Water treatments means to reduce the corrosivity of soft waters

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ABSTRACT
Soft waters tend to reduce the life time of pipes from drinking water distribution systems and the induced corrosion is likely to deteriorate water quality at the consumer's tap. New French legislation (decree 2001-1220 of 20/12/2001) effective since the end of 2003, recommends the supplied water not to be aggressive. Two types of treatments are commonly used to limit the corrosion effect of soft waters with low alkalinity: (1) the addition of phosphate corrosion inhibitors and (2) the neutralization or remineralisation of soft water. In order to provide guidelines for the network operator to choose suitable treatment methods, a comparison must be made based on a technical (reliability and efficacy) and an economical standpoint (treatment cost and impact on pipes renewing). Within this study, a pilot experiment has been performed to compare the impact of phosphate inhibitors with remineralisation on the degradation of pipes commonly used in drinking water distribution systems (cast iron, cement and steel) and household plumbing systems (copper). The impact of water treatments was studied on the water (pH, metal leaching, etc) and on corrosion measurements (electrochemical probes, weight loss coupons). The results obtained over a 15-months period showed that the best water quality was achieved with the remineralisation approach. This water treatment strategy reduces metal pipe corrosion of soft water by 40 % and improves of 50 % both the copper and the iron release reduction.

KEYWORDS
Pipe corrosion, remineralisation, phosphate inhibitors; drinking water distribution system, water quality

INTRODUCTION
The maintenance of distributed water quality up to the consumer's tap represents one of the main concerns of the network operator and sanitary authorities. It requires the knowledge of factors which deteriorate water quality causing internal corrosion of drinking water distribution systems (DWDS).

In DWDS, interactions between supplied water and pipes internal wall are important. They depend on both the nature of materials (cast iron, cement based material, steel) of the pipe and the physico-chemical characteristics (pH, conductivity, alkalinity, carbonate calcium saturation, etc) of the supplied water (Leroy, 1999).

The current study was undertaken to examine at the pilot scale, the impact of two treatments used to limit the corrosivity of soft waters. Indeed, soft waters tend to reduce the life-time of the pipes in public and/or household plumbing distribution systems due to their aggressiveness towards calcium carbonate scale and to their corrosivity towards pipe walls. The induced corrosion has a high economic incidence for water utilities with the failure of the distribution system pipes such as water leakage, pipe breaks, overflows, clogging of pipes with corrosion products. One other effect of corrosion is consumer's complaints, due to a degraded water quality (red water, bad taste and odour as well as eventually health problems depending on the pipe materials). Coloured water often results from either improperly treated water that contains iron or the dissolution of the corrosion scales from corroded iron pipes (Sarin *et al*, 2003). The overall consequences of pipes corrosion might be minimized by cleaning and more frequent renewed. However, such operations often represent an important cost issue, and preventive water treatments usually offer good economical alternatives.

In order to reduce the corrosivity of soft waters or low-alkalinity waters, two types of treatment are commonly used (1) the addition of phosphate corrosion inhibitors or (2) the neutralisation or remineralisation treatment which corrects the mineral composition of the water.

Phosphate inhibitors are one of the most common methods used to prevent iron corrosion in DWDS. The most common types of phosphate inhibitors currently used are polyphosphate (hexametaphosphate) or orthophosphate. The reaction mechanisms of these inhibitors depend on the exact nature of phosphate used. Thus polyphosphates have both a sequestering and an adsorption role: they form complexes with metallic ions (Fe, Mn, Pb) in the water. So, several studies indicate the advantages of using polyphosphate inhibitors for preventing red water phenomena in DWDS (McNeill and Edwards, 2001; AWWARF, 1996). Unlike polyphosphates, orthophosphates are added for scale formation but not for iron sequestration (Wagner, 1992; Benjamin et al., 1990). The orthophosphate acts by enabling the formation of a charged complex that migrates to the cathode by creating a protective polymeric film on the metal surface. Finally, orthophosphate addition is a passivation approach to corrosion control. However, it is claimed that phosphate inhibitors have little effect on iron corrosion at low flow or stagnant conditions (McNeill and Edwards, 2000; Maddison and Gagnon, 1999, Rompre et al., 1999).

The main purpose of the remineralisation is to obtain a passivation of the pipe material by forming a calcium hydroxide or a calcium carbonate shell on its surface. This can be achieved by adding calcium hydroxide, calcium carbonate or sodium hydroxide to the water in order to reach an equilibrium pH in excess of 8, which is relatively high for soft water.

A 24-month pilot study was initiated to compare the effectiveness of these two treatments on four types of materials commonly used in public distribution systems (iron, scraped and non-scraped old cast iron and cement ductile iron) and on one material only used in plumbing distribution systems (copper). The aim of this study is to better understand the interactions between water treatment and pipe corrosion over a long time period. From these results, guidelines are proposed to help the operator to find the optimal strategy that minimises the corrosion rates of iron, copper and cement-based materials in terms of reliability and effectiveness.

After a brief review of the general experimental approach and a discussion of the quality control procedures of the pilot, the results after 15 months of exposure to either treatment of the study will be presented. Finally, the implications of these results to better understand the impact of phosphate inhibitors towards remineralisation have been evaluated.

MATERIALS AND METHODS

Selection of treatments and pilot plant configuration

The pilot plant (Figure 1) is located at the reservoir of the city of Maisons-Laffitte (France). The pilot plant configuration was set up to compare four distinct water qualities, the characteristics of which are reported in table 1.

Table 1. Average water quality characteristics for the four units plant of the pilot from January, 2004 to July, 2005
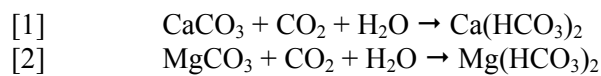
Water quality parameter	Unit 1: soft water	Unit 2 : remineralisation of soft water	Unit 3 : soft water + polyphosphates	Unit 4 : soft water + orthophosphates
Temperature (°C)	20,6 ± 2,5	18,8 ± 2,5	20,6 ± 2,5	20,5 ± 2,5
pH	7,01 ± 0,11	8,38 ± 0,19	7,03 ± 0,12	7,09 ± 0,14
Conductivity (µS/cm)	100 ± 10	275 ± 22	99 ± 1	107 ± 1
Calcium (mg/l CaCO$_3$)	41 ± 5	95 ± 10	42 ± 3	40 ± 5
Hardness (mg/l CaCO$_3$)	35 ± 2	104 ± 2	35 ± 2	35 ± 2
Alkalinity (mg/l CaCO$_3$)	44 ± 6	95 ± 5	44 ± 1	43 ± 1
TOC (mgC/l)	0,4 ± 0,3	0,30 ± 0,01	0,45 ± 0,31	0,21 ± 0,08
Chloride (mg/l)	1,7 ± 0,2	1,9 ± 0,2	2,0 ± 0,1	2,2 ± 0,1
Sulphates (mg/l)	4,0 ± 0,6	40,8 ± 0,6	4,1 ± 0,3	4,4 ± 0,3
Saturation index**	-1,8 ± 0,6	0,5 ± 0,3	-0,83 ± 0,4	-1,73 ± 0,4
Larson index**	0,5 ± 0,1	0,1 ± 0,1	0,5 ± 0,1	0,2 ± 0,1

