Effect of chloramine residual on iron release in drinking water distribution systems

Y. Wang, X. J. Zhang, Z. B. Niu, C. Chen, P. P. Lu and F. Tang

ABSTRACT

Iron release from scale brought about serious problems such as noticeable increases in turbidity and colour of the water in distribution system and taps. Field study and bench scale experiment on iron release from corrosion scale were carried out. In old cast iron pipe, higher iron release occurred with lower chlorine residual concentration, while lower iron release occurred with higher chlorine residual concentration. The reason lay in the structure of scale and the electrochemical reactions occurring on the scale and in the bulk. The passivated-out-layer of scale was formed by ferric oxide. It could be broken down by reductive reaction in an atmosphere of low chlorine residual concentration. In contrast, the situation was quite different with new cast iron pipe, the age of which was only half a year. Iron release was considered as the product of the iron matrix and chlorine since the passivated-out-layer of scale had not formed yet. This iron release was consistent with chlorine residual concentration. It is suggested that maintaining a high chlorine residual concentration in a drinking water distribution system is beneficial to controlling both microorganism' regrowth and iron release.

Key words | chemical stability, chloramine, corrosion scale, drinking water distribution system, iron release

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INTRODUCTION

Maintaining water quality and keeping water stability in drinking water distribution system is a challenge for the water industry (Edwards 2004). The main problem to resolve is water instability in the distribution system especially for iron instability, biological instability and chlorine decay. Iron stability is one problem of chemical stability in distribution systems, including iron pipe corrosion, corrosion scale formation and iron release phenomena. It is very complicated because of the involuted physical, chemical and biological reactions and processes and reticular relationship among them.

Iron release from corrosion scale is the common reason for iron, turbidity and colour exceeding contaminant level. It is very important to study the factors that influence iron release. Many researchers had studied the effect of dissolved oxygen, pH, alkalinity and phosphate on iron

release in pilot-scale pipe-loop, and it was known that iron release rate decreased with pH, alkalinity, and dissolved oxygen increasing (Sarin *et al.* 2001, 2004). The factors of effect on iron release (Niu *et al.* 2007) had been studied in recent years. It was found that the iron release rate decreased with pH, alkalinity, the concentration of dissolved oxygen increasing, and the iron release rate increased with the concentration of chloride increasing.

Chlorine is an important water quality parameter which is widely used for water disinfection. Usually, chlorine must exist in the distributed water to prevent bacterial regrowth. According to the common assumption, iron concentration would higher with higher chloramine. Because of its high oxidation potential, chloramine can react with reductive material. Therefore, people thought that chlorine and chloramine could react with iron on the pipe wall,

and some researchers had found the similar results in batch-reactor with new iron pipes (Cantor *et al.* 2003). Nevertheless, pipe wall (corrosion scale) contacting with water possessed special characteristics (Sarin 2001), and the effect of chloramine may be different. But the effect of chloramine on iron release was not reported, especially under low oxygen concentration condition.

Reactions happening in on the micro-environment of pipe wall in distribution systems are a mystery attracting researchers. People cast their sights on iron release, chlorine decay and biofilm development in the pipe wall. The relationship between iron release and chlorine decay is complicated, and it is useful to keep water quality stability by understanding it. The objective of this study was to describe the effect of chloramine on iron release in drinking water distribution system. The study was conducted in full-scale distribution system and batch-scale experiment. Based on the results, it would provide theoretical and data support for controlling iron release and maintaining chloramine residual in drinking water distribution systems.

MATERIALS AND METHODS

Method of occurrence on full-scale distribution systems

This work was done in drinking water distribution system in a northern city of China. The sampling locations can be classified as three types of pipe characteristics, including old cast iron pipe (used for 15 years), cast iron pipe (used for 2 years), and new cast iron pipe (used for half a year).

Water was sampled and reserved by brown glass bottle, and was analyzed within 8 hours. All the glassware used in the experiment was soaked in 25% (V/V) concentrated HNO_3 for 24 hours, and rinsed with deionised water for three times. The water quality analytical items and methods were listed in Table 1.

