

Iron stability in drinking water distribution systems in a city of China

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Abstract: A field study on the estimation and analysis of iron stability in drinking water distribution system was carried out in a city of China. The stability of iron ion was estimated by pC-pH figure. It was found that iron ion was unstable, with a high Fe(OH)₃ precipitation tendency and obvious increase in turbidity. The outer layer of the corrosion scale was compact, while the inner core was porous. The main composition of the scale was iron, and the possible compound constitutes of the outer scale were α -FeOOH, γ -FeOOH, α -Fe₂O₃, γ -Fe₂O₃, FeCl₃, while the inner were Fe₃O₄, FeCl₂, FeCO₃. According to the characteristics of the corrosion scale, it was thought that the main reason for iron instability was iron release from corrosion scale. Many factors such as pipe materials, dissolved oxygen and chlorine residual affect iron release. Generally, higher iron release occurred with lower dissolved oxygen or chlorine residual concentration, while lower iron release occurred with higher dissolved oxygen or chlorine residual concentration. The reason was considered that the passivated out layer of scale of ferric oxide was broken down by reductive reaction in a condition of low oxidants concentration, which would result more rapid corrosion of the pipe and red water phenomenon.

Keywords: chlorine residual; corrosion scale; dissolved oxygen; drinking water distribution systems; iron release; iron stability

Introduction

Although many water facilities have adopted pretreatment and advanced treatment technologies to improve drinking water quality, iron, turbidity and bacteria in tap water still cannot reach the requirements, indicating that water in distribution systems was biological instability and chemical instability (Yuan and Wang, 2003; Wu and Liu, 1998; Xu and He, 2002). Maintaining water quality and keeping water stability in drinking water distribution systems is a challenge and is viewed as a new frontier by the water industry. Consequently, many researches on the water quality problems in drinking water distribution systems were carried out.

The majority of distribution systems pipes were composed of iron material: cast iron (51.67%) and galvanized steel (23.85%) in China (Xu *et al.*, 2004), similarly, cast iron(38%), ductile iron(22%) and steel (5%) in the USA (Benjamin, 1996). Moreover, a survey in the year of 1997 of the 100 largest water utilities was found that the most common distribution system problem is the corrosion of iron material pipe (Edwards, 2004). Edwards considered that "controlling corrosion in drinking water distribution systems is a grand challenge for the 21st century" (McNeill and Edwards, 2001). According to the data provided by AWWA, 325 billion USD was cost to upgrade water distribution systems over the next 20

years, correspondingly, the USEPA estimate of 77.2 billion USD (McNeill and Edwards, 2001). Complaints of "red water" at the tap is becoming the most troublesome problem for water utilities all over the world (Xu and He, 2002; Benjanun, 1996). Therefore people must know the mechanism of iron stability to solve problems in water distribution systems.

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 the corrosion, scale formation and iron release.

Iron instability not only obstructs the flow of water, but also degrades the water quality. Many problems caused by iron instability are as follows: (1) it can form corrosion scale, increasing head loss and decreasing water capacity (Larson and Sollo, 1967); (2) it can cause iron release from the corrosion scale and severely cause "red water" problem (Sarin, 2001); (3) it can react with dissolved oxygen and chlorine residual in drinking water distribution systems (Sarin *et al.*, 2004; Fratuer *et al.*, 1999); (4) it can provide an excellent breeding ground for microorganism (Tuovinen *et al.*, 1980; LeChevallier *et al.*, 1993); (5) especially it can adsorb and accumulate arsenic (Raven *et al.*, 1998) and radium (Field *et al.*, 1995).

The objective of this study was to estimate the

iron stability, to describe the characteristics of corrosion scale and to analyze the influence factors on iron release in drinking water distribution systems in a city of China. The study was conducted using field experiments. Based on the findings the mechanism and control measurements of iron instability were also discussed.

1 Materials and methods

1.1 Setting of sampling locations

As shown in Fig.1, the sampling locations were set along a orbicular main lined cast iron pipeline (used about 10 years), including finished water, ordinary sampling locations(sampling point 1—7) and dead end(sampling point 8—9). According to the actual case in the city, other sampling locations with unlined cast iron and PVC pipes were also set.