** Parameters determined with Legrand – Poirier – Leroy method

The pilot plant included alternative water treatment strategies under consideration (neutralisation, polyphosphates and orthophosphates addition) in order to minimize the metal released. Four water qualities were therefore obtained by the suitable treatment of tap water from the public network. Each water quality was then used to feed a pilot plant unit, composed of pipe loops with different materials (Figure 1).

The first unit (unit 1) was supplied with soft water that was obtained from the public water network passing through a softener and a reverse osmosis unit. The final composition was as close as possible to natural soft water with low alkalinity (pH ≈ 7, hardness ≈ 40 mg $CaCO_3$/l and alkalinity ≈ 40 mg $CaCO_3$/l). Table 1 shows the expected characteristics of the soft water was obtained with a good accuracy. The soft water supplied unit 2 and also constituted the aggressive and corrosive reference water for anti-corrosion tests of units 2, 3 and 4.

Unit 2 supported the remineralisation approach. This approach involves the formation of $CaCO_3$ scale in order to create a protective scale to block the contact between the electrolyte, the anodes and the cathodes. The process used during this study involved the soft water (same as unit 2) passing through a column of calcareous alga (NeutralG®). The reactions involved are as follows:

[1] $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$
[2] $MgCO_3 + CO_2 + H_2O \rightarrow Mg(HCO_3)_2$

An addition of sodium hydroxide was performed at the exit of the column in order to have a pH close to 8,3. This value gave a saturation index that ranged between 0,3 and 0,4 in order to accelerate the formation of a protective ferricalcite scale on ferric metals (Cordonnier *et al*, 2000).

(a)   (b)

Figure 1. The whole pilot plant (a) and one of the four treatment units (b)

Unit 3 and Unit 4 were fed with phosphate treated soft water (same as Unit 1). Two inhibitors were selected: a hexametaphosphate (polyphosphate) to unit 3 and an orthophosphate to unit 4. These two treatments proceeded to be the most efficient to reduce the corrosivity of the soft water. During the study, the treatment rate was maintained in the influent of each unit plant at 3 mg PO_4/l during the study.

Pilot pipe-loop construction

Each of the five units (Fig. 2) consisted of five independent flow-through PVC loops. Each loop, except the copper loops, has six removable 30 cm long pipe sections of 60 mm inner diameter, that are connected with quick fit coupling, so that each pipe section could be easily sampled for further analyses. These inserts were machined to fit the assemblies and to minimize flow distortions. The inserts were coated with an epoxy resin on the outer surface and edges to limit corrosion to interior surfaces. Pipe section samples were made up of different type of materials:

- loop 1 = Portland cemented ductile iron pipe samples
- loop 2 = steel pipe samples
- loop 3 = scraped old unlined cast iron samples
- loop 4 = old unlined cast iron samples
- loop 5 = a single pipe of length 6 m with a diameter of 12 mm

As a whole, the pilot is composed of twenty loops (4 loops with cement pipe samples, 4 loops with steel pipe samples, 4 loops with old unlined cast-iron pipe, 4 loops with scraped old cast-iron and 4 loops in copper), figuring four independent units fed by four water qualities.

Each cast-iron loop was constructed with samples from old, unlined cast-iron pipe removed from the Syndicat des Eaux d'Ile de France (SEDIF), water distribution system of Saint-Denis. This pipe was 90-100 years old and had an internal diameter of 60 mm (2,4 in.). The internal surface of the pipe was only slightly turbaculated. In order to study the impact of rehabilitation on the water quality and iron release, half of the old cast-iron pipes collected was scraped and installed on a distinct loop in each treatment unit. Detailed information on the quality of water that passed through this pipe over the pipe life-time was not available. The loops made with cemented ductile iron and with steel, brand new pipes were used for the study.
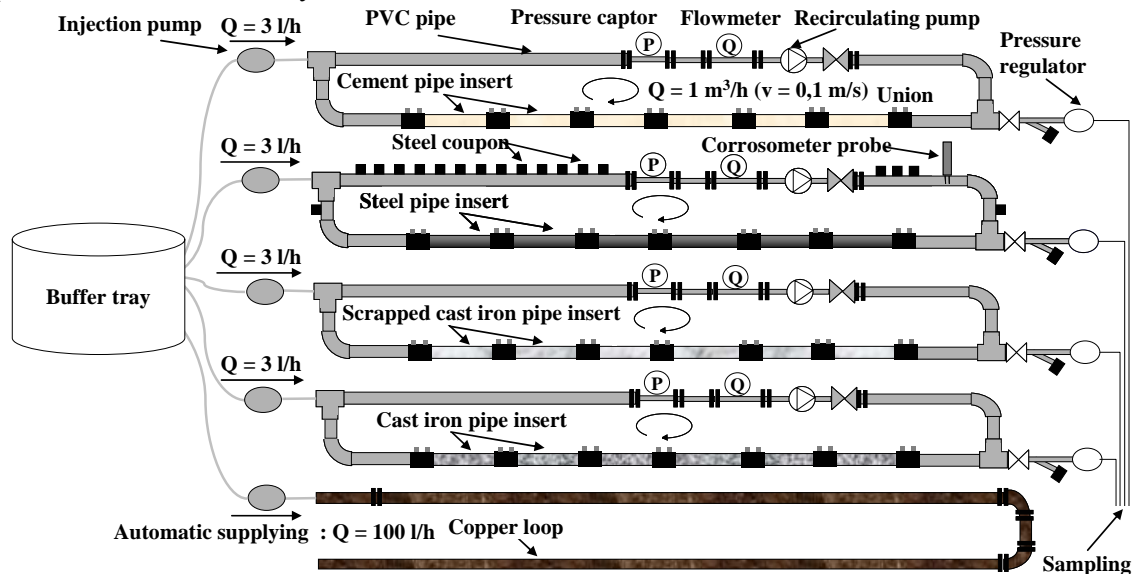