Batch-scale experiment equipment

The research was carried out in Pipe Section Reactor (PSR) which was modified to analyze the effect of chloramine on iron release. This reactor is a continuous stirring tank

Table 1 | The analysis items and methods for water quality

Analytical items	Analytical methods
pH	pHB-4 analysis instrument
Water temperature (°C)	Ethanol thermometer
Total iron (mg/L)	Bathophenanthroline method
Dissolved oxygen (mg/L)	SensION analysis instrument
Chloramine (mg/L)	HACH analysis instrument

reactor and had been used for simulating chlorine pipe wall decay (DiGiano & Zhang 2005).

The pipe section reactor included pipe section, sleeve, stirrer, pilot tube, piezometer, and screw propeller, etc shown in Figure 1. The geometrical dimension of pipe section reactor is listed in Table 2. In the operation process, the screw propeller wheeled with the stirrer, and the water would be forced to move ahead, as a result, an internal circulated flow could be formed between the pipe section and sleeve. The pipe section was obtained from the full-scale distribution systems in a northern city of China which had been used for over 20 years and corroded severely. The sleeve, screw propeller, and flange plugs were made of polytetrafluoroethylene (PTFE), because this material is stable and cannot react with chloramine and other oxidative materials in the water.

The detailed physico-chemical characteristics of the pipe section corrosion scale were analyzed by SEM (Scanning Electron Microscope, JSM-6460LV model JEOL), XRF (X-ray Fluorescence spectroscopy, XRF-1700 model SHIMADZU), XRD (X-ray Diffraction, BRU KER2P4 model X-ray single crystal diffractometer) and XPS (X-ray Photoelectron Spectroscopy, PHI-5300 model).

The experiment using the pipe section reactor comprised the following procedure.
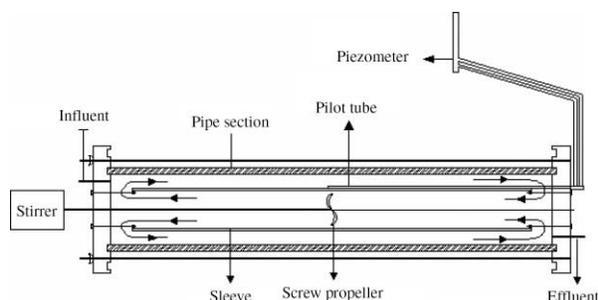

Figure 1 | Diagram of pipe section reactor.

Table 2 | Geometrical dimension of pipe section reactor

Diameter of pipe section (mm)	Diameter of sleeve (mm)	Length of pipe section (mm)	Length of sleeve (mm)	Volume of the reactor (L)
100	50	550	450	3.5

1. Pipe section flushing. Before the experiment, the reactor was filled with water with 20 mg/l chlorine concentration. The velocity of the stirrer was set at the highest value for 10 hours. The purpose for that was to flush the particles adhering to the pipe wall and protect the special physico-chemical structure of corrosion scale.

2. Water quality adjusting. After flushing, the adjusted water was conducted to the reactor. Water quality such as pH, concentration of dissolved oxygen and chloramine was adjusted. Nitrogen gas was used in stripping the dissolved oxygen. 0.1 M sodium hydroxide solution and 0.1 M hydrochloric acid solution were used to adjust pH. Chloramine residual concentration was maintained by titrating chloramine solution. The water quality was determined and the corresponding adjustment was operated to maintaining the special water quality condition.

3. Sampling and analyzing. An experiment under the setting condition would last for 10 hours. 70 ml of water sample was collected undisturbedly every 1 hour. pH, dissolved oxygen and chloramine were measured immediately. Iron concentration of the total samples was finally measured by the Bathophenanthroline method.