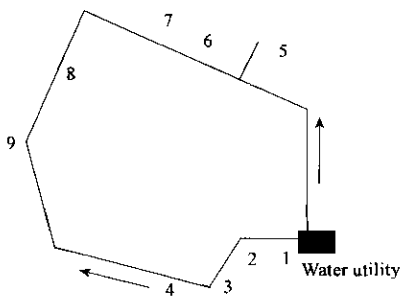


Fig.1 Sampling locations in the distribution systems

1.2 Sampling and analysis methods for water quality

The analysis items of water quality include pH, water temperature, turbidity, iron concentration, dissolved oxygen concentration, chlorine residual and alkalinity. The analysis methods for each item are shown in Table 1.

Table 1 Analysis items and methods for water quality

Analysis items	Analysis methods
pH	pHB 4 analysis instrument
Water temperature, °C	Ethanol thermometer
Turbidity	Hach2100 turbidity analysis instrument
Total iron, mg/L	Bathophenanthroline method
Dissolved oxygen, mg/L	SensION analysis instrument
Chlorine residual, mg/L	DPD titration method
Alkalinity, mg/L as CaCO ₃	Hydrochloric acid titration method

1.3 Sampling, pretreatment and analysis methods for corrosion scale

1.3.1 Sampling method

The corrosion scale was obtained from cast iron pipe and galvanized steel pipe in water distribution systems. In course of distribution systems upgrading,

Table 2 Analysis items and methods for corrosion scale

Analysis items	Analysis methods	Analysis instrument	Sample kind
Microstructure	SEM	KYKY-2800 scanning electron microscope	The outer layer bulk sample The inner core bulk sample
Chemical composition	XRF	SXF-1200 X-ray fluorescence spectroscopy	The powder sample
Crystalline structure	XRD	BRUKER-P4 X-ray diffraction spectroscopy	The outer layer powder sample The inner core powder sample
Compound constitute	XPS	PHI-5300 X-ray photoelectron spectroscopy	The outer layer powder sample The inner core powder sample

the pipes were excavated and cut. The pipes were filled with water and sealed in the two ends, then clean up the external mud of the pipe. The pipes were put into a box filled with cotton and foam in order to prevent the scale being destroyed.

1.3.2 Pretreatment method

The corrosion scale was dried under vacuum condition, and four kinds of scale were prepared. The samples were the outer layer bulk sample, the inner core bulk sample, the outer layer powder sample, the inner core powder sample. The scale was cut with a blade, and the bulk samples were prepared. The bulk samples were powdered with a mortar and pestle.

1.3.3 Analysis method

The analysis items, analysis methods, analysis instrument and sample kind are shown in Table 2. All the experiments were operated in the Analysis Centre, Tsinghua University.

2 Results and discussion

2.1 Analysis of iron stability

2.1.1 Estimation of iron stability

According to the iron concentration in Table 3, the pC-pH figure on Fe(III) is drawn as Fig.2(Larry *et al.*, 1982). In the figure, the bound of iron concentration and pH of the samples were in the solid

Table 3 Iron concentration of the samples

Sampling locations	1	2	3	4	5	6	7	8	9
pH	7.96	7.86	7.91	8.14	8.02	8.14	8.05	7.93	8.10
Iron concentration, mg/L	0.12	0.23	0.29	0.25	0.43	0.54	1.06	0.83	0.43
Iron concentration, $\mu\text{mol/L}$	2.14	4.11	5.16	4.46	7.68	9.64	18.93	14.82	7.68

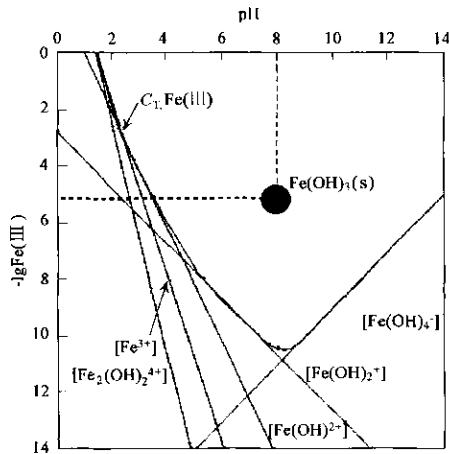


Fig.2 Solubility equilibrium pC-pH figure of iron(III)

ellipse. Consequently, Fe^{3+} in water can form $\text{Fe}(\text{OH})_3(\text{s})$, with a strong precipitation potential. So iron in drinking water distribution systems is unstable.

