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Migration of lead from unplasticized polyvinyl chloride pipes

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Abstract

The effect of water quality parameters, such as water pH, temperature, and total dissolved solids (TDS), and direct exposure to UV-radiation on the migration of lead, tin and other metal stabilizers, such as calcium, cadmium, and barium from unplasticized polyvinyl chloride (uPVC) pipes were investigated using locally manufactured pipes. Specimens of 1 m were used to investigate the effect of water quality parameters using the circulatory method. To investigate the effect of UV-radiation, specimens of 33 cm long were used throughout the research. The investigation was carried out, using the static method at different times of exposure to the UV-radiation. The concentrations of lead, tin, and other metal stabilizers in the water were evaluated using the inductively coupled argon plasma (ICAP) technique. The results on the effect of water quality parameters showed that water pH, temperature, TDS, and time of water circulation were all having an effect on the migration of lead, tin, and other metal stabilizers. On the other hand, exposure to UV-radiation was seen to promote the migration of lead, tin, and other metal stabilizers. A lead concentration of about 0.8 mg/l (ppm) was detected after 14 days of exposure to the UV-radiation.

Keywords: Barium; Cadmium; Calcium; Diffusion rate; Effect of UV-radiation; Migration of lead; pH; TDS; Temperature; Tin; Unplasticized PVC pipes

1. Introduction

Polyvinyl chloride (PVC) is widely used in the building industry. It is very resistant to chemical attack and certain grades are designed for use within the chemical industry such as tank lining. The PVC, like all plastics, is a relatively lightweight material, with a density one-sixth that of steel and half that of aluminum. One of the largest single uses for PVC is that for piping, where it has become the preferred material in many applications such

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as drain, water, wastewater and vent systems, electrical and communications conduits and industrial process piping. Packaging is the second most important outlet for PVC where it is used for a whole variety of applications. These include such diverse areas as cosmetics and toiletries where a well-designed pack can enhance consumer appeal. Blow-molded bottles in PVC are now well established, particularly in Europe, for various products such as mineral waters, cooking oils and fruit squashes. Modern blow-molding machinery can produce over 10,000 bottles of 1.5 l per hour, and the range of sizes can extend to as much as 5 l. Corrugated PVC sheeting is used extensively in both the domestic and industrial environments. Other sectors of use in building include PVC wall cladding, safety glazing, window profiles, and vinyl wall/floor coverings.

Unplasticized polyvinyl chloride (uPVC) pipes are highly preferred in sanitary and plumbing systems due to several reasons such as easy installation, easy cutting, excellent stiffness, decreased water noise, and increased impact resistance. Resistance to corrosion, ability to tolerate slight displacement and soil movement without damage to their physical properties, prevention of the build-up of deposits and corrosive scaling, and easy joining are also among those factors which make uPVC pipes preferable in such applications.

In order for PVC to be processed into various products, it is often heated to temperatures of around 200°C. This would normally cause the polymer to decompose and disintegrate, and thus, heat stabilizers are needed to prevent this. Thus, the term (stabilization) implies a set of methods or techniques used to improve the resistance of the polymer or composite to various degradation-promoting factors during processing, storage, and service [1]. The stabilization of VC-based polymer products is a more serious problem than the stabilization of many other commercial polymers due to the complex nature of degradation of the former and the multitude of requirements for an effective stabilizer. Apart from protecting the polymer from as many degradation-promoting factors as possible, an effective stabilizer must

- have a favorable effect on the processing properties of the polymer;
- have no adverse effect on the service characteristics of the material;
- possess the desired mixture of physical, chemical and other properties.

There are two principal ways in which polymers can be stabilized [2]

1. by adding special stabilizing agents;
2. by chemical modification including conversion of functional groups by reaction of the polymer with low-molecular compounds.

Stabilizers such as metal mixtures of lead, organotin, calcium, barium, and cadmium are being used to control degradation of uPVC pipes during manufacturing process. Burn and Schafer [3] reported that uPVC pipe products manufactured in Australia, Asia and Europe have traditionally been manufactured with lead-based stabilizers, whilst in the United States of America they have been stabilized with tin-based products. Some investigators have raised concerns about the migration of lead from uPVC pipes into potable water [4–8].