According to the experiment results, iron release rate under different conditions could be obtained by the formula (1)

$$\nu = \frac{C \times V}{S \times t} = \frac{C \times \pi \times R^2 \times l}{2\pi \times R \times l \times t} = \frac{500 \times R \times C}{t} \tag{1}$$

ν, iron release rate, mg/h/m^2; C, increase of iron concentration, mg/L; V, volume of the pipe section; S, interior area of the pipe section; R, interior radius of the pipe section, m; l, length of the pipe section; t, elapsed time, h.

4. Pipe section reactor maintenance. If the pipe section reactor was not used, water must keep on flushing the reactor.

RESULTS AND DISCUSSIONS

Occurrence on full-scale distribution systems

Much corrosion scale was found on the cast iron pipe with age of 15 years. The relationship between chloramine and dissolved iron is shown in Table 3 and Figure 2, which was obtained from the field study. High iron concentration occurred with low chloramine, and low iron concentration occurred with high chloramine. The concentration of chloramine in the distributed water from this pipe was lower than 0.3 mg/l. Iron concentration was over 0.3 mg/l, and it cannot meet the requirement in Chinese Drinking Water Quality Standard. When the chloramine

Table 3 | Chlorine residual and total iron in cast iron pipe used for different time

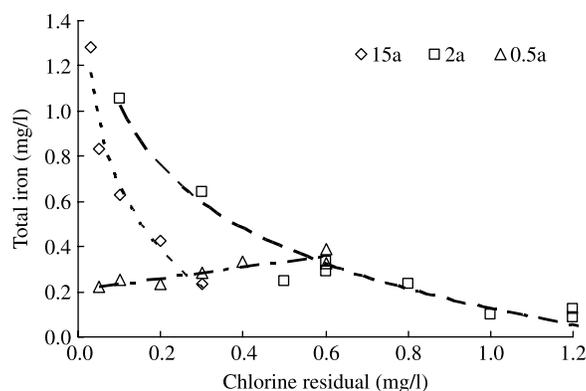| 15a		2a		0.5a	
Chlorine residual (mg/l)	Total iron (mg/l)	Chlorine residual (mg/l)	Total iron (mg/l)	Chlorine residual (mg/l)	Total iron (mg/l)
0.05	0.83	0.10	1.06	0.60	0.33
0.20	0.43	0.50	0.25	0.60	0.39
0.03	1.28	1.20	0.12	0.05	0.22
0.10	0.63	0.60	0.29	0.10	0.25
0.30	0.23	0.80	0.23	0.40	0.34
		0.60	0.33	0.20	0.23
		0.30	0.64	0.30	0.28
		1.20	0.09		
		1.00	0.10		

Figure 2 | Relationship between chlorine residual and total iron in a pipe used for 15 years, 2 years and half a year (pH was about 7.9, DO was 3 to 8 mg/l and alkalinity was about 194 mg/l calculated as $CaCO_3$).

concentration was very low (less than 0.05 mg/l), the iron concentration was over 1.2 mg/l. The colour of this water was light yellow, and the turbidity was higher than 3 NTU. The reasons for this phenomenon lie in two aspects. For one thing, this area was far from the water treatment plant, the retention time was as long as one day and the chloramine decayed greatly. On the other hand, the ferrous substance and biofilm on the old and corroded pipe would react with chloramine and reduce it quickly (LeChevallier *et al.* 1993).

For the cast iron pipe used for 2 years, the relationship between chloramine and released iron is shown in Table 3 and Figure 2. It exhibited the similar trend of the 15-year-old pipe except for higher chloramine residual maintained in the 2-year-old pipe. If the pipe had been used for more than 2 years, it would corrode and corrosion scales would be formed. When the chloramine concentration was over 0.6 mg/l, the iron concentration could be controlled less than 0.3 mg/l, which could satisfy the criteria. When the chloramine concentration was very low (0.05 mg/l), the iron concentration was as high as 1 mg/l.

For the cast iron pipe used for only half a year, the relationship between chloramine and released iron is shown in Table 3 and Figure 2. It was completely contrary with the above 2 pipes. High iron concentration occurred with high chloramine and low iron concentration occurred with low chloramine. Fortunately, the maximum concentration of dissolved iron was below about 0.3 mg/l, even with high chloramine concentration. Because this pipe has been just used for half a year, corrosion scales

have not been formed. So the redox reaction of chloramine and new pipe was different from old pipe.