2.1.2 Comparison between finished water and tap water

The Chinese Ministry of Construction has set the maximum level for iron at 0.30 mg/L for drinking water, but in this study it was found that about 66.7% iron concentration of the samples of tap water were over 0.30 mg/L, several samples were over 1.00 mg/L. The iron concentration of finished water was at the range from 0.23 to 0.26 mg/L. Obviously, the iron concentration of tap water was far higher than finished water. Because the water utility used ferric chloride as coagulant, it has been thought that the coagulant should account for high iron concentration of tap water for a long time. However in this study, we found the coagulant could not bring about high iron concentration.

2.1.3 Relationship between iron concentration and turbidity

Turbidity of all the samples were over 1 NTU, and cannot attain the requirement set by Ministry of Construction of China. Like iron concentration of finished water, high turbidity of tap water was brought up in distribution systems.

In Fig.3, the turbidity increases with iron concentration, it can be seen relationship between the iron concentration and turbidity is linear. The reason is iron formed suspended particles($\text{Fe}(\text{OH})_3(\text{s})$). High iron concentration in water resulted in high amount

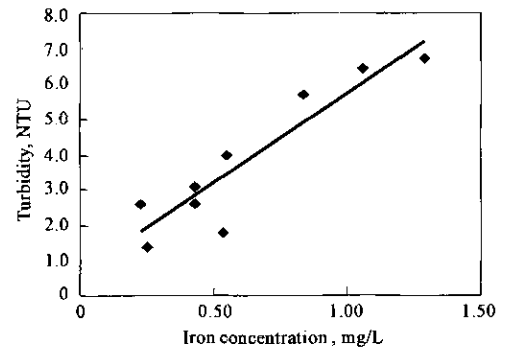


Fig.3 Relationship between iron concentration and turbidity

suspended particles (McNeill and Edwards, 2001). As a result, iron instability rendered high iron concentration and turbidity.

2.2 Characteristics of corrosion scale

Two kinds of pipe were obtained. One was 3.2 cm diameter 10-year old cast iron pipe, while the other was 3.2 cm diameter 8-year old galvanized steel pipe.

2.2.1 Appearance characteristics of corrosion scale

Fig.4 shows that obvious corrosion scale were found on the internal of both cast iron pipe and galvanized steel pipe. The corrosion scale on cast iron pipe was heavily tuberculated, with a thickness of 0.3—0.9 cm. The scale was substantial and hard to destroy. The outer layer was reddish smooth curve surface while the inner core was black compact solid. The corrosion scale on galvanized steel pipe was uniform, with a thickness of 0.1—0.3 cm. The scale was loose and prone to be destroyed. The outer layer was reddish rough curve surface with cracked particles on it, while the inner core was loose black solids.

The appearance characteristics of the scale on cast iron was similar to the former studies(Sarin *et al.*, 2001; Lin *et al.*, 2001). But the scale on galvanized steel pipe appeared different characteristics. The reason for that is the difference of hydraulic condition. The water in cast iron pipe was flowing all the time while galvanized steel pipe was in long-term stagnant condition. The flowing water directly scoured the scale and formed the substantial smooth scale, while the stagnant condition resulted in suspended particles sedimentation and formed loose cracked scale.

