolved in water.
- ▶ The deterioration of the pipes and the corrosion products were determined.
- ▶ Nitrate ions increase the acidity of water in the wells.

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ABSTRACT

Corrosion problems having to do with drinking water distribution systems are related to many processes and factors and two of them are ionic acidity and carbon dioxide, which were considered in this work. The corrosion character of water is determined by the corrosion indexes of Langelier, Ryznar, Larson, and Mojmir. The results show that pipes made of different materials, such as plastics or metals, are affected by corrosion, causing manganese to be deposited on materials and dissolved in water. The deterioration of the materials, the degree of corrosion, and the deposited corrosion products were determined by X-ray diffraction and Scanning Electron Microscopy. High levels of manganese and nitrate ions in water may cause serious damage to the health of consumers of water. Three wells were examined, one of them presented a high content of manganese; the others had high levels of nitrate ions, which increased the acidity of the water and, therefore, the amount of corrosion of the materials in the distribution systems.

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1. Introduction

Corrosion affects the extraction, distribution, and storage of drinking water in several important ways, such as chemical composition, structure, and morphology of the materials (iron, steel, cement, asbestos, PACK o PVC) of pipes, valves, pumps, and storage tanks. These types of corrosion problems tend to deteriorate water quality as well as the hydraulic infrastructure of extraction and distribution systems, resulting in layers of rust that increase the amount of energy required for distribution of water; as hydraulic performance decreases, the cost of distribution and maintenance of water systems increase (Sarin et al., 2004).

Metals such as manganese and iron are related to the corrosion of iron pipes and are the main source of coloration of drinking water in distribution systems (Sarin et al., 2004; Cerrato et al., 2006; Ong et al.,

2007; Peng et al., 2010; Peng and Korshin, 2011). Corrosion in distribution systems restricts water flow, causing deterioration in terms of quality (Sarin et al., 2002, 2004, 2007). The presence of manganese in the systems, which may be soluble in the water, may cause sensory problems such as colored water, stains, dirt in the systems, and complaints by consumers (Sly et al., 1990). From the toxicological point of view, the adverse effects of manganese on human health depend on the route of exposure, the chemical species, and the age and nutrition status of the consumers. It is known that manganese exposure affects nervous system functions and may even cause an irreversible Parkinson-like syndrome known as manganism, which is characterized by weakness, anorexia, muscle pain, apathy, slow speech, emotionless “mask-like” facial expressions, postural difficulties, rigidity, tremors, decreased mental status, and slow, clumsy movements of the arms and legs (Bouchard et al., 2007; Roccaro et al., 2007; US-EPA, 2004; ATSDR, 2000). Studies in animals that have been exposed to different concentrations of manganese have revealed neurotoxic effects (Ong et al., 2007). The Environmental Protection Agency of the U.S.A. has set a

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secondary maximum contaminant level for manganese of 0.05 mg/L (US-EPA, 2004), the World Health Organization has set a level of 0.1 mg/L (WHO, 2004), and Mexican legislation has set a limit of 0.15 mg/L (NOM, 1994).

Cerrato et al. (2006) reported that PVC and iron pipe materials used in hydraulic systems are affected in different ways by deposits of manganese in drinking water systems and can cause problems involving black water since they receive soluble manganese which undergoes biochemical cycles. The steel used in the extraction, distribution, and storage systems for water in Latin America contains manganese in the form of pyrolusite (MnO_2) in a maximum concentration of 1.2% (ASTM A53/A53M-12). In order to reduce the likelihood of corrosion in hydraulic infrastructure, in 1994, Mexico (CNA, 1994b) ruled that the materials composing hydraulic systems should maintain a film of calcium carbonate and that the corrosive tendency of water should be determined by considering quantitative models such as those of Langelier, Ryznar, and Larson. Qualitative models also exist, such as the modified and unmodified Mojmir Mach models (Allende, 1976; Trujillo and Martínez, 2005, 2009). Quantitative models offer better results than qualitative models.

The corrosive nature of water is mainly due to variations in the concentrations of free CO_2 and to other properties, such as hardness, amounts of dissolved oxygen (Allende, 1976; Moreno, 2006), alkalinity, pH (Rahman et al., 2007), dissolved solids (Peng et al., 2010; Sarin et al., 2001), residues from disinfection processes (Ong et al., 2007), acidity, major ions present (Allende, 1976; Trujillo et al., 2008), as well as the presence of nitrates ions (Helfrid et al., 2010). The physicochemical quality of water can be modified by flow configurations, fluctuations in water temperature during the year, microbiological activity, inhibitor applications, humic acid, hydrogen sulfide, alkaline compounds, salts, and the presence of microorganisms (Sarin et al., 2004; Imran et al., 2005; Rodier, 1998).