Lead exposure is a major health concern that is gaining recognition across the entire world. In the United States of America, magazines, newspapers, television, and radio have been spreading the word about its risks, and although only 20% of lead exposure is caused by drinking water, the nation has focused its attention there. The US environmental protection agency (EPA) considers lead as a highly toxic metal. According to the EPA current drinking water standards, the maximum contaminant level goal (MCLG) of lead in drinking water is zero mg/l, while the maximum permissible level (MCL) is 0.015 mg/l (15 ppb) [9]. Moreover, lead is regulated in a Treatment Technique, which requires systems to take tap water samples at sites with lead pipes or pipes that have lead solder. Water systems that exceed the 0.015 mg/l in 10% of tap water samples will be required to take action to reduce lead levels.

Although in adults, lead can increase blood pressure and interfere with hearing, children are at a greater health risk due to lead ingestion than adults. In children, lead can interfere with the formation of red blood cells, delay physical and mental development, and impair mental abilities. At high levels of exposure, lead can cause anemia, kidney damage, and mental retardation. Pregnant women should also be especially cautious about lead exposure, as it can cause premature birth, and reduce the birth weight of babies.

In the Kingdom of Saudi Arabia, uPVC pipes are extensively used in plumbing systems of houses to transport potable water. Moreover, information on the migration of lead from uPVC pipes into potable water with respect to the Kingdom is not available. Based on that, the main objective of the current research is to investigate the effect of water quality and exposure to UV-radiation on the migration of lead from uPVC pipes into water and make recommendations based on the results obtained.

2. Materials and methods

2.1. Sample preparation

Local brand of uPVC pipes was used throughout the investigation. The dimensions and specification of the pipes, used in the research are shown in Table 1.

2.1.1. Circulatory method

The circulatory method was selected to investigate the effect of time of exposure and water quality parameters on the migration of stabilizers such as Pb, Sn, Ca, Cd, and Ba from uPVC pipes into water. Each 1 m pipe specimen was vertically clamped on a stand

Table 1
Dimensions and specifications of pipe specimens

Item	Static method	Circulatory method
Manufacturer	Local	Local
Specimen length (cm)	33	100
Pipe thickness (mm)	4.3	4.3
Pipe inside diameter (mm)	12.7	12.7
Pipe outside diameter (mm)	21.3	21.3
Water volume (ml)	44	4000
Specimen weight (g)	108	330
Manufacturing date	18 July 1995	18 July 1995
Date of experiments	27 October 1997	27 October 1997

and the lower end was connected to a circulatory pump of constant flow rate using Tygon tubing and clamps, which in turn is connected to a water reservoir containing the sample water (extractant). The upper end of the pipe was directly connected to the water reservoir through Tygon tubing. Control experiments were conducted by circulation the water through the Tygon tubes only.

In all the circulatory experiments, it was observed that the water temperature was rising gradually to 45°C due to warming up of the circulatory pump. Each experiment was conducted in duplicate.

2.1.1.1. Effect of time of exposure. Three time intervals (8, 24 and 48 h) were selected for this study, where 4 l of double-distilled water were circulated through the uPVC pipe.

2.1.1.2. Effect of total dissolved solids (TDS). The water samples used in this study were, double-distilled water, Al-Khober drinking water and KFUPM utility groundwater with TDS concentrations of 2, 160 and 2670 mg/l, respectively. About 4 l of each sample were circulated for 48 h.

2.1.1.3. Effect of pH. Four different pH values were selected for this study (5, 6, 7 and 9). These were obtained by adjusting the pH value of the double-distilled water (pH 5) with phosphate buffer. About 4 l of each sample were circulated for 48 h.

2.1.1.4. Effect of temperature. Two temperatures were selected for this study (35 and 45°C). The 35°C was attained by immersing part of the water reservoir in a water bath with controlled temperature. The 45°C was obtained as described previously. About 4 l of the water were circulated for 48 h.

2.1.2. Static method

The static technique was selected in order to investigate the effect of exposure to UV-radiation on the migration of lead and other metal stabilizers from uPVC pipes into water. Each specimen was tightly closed, at one end with a parafilm and uPVC cap, and completely filled with double-distilled water (extractant) to the brim (ensuring that the water is free of air bubbles). The other end was also tightly closed with a parafilm and uPVC cap. The outside surface of the 33 cm long specimens was exposed to direct UV-radiation using four UV-lamps with high-energy radiation (2537 Angstroms). The lamps used were germicidal lamps manufactured by Millipore. Water samples, from the uPVC specimens, were then analyzed for lead and other metals in duplicate, at different times of exposure. Control experiments were conducted by keeping some 33 cm long specimens at room temperature. These uPVC pipe specimens were not exposed to UV-radiation. Water samples were then analyzed for lead and other metals in duplicate and at different times of exposure.