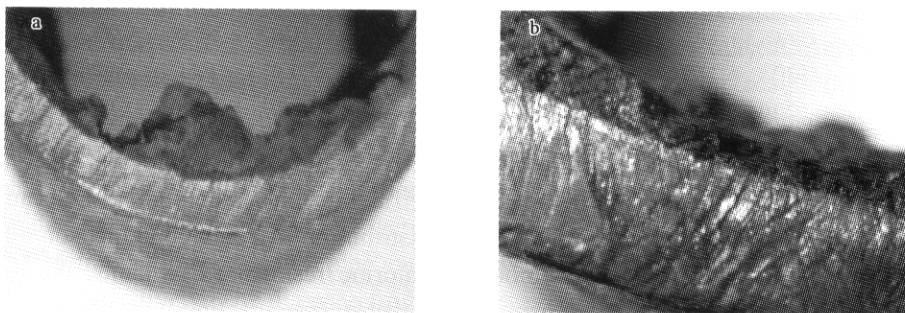


Fig.4 Appearance characteristics of corrosion scale in the cast iron pipe(a) and galvanized steel pipe(b)

2.2.2 Microstructure of corrosion scale

The microstructure of the scale was analyzed by SEM. The results are shown in Fig.5. Both the scale on cast iron pipe and on galvanized steel pipe had a similar microstructure. The microstructure of outer layer was disparate from the inner core. The outer layer was flat and close-grained, while the inner core

was porous. Because of the microstructure characteristics of scale, once water penetrated the outer layer, it can directly pass through the porous core to contact with the iron metal. As a result, corrosion will continue to happen although the corrosion scale had formed.

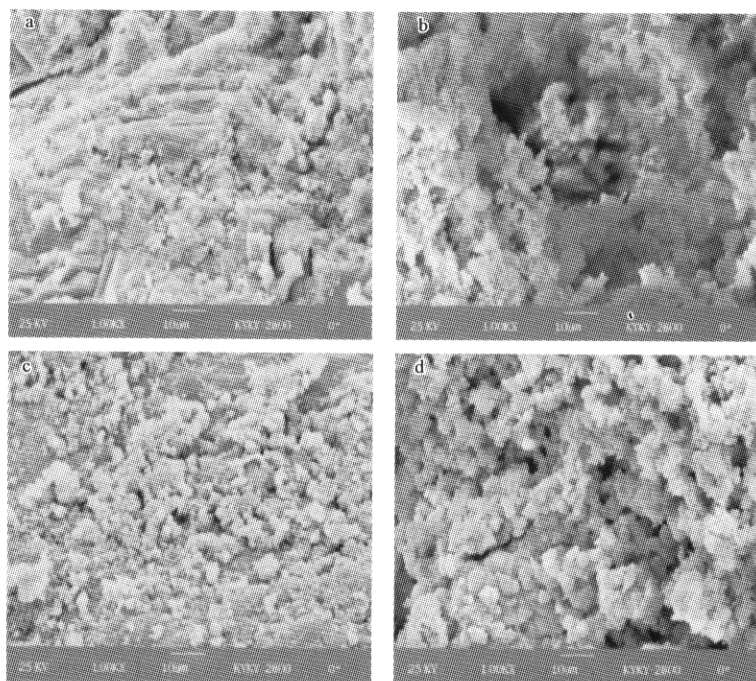


Fig.5 Micrograph of corrosion scale of cast iron pipe(a,b) and galvanized steel pipe(c,d) using SEM
a, c: outer layer; b, d: inner core

2.2.3 Chemical composition of corrosion scale

Because EDS (Energy Dispersive Spectrometer) only detected iron as chemical composition, XRF was used for more exactly chemical composition analysis. XRF can determine elements with atomic number 4 or greater, but EDS can only determine elements with number 11 or greater.

The chemical composition results are shown in Table 4. The main composition of scale on cast iron pipe in turn was iron, oxygen, sulfur, silicon and calcium, while that on galvanized steel pipe was iron, zinc, oxygen, sulfur, silicon and calcium. Iron was the

uppermost composition, with content over 90% (calculated as ferric oxide). Consequently, the scale must be composed of iron compounds.

2.2.4 Crystalline structure of corrosion scale

XRD was used to analyze the crystalline structure. Because of the low precision of the X-ray diffraction spectroscopy, only a few sorts of crystalline structure were detected.

