Diagnosis of the ageing of water pipe systems by water quality and structure of iron corrosion in supplied water

Yoshiyuki Ishiwatari, Iori Mishima, Norihiko Utsuno and Masafumi Fujita

ABSTRACT

To develop a method for screening ageing of water supply systems by analysing the supplied water’s quality, water samples were collected from a water treatment plant, a delivery pump station, two distribution reservoirs and two feed pipes along a water pipe system. Principal component analysis of the water was conducted. In the first principal component, many elements exhibited high factor loadings, whereas the major contributor for the second principal component was iron (Fe). The unlined steel pipe, which was beyond its working lifetime, had a significantly high Fe content in suspended solids. X-ray absorption fine structure (XAFS) analysis showed differences in the abundance ratios of Fe$_3$O$_4$ and \( \alpha \)-FeOOH among the sampling points. It was concluded that the concentration and speciation of Fe in supplied water can be a useful index for detecting the ageing of pipes.

Key words | iron corrosion, pipe ageing, water pipe, water quality, XAFS

INTRODUCTION

A large number of water pipe systems were laid in Japan during the 1970s, which have now passed their 40 years working lifetime (Mimura 2008). Deterioration in the water quality such as the occurrence of red water and an increase in maintenance issues often result from the corrosion of pipes by ageing (Sarin et al. 2004a). Additionally, many water pipes were damaged by the 2011 earthquake off the Pacific coast of Tohoku. Therefore, it is important to develop a prioritisation procedure for replacing aged water pipes along with a replacement schedule.

Water pipe replacement is usually scheduled according to the year in which the line was laid; yet the extent of ageing due to corrosion can differ among pipes laid in the same year. This means that the replacement schedule should be based on the extent of ageing. Observation using an underwater camera (Ogawa 2009) is one investigation method with a reported high precision due to the extent of ageing being verified by human monitoring. However, because of the expense and lengthy duration of an underwater-camera investigation, the technique is unusable for large areas. Thus, the development of an inexpensive, easy screening method to detect ageing pipes is urgently required. Against this backdrop, an affordable and simple screening method to detect ageing pipes based on water quality in a water pipe system is sought.

Quantitative research using water quality indices on the deterioration diagnosis of the water pipe network was conducted by the Japan Water Research Center in Japan. The research described the possibility that the extent of ageing of a water pipe could be determined according to the amount of suspended substances and the consumption rate of residual chlorine (Japan Water Research Center 2008). Considering the chemical composition of water supply samples can provide further information on the extent of pipe ageing.
Barkatt et al. (2009) used X-ray diffraction (XRD) to measure suspended solids in cold tap water obtained from an old building. Although XRD is commonly used to analyse the speciation of iron (Fe), the sensitivity of XRD is too low to effectively analyse the suspended solids gathered from a water supply system. This is because the suspended solids’ concentration in a water supply system is often too low; moreover, Fe oxidation occurs during pre-processing for XRD (Sarin et al. 2000, 2001). This highlights the need for a higher sensitivity technique, which can measure a wet sample, such as X-ray absorption fine structure (XAFS), to analyse Fe speciation of pipe corrosion.

In this study, water quality was analysed at six points along a water supply system, including an ageing unlined steel pipe. To establish a useful index for detecting ageing pipes, differences in the concentrations of the major elements in water and the speciation of Fe in suspended solids among the sampling points were analysed.

**MATERIALS AND METHODS**

**Sampling from a water pipe system**

Water samples were obtained from a water treatment plant, a delivery pump station, two distribution reservoirs and two feed pipes (Figure 1) in Hitachi City, Ibaraki Prefecture, Japan. The processing volume at the water treatment plant is approximately 108,000 m³/d, and the water supply system splits into two at the delivery pump station. There were 0.9-km mortar lining steel pipes with 38 years of service (A2–AA1, Figure 1), a 2.1-km unlined steel pipe with 50 years of service (AA–AA2), a 1.6-km mortar lining steel pipe with 41 years of service (A2–AB1) and a 4.3-km mortar lining ductile cast iron pipe with 20 years of service (AB1–AB2). There was no information from A1 to A2 (10 km). Because the working lifetime of the water pipe is specified as 40 years in Japan (Mimura 2008), the ages of the pipes between A2 and AA1, AA1 and AA2 and A2 and AB1 are regulated for life or more.

