Journal of Civil Engineering and Architecture 14 (2020) 271-279
doi: 10.17265/1934-7359/2020.05.005

Lead and Cadmium Distribution in Tubes of Galvanized Steel by Hot-Dip Used for Drinking Water Supply

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Abstract: The main objective of this work was to evaluate the presence of lead and cadmium in galvanized steel tubes by hot-dip used exclusively for drinking water supply. In this research, samples of galvanized tubes were removed from walls of residential buildings with 30 years of use. In the process of hot galvanizing, the manufacturing standards allow or for low cost conveniences, and the use of primary zinc ingot with 1.6% metallic impurities, such as lead and cadmium, is allowed, enabling the incorporation of these metals into the zinc coating deposited on the carbon steel. The associated corrosion of these tubes can release these toxic metals, contaminating the drinking water used by residents. The samples taken from the tubes were evaluated by a square-wave anodic stripping voltammetry technique, and the results for lead and cadmium suggested randomly distributed levels, indicating that the contents of these contaminants depend mainly on the quality of the added primary zinc and the operational conditions of the immersion bath. The metallographic evaluations performed on the samples of the galvanized tubes showed irregularities in thickness and even a lack of the zinc layer deposited on the carbon steel surface. These facts suggest that galvanized tubes should not be used for drinking water.

Key words: Lead, zinc, hot-dip, galvanized steel, square-wave anodic stripping voltammetry, contamination.

1. Introduction

The hot-dip zinc galvanizing process basically consists of immersing the cast iron or carbon steel artifacts in a molten zinc bath at temperatures ranging from 440-470 °C for 1 to 5 minutes, depending on the desired coating thickness, to form a corrosion-resistant coating. After the immersion step is finished, the piece is removed and cooled, represented in Fig. 1.

During immersion, the diffusion process between the liquid zinc and iron forms a series of intermetallic layers that adhere to the carbon steel (Fig. 2), which provides excellent barrier protection and cathodic protection when there are imperfections or eventual discontinuities on the coating [1-4].

The presence of lead and cadmium in the hot-dip galvanizing process can be understood based on Brazilian standard NBR 5590 [5], which allows the zinc ingots used in the hot-dip galvanizing processes to have the specifications shown in Table 1.

In the technical view, the presence of lead in the molten zinc bath can be explained by the following reasons: increasing the fluidity of the bath, reducing the attack of zinc on the steel substrate, protecting the tank against excessive attack of zinc, preventing its premature wear, increasing ductility, and improving the mechanical properties. The optimum amount of lead in the kettle has been determined to be 1-1.5%, which provides fluidity of the molten zinc, produces spangles, and provides a better quality surface [6]. Lead also favors the formation of a thinner layer, helping to control the growth of intermetallic compounds in reactive steels and reducing zinc consumption [7]. Some tests on galvanized steel tubes and connections, installed from 1950 to 2008, show

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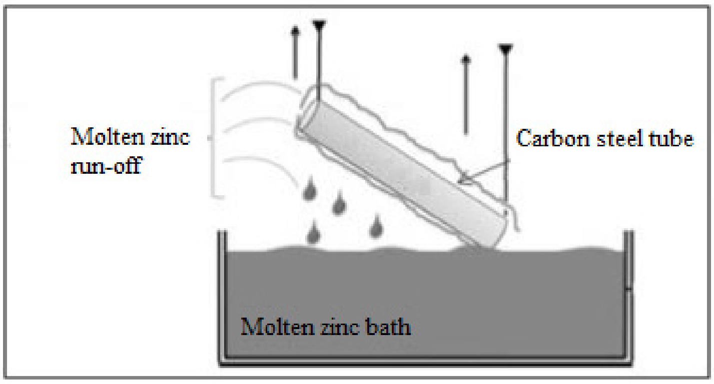

Fig. 1 Hot-dip zinc galvanizing process [1].

