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EFFECT OF INTERNAL POLYURETHANE COATINGS OF CAST IRON PIPES ON THE QUALITY OF TRANSPORTED POTABLE WATER

The paper presents the results of laboratory tests to determine the effect of an internal polyurethane coating in ductile iron pipes on the quality of disinfected and non-disinfected drinking water. A decrease in the pH of water in contact with the polyurethane coating was found, which was slightly higher in the non-disinfected water than in the disinfected water. The coefficient of variation (*CV*) of the pH values for the chlorinated water samples was 5.02% and for the non-chlorinated water was 7.15%. The experiments also showed a rather large effect of polyurethane liner on the increase of TOC concentration in water. The presence of disinfectant further slightly increased the amount of organic compounds released. The *CV* values normalized to one day for TOC were as high as 193.32% and even 199.39% for disinfected water. A significant effect of polyurethane coating was observed on the color change and odor of water. On the other hand, there was no effect of polyurethane coating on alkalinity and chlorine consumption in water. The *CV* values normalized to one day in both cases were very small at 0.97% and 0.53%, respectively.

1. INTRODUCTION

Ductile iron is one of the most popular materials used for mainline construction in water supply systems. Cast iron has been used for the construction of water supply lines for more than 500 years. Around 10 000 000 km of cast iron water pipes have already been laid in the ground worldwide [1]. Despite many advantages of plastic pipes made of PVC and PE, cast iron is still a popular material for water pipes [2, 3]. The advantages of cast iron pipes over plastic pipes are their high resistance to external stresses and

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internal hydrostatic and hydrodynamic pressures, as well as higher circumferential stiffness and resistance to deformation [4]; hence, cast iron pipes are particularly suitable for the construction of mains characterized by large diameters. On the other hand, a disadvantage of cast iron pipes concerning PVC and PE pipes is the corrosiveness. It is less intensive than that of steel pipes. However, it is so intensive that their application without necessary protection can cause quick overgrowing of corrosion sediments, increase of pressure losses, deterioration of water quality and failures.

One of the basic corrosion protection for cast iron water pipes is internal and external linings [5]. In the case of external coatings, they must have high abrasion resistance, while the internal coatings, additionally must be inert to the potable water flowing through the pipes. This limits the number of potential materials that can be used as interior linings. Previously, cement coatings were most commonly used for this purpose, but now, epoxy resins and polyurethanes are increasingly being used as inner linings. These materials are used in brand new pipes, but also operated old pipes during their renovation. These materials, although relatively inert to contact with tap water, require caution in the application. Cement linings have been used since the 1930s [6] and are now fairly well recognized. Numerous studies have indicated that cement coatings in contact with soft water can dissolve and leach large amounts of calcium compounds into the water, resulting in a weakening of the lining structure and damage over a long time [7]. The use of cement coatings in soft water conditions also poses risks to the quality of that water. There can be a significant increase in water pH, alkalinity, and leaching of large amounts of aluminum and heavy metals such as chromium and lead [8]. Heavy metals are admixtures of cement. They may be of natural origin, but usually, they mostly get into the cement during its production. They can enter the cement during abrasion of plant components, especially during grinding, heating, and firing in cement kilns, where heavy metal-rich agricultural waste or old tires are often used as fuel additives [9]. With a factory-made cement coating of ductile iron pipes, the risk of contaminants leaching into the water is far less than with internal linings made by spraying during the renovation of old pipes on-site [10].

In the late 1970s, the epoxy lining was first used in the UK during the rehabilitation of old pipes. In the US, epoxy spray rehabilitation did not start to be used until the mid-1990s. Since then, it has become widely used in many countries around the world and has even replaced cement-based rehabilitation of cast iron pipes. Epoxy coatings are characterized by a smoother surface that creates less resistance to water flow, and thus, allows obtaining higher pipe capacity, necessity to maintain lower pressures in the network, and reduces the growth of biofilm layer, pumping costs, and maintenance. Contrary to cement lining, the epoxy lining is characterized by resistance to the influence of soft water [6]. When epoxy spraying is used to rehabilitate pipes lying in the ground, the advantage over cement spraying is a significantly shorter operation and shutdown time of approximately one day [6]. Studies of pipes rehabilitated with epoxy spray in the UK between 1982 and 1988 [11] revealed some errors that can accompany spraying

on site. In the case of about 50% of pipes, a mixing ratio of epoxy resin and hardener was inappropriate, which was a major cause of imperfect linings [11]. A selection of the proportion of mixed resin and hardener has a direct impact on epoxy lining hardness and strength [6].