Figure 2. Schematic diagram of a treatment unit

Operational procedures: case of loops with cement, steel and cast iron

The inlet and the outlet flow of these loops was about 3 l/h. The initial flow rate through each loop was 1 m^3/h which resulted in a velocity of 1 m/s. and a pressure of 3 bars. The volume of each loop being 18 L, the residence time was about 6 hours. These hydraulics characteristics are close to those which can be met in a real distribution system. They were based on the hydraulic modelling of real drinking water distribution systems in France (Jaeger *et al.*, 2002; Jaeger *et al.*, 2003)

The corrosion impact of the different water qualities on materials was assessed through weekly sampling of the influent and effluent of each of the five treatment units. Sampling were performed to monitor the pH, the temperature, the conductivity, the turbidity, the alkalinity, the water hardness, the calcium carbonate, the total iron in the loops constituted with iron or cast iron and the aluminium level for cement pipe loops and the phosphate rate for the involved loops. The aluminium and total iron measurements were made twice a week during the study using an atomic absorption spectrophotometer (PERKIN ELMER Optima 3300 DV) in accordance with standard methods (NF EN ISO 11885).

Steel corrosion coupon

To each of the four loops installed by using six steel pipe inserts, 18 weight loss corrosion coupons made of mild steel were also installed. These coupons were developed by Anjou Recherche to obtain a reliable tool to measure the corrosion in distribution system. The corrosion coupons were made of a steel washer on a Teflon^{TM} support (Fig. 4.a). These coupons were inserted flush to the pipe wall via a 20/27 fitting (Fig. 4.b). The purpose of the use of such coupons was to evaluate the corrosion in distribution systems which can be subsequently performed at different levels:

- The easiest approach consists of a visual observation of the coupon feature to evaluate the corrosion scale, the presence or lack of corrosion-inhibition product, the eventual presence of pitting. This inspection is totally non-destructive. After the examination, the coupon can be replaced in the pipe for further investigation.

- Further analysis involves weight loss measurements in order to evaluate the quantity of oxidized metal. Such a measure requires a suitable preparation of the coupon in order to remove the adherent scale according to NF ISO 8407. The corrosion rate can be calculated by the following equation :

[3] $$v_{corr} = \frac{M_i - M_f}{m_v \times S \times t} \times 365 \times 10^4$$

where v_{corr} = average corrosion rate (µm/year); M_i = initial mass of the coupon (g); M_f = final mass of the coupon (g); m_v = volumetric mass of the metal (g/cm^3: 7,8 g/cm^3 for steel); S = exposed coupon area (cm^2) and t = exposition time of the coupon (day)

- These coupons can also be used for a more complete corrosion characterization as well: surface analyses to determine the nature of both the corrosion scale or corrosion-inhibition product and biofilm analyses

Within the frame of this pilot study, only first two evaluation levels were considered. The steel coupons weight loss rates were expressed in terms of equivalent rates of penetration in micrometers per year. At 3-month intervals for the first year and at 6-month intervals for the second year, three coupons were examined by removing them from each iron loop and were subsequently replaced with a new set of the same type. Thus, the final set will include coupons exposed for 3, 6, 9, 12, 18 and 24 months, providing replicates of the 6, 12, 15, 18, 21 months exposures.
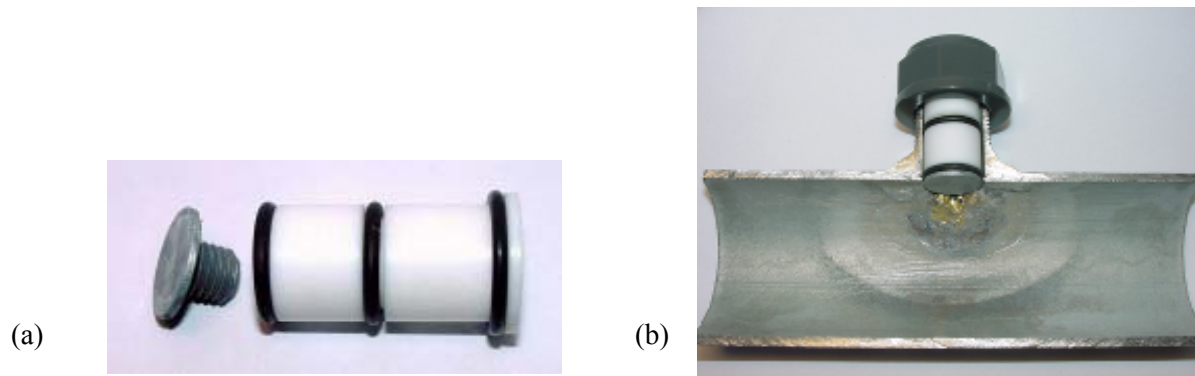

(a)   (b)

Figure 3. Steel corrosion coupon and Teflon^{TM} support (a) and steel corrosion coupon inserted in pipe (b)

Mild steel corrosion probes (corrosometer)

Corrosion probes were also used. They consisted of a transducer (type Corrater 9030+^{TM} from Rohrback Cosasco Systems) that was linked to a probe with two mild steel electrodes. This device determines the polarization resistance of the corrosion process. The resistance is used to assess the intensity of the corrosion current (i_{corr}), by using the Stern and Geary equation [Eq. 4]. The corrosion rate is then calculated from the corrosion current that is derived from the Faraday's law.

[4] $$R_p = \frac{1}{2,3.i_{corr}} \frac{b_a.b_c}{b_a + b_c} = \frac{B}{i_{corr}}$$

where b_a and b_c are the Tafel coefficients which are considered constant and ranging from 40 mV to 150 mV respectively. The value of B factor can be estimated around 20 mV.

In the framework of the pilot study, mild steel probes were installed on each of the five steel-loops. The corrosion rate was measured continuously.

Operational procedures: case study using copper loops

Currently, copper pipes are used in most household plumbing systems. In order to quantify the impacts that the studied treatments have on the copper release, copper pipe have been installed onto the pilot (Fig. 2). As a simulation of the behaviour of these systems, the copper loop has a different pattern in comparison with the others loops.

