Analysis of Iron and Manganese Release Effect in Drinking Water Systems from a New Perspective

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Abstract. In recent years, with the continuous attention to the quality of drinking water and the intensive research on the corrosion of water distribution systems, the problem of metal ions release has attracted more and more attention by researchers. This paper studies metal ions release in drinking water systems from the perspective of occluded water. It has been found that the concentration of iron and manganese ions in the bulk water increases with the concentration of chloride and sulfate ions when only the effect of occluded water on metal ions release is considered. This result is consistent with previous studies. The concentration of iron and manganese ions in the bulk water does not decrease as the pH increases. At the same time, the presence of pipe scales is also a potential threat to the quality of drinking water. It has been found that the concentration of iron and manganese ions in the bulk water also increases as the amount of pipe scales increases. Fe$_3$O$_4$ has an adsorption effect on iron, and a single component pipe scale cannot hinder the migration of manganese in the occluded water.

1. Introduction

All water quality parameters of the finished water meet the health and hygiene requirements for drinking water; however the tap water which the customers exactly used might be contaminated, including an increase in turbidity, chromaticity, iron concentration, bacteria and other water quality problems [1]. The drinking water experiences a long hydraulic retention time (HRT) of storage and transportation in water distribution systems (WDS) [2], therefore, the pipes in WDS as well as the interaction between pipe surfaces and bulk water are crucial to the drinking water quality.

Unlined cast iron pipe is still widely existed in current WDS all over the world, particularly in some less developed and large cities. At present, iron pipes still hold a large proportion in WDS worldwide. According to the surveys in Italy and Beijing, China, in WDS, cast iron, ductile iron and steel pipes account for three-quarters of the total, mainly for water pipes, while service pipes are mainly made of galvanized iron and plastic [3, 4]. This situation is estimated to last for long as the pipe networks are expensive to be upgraded [5]. Internal corrosion of metal pipes is a common problem in WDS.

In order to alleviate the shortage of water resources and over exploitation of groundwater, the implementation of a variety of water sources for comprehensive utilization and even long-distance water transfer across river basins is an important strategy for solving water resources problems in many cities at home and abroad. However, sudden changes in the chemical composition of water, such as pH, SO$_4^{2-}$, Cl$^-$, alkalinity, and hardness of the pipe network caused by different water sources, can easily break the balance between the scale-water in WDS, resulting in a large amount of scale components, especially iron corrosion products, to the bulk water [6-9]. As a result, turbidity of water and color increase, causing serious “Yellow Water” problems.
Corrosion of the pipe network occurs on the inner surface of the pipe, and the solution medium in contact with it is the solution inside the pipe scale. This solution is occluded water. There is a great difference between occluded water and bulk water. The occluded water is weakly acidic and contains a lot of ions such as iron, manganese, chlorine and sulfate [10]. The influence of different factors on the release of metal ions is analyzed for bulk water, but their effect on the occluded water is not considered. A large amount of iron and manganese ions, which are abundant in occluded water, are likely to migrate among occluded water, corrosion scale and bulk water under certain conditions. Iron and manganese ions are thus released into the bulk water and lead to secondary pollution of drinking water. Therefore, it is very necessary to introduce the occluded water into the study of secondary pollution of drinking water. This work sought to identify and evaluate the change of metal ions in bulk water and occluded water under different conditions of water quality (sulfate, chloride, pH), hydraulic conditions (flowing and stationary), and scale component.

2. Experiment Set-up and Operation
A detailed schematic of the simulated occluded cell is shown in figure 1. The volume of the occluded water is 8 mL and the volume of the bulk water area is 110 mL. In the experiment, the anode electrode material is ductile iron. In addition to the scale composition experiment, the simulation corrosion scale of all experiments is a mixture of Fe₂O₃, Fe₃O₄, Fe(OH)₃ in the proportion of 6.5:3.5:1.

Experiment 1: The cathode working electrode is a glassy carbon electrode, and the anode working electrode material is ductile iron. Before the experiment, the surface of the anode working electrode was sanded from No. 360 to No. 2000, and then rinsed with ultrapure water, then the oil was removed with absolute ethanol. The experiment was operated under the condition of the flow velocity of 400 mL/min and the current of 0.1 mA. The water quality parameters of bulk water and occluded water are shown in Table 1. The occluded water was deoxygenated by nitrogen for 2 hours. When adjusting one of the water quality parameters, the other parameters remain unchanged. The experiment ran for 24 hours. The experimental operation of the flow rate on the release of iron and manganese in the occluded water is the same as the above experimental operation. The bulk water flow rate is designed to be 400 mL/min and 0 mL/min respectively.