Studies on the effect of epoxy linings on water quality deterioration are mainly related to the direct leaching of organic substances and microorganism growth that use these compounds as substrates [12]. 30-day research by Alben et al. [13] showed the leaching of large amounts of organic compounds from epoxy lining into water. Among others, they identified methyl isobutyl ketone (MIBK) and xylenes [13]. Similar studies of several epoxy lining samples for 72 h were conducted in Canada [6]. Very high concentrations of TOC in water, at a level of 34.0–345.0 mg/dm³ and benzene, toluene, ethylbenzene, and xylene (BTEX) from 0.2 to 48.0 mg/dm³ for all samples were noted then [6]. Studies by Pierce [14] indicated that TOC leaching is still quite high even for linings that have been in service for years [14]. Epoxy coatings have also been shown to affect the formation of odors and tastes in water [15, 16], but after a month of contact with water, plastic smell and taste slowly disappeared [15]. Conducted research confirmed a significant impact of epoxides on TOC concentration, as well as on disinfectant consumption [16, 6]. Free chlorine was reduced faster than chloramines [16]. A slight increase in THM and HAA5, more significant in chlorinated water, was also observed [6]. The most commonly used epoxy resin for spraying epoxy coatings contains bisphenol A (BPA) monomer. Hence, the use of this type of lining for contact with drinking water in some countries is prohibited [17]. The concentrations of this substance in water contacted with modern epoxy linings are much lower than with older types of epoxy [17]. In contrast, bisphenol F, 4-nonylphenol and 4-t-octylphenol are rarely found in water contacting epoxies [17]. Higher temperatures and longer operating times enhance the leaching intensity of bisphenol A [17]. The impact of epoxy on water causing a slight decrease in water pH occurs in pipes that have been in service for a long time [17].

When it comes to the impact of polyurethane coatings on drinking water quality, studies by Deb et al. [6] showed a decrease in water pH from 8.0 to 6.0 during experiments in which a 30-day polyurethane coating was in contact with water for 24 h. Free chlorine reduction in water as a result of contact with polyurethane coatings and a gradual decrease of chlorine consumption with the time of pipes' operation were observed, as well as an increase of TOC concentration that was significantly greater for chlorinated water than for non-chlorinated water [6]. Leaching TOC reacted with free chlorine to form HAA5, but no THM was recognized [6]. Moreover, a faint moderating odor released from the polyurethane coating, and persisted for 30 days of testing.

Because of a small number of studies on the effects of protective polyurethane coatings applied to cast iron pipes on drinking water quality, the authors decided to expand the state of knowledge in this field by conducting laboratory studies to analyze these effects. The authors of this paper show the results of the impact of polyurethane coatings

on water pH, alkalinity, TOC concentration, chlorine consumption, water color, odor, and taste.

2. MATERIAL AND METHODS

Laboratory set-up. Experiments were carried out in a laboratory under static conditions. For this purpose, two similar test stands (TS-1 and TS-2) were constructed (Figs. 1, 2).

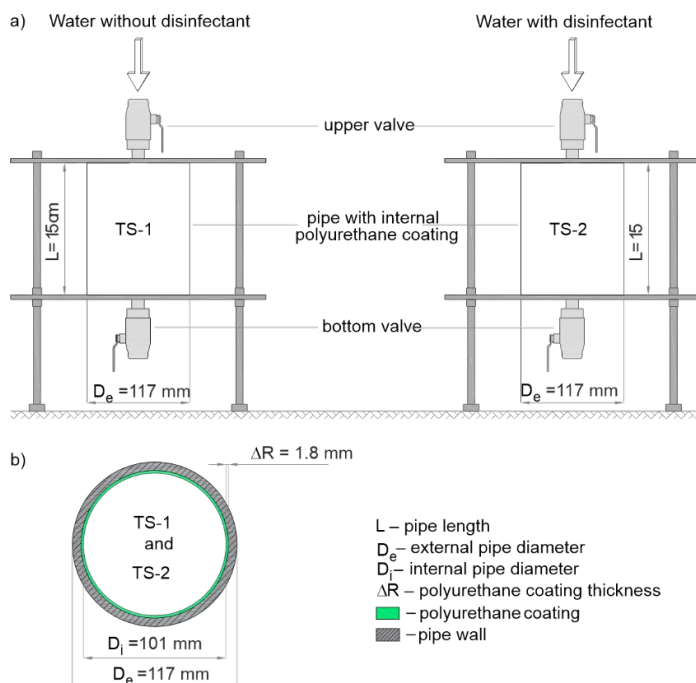


Fig. 1. Laboratory test stands (TS-1 and TS-2): a) side view of the test stands, b) pipe cross-section with an internal polyurethane coating