A control system has been installed in order to simulate a household using copper piping for its water system. This protocol is based on research work led by European laboratories and coordinated by the Centre de Recherche et de Contrôle des Eaux de Paris (CRECEP) (European Commission, 2000; DIN, 1999). Thus, water was fed for 6 hours every day. The initial flow rate through each copper loop was 100 l/h which resulted in a consumption of 600 l/day which is representative for about four households. The copper measurements in the outlet water were made once a week during the study on a PERKIN ELMER Optima 3300 DV atomic absorption spectrophotometer in accordance with Standard Methods (NF EN ISO 11885). Three samples were also collected weekly in order to monitor copper release after two different stagnation times (30 minutes and 9 hours).

RESULTS AND DISCUSSION

Effect of water treatments on copper release

The main objective of this phase was to examine the effect of different water treatment strategies on the copper-released. Copper concentration were monitored in the effluent of all the 4-copper loops for two stagnation times (30 minutes and 9 hours). The results are represented graphically in Figures 4 and 5.
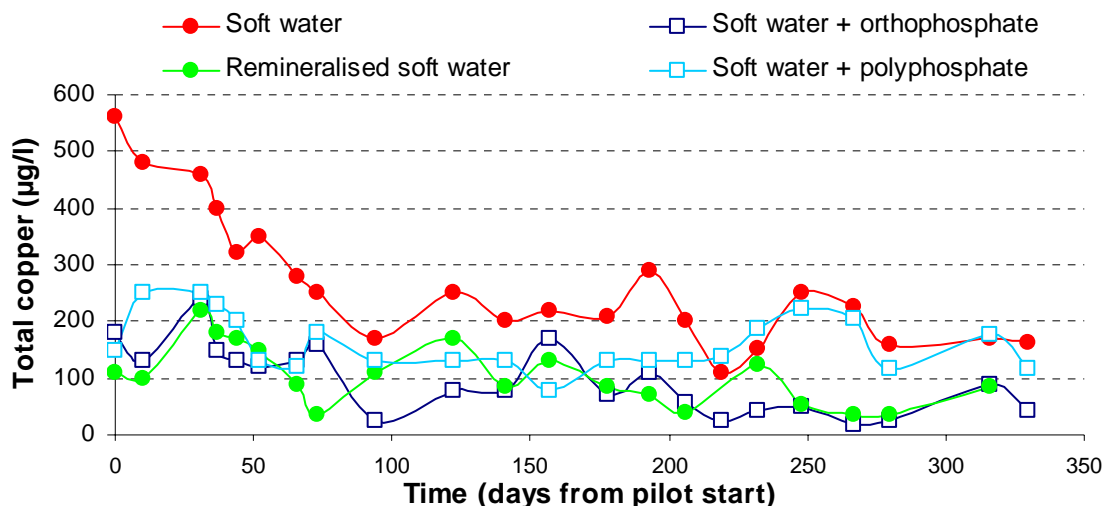

Figure 4. Copper levels in brand new pipes after 30-minutes stagnation

As shown in Figure 4, the lowest copper levels (< 100 µg/l) were measured at the outlet of remineralisation and orthophosphate treated loops followed by polyphosphate (< 200 µg/l). The highest copper levels were measured in the effluent of copper loop supplied with the soft water loop (> 200 µg/l). A decreasing trend of copper levels in the soft water was observed with time. With remineralisation and orthophosphate treatment, these 30 minutes-stagnation show an average improvement of at least 60% for the copper release reduction. This improvement calculation is based on the following equation:

$$[5] \quad \% \text{ improvement} = \frac{(\text{Total copper release with treatment} - \text{Total copper release without treatment}}{\text{Total copper release without treatment}} \times 100$$

Unlike these two treatments, the impact of polyphosphate is slightly less pronounced with only 40 % of improvement.

For the 9-hours stagnation period (Fig. 5), the same trends were observed as shown in Figure 4. The lowest copper levels were measured at the outlet of remineralisation unit with an improvement of 75% in comparison with soft water. In the same time, orthophosphate also gives goods results with an improvement that was close to 40%. Contrary to these two treatments, the effectiveness of polyphosphate is less significant with an improvement lower than 25 %.
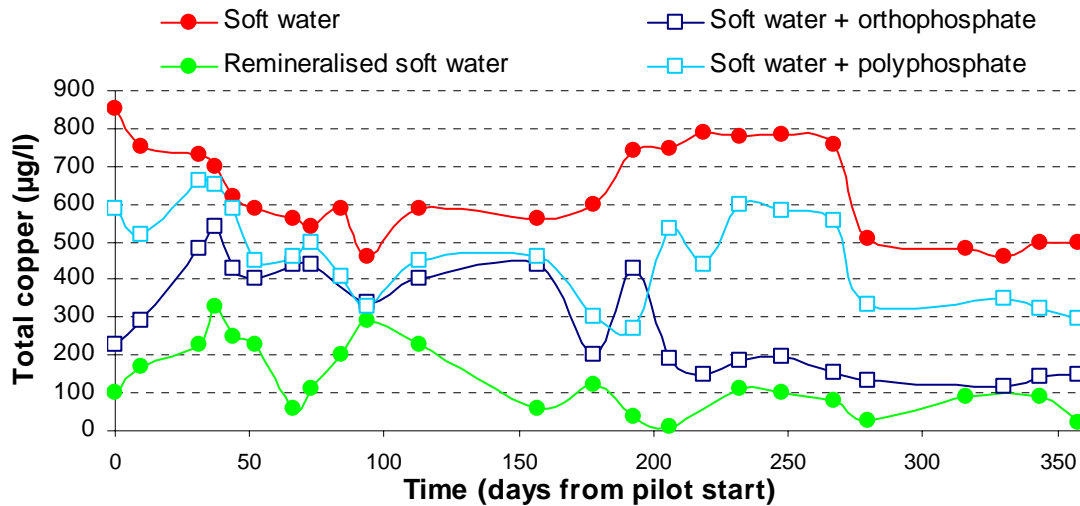

Figure 5. Copper levels in brand new pipes after 9-hours stagnation

In summary, for all stagnation times, the lowest copper levels were measured in the effluent of remineralisation copper loop. Nevertheless, phosphate-based inhibitors appeared to provide a significant degree of beneficial protection to the copper pipes supplied with soft water whose characteristics are $pH \approx 7,0$ and alkalinity ≈ 40 mg/l as $CaCO_3$.

In comparison with polyphosphate, orthophosphate had lower copper release and its performance was more significant for the two stagnation time studied. Dosing of 3 mg PO_4/l orthophosphate led to reductions in copper release from 70 % for 30 minutes-stagnation time to 40 % for 9-hours stagnation time. For polyphosphate, a dosing of 3 mg PO_4/l led to reductions in copper release from 40 % for 30 minutes-stagnation time to 20 % for 9-hours stagnation time.