2.1.3. Sample pre-treatment

Prior to analysis, water samples were filtered using a 45-micron filter paper and acidified using 5% concentrated nitric acid. The final volume of each sample was concentrated to 25 ml by evaporation at steady temperature of 95°C on hot plate. Samples were analyzed for lead and other metals using inductively coupled argon plasma (ICAP) technique.

2.2. Sample analysis

2.2.1. Inductively coupled argon plasma (ICAP)

A Jarrel-Ash ICAP (model 9000) with an RF power at 1.3 kW, an Argon coolant gas flow of 20 l /min and a gas pressure of 23 psi, was used in analysis of water samples.

3. Results and discussion

3.1. Circulatory method

In the circulatory method, the effect of water pH, water temperature, total dissolved solids (TDS) concentration, and time of exposure on the migration of lead and other metal stabilizers from uPVC pipes was investigated. It is worth mentioning that control experiments were conducted by circulating water through Tygon tubes using the same type of pumps. Lead and tin were not detected during control experiments. The results reported in this section are based on considering those obtained from the control experiments.

3.1.1. Effect of time of exposure

Fig. 1 shows the effect of time of exposure on the migration of lead and tin from uPVC pipes. The figure clearly demonstrates the steady increase in lead concentration migrated from the uPVC pipes into the circulated water, with respect to time. After 10 h of exposure, lead concentration reached a value of 0.43 mg/l, and by the end of the experiment (48 h), it

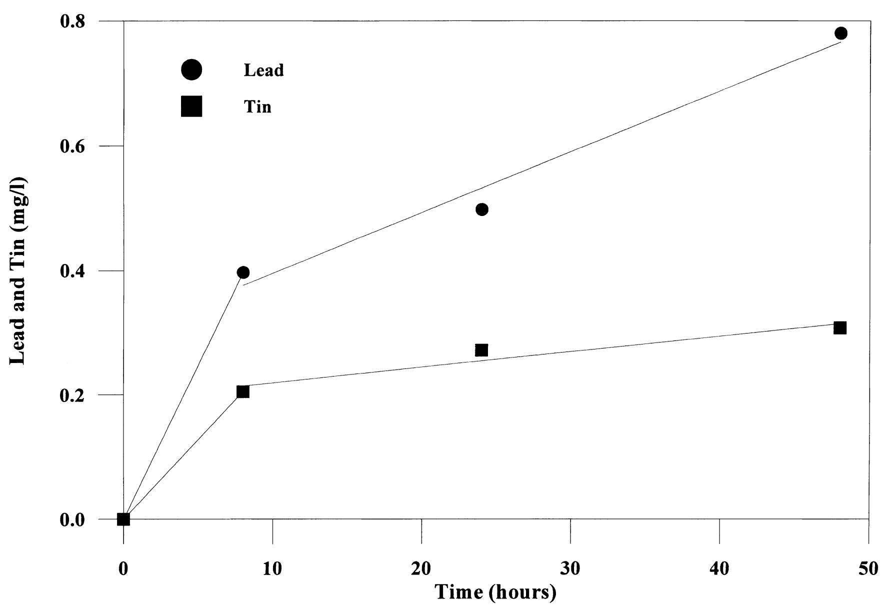

Fig. 1. Effect of time of exposure on the migration of lead and tin from uPVC pipes.

increased to 0.78 mg/l. It is clear that such concentration is very much higher than the lead standard in drinking water. According to the US EPA current drinking water standards, the MCLG of lead in water is 0 mg/l, while the MCL is 0.015 mg/l. Based on that, after 48 h of circulation, lead concentration was found to be >50 times more than the MCL.

Moreover, the figure clearly shows that migration of lead and tin took place in two distinct phases. In the case of lead, the first phase can be represented by the following equation:

$$\text{Lead (mg/l)} = 0.0496 \times \text{time (h)}$$

with a diffusion rate of lead of 0.0496 mg/l/h. In the second phase, the migration can be represented by

$$\text{Lead (mg/l)} = 0.00975 \times \text{time (h)} + 0.2984$$

with a diffusion rate of lead of 0.00975 mg/l/h.