A substantial part of each of the two test stands was a piece of ductile cast iron water pipe ($L = 15.0$ cm, $D_e = 117$ mm, $D_i = 101$ mm), with an internal prefabricated polyurethane coating ($\Delta R = 1.8$ mm). The upper valve was for pipes' interiors water filling, while the bottom valve was for pipes' water emptying. The experiments consisted of alternating water pipes' filling and emptying over a 64-day period. The volume of water inside the pipes was about 1.2 dm³. After the water pipes' filling, water was kept inside for some time, and then, water was replaced by another water. The elaborated schedule of periodic water replacements (Table 1) included both shorter and longer water stagnation periods; these enabled to monitor of water quality changes after different times

of water contact with polyurethane coating. Ductile cast iron pipe on the first test stand (TS-1) was in contact with water without disinfectant (it was treated with soft water collected at the outflow from the largest water treatment plant for Cracow, the second large city in Poland); in turn, the second one (TS-2), was in contact with chlorinated water. For the chlorinated water solution preparation under laboratory conditions ($0.36 - 0.39 \text{ mg Cl}_2/\text{dm}^3$), sodium hypochlorite NaOCl was used.

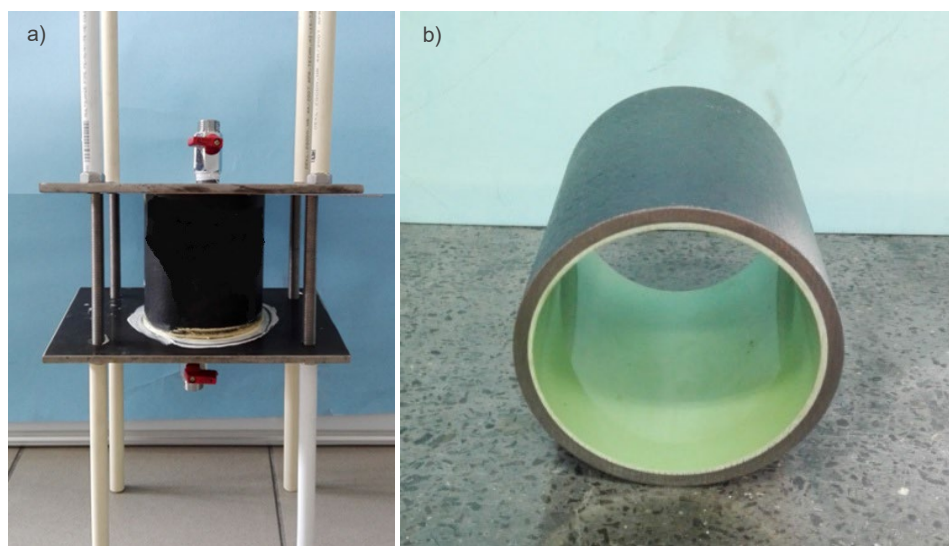


Fig. 2. Laboratory test stand (a), and ductile cast iron pipe with an internal polyurethane coating (b)

Table 1

The schedule of water replacements (pipes' filling and emptying)

Day	0	1	2	4	7	9	12	16	19	36	64
Water replacements		I	II	III	IV	V	VI	VII	VIII	IX	
Empties		1	2	3	4	5	6	7	8	9	10
Fills	1	2	3	4	5	6	7	8	9	10	

Measurements and the elaboration of results. Over the 64-day investigation period, in total, 20 water samples after contact with polyurethane coating were tested; these included 10 water samples collected from the first test stand (TS-1) (water without disinfectant) and 10 samples collected from the second test stand (TS-2) (water with disinfectant). In all collected water samples, as well as in water before contact with a polyurethane coating, some physicochemical and organoleptic water quality parameters, i.e., pH, alkalinity, total organic carbon (TOC), chlorine concentration (residue and consumption), color, odor, and taste were tested using the measurement methods as is presented in

Table 2. For testing chlorine consumption, water color, odor, and taste changes as a result of contact with polyurethane coatings, control water samples (i.e., reference water) were used; these were water samples with similar initial parameters not contacting with polyurethane coating. During the experiments, the temperature of the tested water was controlled; the temperature was kept on a steady level of about 20 °C.