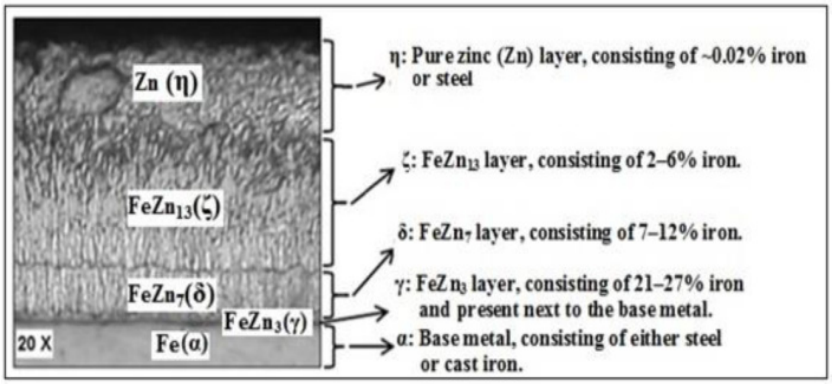

Fig. 2 Micrograph of the alloy (Zn-Fe) layers is shown (20× magnification) with basic descriptions of their respective compositions [1].

Table 1 Chemical composition of primary zinc for the hot-dip zinc galvanizing process [5].

Type	Minimum zinc content (%)	Maximum impurities content		
		Lead (%)	Cadmium (%)	Iron (%)
Extra fine	99.99	0.003	0.003	0.003
Fine	99.9	0.07	0.03	0.02
Common	98.0	1.60	0.50	0.05

that the lead concentration in the original zinc coating can vary from undetected to almost 2%, depending on the manufacturer and type of connection [8].

From an economic approach, there is a significant reduction in the processing cost when using common zinc ingot (with 1.6% lead). The cost of this zinc ingot is 40% cheaper (low-cost) than the fine ingot, and the lead has a density greater than zinc, protecting the bottom of the heating tubes of the tank and, consequently, increasing the useful life of the tank.

The cadmium contamination comes from the zinc ingot, as shown in Table 1; the common zinc ingot has 16 times more than the extra fine type [5].

It can be assumed that the lead in hot-dip galvanizing baths is allowed, as it is based on improving operational conditions and reducing costs in the final product. However, it is scientifically proven that lead is harmful to the environment, toxic to man, and can create serious public health problems, especially when it is associated with drinking water. It is a potent neurotoxin that can cause damage to almost all organs, bringing several risks to humans, including gastrointestinal and cardiovascular defects, high blood pressure, kidney problems, anemia, embryotoxicity, bone marrow suppression, and seizures. In addition, it is important to note that low concentrations over a long period of time can also have a bio-cumulative effect, and finally, the residents of old buildings should be alerted of the preferential risk of contamination in premature babies, children and pregnant women [9, 10].

Research conducted on building drinking water systems shows that lead release is generally due to galvanic corrosion and corrosion-erosion associated with lead-contaminated galvanized pipes, welded tanks (Sn-Pb), boilers, valves, and taps made of bronze and brass containing lead, etc. Exposure to lead contamination can occur faster inside residential buildings because drinking water is stagnant for long periods of time, depending on its use. This may mean that the concentrations of lead in the taps of residences may be higher than that coming from a water treatment plant [11].

This paper aims to evaluate the lead and cadmium content in galvanized tubes using the Square-Wave Anodic Stripping Voltammetry (SWASV) technique and metallographic analyses present considerations on the use of galvanized tubes for drinking water.

2. Material and Methods

Fig. 3 shows galvanized tubes that supply municipal (potable) water to the bathrooms, kitchens, and service areas of two residential buildings that were built 30 years ago. Fig. 3 highlights a water leak and valve made of brass, illustrating galvanic corrosion. In Figs. 4 and 5, the tubes used as specimens for chemical and metallographic analyses are presented. Corrosion is noted from the inside out, and in some cases, crevice corrosion and galvanic corrosion caused by iron (carbon steel)-brass or iron (carbon steel)-bronze connections are observed under the deposit.