Figure 2 shows the flow of analysis for the sampled water. A water sample was used to analyse the concentration of elements. Suspended solids were gathered by filtration using a membrane filter with a 0.45-μm pore size. For quantitative analysis of elements in suspended solids, 7 L of sampled water were filtered. For speciation analysis of Fe in suspended solids, 20 L or 10 L (at AA2) was used.

**Chemical analysis**

**Chemical elements in water**

The concentration of sodium (Na), magnesium (Mg), aluminium (Al), silicon (Si), phosphorus (P), sulphur (S), potassium (K), calcium (Ca), manganese (Mn), zinc (Zn), lead (Pb), chromium (Cr), nickel (Ni) and Fe in water was analysed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and ICP-mass spectrometry (ICP-MS). Suspended solids were dissolved in acid, and the speciation of Fe was determined by XAFS.

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**Figure 1** | Sampling points along the water supply system.

**Figure 2** | Analysis of the flow for water samples.
spectroscopy (ICP–AES) (Ciros 120, Rigaku) and inductively coupled plasma mass spectrometry (ICP–MS) (Agilent 7500, Agilent) (Figure 2).

**Chemical elements in the suspended solids**

The suspended solids collected on the membrane filter were dissolved in 10 mL of 60% nitric acid and 5 mL of 60% perchloric acid at 150°C. Next, they were diluted to 50 mL with deionised water, and their Al, Si, Ca, Mn, Fe and Zn concentration was analysed by ICP–AES. The results were normalised to the original water volume by considering 140:1 concentration upon deposition and dissolution.

**Speciation of Fe in suspended solids**

XAFS analysis was performed to characterise the Fe structure in the suspended solids obtained from filtration (Figure 2). Suspended solids were kept in water. The Fe K-edge XAFS spectra were measured in a wet state using BL-3 at the Synchrotron Radiation Center of Ritsumeikan University, Japan, equipped with an Si (220) double-crystal monochromator. The fluorescence yield mode (Asaoka et al. 2012) was used for the samples and the transmission mode (Takeuchi et al. 2011) was used for the standard reference materials.

**Statistical analysis**

Principal component analysis (PCA) was performed using the total concentration of chemical elements obtained from ICP–AES and ICP–MS measurements to quantitatively determine the influential factors to water quality in the pipes. Statistical software SPSS Statics 18 was used for calculations. A concentration value lower than the minimum limit value was calculated as zero.

Data obtained by XAFS analysis were subjected to partial least squares regression using EXCEL Tahunryoukaiseki Ver. 6.0 (ESUMI), to calculate the ratio for each oxidation form of Fe.

**RESULTS AND DISCUSSION**

**Chemical elements in water**

Table 1 shows the water quality results for each sampling point. No large difference in water quality was observed, except the highest concentration of Fe was found at AA2. The ratios of the suspended solid and dissolved elements to their total concentration were calculated using the data shown in Table 1 and Figure 5. Around 0.1% of Si and 0.01% of Ca were present in suspended solids form in all of the sampling points. Al in suspended solid form ranged from 2 to 18%, and Fe ranged from 17 to 65%. The highest Fe ratio of 65% was found at AA2.

To quantitatively identify significant indices for distinguishing a diversity of water quality among the sampling points, PCA was performed using the data listed in Table 1. The analysis showed that the elements present in concentrations below the minimum limit value were excluded. In these cases, data on Na, Mg, Al, Si, K, Ca and Fe were used for the analysis.