Table 2

Water quality parameters before and after contact with polyurethane coatings and measurement methods used

Parameter	Measurement method	Water quality parameters			
		initial		tested	
		without disinfectant	with disinfectant	without disinfectant	with disinfectant
pH	potentiometry; pH meter CX-551 ELMETRON	8.05–8.41		T	T
Alkalinity, mmol/dm ³	titration	2.9–3.2		T	NT
TOC, mg C/dm ³	high-temperature oxidation with IR detection; organic carbon analyzer Skalar Formacs HT	2.38–4.11		T	T
Cl ₂ concentration (residue and consumption, mg Cl ₂ /dm ³)	spectrophotometry; absorbance measurement; SPEKOL 11, orthotolidine solution as a reagent	not measured	0.36–0.39	NT	T
Color	visual evaluation	no color		T	T
Odor	organoleptic method	no smell	–	T	NT
Taste		no taste	–	T	NT

T – tested, NT – not tested water quality parameters in water after contact with polyurethane coating.

To quantify the effect, or lack thereof, of the polyurethane liner on selected water quality parameters, simple statistical calculations were performed. Standard deviations and coefficients of variation were determined to describe time dependences of such parameters as pH, TOC, alkalinity, and chlorine consumption in samples in contact with polyurethane relative to control samples (raw water without contact with polyurethane liner)

$$SD = \sqrt{\sum_{i=1}^n (x_i - \mu_i)^2 p_i} \quad (1)$$

where: SD – standard deviation of values in samples contacting polyurethane relative to control samples, x_i – i th point value in the data set of samples in contact with polyurethane,

n – number of data points in the data set of samples in contact with polyurethane, p_i – probability of i th point (proportional to the contact time of the i th sample with polyurethane), μ_i – the i th point value of the control sample data set (not in contact with polyurethane)

$$CV = \frac{SD}{\bar{x}} \times 100\% \quad (2)$$

where: CV – coefficient of variation, \bar{x} – mean value over a data set of control samples (not in contact with polyurethane).

3. RESULTS

As shown in Fig. 3, pH of water in contact with polyurethane coating decreased slightly on the first day of the experiments. For the sample without disinfectant, pH decreased from 8.08 to 7.95, and for the disinfected water to 8.01. As the contact time increased, pH of water became lower and lower despite water changes according to the schedule shown in Table 1. On day 64 of the experiments, the pH of non-disinfected water contacting the coating for 28 days without replacement reached 7.50 and 7.68 in the disinfected water sample (initial pH 8.20). During the 64-day testing, there was no clear decrease in the effect of the polyurethane liner on the pH value; on the contrary, the influence increased with the time of operation. According to the results shown in Fig. 3, the effect of polyurethane coating on the decrease in pH of the water was less, when it was disinfected with sodium hypochlorite beforehand.

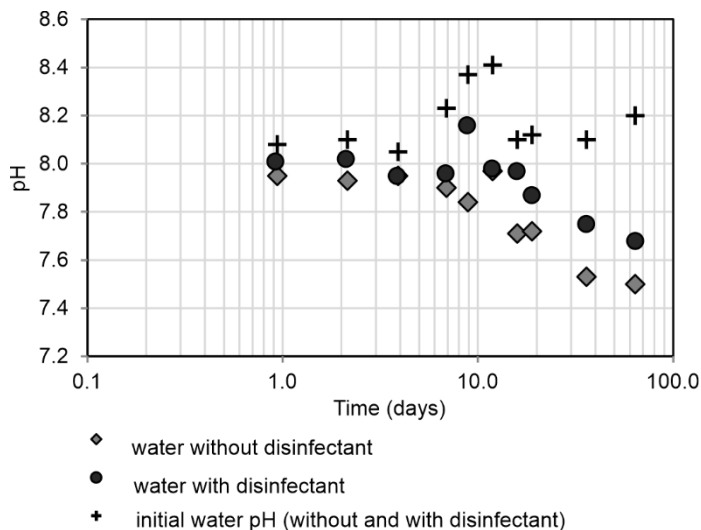


Fig. 3. Time dependences of pH of water without and with disinfectant as a result of contact with polyurethane coating

The mean pH over the study period was determined to be 8.18 in raw water not in contact with polyurethane liner. Based on equations (1) and (2), the standard deviation SD was calculated for the study period equal to 0.58 of the pH values of the water samples in contact with the polyurethane lining relative to the control samples at the same time, and the coefficient of variation CV equal to 7.15%. For chlorine disinfected water samples, the standard deviation, and the coefficient of variation were lower at $SD = 0.41$ and $CV = 5.02\%$. In all cases, the pH of the samples in contact with the polyurethane liner was lower than those of the samples not in contact with the liner.