The results indicate that the diffusion rate of lead was slowing down as time passes. This is attributed to the migration of the surface lead, which will occur at the start of the experiment. As time passes, the amount of lead migrated the uPVC pipe was seen to decrease.

In the case of tin, the following two phases can be represented:

$$\text{Tin (mg/l)} = 0.0256 \times \text{time (h)} \quad \text{(phase 1)}$$

$$\text{Tin (mg/l)} = 0.00244 \times \text{time (h)} + 0.1953 \quad \text{(phase 2)}$$

The results show that tin behaved in the same manner as lead, which can be attributed to the same reasons given above.

On the other hand, the results on the migration of other stabilizers such as barium, cadmium, and calcium are shown in Table 2. The table obviously shows that all metal stabilizer concentrations were increasing with respect to time of exposure. Tin was found to increase to 0.27 and 0.31 mg/l after 24 and 48 h of exposure, respectively. Barium and cadmium were found to increase to 0.42 and 0.1 mg/l, respectively, after 48 h of exposure to double distilled water. Moreover, calcium concentration increased to 46 and 49 mg/l after 24 and 48 h of exposure, respectively.

3.1.2. Effect of water pH

The effect of water pH on the migration of lead and other metal stabilizers was investigated at pH values between 5 and 9. Fig. 2 shows the effect of pH on the migration of lead and tin from uPVC pipes. The figure clearly demonstrates that as pH was decreased, the amount of lead migrated from the uPVC pipes increased. At pH value of 5, about 1 mg/l of lead was

Table 2
Effect of time of exposure on the migration of Ba, Ca, and Cd, from uPVC pipes

Time (h)	Ba (mg/l)	Ca (mg/l)	Cd (mg/l)
0	0	0	0
8	0.113	45	<0.05
24	0.152	46	<0.05
48	0.416	49	0.088

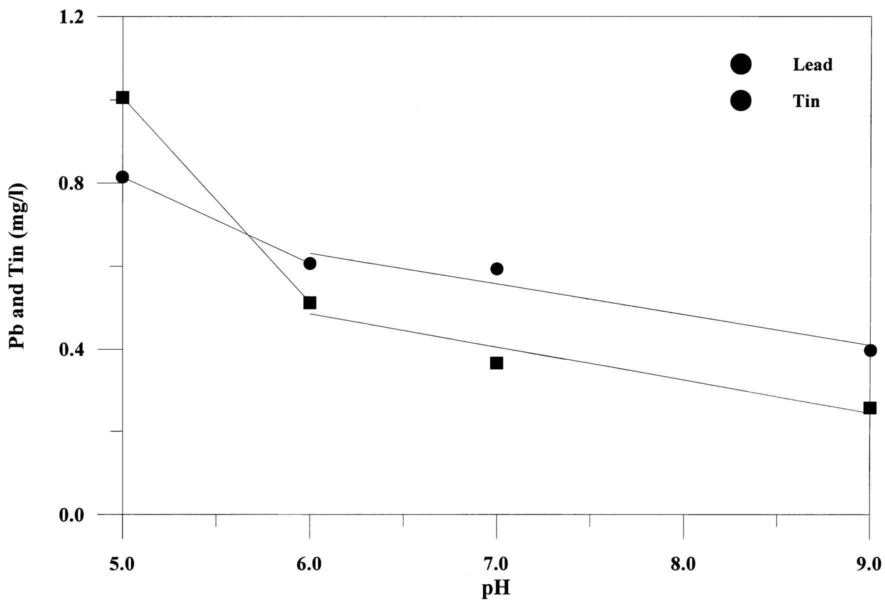

Fig. 2. Effect of water pH on the migration of lead and tin from uPVC pipes.

found to migrate to the water after 48 h of exposure. The figure also shows that between pH value of 7 and 9, the increase in lead concentration was not significant, which indicates that alkaline environment has insignificant effect on lead migration from uPVC pipes. Burn and Sullivan [8] investigated the effect of commissioning procedures on the level of extracted lead from new uPVC water reticulation mains. They reported that acidic conditions enhance extraction of lead. Moreover, Koh et al. [10] investigated the factors affecting the migration of lead from uPVC pipes. They concluded that lead migration is enhanced by the presence of low concentrations of anions such as Cl^-, $HPO_4{}^{2-}$, NO^{3-}, and $SO_4{}^{2-}$.