Figure 3 shows the PCA. The accumulated proportion until the second principal component was 86.1%, with the

<table>
<thead>
<tr>
<th>Sites</th>
<th>Na (mg/L)</th>
<th>Mg (mg/L)</th>
<th>Al (mg/L)</th>
<th>Si (mg/L)</th>
<th>P (mg/L)</th>
<th>K (mg/L)</th>
<th>Ca (mg/L)</th>
<th>Mn (mg/L)</th>
<th>Fe (mg/L)</th>
<th>Zn (mg/L)</th>
<th>Pb (mg/L)</th>
<th>Cr (mg/L)</th>
<th>Ni (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>9.39</td>
<td>3.19</td>
<td>0.016</td>
<td>8.19</td>
<td>&lt;0.005</td>
<td>2.06</td>
<td>13.3</td>
<td>&lt;0.005</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.001</td>
<td>&lt;0.005</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>A2</td>
<td>9.15</td>
<td>3.11</td>
<td>0.015</td>
<td>7.84</td>
<td>&lt;0.005</td>
<td>1.96</td>
<td>12.9</td>
<td>&lt;0.005</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.001</td>
<td>&lt;0.005</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>AA1</td>
<td>9.37</td>
<td>3.11</td>
<td>0.024</td>
<td>8.21</td>
<td>&lt;0.005</td>
<td>2.00</td>
<td>12.9</td>
<td>&lt;0.005</td>
<td>0.011</td>
<td>&lt;0.010</td>
<td>&lt;0.001</td>
<td>&lt;0.005</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>AA2</td>
<td>9.18</td>
<td>3.08</td>
<td>0.019</td>
<td>8.18</td>
<td>&lt;0.005</td>
<td>2.02</td>
<td>12.8</td>
<td>&lt;0.005</td>
<td>0.033</td>
<td>&lt;0.010</td>
<td>&lt;0.001</td>
<td>&lt;0.005</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>AB1</td>
<td>9.14</td>
<td>3.04</td>
<td>0.012</td>
<td>7.90</td>
<td>&lt;0.005</td>
<td>1.95</td>
<td>12.7</td>
<td>&lt;0.005</td>
<td>&lt;0.010</td>
<td>&lt;0.010</td>
<td>&lt;0.001</td>
<td>&lt;0.005</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>AB2</td>
<td>9.26</td>
<td>3.10</td>
<td>0.015</td>
<td>8.19</td>
<td>&lt;0.005</td>
<td>2.00</td>
<td>12.8</td>
<td>&lt;0.005</td>
<td>0.014</td>
<td>&lt;0.010</td>
<td>&lt;0.001</td>
<td>&lt;0.005</td>
<td>&lt;0.001</td>
</tr>
</tbody>
</table>
The first principal component accounting for 58.2% of the variance and the second accounting for 27.9%. Therefore, the major tendency in water quality was explained by the first and second principal components. Results of the first principal component (PC1) score showed differences among the six sampling points. These points were plotted along the second principal component (PC2).

To specify a meaningful index for each principal component, the factor loading for each principal component was examined (Table 2). In PC1, many elements exhibited high factor loadings, Na, Mg, Si, K and Ca were over 0.8, whereas Al and Fe were 0.555 and 0.118, respectively. In contrast, only Fe was a high contributor for PC2. This indicates that Fe shows different behaviour with other elements in water. Particularly, the presence of Fe in suspended solid form appears to have a relationship to the ageing unlined steel pipe.

### Chemical elements in suspended solids

If the walls of a water pipe are corroded, it is assumed that the Fe corrosion scales are discharged into the water due to pipe flaking. To evaluate the suspended solid concentrations among the sampling points, they were collected using the 0.45-μm membrane filter and were visually observed.

Figure 4 shows the membrane filters after passing through 20 L of sampled water and then dried naturally. AA1, AA2, AB1 and AB2 had more colour compared to that of A1 and A2. The filter from AA2 had a distinct brownish colour, indicating a large collection of suspended solids. The filters of AA1, AB1 and AB2 had slightly brownish colour.