For the corrosion scale from cast iron pipe, the crystalline structure was α -FeOOH (goethite) and γ -FeOOH (lepidocrocite), while the inner core was Fe₃O₄ (magnetite). The results are consistent with Sarin,

Table 4 The composition of cast iron pipe and galvanized pipe(calculated as oxide weight percentage. %)

Chemical composition	Fe ₂ O ₃	SiO ₂	ZnO	SO ₃	Al ₂ O ₃	Na ₂ O	CaO	MnO	Cr ₂ O ₃	Cl	P ₂ O ₅	MgO
Cast iron pipe	93.38	1.99	0.09	3.42	0.27	0.02	1.02	0.11	0.07	0.30	0.15	0.03
Galvanized steel pipe	92.10	2.58	1.75	1.41	0.73	0.05	1.09	0.08	0.06	0.08	0.07	0.01

Lin and Kevin's studies (Sarin *et al.*, 2001; Lin *et al.*, 2001; Kevin, 1996). On the other hand, the crystalline structure of outer layer from galvanized steel pipe was Fe₂O₃ (iron oxide), while the inner core was amorphous. The reason for that may also is hydrodynamic effect. Flowing condition is in favor of forming crystalline.

An interesting phenomenon was that for both scales, the crystalline structure of outer layer was

ferric compounds, while the inner core was mixed ferric and ferrous compounds. Because bulk water in distribution systems contained dissolved oxygen and chlorine residual as oxidants, the redox potential at outer layer contacting bulk water was higher than the inner core. In higher redox potential condition, ferric compounds were formed, while ferrous compounds were formed in low redox potential condition(Fig.6).

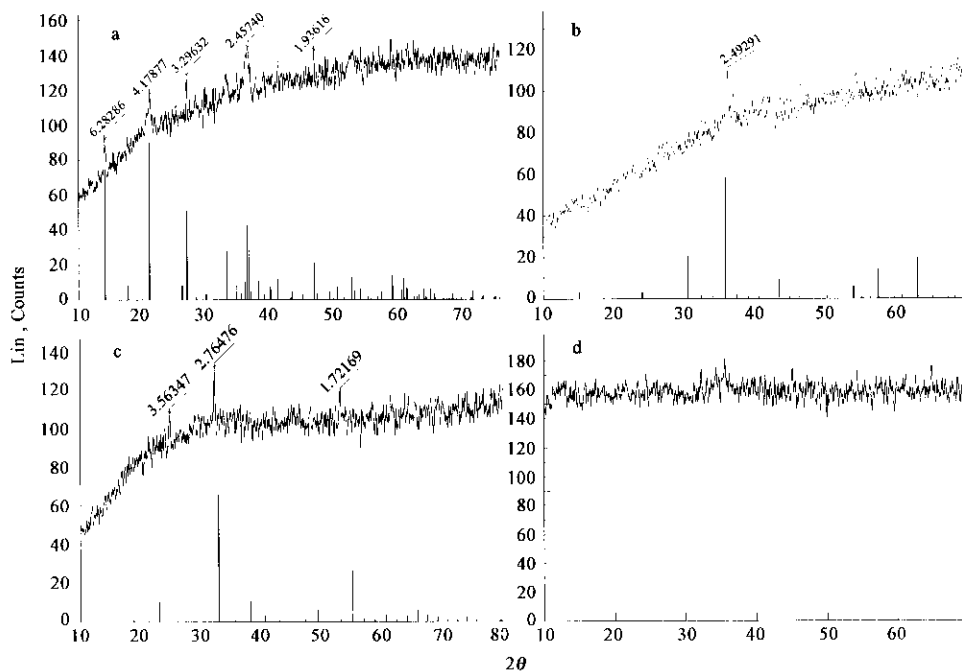


Fig.6 Corrosion scale in corroded cast iron pipe(a, b) and galvanized steel pipe(c,d) analyzed by XRD

2.2.5 Compound constitute of corrosion scale

Because XRD cannot list the whole compounds of corrosion scale, XPS was used to determine the possible compound constitute.