The figure also shows that migration of lead and tin took place in two different phases. Lead migration can be expressed by:

$$\text{Lead (mg/l)} = -0.208 \times \text{pH} + 1.854 \quad \text{(phase 1)}$$

$$\text{Lead (mg/l)} = -0.0735 \times \text{pH} + 1.0726 \quad \text{(phase 2)}$$

with diffusion rates of lead of −0.208 and −0.0735 mg/l/pH unit for the first and second phases, respectively. The minus sign indicates that diffusion rates were decreasing with pH increase.

For tin, the following equations can represent its migration from uPVC pipes:

$$\text{Tin (mg/l)} = -0.494 \times \text{pH} + 3.476 \quad \text{(phase 1)}$$

$$\text{Tin (mg/l)} = -0.0803 \times \text{pH} + 0.968 \quad \text{(phase 2)}$$

with diffusion rates of tin of −0.494 and −0.0803 mg/l/pH unit for the first and second phases, respectively.

Table 3
Effect of water pH on the migration of Ba, Ca, Cd, and Sn from uPVC pipes

pH	Ba (mg/l)	Ca (mg/l)	Cd (mg/l)
5	0.113	45	0.0102
6	0.084	22	0.089
7	0.078	17	0.078
9	0.064	9	0.053

The effect of water pH on the migration of other metal stabilizers from uPVC pipes is shown in Table 3. The table shows that as water pH was decreased, concentrations of Ca, Cd, and Ba increased. This could be attributed to the same reasons given above.

3.1.3. Effect of water temperature

The effect of water temperature on the migration of lead and other metal stabilizers was investigated at two different temperatures, namely 35 and 45°C. Table 4 summarizes the results obtained on the temperature effect. The table clearly shows that the migration of lead and cadmium was not found to be significantly affected by the increase in water temperature. On the other hand, tin, barium, and calcium concentrations were found to increase when the water temperature was raised from 35 to 45°C by 42, 85 and 29%, respectively. Burn and Sullivan [8] reported that temperature could also affect the extraction of lead, with lead extraction from the surface of the pipe occurring faster at higher temperatures. The reason for the results obtained on lead migration could be attributed to the low range of temperature considered in the investigation.

3.1.4. Effect of total dissolved solids (TDS)

The effect of TDS concentration on the migration of lead and other metal stabilizers was conducted using double-distilled water, tap water, and brackish water having TDS concentrations of 2, 160 and 2670 mg/l, respectively.

Fig. 3 shows the effect of TDS concentration on the migration of lead and tin from uPVC pipes. The figure shows that tin migration took place in two distinct phases, where the diffusion rate of tin in the first phase was higher than that in the second phase. This could be attributed to the same reasons given on the effect of time of exposure and water pH. The migration of lead and tin can be expressed by the following equations:

$$\text{Lead (mg/l)} = 0.00025 \times \text{TDS (mg/l)} + 0.53$$

$$\text{Tin (mg/l)} = 0.0035 \times \text{TDS (mg/l)} + 0.34 \quad \text{(phase 1)}$$

$$\text{Tin (mg/l)} = 0.00069 \times \text{TDS (mg/l)} + 0.80 \quad \text{(phase 2)}$$

Table 4
Effect of water temperature on the migration of Ba, Ca, Cd, Pb and Sn from uPVC pipes

Temperature (°C)	Ba (mg/l)	Ca (mg/l)	Cd (mg/l)	Pb (mg/l)	Sn (mg/l)
35	0.082	28	0.095	0.669	0.489
45	0.152	36	0.098	0.673	0.673