Chloramine is one of the most important oxidants in water distribution systems, and it can react with iron metal and ferrous compounds to influence corrosion formation and iron release. High concentration of chloramine could control iron release from corroded in two ways. One was high chloramine could prevent Kuch phenomena happening, the other one was the low solubility of iron compounds.

In the corroded pipelines maintaining a high chloramine residual concentration in drinking water distribution system is beneficial to iron release control. According to the characteristics of corrosion scale, the Kuch mechanism can explain the effect of chloramine on iron release (Kuch 1988). The outer layer of the corrosion scale was in contact with bulk water and in strongly oxidative condition. The primary constituents of the outer layer were ferric compounds, and the outer layer can act as a passivated layer to prevent iron release. When the chloramine was depleted, ferric compounds were reduced to maintain the electrical chemical reaction. The passivated layer was destroyed and the primary constituents of the scale became ferrous compounds. As a result of high solubility of ferrous compounds, severe iron release phenomenon happened.

The solubility of ferric compounds was low when pH was over 4. When the released ferrous ions contacted chloramine in the bulk solution, they were oxidized to ferric ions immediately, which then precipitated as red or yellow ferric hydroxide particle and adhered to pipe wall to prevent iron release.

For new iron pipe, corrosion scales had not formed yet. The effect of chloramine was supposed to act in the mode of direct reaction with iron matrix. The reaction formulas were as follows.

$$NH_2Cl + Fe + H_2O \rightarrow Fe^{2+} + Cl^- + NH_3 + OH^-$$

$$NH_2Cl + 2Fe^{2+} + H_2O \rightarrow 2Fe^{3+} + NH_3 + OH^-$$
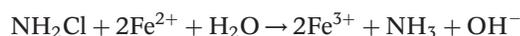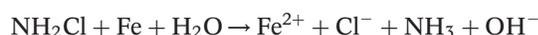
Ferrous ion could be dissolved to the bulk water, and reacted with chloramine into ferric sequentially. Because of the low solubility of ferric ion, it may precipitate and form corrosion scale gradually.

Table 4 │ Composition of the corrosion scale (calculated as oxide weight percent)

Fe_2O_3	SiO_2	ZnO	SO_3	Al_2O_3	Na_2O	CaO	MnO	Cr_2O_3	Cl	P_2O_5	MgO
93.38	1.99	0.09	3.42	0.27	0.02	1.02	0.11	0.07	0.30	0.15	0.03

Physico-chemical characteristics of corrosion scale

The characteristic of the corrosion scale from pipe section reactor was analyzed, including microstructure, chemical composition, crystalline structure and compound constitution. The main component of the scale was iron, then oxygen, sulfur, silicon and calcium in turn according to XRF analysis, as shown in Table 4. The structure of the corrosion scale composed of top surface layer, shell-like layer and porous core shown in Figure 3.

The possible compound constitution of the outer scale including top surface and shell-like layers was α-FeOOH, γ-FeOOH, α-Fe$_2$O$_3$, γ-Fe$_2$O$_3$, FeCl$_3$, while the inner was Fe$_3$O$_4$, FeCl$_2$, FeCO$_3$ (Niu *et al.* 2006). From the XRD experiment results shown in Figure 4, it could be found that the dominant compound of outer layer were compact α-FeOOH (CAS 81-0462) and Fe$_3$O$_4$ (88-0315), while the inner was incompact γ-FeOOH (76-2301).

According to the characteristics of the corrosion scale, the corrosion scale is the source of iron release. The special physico-chemical characteristics of the corrosion scale determined many water quality parameters may influence iron release. pH and alkalinity influenced the precipitation-dissolution equilibrium of iron compounds, while dissolved oxygen and chorine influenced oxidation-reduction equilibrium. Kuch mechanism was also based on the characteristics.