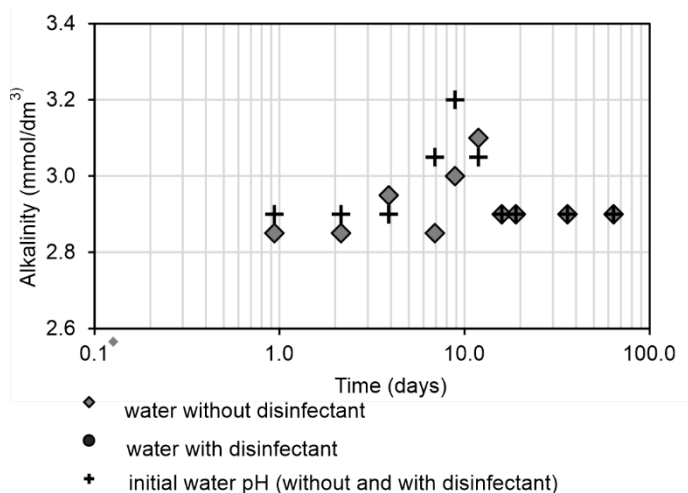


Fig. 4. Time dependences of alkalinity of water without disinfectant as a result of contact with polyurethane coating

The alkalinity values determined during the experiments (by collecting water without disinfectant from the test stand TS-1) indicate that there was almost no effect of the polyurethane coating on water alkalinity throughout the 64-day investigation period (Fig. 4). The standard deviation of the alkalinity of the water samples in contact with the polyurethane liner over the 64 days relative to the alkalinity of the water not in contact with the polyurethane liner during that time, was only $SD = 0.072$ mmol/dm³ with a mean alkalinity value of 2.9 mmol/dm³ and $CV = 2.44\%$, confirming almost no effect of the liner on water alkalinity. When the alkalinity values of the samples were standardized to one day, the SD and CV values were even lower at $SD = 0.029$ mmol/(dm³·day) and $CV = 0.97\%$.

Results of the total organic carbon measurements shown in Fig. 5 indicate a very intensive transfer of organic compounds from polyurethane coating into the water. A 10-fold increase in TOC concentrations in water was observed immediately during the first day after water contact with the new polyurethane coatings; TOC concentrations reached values of nearly 50 mg C/dm³ then. Successively, over time, the increase in TOC concentration per unit time due to the water contact with polyurethane liner was

decreased. The effect of chlorine compounds added to water on the intensity of organic compounds leaching from polyurethane coating was almost negligible. After the first day of the experiments, TOC concentration in disinfected water increased by about 2% more than in non-disinfected water.

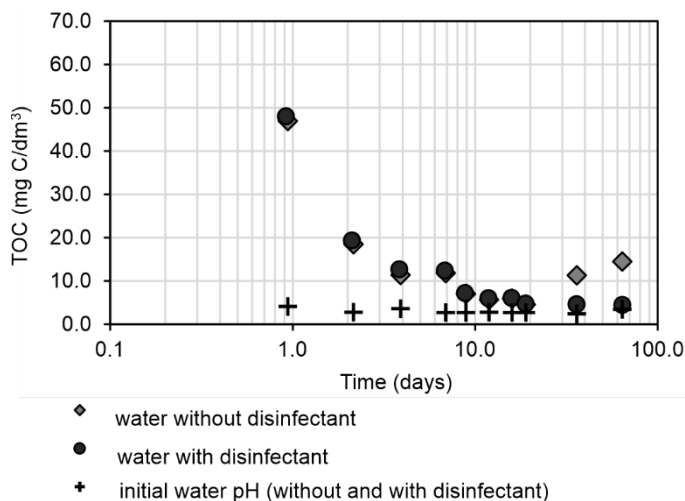


Fig. 5. Time dependences of total organic carbon (TOC) concentration in water without and with disinfectant as a result of contact with polyurethane coating