The reasons behind the phosphate impact on copper release reduction are not well known. Thus, in order to better understand the action of phosphate on copper pipe, some pipe sections were removed from each of copper pipe loops. The scale on each sections were analysed with a Fourier transform infrared spectrophotometer. The pipe sections supplied with soft water and orthophosphate addition, the results show that the orthophosphate appears to accelerate the formation of a uniform cuprite (Cu_2O) layer on the copper pipe wall. This layer seems to be relatively dense and provides structural integrity to the scale. Analysis of sections supplied with soft water and polyphosphate treatment show the presence of copper polyphosphate and a cuprite film layer. Unlike orthophosphate, these precipitates occur in an overlying porous film layer leading to a protective layer that is less uniform than layers observed on the copper pipe treated with orthophosphate. These effects can explain the reduced effectiveness of polyphosphate in limiting copper released.

Regarding remineralisation, analysis of the copper pipe sections shows the presence of an adherent and protective scale of cuprite. Moreover, the presence of calcite has also been identified during these studies. Contrary to previous results, analysis of the pipe sections supplied with soft water show the presence of malachite ($Cu_2(OH)_2CO_3$) and low quantity of cuprite solids. This thin and porous scale can explain the high copper release observed in figures 4 and 5.

In summary, for copper pipes supplied with a soft water treated or not, copper release decreased in the following order:

Remineralisation treatment > orthophosphate >> polyphosphate > no treatment

Effect of Portland cemented ductile iron pipes on water quality

Previous studies have revealed that the degradation of cement based materials involves the dissolution of calcium hydroxide with an associated increase of the water's original pH which also can be accompanied by aluminium dissolution (Kristiansen *et al,* 1978; Vik and Weidborg, 1991; Conroy and Oliphant, 1991). The main objective of the water quality monitoring performed on outlet cemented ductile iron loops is to assess the impact of soft water treatments on this type of pipe material.

The tables 3 and 4 show respectively the pH level measured after a contact time of 6 hours and the aluminium released.

Table2. pH levels before and after a contact time of 6 hours in cement loops

Time (months)	Unit 1 : soft water		Unit 2 : remineralisation of soft water		Unit 3 : soft water + orthophosphate		Unit 4 : soft water + polyphosphate	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
0	7,01	7,40	8,25	8,20	6,95	7,40	6,97	7,54
0,25	7,04	7,42	8,18	8,20	7,00	7,42	7,01	7,59
0,5	7,02	7,46	8,54	8,50	7,00	7,46	7,00	7,63
0,75	6,99	7,57	8,41	8,40	6,95	7,57	6,96	7,55
1	7,01	7,62	8,30	8,3	6,98	7,62	6,96	7,44
2	6,99	7,75	8,35	8,35	6,95	7,75	6,98	7,37
3	7,03	7,80	8,20	8,20	7,01	7,80	7,02	7,34
6	6,96	7,72	8,41	8,41	6,98	7,72	6,98	7,33
9	7,05	7,61	8,30	8,30	7,03	7,19	7,05	7,19
12	6,98	7,5	8,30	8,30	6,94	7,19	6,94	7,18

As shown in Table 2, the highest pH values were measured at the outlet of units 1, 3 and 4 during the first 3-months of the study. Apart from unit 3, the three other water qualities lead to a gap of pH 0,7 between the influent and the effluent. This difference is significant as only two meters of cemented ductile iron were installed on each loop. In real DWDS, this increase can be largely higher. This increase is mainly due to the migration of basic compounds in the water (e.g. KOH, NaOH, $Ca(OH)_2$) contained in cement pores.

After 9-months of use, the pH values measured in the effluent of the loops that were treated with phosphate clearly decrease. This decrease was correlated with both low phosphate levels in the effluent and analysis of scale on the pipe sections show high phosphate levels. These results proved that the formation of a protective layer occurred with the cemented ductile iron pipes. Nevertheless, there is always a small difference of 0,2 to 0,3 in the pH between the inlet and the outlet of cement loops. Contrary to phosphate treatments, remineralisation avoids this pH increase due to its scaling properties leading to the formation of stable calcium carbonate scales that block material pores.

Table 3 Aluminium concentrations before and after a contact time of 6 hours in cement loops (μg/l)

Time (months)	Unit 1 : soft water		Unit 2 : remineralisation of soft water		Unit 3 : soft water + orthophosphate		Unit 4 : soft water + polyphosphate	
	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
0	< 20	30	< 20	20	< 20	20	< 20	20
0,25	< 20	40	< 20	20	< 20	40	< 20	40
0,5	< 20	50	< 20	20	< 20	50	< 20	40
0,75	< 20	50	< 20	30	< 20	50	< 20	40
1	< 20	60	< 20	30	< 20	50	< 20	60
2	< 20	60	< 20	30	< 20	60	< 20	50
3	< 20	50	< 20	30	< 20	60	< 20	40
6	< 20	40	< 20	< 20	< 20	30	< 20	30
9	< 20	30	< 20	< 20	< 20	< 20	< 20	< 20
12	< 20	< 20	< 20	< 20	< 20	< 20	< 20	< 20

Regardless of the four treatment units, aluminium leaching was found to be between 20 - 70µg/l at the outlet of cemented ductile iron loops during the first 12-months of use (Table 3). Note that for the soft water unit, the aluminium leaching was greatest during the first 9-months exploitation. This low alkalinity water appeared to cause a fast degradation of the cement coating. This degradation can be

reduced with the help of suitable treatments. Regarding unit 2, the leaching started to be less significant from the third month. Some of the pipe sections were removed from this unit in order to examine the nature of scales. These observations showed the fast formation of calcite which can explain the decrease in the leaching rate. In case of units 3 and 4, the absence of leaching from the sixth month is correlated with the decrease in pH observed in table 2. These results tend to confirm the formation of a protective layer on the pipe wall. Therefore, the protection of the cemented ductile iron is faster with a remineralisation treatment than with phosphate treatment.