The results appeared that the possible compound constitute was similar between scale from cast iron pipe and galvanized steel pipe. The compounds of outer layer may be α -FeOOH, γ -FeOOH, α -Fe₂O₃, γ -Fe₂O₃, FeCl₃, while inner core was Fe₃O₄, FeCl₂, FeCO₃. It is consist with Sontheimer's result (Sontheimer *et al.*, 1981), but green rust (Fe₄²⁺ Fe₂³⁺ (OH)₁₂CO₃) known as an important compound of corrosion scale was not found(Refait *et al.*, 1998). It is because that the corrosion scale had been stayed for a month before XPS analysis, the green rust had already been oxidized to other iron compounds.

2.3 Influence factors on iron release

According to the characteristics of corrosion scale, corrosion scale provided favorable conditions for iron release, and it is the significant reason for iron instability in drinking water distribution systems. Many water parameters including dissolved oxygen (Sarin and Edwards., 2004), chlorine residual(Abigail and Edwards, 2003), pH(Beckett, 1998; Clement *et al.*, 2002), alkalinity (Pisigan and Singley, 1987), temperature (McNeill and Edwards, 2002a) and phosphate (McNeill and Edwards, 2002b), influence iron release from corrosion scale to bulk water in drinking water distribution systems. Because this study was carried out in full-scale water distribution systems, the changeful parameters were dissolved oxygen and chlorine residual. The other parameters were usually stable. As a result, the effects of pipe material, dissolved oxygen and chlorine residual on

iron release were discussed as follows.

2.3.1 The effect of pipe material

Unlined cast iron pipes, lined cast iron pipes and PVC pipes were the ordinary pipes used in water distribution systems in the city. Four sampling locations were set to compare the iron concentration in different pipe materials. Location A, B, C, D were PVC pipe, lined cast iron pipe, lined cast iron pipe and unlined cast iron pipe, respectively. The distance from location A to the water utility was the same as that of location B, so as C and D. The results are shown in Table 5. Iron concentration in PVC pipe was lower than that in lined cast iron pipe, and it was the highest in unlined cast iron pipe. This result may be explained that the internal of PVC pipe and lined cast iron had little corrosion scale, but the unlined cast iron pipe had thick corrosion scale to release.

Table 5 Concentration of iron in different pipe materials

Sampling location	Iron concentration, mg/L				Average value
	1	2	3	4	
A	0.119	0.073	0.052	0.073	0.079
B	0.124	0.088	0.160	0.099	0.118
C	0.325	0.387	0.284	0.253	0.312
D	1.283	0.629	0.426	0.233	0.643

2.3.2 The effect of dissolved oxygen

The relationship between dissolved oxygen and concentration of iron is shown in Fig.7. High iron concentration occurred with low dissolved oxygen, and low iron concentration occurred with high dissolved oxygen. Generally, the concentration of dissolved oxygen was 7–9 mg/L and the corresponding iron concentration was under 0.20 mg/L, but in the dead ends, dissolved oxygen was 2–4 mg/L and iron concentration was over than 0.60 mg/L then. The results are consist with that studied by Sarin with pilot pipe-loop systems(Sarin *et al.*, 2004).

Dissolved oxygen is one of the most important oxidants in water distribution systems, and it can react