Water has the ability to contain different amounts of free CO_2 , which determines the behavior of calcium carbonate in the water. CO_2 in equilibrium is the quantity which should be present in water to maintain the bicarbonate species in solution. Excess CO_2 reacts with calcium carbonate (CaCO_3), increasing the concentration of bicarbonate in the water to maintain equilibrium (Merkel and Friedrich, 2008).

The aim of this paper was to evaluate effects of the materials used and the corrosion of the distribution systems of drinking water by the determinations of the physicochemical variations of water and the characterization of the corrosion products.

2. Materials and methods

2.1. Sampling

Three wells with low mineralization were considered for this research. The first one with carbon steel (PZ1), the second well stainless steel (PZ2) and the third well with manganese steel infrastructure (PZ3). PZ1 is located in a village center, PZ2 and PZ3 are located in an industrial area. PZ2 is located in a hydrating milk plant which produces 5,432,320 L of milk monthly and is distributed to children from the ages of 6 months to 12 years of age, females from 13 to 15 years of age in gestation or lactation periods, old chronically ill people between 45 and 59 years of age, disabled persons over 12 years old, and adults over 60 years old. PZ3 was used for agricultural purposes, which was rehabilitated and put into operation for the extraction of drinking water. This well, PZ3, is currently closed due to water quality problems. The water from these wells reaches a distribution tank (TQ) and then goes to consumers.

The samples were taken directly from PZ1 (21 times), PZ2 (14 times), PZ3 (8 times) and the storage tank (TQ) (18 times), three samples were taken in each sampling time. Before collecting the samples, the areas were cleaned in an attempt to remove all interference; then, the water was allowed to flow for 5 min before the samples were taken.

2.2. Analysis of samples

pH, temperature, electric conductivity, amounts of dissolved solids, dissolved oxygen, and saturation percent were determined in situ. Acidity, alkalinity, hardness, and amount of chloride ions were determined by volumetric titrations. Levels of nitrates, nitrites, sulfates, and phosphates were determined by UV-vis spectroscopy. Amounts of Ca, Mg, Na, K, Fe, Mn, and Si were determined by atomic absorption spectrometry. The samples were stored at 4 °C until they were analyzed; all processes were conducted according to standard methods (APHA-AWWA-WPCF, 2005).

2.3. Samplings of solids

Solids were collected from the hydraulic infrastructure (distribution tank; pipes composed of iron (SAC), polyvinyl chloride (PVC), and polyethylene of high-density PACK; solid sediments from TQ (SST); and solids from tap water (SCT)). These bonded materials were carefully removed and stored in glass containers and analyzed by X-ray diffraction (XRD) and Scanning Electron Microscopy.

2.4. Scanning Electron Microscopy

For Scanning Electron Microscopy (SEM) observations, the solids were mounted directly on holders and then observed at 10 and 20 kV in a JEOL JSM-5900-LD electron microscope. Microanalysis was done with an EDS (Energy X-ray Dispersive Spectroscopy) system.

2.5. X-ray diffraction (XRD)

Powder diffractograms of the solid samples were obtained via a Siemens D500 diffractometer coupled to a copper anode X-ray tube. The conventional diffractograms were used to identify the compounds and to verify crystalline structure.

2.6. Corrosion indexes

2.6.1. Qualitative models

Corrosion tends to increase the concentrations of certain metals in tap water like toxic metals: lead, cadmium nickel, copper, iron and zinc, which cause staining of fixtures or metallic taste or both. The Langelier saturation index (Langellier, 1936) is probably the most widely used indicator of water scale potential of water corrosivity. It is based on the effect of pH on the equilibrium solubility of CaCO_3 . The pH at which water is saturated with CaCO_3 , is known as the pH of saturation (pH_s). The Langelier index provides a qualitative value in reference to the stability of water by applying Eq. (1), which is the difference between the measured water pH and the pH of equilibrium or saturation (1.1) (CNA, 1994a, 1994b):

$$(I_L = \text{pH} - \text{pH}_s) \quad (1)$$

$$\text{pH}_s = 9.3 + A + B - C - D \quad (1.1)$$

pH_s	pH of saturation of Langelier
A	$(\log_{10} \text{SDT} - 1) / 10$
B	$-13.12 \log_{10} (\text{T}^\circ\text{C} + 273) + 34.55$
C	$\log_{10} [\text{Ca}^{2+} \text{ as mg/L CaCO}_3]$
D	$\log_{10} [\text{Alkalinity as CaCO}_3 \text{ mg/L}]$
SDT	Total dissolved solids.

If the index is equal to zero, water is in chemical equilibrium; if it is positive, it is encrusting; and if it is negative, it is corrosive (Pierre, 2008). Allende (1976) indicated that the Langelier index does not provide an estimation of the degree of corrosion or encrusting of water.

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