# Evaluation of the effect of sulfate, alkalinity and disinfector on iron release of iron pipe and iron corrosion scale characteristics under water quality changing condition using response surface methodology

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**Abstract**: The response surface methodology (RSM), particularly Box-Behnken design model, was used in this study to evaluate the sulfate, alkalinity and free chlorine on iron release of pipe with groundwater supply history and its iron corrosion scale characteristics under water quality changing experiment. The RSM results together with response surface contour plots indicated that the iron release of pipe section reactors was positively related with Larson Ratio and free chlorine. The thin Corrosion scales with groundwater supply history upon collection site contained $Fe_3O_4$ (18%), $\alpha$-FeOOH (64%), $FeCO_3$ (9%), $\beta$-FeOOH (8%) and $\gamma$-FeOOH (5%), besides their averaged amorphous iron oxide content was 13.6%. After the RSM water quality changing experiment, $Fe_3O_4$, amorphous iron oxide and intermediate iron products ($FeCO_3$, Green Rust (GR)) content on scale of $Cl_2Rs$ increased, while their $\alpha$-FeOOH contents decreased and $\beta$-FeOOH disappeared. The high iron released $Cl_2Rs$ receiving higher LR water (1.40-2.04) contained highest $FeCO_3$ (20%) and amorphous iron oxide (42%), while the low iron release $Cl_2Rs$ receiving lower LR water (0.52-0.73) had higher GR(6.5%) and the amorphous iron oxide (23.7%). In high LR water (>0.73), the thin and non-protective corrosion scale containing higher amorphous iron oxide, Fe(II) derived from new produced $Fe_3O_4$ or $FeCO_3$ or GR was easy for oxidants and sulfate ions penetration, and had higher iron release. However the same unstable corrosion scale didn't have much iron release in low LR water (≤0.73). RSM experiment indicated that iron release of these unstable corrosion scales had close relationship with water quality (Larson Ratio and disinfectant). Optimizing the water quality of new source water and using reasonable water purification measures can help to eliminate the red water case.

## 1. Introduction

Due to the groundwater depletion and regulatory constraints, many countries or districts had decreased groundwater utilization and increased utilization of other surface water sources for the increasing drinking water supply. Difference between the finished water quality of these alternate supplies and old groundwater source might disrupt the existing distribution scale on pipes which had adverse effects on distribution water quality. Red water issue had occurred in some areas in a northern city of China, soon after 80% of the local source water was replaced by long-distance introduced source water from a neighboring province in October, 2008 [1, 2]. Heavy red water occurred only in areas historically supplying local groundwater, and the areas without red water were historically supplied with local surface waters. Compared with the groundwater sources, the new water source had higher sulfate concentration (198 mg·L$^{-1}$), higher chloride (51 mg·L$^{-1}$) and lower alkalinity (120 mg·L$^{-1}$). Larson Ratio (LR) has been used to evaluate the corrosive of water against iron-based pipes, which was developed from the relative corrosive behaviors of chlorides and sulfates to the protective properties of bicarbonate for iron pipe corrosion, and LR value above 0.5 was considered corrosive [3]. The LR of the new water source was 1.7, which was obviously in corrosive range. According to the previous studies the thin corrosion scale mostly discovered in pipes historically transporting groundwater had no magnetite detected or with M/G ratio of less than 1.0, and contained higher contents of unstable ferric components such as γ-FeOOH, β-FeOOH and amorphous iron oxide. The LR of local groundwater was in the range of 0.22-0.4, so the pipes historically transporting groundwater were less corroded [1].

Alkalinity, sulfate and disinfector are primary water quality parameters affecting iron corrosion. Switching to alternative water sources or long distance transported new source water is becoming a trend for water shortage cities in the world. In order to prevent the red water cases resulted from source water switch, pipe section reactors harvested in groundwater treatment plant service areas were used for RSM experiment to identify acceptable water quality for iron release control. New experimental waters with adjusted sulfate, alkalinity and free chlorine concentration designed by RSM experiment were supplied to pipe section reactors for effluent total iron release. After 11d-RSM experiment, the scale samples of pipe section reactors with different iron release degree were collected for XRD and amorphous iron analysis to investigate the scale physiochemical changes. The results obtained in this work could help providing the water quality regulation method for less corrosive pipes historically transporting groundwater.

## 2. Materials and methods

### 2.1 Preparation of iron pipe section reactor

The cast-iron pipe was approximately 20 years old and harvested from Beijing drinking water distribution system (DWDS) area, denoted as PipeB-GW3. Historically, PipeB-GW3 was transporting local groundwater (denoted as GW3) treated by groundwater treatment plant 3 (GWTP3). It was cut into 10 cm short sections with relatively little damage to the pipe scales and the exposed metal surfaces at both ends of each section were coated with epoxy to prevent water contact. Short pipe sections were installed with polyvinyl chloride (PVC) plate covers and magnetic stirrers into pipe section reactors (shown in figure 1). The pipe section reactors filled with GW3 water were carefully transported to laboratory avoiding any scale damage by collision.