Experiment 2: According to the purpose of this experiment, quantitative analytical pure chemicals such as Fe₂O₃, Fe₃O₄, Fe(OH)₃, CaCO₃, SiO₂ and other simulated scales were filled in the container. The electrodes used in the experiment and the operation are the same as above. The peristaltic pump was adjusted to a speed of 25 rpm to allow the solution to flow at a constant rate in the bulk water. Adjust the voltage of the external battery so that the current is maintained at around 0.10 mA. During the experiment, samples were taken at 0 h and 48 h after the operation of the device. The water quality of experiment 2 is shown in Table 2.

![Figure 1. Schematic of a simulated occluded cell: 1) Occluded anode electrode; 2) Occluded cavity; 3) Bulk water inlet; 4) Cathode electrode; 5) Bulk water outlet; 6) Simulated scale area; 7) Bulk water area.](image)
Table 1. Bulk water and occluded water quality parameters in experiment 1

| Water quality parameters | Bulk water | Occluded water |
|--------------------------|------------|----------------|
| pH                       | 7.5        | 4.1            |
| Fe (mg/L)                | 0.83       | 1001.63        |
| Mn (mg/L)                | 0.01       | 15.345         |
| Cl (mg/L)                | 89.15      | 475.20         |
| SO\textsubscript{4} (mg/L) | 185.39    | 1348.31        |

Table 2. Bulk water and occluded water quality parameters in experiment 2

| Water quality parameters | Bulk water | Occluded water |
|--------------------------|------------|----------------|
| pH                       | 7.0        | 4.0            |
| Mg (mg/L)                | 20.12      | 15.53          |
| Ca (mg/L)                | 0.61       | 0.38           |
| Fe (mg/L)                | 0.012      | 1011.71        |
| Mn (mg/L)                | 0.005      | 16.35          |
| Cu (mg/L)                | 0          | 1.03           |
| Cr (mg/L)                | 0.002      | 0.074          |
| Zn (mg/L)                | 0          | 0.016          |
| Al (mg/L)                | 0          | 0.27           |
| NO\textsubscript{3} (mg/L) | 9.09       | 0              |
| Cl (mg/L)                | 71.54      | 552.47         |
| SO\textsubscript{4} (mg/L) | 137.15    | 1454.66        |
| DO (mg/L)                | 7.95       | ≤0.5           |

3. Experiment Results and Discussion

Experiment 1 designed the effect of three gradients and three experimental factors on the release of iron and manganese in pipelines. The three gradient experimental factors are as follows: rank 1 pH, chloride, sulfate are 6.5, 89.15 mg/L, 185.39 mg/L respectively, rank 2 pH, chloride, sulfate are 7.5, 169.12 mg/L, 327.95 mg/L respectively, rank 3 pH, chloride, sulfate are 8.5, 228.76 mg/L, 457.31 mg/L respectively. The experiment used the control variable method to study the effect of single factor on the release of iron and manganese from drinking water systems. When one of the factors is changed, the other factors maintain pH, chloride ion and sulfate ion respectively of 7.5, 89.15 mg/L and 185.39 mg/L. The release of iron and manganese ions is substantially proportional to the chloride and sulfate ions. In this experiment, the effect of pH on the release of iron and manganese in the pipeline is different from that of previous studies. The iron and manganese released at a pH of 7.5 are the most, and the release amount of iron and manganese when the bulk water at a pH of 8.5 is higher than the release amount of iron and manganese when the bulk water at a pH of 6.5 (Figure 2). This indicates that iron and manganese are more easily released from the occluded water and the scale to the bulk water when the initial pH of the bulk water is 8.5. The influence of water quality parameters in the bulk water on the concentration of iron ions in the occluded area is similar to that of the bulk water. The iron in the occluded area increases with the concentration of chloride and sulfate. First, the concentration of manganese ions in the occluded water is the highest at pH 7.5, and the concentration of manganese ions in the other two gradients is substantially equal (Figure 2). The manganese ion in the occluded area was the smallest at a chloride ion concentration of 130 mg/L and the largest at 65 mg/L (Figure 2). It can be seen from figure 3 that the concentration of iron and manganese in the bulk water in the flowing state is higher than the concentration of iron and manganese in the stagnant state. This may be due to the violent water disturbance in the flow state causing the release of iron and manganese from the scale and occluded water into the bulk water. The concentration of iron and manganese in the occluded water has little to do with the state of the water flow. The effect of sulfate ion on the manganese ion in the occluded area is opposite to that of the bulk water. As the concentration of sulfate ion increases, the manganese ion gradually decreases. The influence of chloride and sulfate on the manganese ion in the occluded area is inconsistent with previous studies.
Experiment 2 designed the effect of different scales on iron and manganese in the occluded water. Iron and manganese in the occluded area increase as the amount of pipe scale increases (Figure 4). This indicates that part of the iron and manganese in the occluded area may come from the dissolution of the pipe scale. The scale can not only serve as a source of iron and manganese in the bulk water and occluded water, but also the adsorption of the pipe scale can also cause changes in the composition of metal ions in the bulk water and the occluded water. We designed the following sets of experiments to study the effects of different scale components on bulk water and occluded water. It can be seen from Figure 5(a) that in the bulk water iron ion concentration is the highest in the Fe$_2$O$_3$ group, followed by SiO$_2$, CaCO$_3$, Fe$_3$O$_4$ and Fe(OH)$_3$. For the metal pipe scale, the iron in the Fe$_2$O$_3$ is more easily released into the bulk water, and the iron ions in the Fe$_3$O$_4$ and the Fe(OH)$_3$ are not easily dissolved and released into the bulk water under the experimental conditions. It can also be considered that in the theory of occluded cells, the presence of pipe scale plays a role in the selective permeability, and in the scale, Fe(OH)$_3$ and Fe$_3$O$_4$ play a major hindrance to avoid iron release in the occluded water. Manganese is released directly into the bulk water. However, SiO$_2$ and CaCO$_3$ release have no obstruction effect on the metal ion, and the iron and manganese in the occluded water are directly released into the bulk water, so the concentration of iron and manganese in the bulk water is higher. It can be seen from Figure 5(b) that the concentration of iron ions in the occluded area of the five experimental experiments is increased. It can be judged that the iron ions in the occluded area are mainly from the corrosion of the ductile iron, rather than the dissolution of iron in the pipe scale and released to the occluded area. From the figure 5(c), we can see that under different conditions of scale composition, the concentrations of manganese ions in the bulk water after 48h are all increased, which means that the manganese in the main water is not mainly from the scale. It can be seen from Figure 5(d) that under different pipe scale conditions, the manganese ion concentrations in the occluded area of the five groups of experiments are reduced, because that a large amount of manganese in the occluded area is released into the bulk water. This also shows that the source of manganese in the bulk water is mainly occluded water.