Iron release studies

The goal of this phase was to examine the effect of different water treatment strategies on iron-release rates. The iron released was monitored for all the 15-loops that had metallic sections (e.g. cast iron and steel). Some studies showed orthophosphate efficiently reduced both the lead and the copper solubility at the consumer's tap. Nevertheless, phosphate treatments may have negative impacts on iron corrosion (McNeill *et al*, 2000). The impact of different treatment strategies on iron corrosion was observed by analysing the composition of the effluent of the 12 metallic pipe-loops (cast iron and iron). In the same time, the comparison of remineralisation towards phosphate based inhibitors was also carried out.
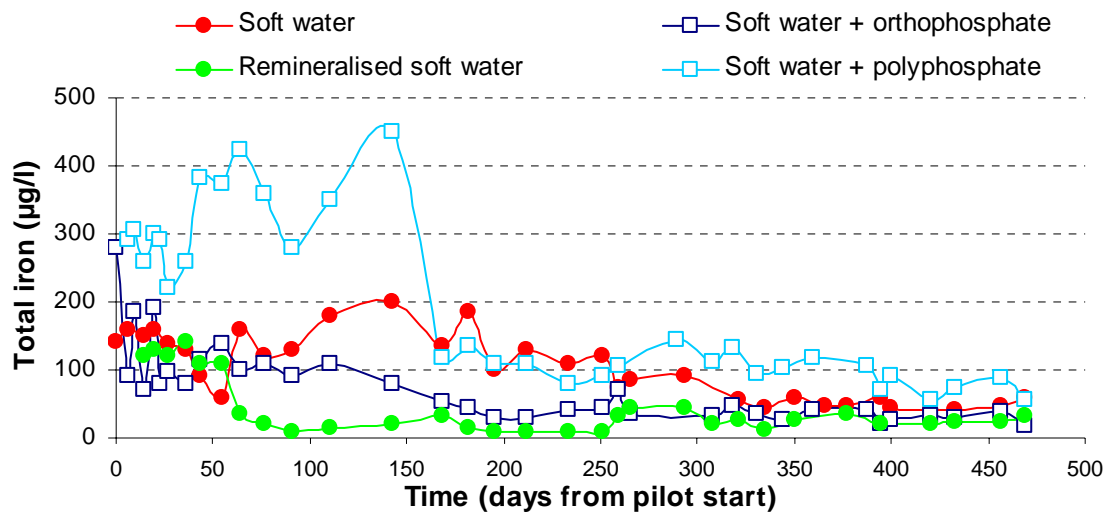

Figure 6. Iron release observed in loops with old unlined cast iron pipes

The figure 6 illustrates the iron released in the effluent of cast iron loops for each of the treatment strategies. These curves show the efficiency of both remineralisation and orthophosphate with total iron concentration two times lower than the concentrations observed at the outlet of the loop supplied with soft water. The polyphosphate treatment does not have a significant impact on soft water as shown with total iron content greater than the three others types of water (> 100 µg/l). These last results can be explained by the sequestering character of polyphosphate which forms complexes with Fe(III) in water thus the total iron measurements can be taken into account with the Fe-PO$_4$ complex produced.

As shown in Figure 7, the scrapping has a significantly impact on iron released with concentrations greater than the maximum admissible concentration of 200 µg/l during the first 2-months exploitation. At these high values, red water was observed. After two months, total iron release at the outlet of both remineralised soft water and untreated soft water loops were lower than 100 µg/l. These results are closer than those observed previously in Figure 6. During this phase, the red water effect disappeared. As for these two types of water, the improvement of water quality and the observation of pipe sections underlined the formation of an adherent scale deposits on the surface of scraped cast iron pipes. This type of scale strongly reduces corrosion rate and the dissolution of Fe(II) in water whose oxidation leads to the formation of ferric oxides (Fe$_2$O$_3$) that become suspended into the water and are visible in red water.

In the case of phosphate treatments, Figure 7 shows an important iron release (> 200 µg/l) during the first 5-months of the study. Thus, the total iron tends to progressively decrease due to the formation of a protective scale of ferric phosphate on the surface of scraped sections.
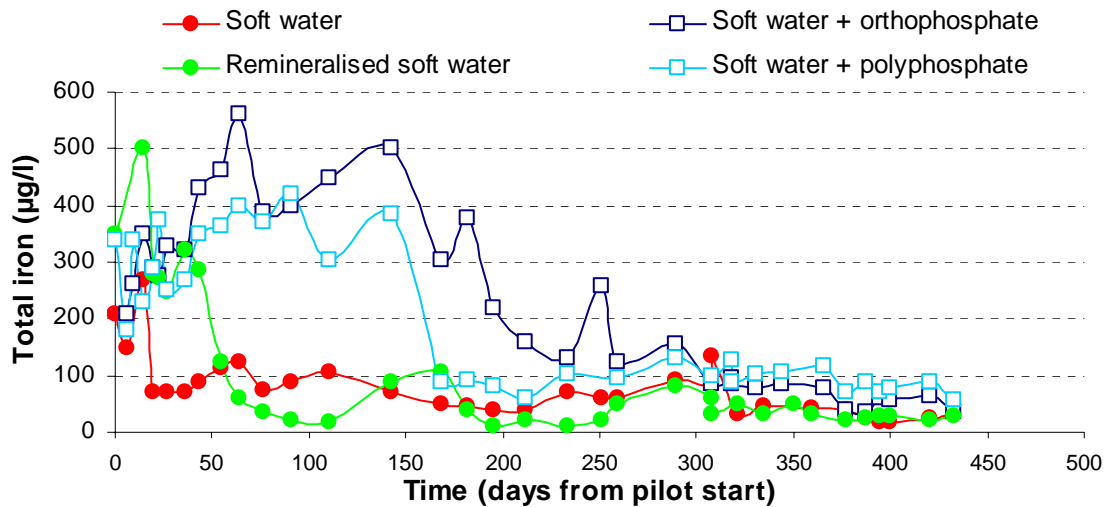

Figure 7. Iron release observed in loops with scraped old unlined cast iron pipes

The iron released in the effluent of loops with iron pipes is close to the one in the effluent of scraped cast iron loops (Fig. 8). As observed in Figure 7, the iron released at the outlet of both remineralised soft water and non-treated soft water decrease after 60 days. In the same time, phosphate treatments become active after only 150 days. The similarity in the results can be explained by the fact that scraped cast iron pipes present a surface similar to a new iron pipe whose the surface is uncovered.