The concentrations of elements in the suspended solids that were collected on the filters are shown in Figure 5. Concentration was calculated on the basis of the filtered water volume. Although suspended solids were in the μg/L range, analysis with high reliability was possible because the samples were concentrated by filtration. A high Fe concentration was shown for AA2, and the continuing order of concentration was as follows: AB1, AB2 and AA1. It may be suggested that Fe is the main cause of the brownish colour, and that it originates in corrosion scales because the AA2 sample was from an ageing unlined steel pipe.

### Speciation of Fe in suspended solids

To examine the speciation of Fe in suspended solids, the solids collected by filtration were analysed by XAFS. XAFS spectra of standard reference materials of various Fe oxides are shown in Figure 6, and those of suspended solids, which were sampled from the water supply system, are shown in Figure 7. An increase in the Fe oxide intensity is shown in the photon energy area in Figure 6. XAFS analysis detected Fe oxide in A1, in which the amount of suspended solids was the least of the six sampling points although this could not be detected by XRD.

Corrosion scales in water supply pipes in the USA include goethite (α-FeOOH), magnetite (Fe₃O₄), maghemite (γ-Fe₂O₃) and siderite (FeCO₃) (Sarin et al. 2004b), while in Japan these include Fe₂O₃, α-FeOOH, Lepidocrocite

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**Table 2** | Factor loading of the first and second principal components

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>PC1</td>
<td>0.920</td>
<td>0.858</td>
<td>0.555</td>
<td>0.805</td>
<td>0.927</td>
<td>0.815</td>
<td>0.118</td>
</tr>
<tr>
<td>PC2</td>
<td>–0.084</td>
<td>–0.453</td>
<td>0.575</td>
<td>0.510</td>
<td>0.072</td>
<td>–0.539</td>
<td>0.923</td>
</tr>
</tbody>
</table>
Further, in USA, suspended solids in tap water from cold water taps in a 90-year-old building generally include Fe$_3$O$_4$, $\gamma$-FeOOH and $\alpha$-FeOOH (Barkatt et al. 2013).

The XAFS spectral shapes of standard reference materials were similar (Figure 6), indicating that speciation of all the standard reference materials was unnecessary to identify the unknown speciation of the sample. Fe$_3$O$_4$ and $\alpha$-FeOOH were selected because they were principal components in corrosion scales in the above-mentioned reports (Nagata et al. 1992; Sarin et al. 2004b; Barkatt et al. 2009). XAFS spectra for sampling points other than A1 were calculated. Data from XAFS analysis of A1 had noise, and corrosion was not expected to have an influence.

Further, the ratio of Fe$_3$O$_4$ between AA1 and AA2 slightly increased, but decreased significantly from AB1 to AB2.
According to the result obtained by ICP–AES (Figure 5), the concentration of Fe increased from AA1 to AA2, but remained constant from AB1 to AB2. This suggests that the behaviour of speciation and concentration is independent.

It is assumed that differences in the oxidation forms of Fe along AA and AB originated from differences in the Fe behaviour. Oxidation forms of Fe in the water resulted from its release from the pipe surface, advection from upstream and flaking of corrosion scales that include well oxidized Fe. The oxidation state can possibly reflect the record of Fe movement. Therefore, measuring the Fe speciation could be a useful tool to determine the internal condition of a water pipe.

CONCLUSIONS

PCA showed that Fe is an important water quality characteristic for detecting the ageing of pipes in water supply. Larger Fe concentrations associated with suspended solids were found on ageing unlined steel pipe. The ratio of Fe as suspended solids in total Fe concentration at the ageing unlined steel pipe investigated was higher than that of other sampling points along the water supply system. The differences in the oxidation forms of Fe observed in two lines of the system indicate that measuring the Fe speciation can be used as a tool to analyse the internal conditions of a water pipe. It is proposed that the concentration and speciation of Fe in water are useful indices for detecting ageing of unlined steel pipes from water supply systems.

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