![Figure 2](image_url)

**Figure 2.** Metal ion concentration under different water quality parameters and ranks (a) Iron ion concentration in bulk water, (b) Iron ion concentration in occluded water, (c) Manganese ion concentration in bulk water, (d) Manganese ion concentration in occluded water.
Figure 3. (a) Concentration of iron ions in bulk water and occluded water under different flow conditions, (b) Concentration of manganese ions in bulk water and occluded water under different flow conditions. B-bulk water, O-occluded water.

Figure 4. Effect of different scale content on iron and manganese concentration in occluded water.

Figure 5. Effect of different scale components on iron (a, b) and manganese (c, d) ion concentration in bulk water (a, c) and occluded water (b, d). A-Fe₃O₄, B-Fe(OH)₃, C-CaCO₃, D-Fe₂O₃, E-SiO₂.
4. Conclusions
This paper cites a special area of occluded water to study the effects of various parameters on iron and manganese release from the perspective of occluded water. In this paper, the effects of water quality parameters, hydraulic parameters and the composition and content of pipe scale on the concentration of iron and manganese ions in occluded water and bulk water were studied. It was found that in the three states of pH 6.5, 7.5, and 8.5, when the pH of the bulk water was 7.5, the corrosion rate of the cast iron electrode and the release rate of iron and manganese reached the maximum at the same time. The flow rate has a certain influence on the release of manganese, and the flow state is more likely to cause the release of iron and manganese than the stagnant state. Within a certain concentration range, $\text{SO}_4^{2-}$ and $\text{Cl}^-$ in the bulk water promote the release of iron and manganese. The concentration of iron and manganese ions in the occluded water increases with the increase of the pipe scale content. When the amount of pipe scale increases to 0.8g, the concentration of iron and manganese ions in the occluded water is the largest, which also proves that some of the iron and manganese in the occluded water come from dissolving of the scale. In the bulk water iron content of the Fe$_3$O$_4$ group is lowered due to the adsorption of the scale, and other scale components do not act as adsorption. The concentration of manganese ions in the five scales of Fe(OH)$_3$, Fe$_3$O$_4$, Fe$_2$O$_3$, CaCO$_3$ and SiO$_2$ increased, indicating that a certain kind of pipe scales cannot hinder the migration of manganese in occluded water. In order to control the content of iron and manganese in drinking water distribution systems, this paper proposes control measures from the perspective of occluded water. Reducing the hydraulic disturbance, pH, sulfate and chloride ion concentration is beneficial to reduce the metal concentration in the bulk water.

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6. References
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