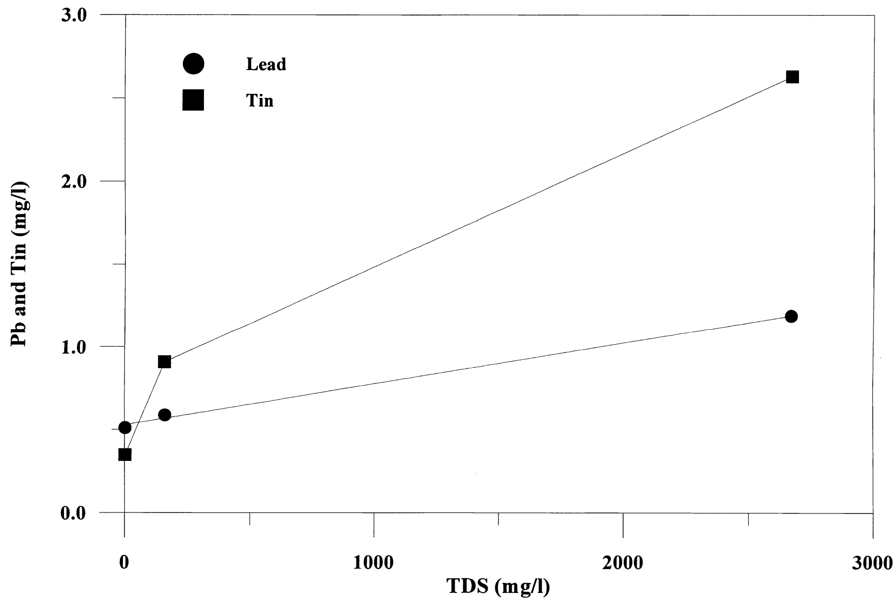

Fig. 3. Effect of total dissolved solids (TDS) on the migration of lead and tin from uPVC pipes.

with diffusion rate of 0.00025 (mg/l)/(mg/l) TDS for lead, and 0.0035 and 0.00069 (mg/l)/(mg/l) TDS for tin in the first and second phases, respectively.

The results on migration of barium, calcium, and cadmium are presented in Table 5. The results clearly demonstrate that as TDS concentration was increased, the concentrations of metal stabilizers migrated from the uPVC pipes also increased. The results are in agreement with those reported by Koh et al. [10]. They concluded that extraction lead from uPVC pipes can be enhanced by the presence of low concentrations of anions such as Cl^-, $HPO_4{}^{2-}$, NO^{3-} and $SO_4{}^{2-}$.

3.2. Static method

In the static method, the effect of exposure to UV-radiation on the migration of lead and other metal stabilizers from uPVC pipes was investigated at different times of exposure. In this investigation, control experiments were conducted by exposing the uPVC pipes to water at room temperature for different periods of time. The control experiments showed no sign

Table 5
Effect of total dissolved solids (TDS) on the migration of Ba, Ca, and Cd, from uPVC pipes

TDS (mg/l)	Ba (mg/l)	Ca (mg/l)	Cd (mg/l)
2	0.067	56	0.07
160	0.085	454	0.09
2670	0.224	4881	0.124

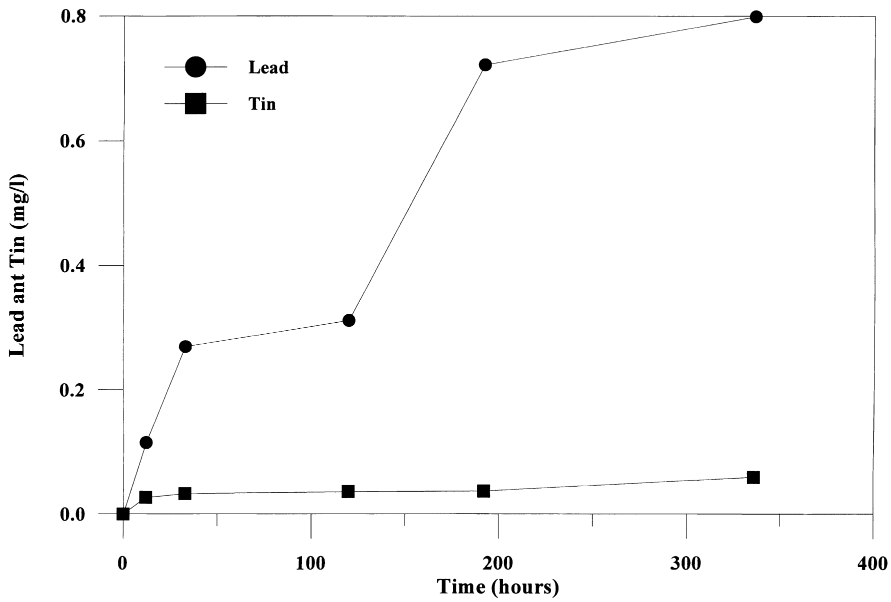

Fig. 4. Effect of time of exposure to UV-radiation on the migration of lead and tin from uPVC pipes.

of migration of lead and other metal stabilizers. During the UV-exposure investigation, it is worth to mention that the water temperature reached a maximum value of 35°C after 24 h of exposure, and remained at that level till the end of the study. Moreover, visual inspection of two pipe specimens, exposed to UV-radiation for 14 days, revealed that the effect of UV penetrated to about 50% of the pipe thickness at some locations.