The impact of orthophosphate was not immediately effective due to the slow implementation of an adherent film on a pipe surface due to the lack of initial scales. However, observations of water quality at the outlet of both scraped cast iron and iron pipes treated with phosphate didn't show any red waters phenomena in spite of high total iron values. These observations may be explained by the complexation of ferrous iron which involved in the removing of red waters, but this increases the total iron that is released.
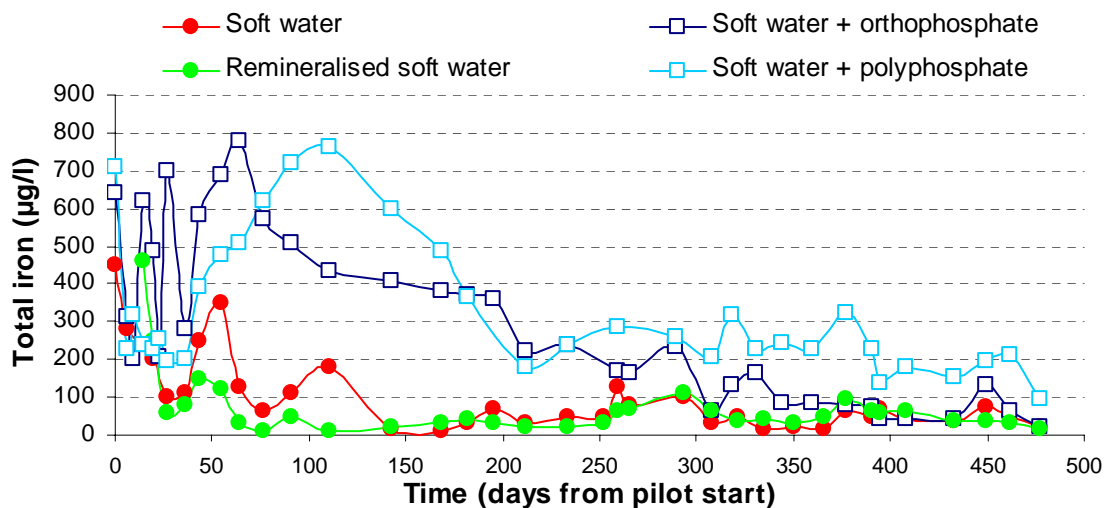

Figure 8. Iron release observed in loops with brand new iron pipes during the study

Finally, if we consider all of the experimental parameters (two inhibitors, three pipes-loops types), there were six different combinations of conditions. For five of the six conditions, the addition of either orthophosphate or polyphosphate increased the iron released in comparison with the results obtained for soft water (Figures 6 – 8). There was only one condition where the addition of

orthophosphate reduced iron release, the case of old unlined cast iron pipe-loop, where orthophosphate enabled an average iron reduction of 60 % in total iron release.

In response to the remineralisation, the iron levels are lower than 50 mg/l for all the types of iron pipes considered. As shown in Figures 8, 9 and 10, the remineralisation reduced iron release over a period of 2 months. This period can probably be attributed to the implementation of an equilibrium at the surface of the pipe material. Indeed, at the start of the study, pH and alkalinity slightly fluctuated so the formation of a protective scale took some time. Changes in alkalinity from 35 – 40 mg/ to 80 – 90 as CaCO3 showed that higher alkalinity resulted in lower iron release (Sarin *et al*, 2002). Calcite (CaCO3) plays a role in reducing the iron released in old unlined cast iron pipes by reducing the porosity of the scale. It is possible that a wide variety of conditions can exist locally as calcium carbonate deposits may form and block some of the pores inside corrosion scales. A comparison of iron release behaviour for the phosphate inhibitors and remineralisation shows that iron release was reduced to lower levels for remineralisation. Contrary to phosphate inhibitors, the remineralisation enables the formation of iron corrosion scale on the uncovered surface of the pipe wall (iron and scraped cast-iron).

Steel coupons

The iron corrosion rates in the pilot study are illustrated by weight loss measurements in Figure 9. The highest corrosion rates were found for the soft water and soft water treated with the two corrosion inhibitors. The lowest corrosion rate was observed for the re-mineralised soft water.
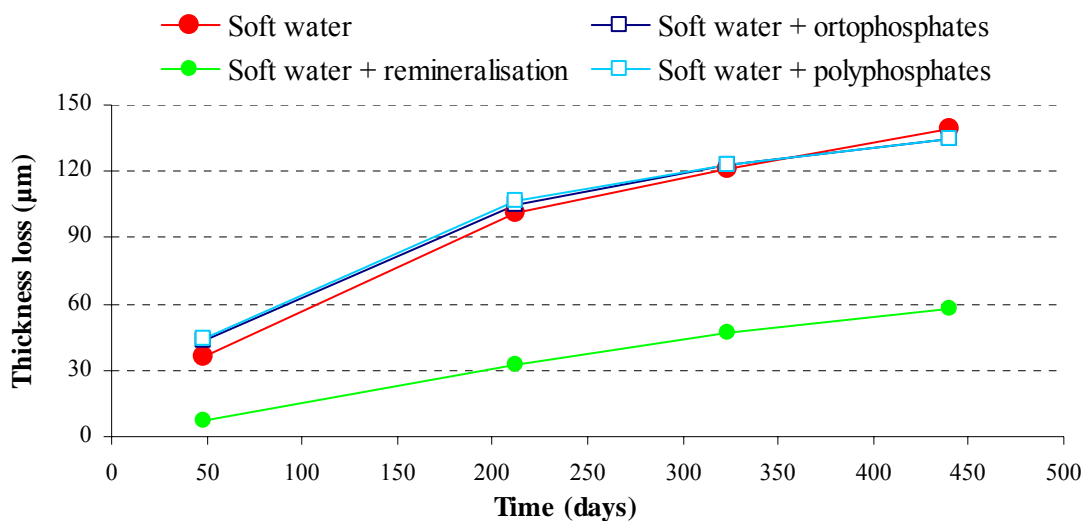

Figure 9. Iron corrosion measured with coupons (all points are averages of three samples)

The remineralisation assumed to form a protective layer composed mainly of calcium carbonate, the corrosion rates decreased after a short period, while no similar decrease was observed when a water quality that was supposed to be protected by a passivation scale such as phosphate inhibitor. The initial corrosion during the first ten months of the study was higher for the soft water treated with corrosion inhibitors than for the soft water. In fact, the protective layers are rarely established over the short term when inhibitor treatments are used (Hem *et al,* 2001). Based on the two last coupon samples (i.e. between 10 month and 14 month in Figure 9), the corrosion rate of steel was calculated for each water quality (Table 4).

Table 4. Summary of iron corrosion rate measured with coupons during the last three months of the pilot study

Water quality	Average corrosion rate with coupons (µm/y)	Average corrosion rate with probe (µm/y)
Soft water	57 ± 5	51
Re-mineralized soft water	33 ± 5	35
Soft water + orthophosphate	40 ± 5	45
Soft water + polyphosphate	50 ± 5	48

As shown in Table 4, the corrosion rates measured with coupons were highest for iron exposed to the soft water and soft water treated with polyphosphate. The re-mineralised treatment enables a reduction of the iron corrosion by 40%. The treatment with polyphosphate seems to have less of an effect on corrosion inhibition. Increased corrosion is often caused by the complexing and sequestering properties of polyphosphate leading to the formation of thinner protective layers. Contrary to polyphosphate, orthophosphate reduced the iron corrosion by 30%. This inhibiting effect can be due to the corrosion products which have formed insoluble phosphates and have improved the protective scale quality by increasing its impermeability and adherence (AWWARF, 1996).