2.1 Analysis of Lead and Cadmium in Samples of Galvanized Tubes by SWASV

2.1.1 Preparation of Samples and Metallic Standards of Zinc, Lead, and Cadmium

The selected tubes were washed with water and a plastic sponge, degreased with acetone and ethanol, and dried with hot air. An area of 2.5 cm^2 was fixed to the surface of the tube (Fig. 6), and with a high hardness scraper, filings of the galvanized zinc coating were obtained. All samples were taken from the outside of the tubes, avoiding the corroded areas.

The solubilization of each sample was carried out with the addition of 37% hydrochloric acid (0.2 mL), followed by the addition of 65% nitric acid (0.05 mL).

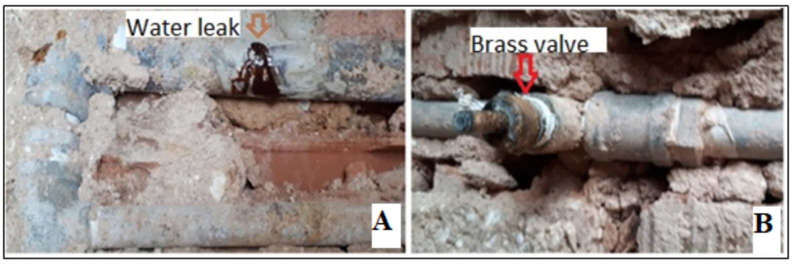

Fig. 3 Galvanized tubes and connections in a residential building.

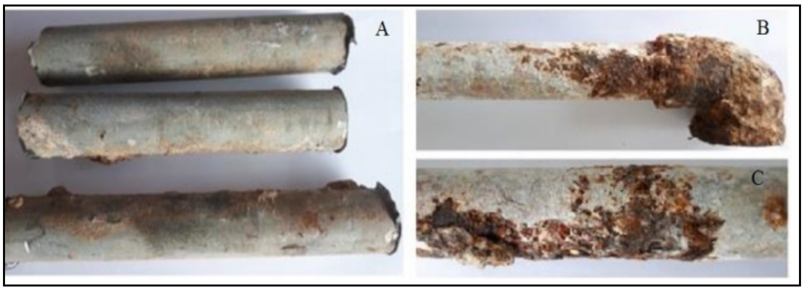

Fig. 4 (a) Galvanized tubes removed from dry walls and (b and c) tubes and connections removed from wet walls in a residential building.

Fig. 5 Internal and external corrosion in galvanized tubes.

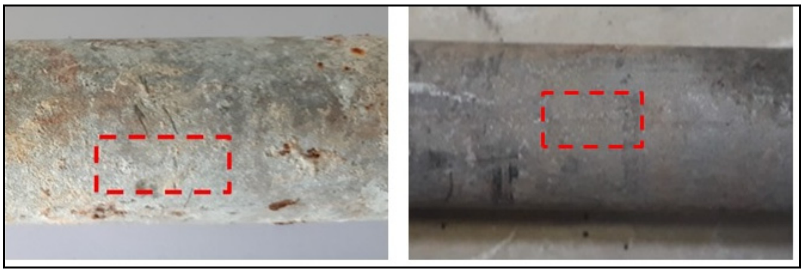

Fig. 6 The scraping area for galvanized zinc samples is shown (highlighted with red boxes).

After complete solubilization, systems were diluted in deionized water, and the pH was adjusted to approximately 6 with 0.2 mL of sodium hydroxide (6 M NaOH) for electroanalytical assessment; the final volumes were adjusted to 10.00 mL with deionized water in volumetric flasks.

The metallic standards were prepared by direct dilution from 1000 mg/L stock standards, with concentrations of 4.0 × 10^{-4} M zinc (Zn^{2+}) and 7.0 × 10^{-5} M lead (Pb^{2+}) and cadmium (Cd^{2+}).