Fig. 4 shows the effect of time of exposure to UV-radiation on the migration of lead and tin. The figure shows that lead and tin concentrations were increasing steadily with time. After 12 h of exposure to UV-radiation, lead and tin concentrations were found to reach 0.115 and 0.08 mg/l, respectively. Such concentration of lead is about eight times more than the MCL of lead in drinking water. Lead concentration increased to 0.312 and 0.799 mg/l after 5 and 14 days of exposure to UV-radiation, respectively. On the other hand, tin concentration reached values of 0.091 and 0.114 mg/l after the same period of exposure. The results also show that >14% of the total lead migrated during the first 12 h of the experiment. Moreover, the figure clearly shows that migration of lead took place in four distinct phases. The following are the diffusion rates of lead for the four phases:

$$\text{Diffusion rate} = 0.0082\ \text{mg/l/h} \quad \text{(phase 1)}$$

$$\text{Diffusion rate} = 0.00048\ \text{mg/l/h} \quad \text{(phase 2)}$$

$$\text{Diffusion rate} = 0.0057\ \text{mg/l/h} \quad \text{(phase 3)}$$

$$\text{Diffusion rate} = 0.00053\ \text{mg/l/h} \quad \text{(phase 4)}$$

The first phase represents the migration of the surface lead which takes place at the start of the experiment. The diffusion rate of lead will then decrease with respect to time (second

Table 6
Effect of time of exposure to UV-radiation on the migration of Ba, Ca, and Cd, from uPVC pipes

Time (h)	Ba (mg/l)	Ca (mg/l)	Cd (mg/l)
0	0	0	0
1	0.001	0.3	–
12	0.002	1.1	0.002
33	–	1.5	–
120	0.006	–	0.003
192	–	1.6	0.04
336	0.01	1.7	0.01

phase). The third phase could represent the diffusion of lead from the matrix of the uPVC pipe, which have been attacked by the UV-radiation. Similarly, the diffusion rate was seen to decrease with respect to time. Based on temperature measurements and visual inspection of two pipe specimens, this effect could be attributed to a combination of UV-radiation and elevated temperatures (35°C).

The migration of other metal stabilizers is shown in Table 6. The table clearly shows the steady increase in concentration of all metal stabilizers with respect to time of exposure.

4. Summary and conclusions

The effect of water quality parameters and exposure to UV-radiation on the migration lead, tin, and other metal stabilizers from uPVC pipes was investigated. The pipes used throughout the investigation were local and 27 months old. The investigation also demonstrated the adverse effect of exposure of uPVC pipes to direct UV-radiation and acidic water. After 14 days of exposure to UV-radiation of high-radiation energy (2537 Å), the uPVC pipes released about 0.8 mg/l of VCM into the water in contact. This lead concentration is 50 times higher than the MCL in drinking water, which was set by the US EPA. The effect of UV-radiation could be attributed to a combined effect of both of heat and UV light. Empirical models, to predict lead concentration with respect to time of exposure, water pH, and TDS concentration, were formed. The experimental diffusion rates of lead and tin at different conditions were calculated. Based on the results of the investigation, precautions have to be taken when uPVC pipes are used in hot climates like that of the Kingdom of Saudi Arabia. When used in households, uPVC pipes have to be well insulated from direct sun light and heat. In order to reduce migration of lead and other metal stabilizers from uPVC pipes during service, commissioning procedures must be conducted. Moreover, manufacturers need to improve their stabilization methods in order to improve the resistance of the polymer or composite to UV degradation during processing, storage, and service. The UV-radiation stabilized PVC is obtained when a combination of anacrylic or methacrylic acid ester and 2,2-dihydroxybenzophenone is used as the stabilizing agent. More work needs to be conducted in order to investigate the effect of the level of UV-radiation energy and water temperature on the migration of lead and other metal stabilizers from uPVC pipes into water in contact.

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