Effect of chloramine concentration on iron release in pipe section reactor

Dissolved oxygen (DO) is an important influence on iron release, and high concentration of dissolved oxygen can control iron release in water distribution system (Sarin *et al.* 2001). In order to know if chloramine can control iron release under low oxygen concentration, water (the concentration of DO was 0.5 mg/l) under different pH, and chloramine concentration was conducted into the pipe

section reactor whose pipe section was cast-iron and used for 20 years, and then iron release rate was obtained.

The gradient of pH was fixed at 6.8, 7.5 and 8.0, and chloramine concentration at 0, 0.05, 0.15, 0.3, 1.0 mg/l. During the experiment, pH, DO concentration and chloramine concentration were maintained stable (pH fluctuated within 0.2, DO fluctuated 0.3 mg/l and chloramine fluctuated 0.05 mg/l), and the iron release rate was determined. Iron release rate under low oxygen concentration conditions were listed in Figure 5.

When chloramine did not exist, iron release rates at pH = 6.8, 7.5, and 8.1 (DO = 0.5 mg/l, chloramine = 0 mg/l) were 0.590, 0.265, 0.173 mg/h/m^2, respectively. When chloramine concentration was 1 mg/l, iron release rates decreased greatly, and were recorded as 0.183, 0.165 and 0.018 mg/h/m^2, respectively. Chloramine can control iron release efficiently when chloramine concentration was above 0.3 mg/l. Low chloramine concentration can bring severe iron release. It could be concluded that iron release was low at high chloramine concentration, while high at low chloramine concentration. According to Kuch mechanism (Kuch 1988), in low reductive environment, ferric oxides as electrons accepter would be reduced to ferrous
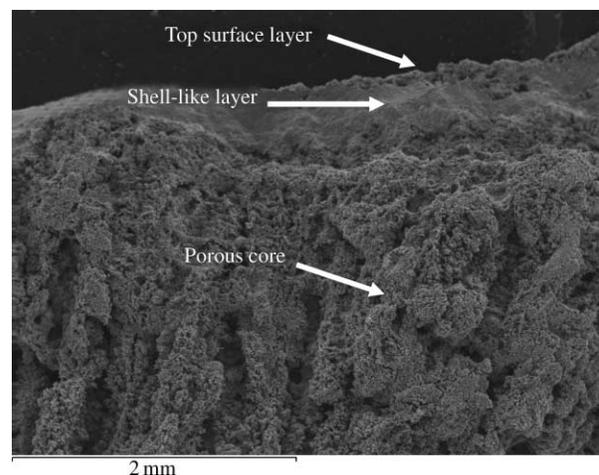
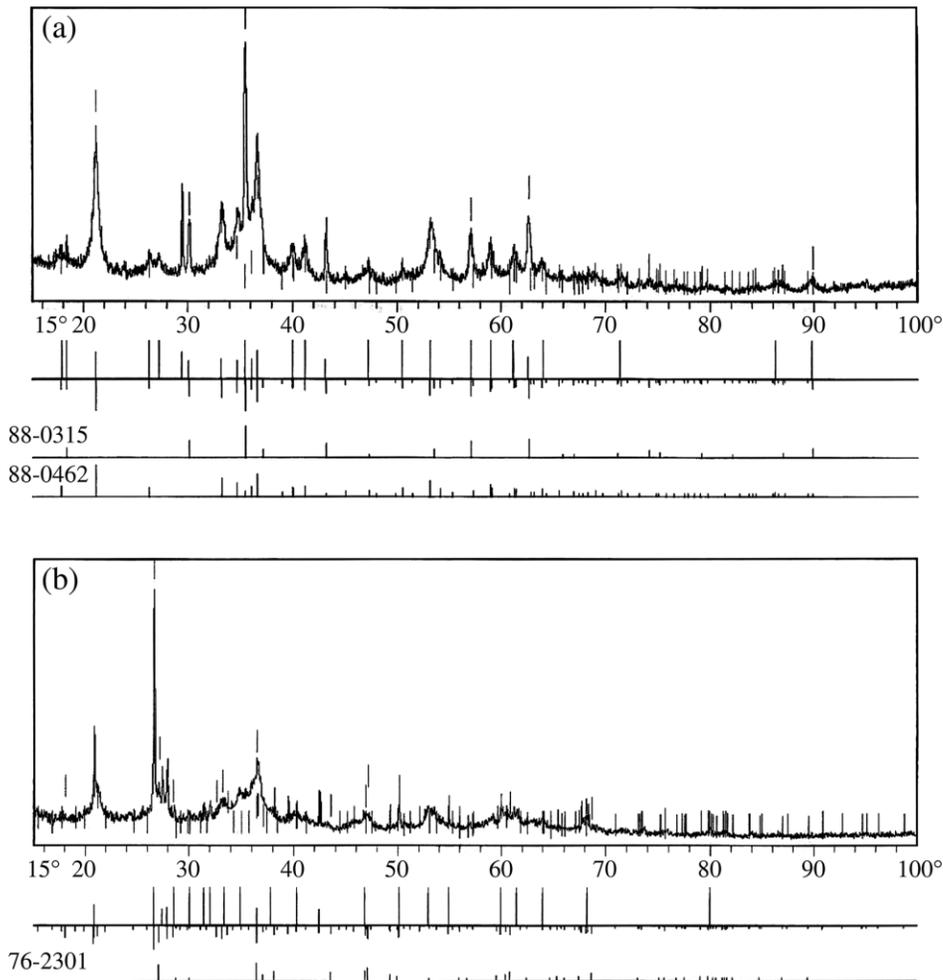**Figure 3** │ SEM photograph of the corrosion scale.