Statistical analyses were conducted to quantify the effect of the polyurethane liner on the increase in TOC in the water samples during the 64 days of testing. Calculated from equation (1), the standard deviation of the TOC concentration in samples in contact with polyurethane relative to samples without contact was 10.67 mg C/dm^3 with a mean TOC value of 2.97 mg C/dm^3 in the reference samples. The coefficient of variation CV for the samples in contact with polyurethane relative to those without contact calculated from equation (2) was equal to 359.52%. Because the contact times of the water samples with the polyurethane liner were greater at a later stage of the study, the TOC values were standardized by converting them to 1 day. The calculated SD value for the standardized TOC values was $5.74 \text{ mg C}/(\text{dm}^3 \cdot \text{day})$ and the CV was 193.32%. For the additionally chlorinated water, the standard deviation of the polyurethane contacting samples relative to the non-contacting liner water was $SD = 6.66 \text{ mg C}/(\text{dm}^3 \cdot \text{day})$, and $CV = 224.59\%$. For the standardized TOC values, the SD and CV values were $5.91 \text{ mg C}/(\text{dm}^3 \cdot \text{day})$ and 199.39%, respectively.

The effect of polyurethane coatings on the rate of disinfectant consumption in water was also analyzed as shown in Fig. 6. It was observed that after the first day, the concentration of chlorine remaining in water in contact with polyurethane liner was lower than in the control water sample, i.e., in water sample with the same initial amount of

sodium hypochlorite ($0.36 \text{ mg Cl}_2/\text{dm}^3$), but not contacting with polyurethane. However, in subsequent days of the experiment, the residual chlorine concentration in water samples in contact with polyurethane coating was similar to, and over time, even bigger than the residual chlorine concentration in control water samples. The intensity of chlorine consumption per day (Table 3) was the greatest on the first day of the experiments; over time, it was lower. Just after a few days, it was observed that the intensity of chlorine consumption was greater in control water samples than in water contacting with polyurethane coating.

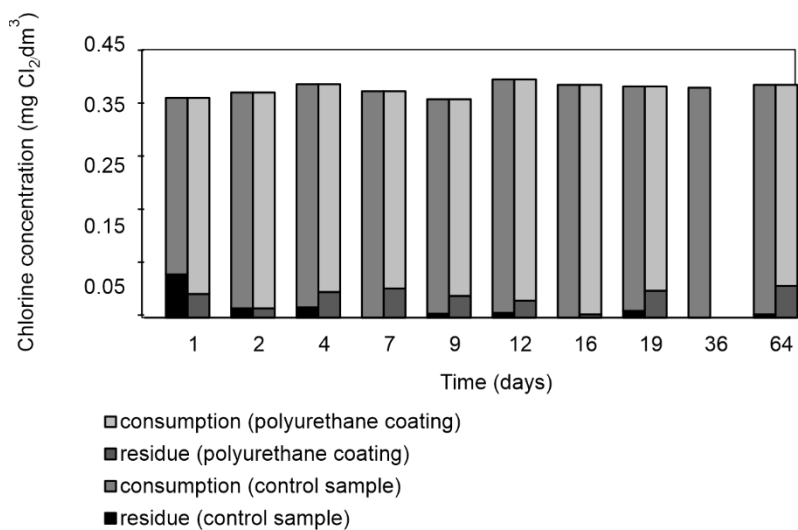


Fig. 6. Chlorine residue and chlorine consumption in water as a result of contact with a polyurethane coating and in control water samples

Table 3

Chlorine consumption intensity in water as a result of contact with polyurethane coating and in control water samples

Day	0	1	2	4	7	9	12	16	19	36
Polyurethane coating	0.352	0.300	0.198	0.109	0.164	0.123	0.095	0.111	–	0.012
Control sample	0.310	0.300	0.213	0.125	0.179	0.129	0.097	0.121	0.022	0.014

The effect of polyurethane lining on the intensity of chlorine consumption was not demonstrated during the 64-day study, which was also confirmed by statistical analyses. At a mean chlorine consumption intensity of $0.15 \text{ mg Cl}_2/(\text{dm}^3 \cdot \text{day})$ in the control samples, the standard deviation value for the samples contacting the polyurethane liner was $SD = 0.0078 \text{ mgCl}_2/(\text{dm}^3 \cdot \text{day})$ and the coefficient of variation $CV = 0.53\%$.