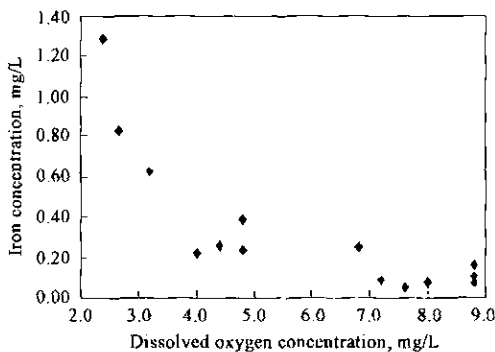


Fig.7 The relationship between dissolved oxygen and iron in distribution system

with ferrous compounds to influence corrosion formation and iron release. According to the characteristics of corrosion scale, the mechanism of the effect of dissolved oxygen on iron release was hypothesized. The outer layer of the corrosion scale contacted with bulk water and was in high redox potential condition. The primary constitutes of outer layer were ferric compounds, and the outer layer can act as a passivated layer to prevent iron release. When the dissolved oxygen was depleted, ferric compounds were reduced to maintain the electrical chemical reaction. The passivated layer was destroyed and the primary constitutes of the scale became ferrous compounds. As a result of high solubility of ferrous compounds, severe iron release phenomenon happened. Consequently, high concentration of dissolved oxygen can prevent iron release in drinking water distribution systems.

2.3.3 The effect of chlorine residual

As seen in Fig.8, the relationship between chlorine residual and iron concentration exhibited the similar trend. The reason for that was based on two hypotheses. One is from the point of chemical analysis; the other is from biological view.

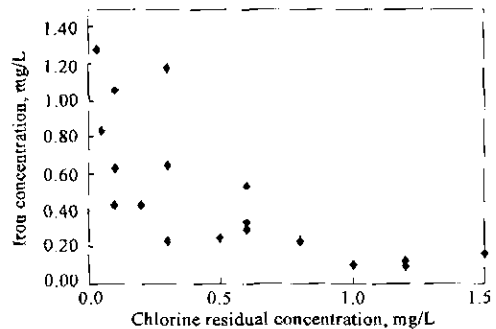


Fig.8 The relationship between chlorine residual and iron in distribution system

From the chemical point, the explanation is the same as the mechanism of effect of dissolved oxygen on iron release.

From the biological point, chlorine residual is not only an oxidant, but also a disinfectant. It can inactivate microorganism on the corrosion scale. The bacteria especially iron bacteria can induce iron release(Xu, 2000), so in high concentration of chlorine residual iron bacteria must be inactivated and prevent iron release phenomenon.

3 Conclusions and suggestions

Iron stability is an extraordinary complicated problem in drinking water distribution systems. Iron is unstable in the drinking water distribution systems,

with a strong Fe(OH)₃ precipitation potential.

Ferric compound coagulant could not bring about high iron concentration, the real reason for that is iron release from corrosion scale. The relationship between the iron concentration and turbidity is linear, and high iron concentration in water resulted in high amount suspended particles.

The outer of the scale was compact, while the inner was porous. The main composition of the scale was iron, and the possible compound constitute of the outer scale was α -FeOOH, γ -FeOOH, α -Fe₂O₃, γ -Fe₂O₃, FeCl₃, while the inner was Fe₃O₄, FeCl₂, FeCO₃. According to the characteristics of the corrosion scale, the corrosion scale is the source of iron release.

Pipe material, dissolved oxygen and chlorine residual influence iron release from corrosion scale to bulk water in drinking water distribution systems. Maintaining a high dissolved oxygen and chlorine residual concentration in drinking water distribution system is also beneficial to iron release control to reduce pipe corrosion.

There are still many other factors influencing iron release phenomenon, for example, hydraulic condition is also a very important factor affecting iron release. As a result, further study should be continued.

References:

- Abigail F C, Jac K P, Prasit V *et al.*, 2003. Effect of chlorine on corrosion in drinking water systems [J]. American Water Works Association, 95(5): 112—123.
- Beckett M A, 1998. The investigation of iron release phenomena using pilot-scale pipe loop[D]. University of Illinois at Urbana- Champaign.
- Benjamin M M, 1996. Internal corrosion of water distribution systems [Z]. 2nd ed. American Water Works Association Research Foundation.
- Clement J A, Hayes M E, Sarin P *et al.*, 2002. Development of red water control strategies[Z]. AWWA Research Foundation.
- Edwards M, 2004. Controlling corrosion in drinking water distribution systems: a grand challenge for the 21st century[J]. Water Science and Technology, 49(2): 1—8.
- Field R W, Fisher E L, Valentine R L *et al.*, 1995. Radium-bearing pipe scale deposits-Implications for National waterborne radon sampling methods [J]. American Journal of Public Health, 85(4): 567—570.
- Fratuer I, Deslouis C, Kiene L *et al.*, 1999. Free chlorine consumption induced by cast iron corrosion in drinking water distribution systems[J]. Water Research, 33(8): 1781—1790.
- Kevin J, 1996. Investigation of iron release from galvanized pipe section [D]. B.S. thesis. University of Illinois at Urbana- Champaign.
- Larry D B, Joseph F J, Barron L W *et al.*, 1982. Process chemistry for water and wastewater treatment [C]. New Jersey: Prentice Hall, Inc, Englewood Cliffs.
- Larson T E, Sollo Jr F R, 1967. Loss in water main carrying capacity[J]. American Water Works Association, 59(12): 1565—1572.
- LeChevallier M W, Lowry C D, Lee R G *et al.*, 1993. Examining the relationship between iron corrosion and disinfection of biofilm bacteria[J]. American Water Works Association, 85(7): 111—123.
- Lin J P, Ellaway M, Adrien R *et al.*, 2001. Study of corrosion materials accumulated on the inner wall of steel water pipe [J]. Corrosion Science, 43(11): 2065—2081.
- McNeill L S, Edwards M, 2001. Iron pipe corrosion in distribution systems[J]. American Water Works Association, 93(7): 88—93.
- McNeill L S, Edwards M, 2002a. Phosphate inhibitor use at US utilities [J]. American Water Works Association, 94(7): 57—63.
- McNeill L S, Edwards M, 2002b. The importance of temperature in assessing iron pipe corrosion in water distribution systems [J]. Environmental Monitoring and Assessment, 77(3): 229—242.
- Pisigan R A, Singley J R, 1987. Influence of buffer capacity, chlorine residual and flow rate on corrosion of mild steel and copper[J]. American Water Works Association, 79(2): 62—70.
- Raven K P, Jain A, Loeppert R H *et al.*, 1998. Arsenite and arsenate adsorption on ferrihydrite-Kinetics, equilibrium, and adsorption envelopes [J]. Environmental Science and Technology, 32(3): 344—349.
- Refait P, Abdelmoula M, Genin J M *et al.*, 1998. Mechanisms of formation and structure of green rust in aqueous corrosion of iron in the presence of chloride ions [J]. Corrosion Science, 40(9): 1547—1560.
- Sarin P, 2001. Iron release from corrosion scales in old iron/steel drinking water distribution pipes[D]. The USA: UIUC.
- Sarin P, Snoeyink V L, Bebeeb J *et al.*, 2001. Physico-chemical characteristics of corrosion scales in old iron pipes [J]. Water Research, 35(12): 2961—2969.
- Sarin P, Snoeyink V L, Bebeeb J *et al.*, 2004. Iron release from corroded iron pipes in drinking water distribution systems: effect of dissolved oxygen[J]. Water Research, 38(5): 1259—1269.
- Sontheimer H, Kolle W, Snoeyink V L *et al.*, 1981. The siderite model of the formation of corrosion-resistant scales[J]. American Water Works Association, 73(11): 572—579.
- Tuovinen O H, Button K S, Vuorinen A *et al.*, 1980. Bacterial, chemical, and mineralogical characteristics of tubercles in distribution pipelines[J]. American Water Works Association, 72(11): 626—635.
- Wu H W, Liu W J, 1998. The characteristics and control measures of scale in drinking water distribution systems [J]. China Water and Wastewater, 14(3): 37—39.
- Xu B J, 2000. The theory of water treatment [M]. Beijing: The Chinese Construction Industry Publishing Company.
- Xu B, He Y J, 2002. The practice and discussion on improving water quality in water distribution systems [J]. Water and Wastewater, 28(12): 13—16.
- Xu B F, Hu Y F, Yang Z *et al.*, 2004. The analysis of common pipe materials in water distribution systems [J]. Design of Colored Metal, 31(1): 60—63.
- Yuan Z B, Wang Z S, 2003. The study on prevention of water polluting in drinking water distribution systems [J]. Tianjin Construction Sciences, (2): 30—31.

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