2.1.2 Description of the Analysis

The determinations were performed using an Ivium® CompactStat® potentiostat/galvanostat, coupled to a laptop with the Ivium® software for operation. The Cd^{2+} and Pb^{2+} analyses were performed using the Square-Wave Anodic Stripping Voltammetry (SWASV) technique, using a carbon composite electrode modified by an *in situ* electrodeposited bismuth film; calibration was completed by the standard addition method. For this purpose, a three-electrode electrochemical cell with a capacity of 25.0 mL was used with carbon composite (65% graphite powder dispersed into 35% polyethylene terephthalate glycol (PETG) binder) as the working electrode (sensor), $Ag|AgCl_{(KCl\ sat.)}$ as the reference electrode, and an AISI 316L stainless steel needle as the counter electrode [12].

The methodology used was based on studies by Furtado et al. [13] in which approximately 1.0 mg of bismuth nitrate was added directly to the electrochemical cell. The following voltammetric parameters were used: -0.85 V deposition potential for 120 seconds, followed by square-wave voltammetry with a frequency of 20 Hz, 50 mV of amplitude, and 10 mV of potential increase in anode sense from -0.9 to 0.1 V. After voltammetry, 0.3 V of potential was applied for 60 seconds to ensure total cleaning of the electrode surface. As the background electrolyte, sodium acetate buffer (pH 6.0) was used.

The limits of quantification and detection were obtained with an analytical curve, constructed using 10 successive additions of 200 μL of Cd^{2+} and Pb^{2+} standards, both 7.0 × 10^{-5} M, and the respective current measurements were recorded by the method described above. Such values were calculated based on the standard deviation of 10 background noise measurements, and the results are shown in Table 2. The analytical curves were constructed from the

Table 2 Analytical parameters obtained for the simultaneous determination of lead and cadmium using the composite electrode.

Analytes	Analytical curve	Linear region (µmol/L)	LD (µmol/L)	LQ (µmol/L)
Pb^{2+}	$I_p = 19.4\ C - 2.90 \times 10^{-5}$; $R^2 = 0.994$	1.09 - 4.70	0.18	0.60
Cd^{2+}	$I_p = 10.3\ C - 2.59 \times 10^{-5}$; $R^2 = 0.994$	1.09 - 4.70	0.30	1.00

C means metal concentration, I_p means peak current measured during stripping electroanalysis, LD and LQ are limits of detection and quantification, respectively; R^2 is the Pearson correlation coefficient.

Table 3 Results of samples A and B that presented indexes above the lead detection limit.

Units	Sample "A"	Sample "B"
	Pb^{2+}	Pb^{2+}
µmol/L	2.54 ± 1.30	7.10 ± 0.39
% mass	0.0243	0.0678

addition of a standard containing the two proposed analytes, in cells with 25.0 mL of 0.1 M sodium acetate buffer pH 6.0.

2.2 Metallographic Analysis of Galvanized Steel Tubes

For the metallographic analysis of the cross-section of the zinc layer, 10 galvanized tubes were selected and removed directly from the residence walls, selecting the external area of the tube without corrosion spots. The specimens were cut to a height of 15 mm and sanded in a polishing machine with 100 to 1,200 grade sandpaper. After this procedure, the samples were washed and passed through ultrasonic cleaning equipment for 3 minutes, in order to remove possible residues that may have been added during sanding. After cleaning, the samples were polished in a polishing machine with a 1 µm alumina (Al_2O_3) solution. The microstructure of the sample was examined by optical microcroscopy after etching the sample with 2% Nital for 15 seconds.

3. Results and Discussions

3.1 Results of Analysis of Lead and Cadmium in Samples of Galvanized Tubes by SWASV

A set of 10 samples of galvanized tubes with non-corroded zinc coating on the outside, with a fixed area of 2.5 cm^2, were selected to determine the lead and cadmium contents in the zinc layer.