Mild Steel corrosion probes

The corrosion rates measured with probes during the first ten months of the pilot study are shown in Figure 10. For all the water qualities, a fast decrease of the corrosion rate was observed during the period which followed the immersion. This phenomenon is due to the higher reactivity of the uncovered metallic surface. This phenomenon decreases during the formation of corrosion scale more or less protective. After one month, the corrosion rate of re-mineralized water tends to stabilise. This is contrary to soft water and soft water treated with phosphate inhibitor which didn't achieve stabilisation until the height month. The Table 4 addresses the corrosion rates at the stabilisation plateau for each water quality.
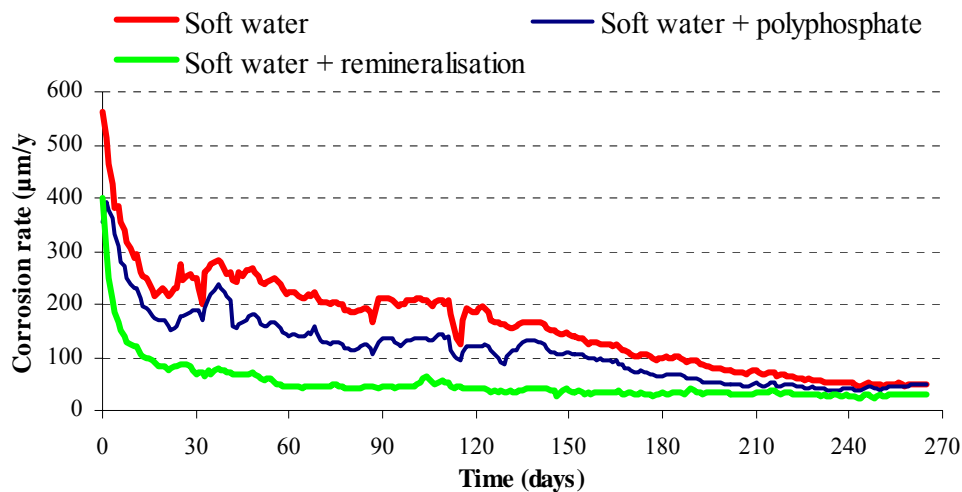

Figure 10. Iron corrosion rates measured with probes

The results of the probes confirm the results from the coupon tests, showing that the remineralisation of the soft water gives lower iron corrosion than soft water treated with polyphosphate inhibitor. The lowest corrosion rates have been observed for both corrosion tools with the remineralised soft water. It is possible to easily distinguish the stronger corrosion rates (soft water and soft water treated with polyphosphate) and the lower to moderate corrosion rates (re-mineralised water and reference water) with the corrosion probes and the steel coupons.

Discussion

The main objective of this study was to examine the impact of three water treatment strategies such as phosphate-based inhibitors and remineralisation (pH and alkalinity adjustment) that limit the corrosivity of soft water. This study was performed on a pipe-loop system in order to compare the effectiveness of these treatments on pipe materials used in both drinking water distribution systems (cast iron, scraped-cast iron and steel) and household plumbing systems (copper). Several methods were employed to make a detailed comparison to help the network operator to choose a suitable treatment. Therefore, the main purpose of this study was not to speculate on the processes and physicochemicals reactions involved in the pilot survey.

The results of the copper release studies provided information on the copper levels for different water qualities. The monitoring of copper leaching was performed for two stagnation times in copper pipe. Phosphates inhibitors and the remineralisation provided some significant degree of protection

over of the soft water. The remineralisation is the better approach to use for limiting the copper concentration at the consumer's tap, especially after long stagnation times.

The analytical survey performed on the different materials used that are representatives of those used in drinking water distribution systems underlines the beneficial impact of the remineralisation approach to reduce the iron released when exposed to soft water. Unlike the remineralisation, the action of phosphate inhibitors was rarely significant for controlling the iron released. Overall, these inhibitors tend to increase iron concentration of the water. Compared to polyphosphate, the orthophosphate treatment was better at limiting the iron released. Nevertheless, this was on old unlined cast iron pipes where these existing scales with high impermeability thus giving a reduced iron release. However, unprotected metallic pipes such as scraped cast iron and brand new steel pipes installed on the pilot, orthophosphates and polyphosphates didn't appear to provide any significant effect to reduce iron released over that obtained from the soft water.

The corrosion probe experiment and the steel coupon experiment gave similar results and showed the remineralisation of soft water reduced corrosion rate below that measured in the soft water. This water treatment tends to reduce the iron corrosion rate by 40 %.Contrary to remineralisation, orthophosphate reduced the corrosion rate by 30 % but only during the last three months of the study. This inhibiting effect can be due to the corrosion products. The inhibiting effect from orthophosphates can be due to the corrosion products which have formed insoluble phosphates and have improved the protective scale quality by increasing its impermeability and adherence Unlike these two pre-cited treatments, polyphosphates tend to increase scale thickness and overall weight loss. In fact, the major role of polyphosphate is to reduce red water phenomenon due to its complexing and sequestrating properties. These properties have no beneficial impact to reduce corrosion rate as the protective layers are not formed to the same degree of thickness. Overall polyphosphate tend also to increase total iron levels at the consumer's tap due to the complexation of ferric iron (Fe^{3+}).

CONCLUSIONS

This study provides detailed information for water utilities supplied with corrosive soft water to better manage their network and improve the water quality at the consumer's tap. The remineralisation treatment is reliable on all types of materials (scraped or not). This treatment approach can protect the all type of pipes from corrosion. This study also examined two different tools used to evaluate and follow the corrosion rate in a distribution system (coupons and electrochemical probes). Corrosion probes data corroborated the steel coupons data. Both techniques easily distinguish corrosive or no corrosive waters. For waters utilities, the probes are relatively expensive but the coupons are cheap. The coupons can be easily installed in both a distribution system and a household plumbing system and visual observations can be also performed to help network managers. Moreover, these coupons can also be used for biofilm analyses. Finally, these two tools constitute interesting devices to help water utilities to better survey and manage their drinking water distribution system.

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