Figure 4 | Corrosion scale analyzed by XRD. (a) Outer layer, (b) Inner layer.
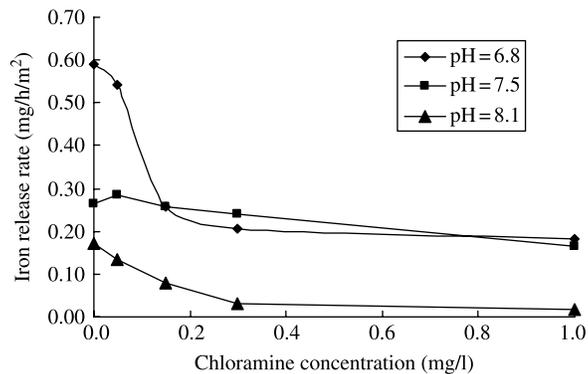

Figure 5 | Effect of chloramine on iron release rate (DO = 0.5 mg/l).

ions and dissolved to the bulk solution. Then the outer layer of corrosion scale (made of ferric compounds) was destroyed, and the inner core (made of ferrous compounds) was contact with bulk water directly, and large amount of iron diffused to the bulk water.

In full-scale water distribution systems, the concentration of chloramine varied largely in different parts. In the main pipes, the flow velocity was fast, the concentration of chloramine was high and the iron release rate was low accordingly. But in the dead ends and stagnant region, the concentration of chloramine was low which leading in large amount of iron release and "red water" problem (Sarin *et al.* 2004).

CONCLUSIONS

According to the experiment results, the following conclusions could be drawn.

1. In the corroded pipelines maintaining a high chloramine residual concentration in drinking water distribution system is beneficial to iron release control. The reason is that high concentration chloramine can prevent Kuch mechanism happening and help the formation of ferric compounds which could precipitate easily.

2. For the heavily corroded cast iron pipes, high iron concentration occurred with low chloramine, and low iron concentration occurred with high chloramine which could be explained by Kuch mechanism. For the non-corroded cast iron pipes, high iron concentration occurred with high chloramine, and low iron concentration occurred with low chloramine which was due to the direct reaction of chloramine with iron.

3. With PSR test, the reductive condition with low chloramine and low oxygen concentration can bring severe iron release. Chloramine residual above 0.3 mg/l can prevent iron release under low dissolved oxygen concentration condition efficiently.

ACKNOWLEDGEMENTS

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