The observations showed a significant effect of the polyurethane coatings on water colour changes; a yellowish water colour was observed. For water without disinfectant, the effect was significantly greater than for water disinfected with sodium hypochlorite.

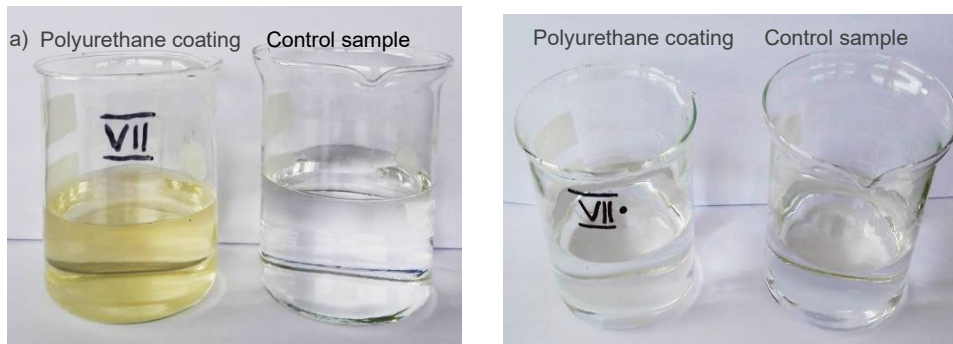


Fig. 7. Water samples after contact with polyurethane coatings, 16th day of the experiments, after 4 days of no water replacement: a) water without disinfectant, b) water with disinfectant

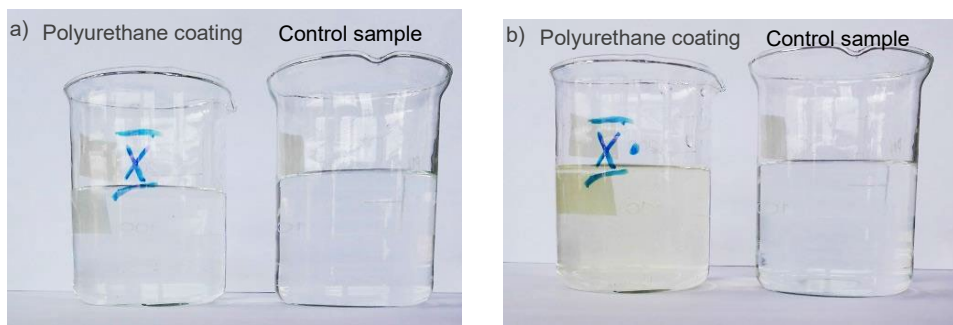


Fig. 8. Water samples after contact with polyurethane coatings, 64th day of the experiments, after 28 days of no water replacement: a) water without disinfectant, b) water with disinfectant

Figure 7 shows the photos of the samples on the 16th day of the experiments, after 4 days of no water replacement: once without adding sodium hypochlorite (Fig. 7a) and once after adding the disinfectant (Fig. 7b). The color of water in contact with polyurethane coating was more intensive when it was not disinfected before, and almost imperceptible discoloration after disinfection. Only after about 60 days of contact between the polyurethane coating and water, the penetration of staining substances from polyurethane into the water decreased to a level that eliminated the visual effect of coating on water color. Figure 8 shows that on day 64th, despite no water replacement for as long as 28 days, the coloration of water was insignificant. Minimally more colored in this case was water that had been disinfected earlier (Fig. 8b).

Water samples collected from the test stand TS-1, where a ductile cast iron pipe with an internal polyurethane coating was installed (water without disinfectant), were

also subjected to ongoing analysis of organoleptic properties for any changes in smell and taste. A specific, chemical smell and aftertaste of water contacting with polyurethane coating were quite noticeable in the initial period of the experiments (during the first few dozen hours of contact) and to a lesser extent, towards the end of the study, when the time intervals between successive water replacements, and thus, the time of contact between the polyurethane and water without water replacement, was relatively long. The statistical measures calculated based on equations (1) and (2) and the experimental results such as the mean value in reference samples (\bar{x}), standard deviation of the polyurethane contacting samples relative to the non-contacting liner (SD), and coefficient of variation (CV), were discussed in earlier sections and are summarized in Table 4.