In the 10 samples analyzed, the presence of cadmium was not detected, which may simply mean that this analyte is found in quantities below the detection limit. For the method, the detection limit for cadmium is 0.30 µmol/L, which represents 0.0016% of the sample mass. In contrast, the presence of lead was detected in two samples (A and B). In the other samples, the detection limit for lead is 0.18 µmol/L, which represents 0.0017% of the sample's mass to be detected.

The voltammograms shown in Fig. 7 represent the lead analysis for the two samples that were above the detection limit. The red line represents the average pattern obtained from successive measurements of the electrolyte. The results of the curves show that the additions were satisfactory in linearity, indicating that the prepared electrode is compatible with the determination of Pb^{2+} and Cd^{2+} in the samples removed from the galvanized tubes. Thus, the lead values found in samples A and B are shown in Table 3.

3.2 Metallographic Analysis of Galvanized Steel Tubes

The micrographs shown in Fig. 8 show the outside of the tube. The Zn-Fe layers formed by immersing carbon steel (Fe) in molten zinc are made up of the four phases, as shown in Fig. 2. The three Fe-Zn

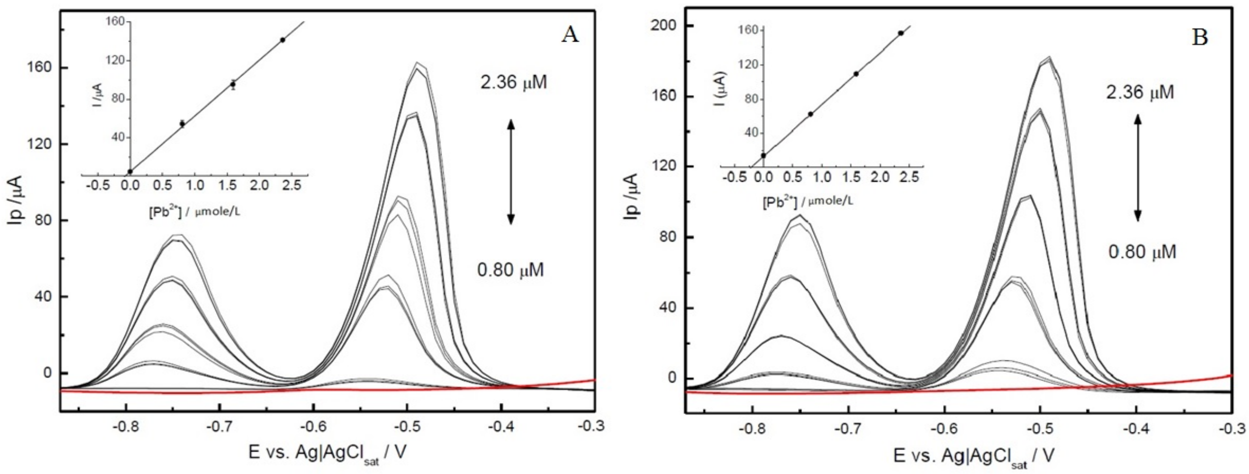

Fig. 7 Voltammograms obtained from standard addition stripping electroanalysis for samples A and B, respectively.

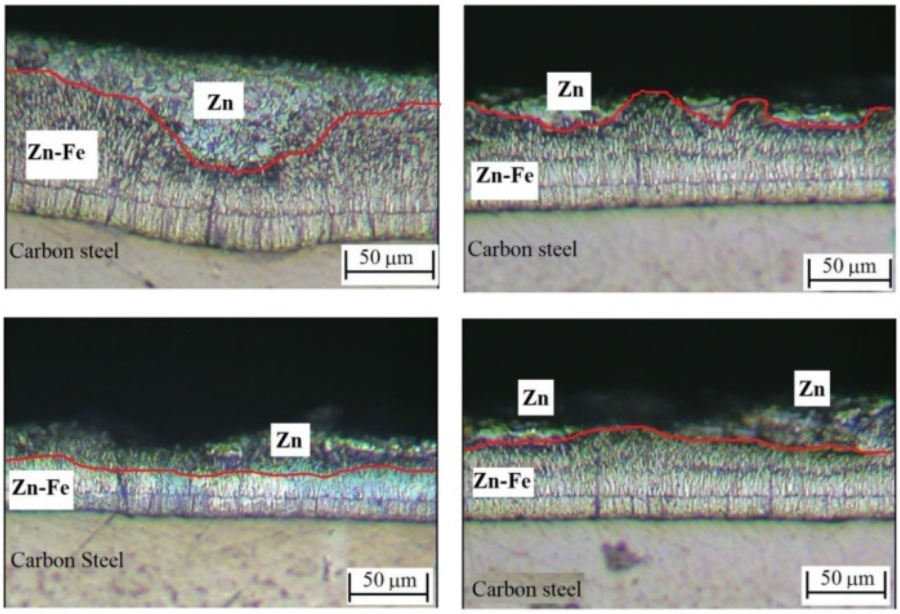

Fig. 8 Micrographs illustrating irregularities in the zinc layer.

phases are (γ) $FeZn_3$ phase containing 21-27% iron, (δ) $FeZn_7$ containing 7-12% iron, and (ξ) $FeZn_{13}$ containing 2-6% iron. The layer of nearly pure zinc (η) is irregular and discontinuous, ranging from 5 to 80 µm thick. The micrographs shown in Fig. 9 also show the outside of the tube where defects and discontinuities of the coating are observed, favoring the corrosive process [2-4].

3.3 Considerations

It is important to note that these results refer to the external part of the pipe, where there was no corrosion. Based on this premise, the condition of these samples taken can be considered as being intact on these walls for 30 years, as they are completely dry (Figs. 3a and 3b). However, in Fig. 3a, there is a leakage point from the inside out. This occurrence corroborates the fact that this water leakage migrates to the walls, making them moist and, consequently, favoring external corrosion of the tubes, as shown in Figs. 4b and 4c. Another premise, based on the presented micrographs (Figs. 8 and 9), suggests that the low thickness and defects may also happen inside of the tubes, favoring localized and generalized corrosion.

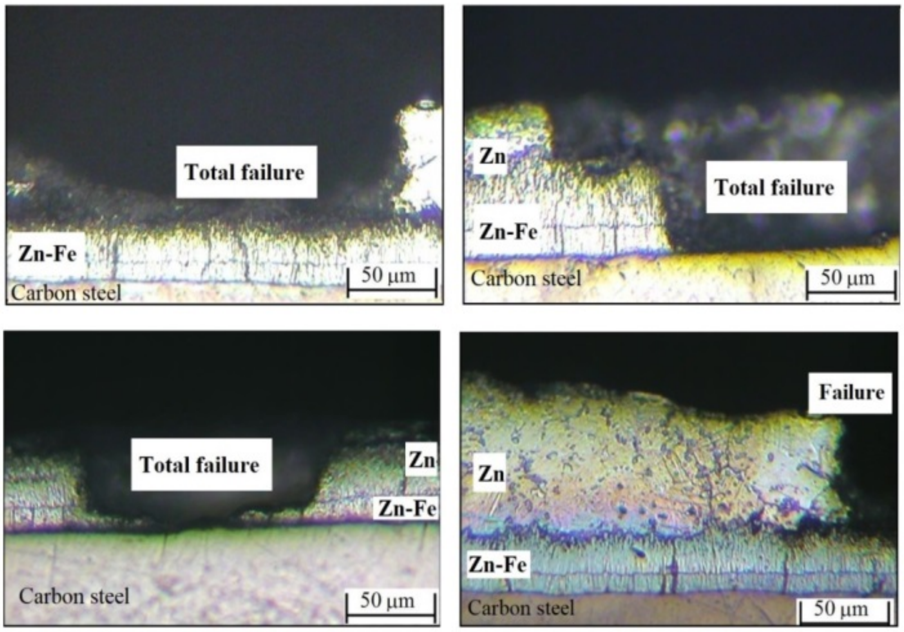

Fig. 9 Micrographs illustrating zinc coating failures.