Table 4

Statistical measures of mean value, standard deviation and variation coefficient

\bar{x}	SD	CV [%]	Chlorinated samples		Standardized		Chlorinated samples	
			SD	CV [%]	SD	CV [%]	SD	CV [%]
pH								
8.18	0.58	7.15	0.41	5.02	–	–	–	–
Alkalinity [mmol/dm ³]					Alkalinity [mmol/(dm ³ ·day)]			
2.9	0.072	2.44	–	–	0.029	0.97	–	–
TOC [mg C/dm ³]					TOC [mg C/(dm ³ ·day)]			
2.97	10.67	359.2	6.66	224.59	5.74	193.32	5.91	199.39
Chlorine consumption (mg Cl ₂ /(dm ³ ·day))								
0.15	–	–	–	–	–	–	0.0078	0.53

Table 4 does not include pH values standardized to a period of one day because it is the value opposite to the decimal logarithm of hydrogen ion concentration. In such a case, converting these values to 1-day period could result in a very high error.

4. SUMMARY

Summarized findings of the conducted laboratory experiments on the impact of polyurethane coatings on the quality of transported potable water are as follows:

- A slight decrease of the water pH after contacting with polyurethane coating from the initial value of about 8.1–8.4 to about 7.7–8.1 (disinfected water) and about 7.5–8.0 (non-disinfected water) was observed. The decrease in pH was maintained throughout the whole investigation period, i.e., for 64 days. In the case of sodium hypochlorite disinfected water, the effect was slightly less than in the case of non-disinfected water. Observations were confirmed by calculated statistical measures. The mean value in reference samples was 8.18. The SD for undisinfected water contacting polyurethane was 0.58 and CV was 7.15%, while for disinfected water the SD was 0.41 and CV was 5.02%.

- Almost no effect of the polyurethane coating on non-chlorinated water alkalinity was observed. This small effect was confirmed by the small values of the statistical measures. With a mean value of 2.9 mmol/dm^3 , the SD was only 0.072 mmol/dm^3 and the $CV = 2.44\%$, and with the values standardized to one day, the SD was even smaller at $0.29 \text{ mmol}/(\text{dm}^3 \cdot \text{day})$ and the $CV = 0.97\%$.

- Very intensive leaching of organic compounds from polyurethane coating into the water was observed. A 10-fold increase in TOC concentration was observed on the first day after water contact with the new polyurethane coating, reaching the value of about 50.0 mg C/dm^3 . The increase in TOC concentration per unit time successively decreased with the time of coating operation. Adding sodium hypochlorite to the water only slightly increased the leaching of organic compounds from the coating into the water. Intensive leaching of TOC from the polyurethane liner was confirmed by high SD and CV values of 10.67 mg/dm^3 and 359.2% , respectively, and when standardized to one day $SD = 5.74 \text{ mg C}/(\text{dm}^3 \cdot \text{day})$ and $CV = 193.32\%$ (the average TOC value in the reference samples was 2.97 mg C/dm^3). When disinfectant was added in the first days of the study, the intensity of TOC release was slightly higher than that of the undisinfected samples, but this trend reversed at the end. The calculated SD and CV values for the disinfected samples were 6.66 mg/dm^3 and 224.59% , respectively, which were lower than for the samples without disinfection. However, for the values standardized to one day, the values were minimally higher than for the samples without disinfection and were $SD = 5.91 \text{ mg C}/(\text{dm}^3 \cdot \text{day})$ and $CV = 199.39\%$.

- A slight effect of the polyurethane coatings on chlorine consumption in water was observed. During the first day of testing, polyurethane liner caused an increase in chlorine consumption and a decrease in the amount of useful chlorine remaining. In subsequent days of water contact with a polyurethane coating, chlorine consumption decreased, while the amount of useful chlorine remaining increased. The change in water pH caused by the influence of polyurethane may have contributed to this. The difficulty to demonstrate the effect of polyurethane lining on chlorine consumption in water is confirmed by small values of $SD = 0.0078 \text{ mg Cl}_2/(\text{dm}^3 \cdot \text{day})$ and $CV = 0.53\%$.

- A significant effect of the polyurethane coatings on the water color change to yellowish color was observed in the first dozen days of the coating operation. It was especially noticeable in non-disinfected water. In the case of sodium hypochlorite treated water, this effect was not observed.

- Perceptible specific chemical smell and aftertaste of water contacting the polyurethane coating were noted during the first few dozen hours of operation and this effect gradually decreased. After 64 days, changes in smell and taste of the water after contact with polyurethane coating were still perceptible to a minimum degree.

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