Based on Fig. 3b, it can be assumed that a brass valve connected to the galvanized pipe can internally accelerate the corrosive process by galvanic corrosion, which is defined by the connection of two different metals immersed in drinking water. These facts can be substantiated by works presented in the referenced literature [14-15].

According to Pawlowski et al. [16] the possibility of failures in the galvanized tubes depends on the zinc bath, the operational conditions during the coating process, the application of the pipes in civil construction, and the quality of the water that flows inside the pipes.

Of the 10 galvanized tube samples removed from the walls of these 30-year-old residential buildings, only two samples showed 0.0243% and 0.0678% of lead, referenced to an area of 2.5 cm^2.

Considering that 0.0678% lead was detected from an external area of 2.5 cm^2 of a galvanized tube by chemical analysis and that metallographic analyses showed that the zinc coating varied from 5 to 80 µm, it is possible to estimate the lead mass that could have contaminated the drinking water in this residential facility. The contamination was estimated for a tube with a diameter of 2.54 cm and length of 1 meter using the formula $M = dSt$, where M is the mass of the coating (g), S is the total area (cm^2), d is the density of zinc (7.14 g/cm^3), and t is the coating thickness (µm).

For these galvanized tubes with 5 to 80 µm of zinc coating, the estimated lead mass that could contaminate drinking water was 30.94 and 1.91 mg of lead, respectively. Although the lead concentration is small in the lining of the pipes, the lead concentration in the water depends on the diameter of the pipe, total linear length, service life, and water flow.

On the other hand, these estimated values may be high, considering that lead is cumulative, and the Ministry of Health of Brazil establishes, by Consolidation Ordinance No. 5 of September 28, 2017 [17], that the maximum allowed value for soluble lead in drinking water is 0.01 mg/L. Generally, these recommendations are directed to the treatment and water distribution network in residencies, school, hospitals, etc. However, lead contamination that occurs in building hydraulic installations is not evaluated because Brazilian Standard NBR 5626 [18] prohibits the use of lead pipes for building hydraulic installation, but it allows hot-dip galvanized.

4. Conclusions

Based on the referenced literature and laboratory tests carried out, conclusions can be summarized as follows:

- The hot-dip galvanizing process is simple, produces a thick coating of zinc, and is low cost. However, the quality of the zinc barrier formed in carbon steel does not guarantee that there are discontinuities or irregularities in the zinc coating.
- The standards of the hot-dip galvanizing process allow the primary zinc ingots that are added to the molten zinc bath to contain up to 1.6% lead. Lead increases the fluidity of molten zinc, favors the formation of thinner layers, can participate in controlling the growth of intermetallic compounds, and reduces the consumption of zinc.
- Extra fine zinc ingot, with 0.003% lead, is often more expensive than common zinc ingot, which has 1.6% lead; therefore, for technical-economic considerations, common ingot is used more frequently.
- The addition of lead to the zinc bath can benefit the hot-dip process. However, it can contaminate also the pipelining in a heterogeneous way; that is, lead can be either detectable or below the detection limits.
- SWASV, using electrodes composed of graphite/PETG and bismuth film, in situ, showed good results for simultaneous identification of lead and cadmium in 10 samples. In two samples, the lead content was 0.0243% and 0.0678% for an area of 2.5 cm^2. In the other samples, lead and cadmium were both below the detectable limits for this technique.
- Metallographic analyses, carried out on the outside of the galvanized tubes removed from the dry walls (where there was no corrosion), showed irregularities, discontinuities, and failures in the zinc coating on the carbon steel.
- Finally, considering both paths of lead absorption (oral and cutaneous), in addition to being a bioaccumulative metal, where concentration levels are more sensitive in children, pregnant women, and the elderly, compared to adults, tubes coated with zinc by the hot-dip process must be banned for drinking water installations.

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