### 2.2 Experimental solution preparation

The characteristics of the old source water of pipeB-GW3, base solution used and BBD experimental water were listed in Table 1. It is observed that the old source water had low sulfate, DO and high alkalinity, whereas base solution and experimental water had higher sulfate and DO.
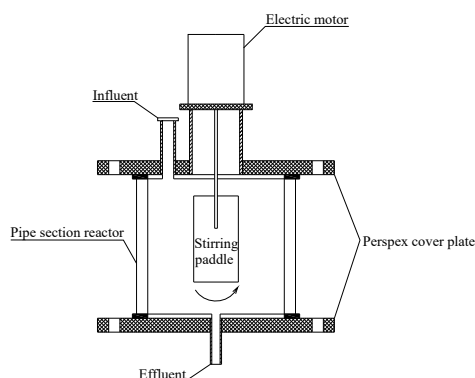
**Figure 1.** Scheme of experimental setup.
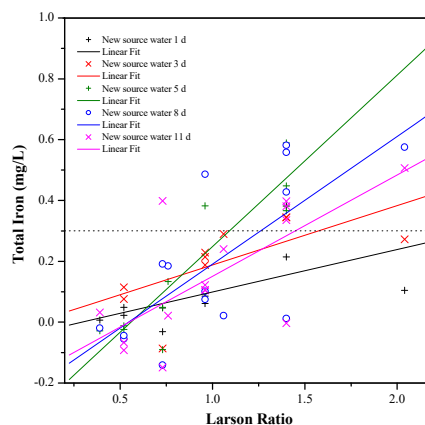


**Figure 2.** Under water quality changing experiment 1d, 3d, 5d, 8d and 11d, the relationship between effluent total iron concentrations for free chlorine pipe section reactors and Larson Ratio.

*2.3 Batch mode study and water quality measurements*

Before the BBD experiments, pipe section reactors were first filled with GW3 water and run for 3 days to acquire blank values of iron release in each pipe section. According to the BBD experimental design, each pipe section reactors (marked by En) were then filled with its new experimental water for 11 days. The new experimental water was renewed into pipe section reactor every day after unloading of 1d-run solution. During water quality changing period, the effluent total iron concentration tested in the end of 1, 3, 8 and 11d for given pipe section reactor was the actual measured data reduced by its corresponding blank value. Water samples were collected from the reactor outlet at the end of 1 d run and measured according to Standard Methods [4]. The monitored parameters of experimental water included pH, dissolved oxygen (DO), conductivity, alkalinity, sulfate and chloride (Table 1).

**Table 1.** Water quality characteristics of original source water of PipeB-GW3 and BBD experimental water (units: alkalinity in mg·L$^{-1}$ as CaCO$_3$; conductivity in μs·cm$^{-1}$; others in mg·L$^{-1}$).

| Water quality | Original source water | BBD experimental water | Analysis equipments |
|---|---|---|---|
| alkalinity | 194.5 | Variables (130,190,250) | Acid base titration |
| conductivity | 408 | Variables (540-780) | Multiparameter meter sension156 |
| DO | 6.5 | 8.1 | HACH Co., USA |
| pH | 7.3 | Variables (7.7-8.0) | |
| Cl- | 23.1 | 40.2 | Ion Chromatography System-1000 |
| SO42- | 24.7 | Variables (40,120,200) | Dionex Co., USA |
| LRa | 0.26 | Variables (0.39-2.0) | Calculated by equation |
| free chlorine | 1.0 | Variables (0-2.0) | DPD titration by HACH DR2800 |

[a] LR, Larson ratio, $R = \dfrac{[Cl^-] + 2[SO_4^{2-}]}{[HCO_3^-]}$      where $[Cl^-]$，$[SO_4^{2-}]$, $[HCO_3^-]$ is expressed in moles per liter.

*2.4 Response surface methodology and statistical analysis*

A Box-Behnken design (BBD) model for above three variabies each at two levels (i.e. low level and high level) was adopted as the experimental design model (Table 2). A total of 15 experiments were employed to calculate coefficients of the polynomial equation that was fitted on the experimental data [5]. The experimental design was generated using Design-Expert 7.0 while the graphics using MAT-LAB software.

Table 3 showed the independent variables (sulfate, alkalinity and free chlorine concentration), the coded value of the variables together with output observed response (total iron release). Each experimental run was carried out with the maintained process variable conditions as given in the design matrix. The effluent iron release concluded in Table 3 was the average value for the tested values of 1, 3, 8 and 11d. A first-order polynomial model fitted to the experimental data obtained from the experimental runs conducted on the basis of BBD model was explained by the following equation:

$$Y = \beta_0 + \sum \beta_i x_i \quad (1)$$

Where $Y$ is the total iron release, $\beta_0$ the offset term, $\beta_i$ the first-order main effect, $x_i$ are the experimental variables studied, i.e. sulfate, alkalinity and free chlorine concentration, respectively. The fit quality of the model was determined by the coefficient of determination ($R^2$) and the analysis of variance (ANOVA) (Table 4).

**Table 2.** Experimental factors, range and level of variables ($mg \cdot L^{-1}$).

| variables | Low level | Medium level | High level |
|---|---|---|---|
|  | (-1) | (0) | (-1) |
| alkalinity | 130 | 190 | 250 |
| sulfate | 40 | 120 | 200 |
| free chlorine | 0 | 1 | 2 |

*2.5 Iron corrosion scale characterization*
At the end of 11d batch mode study, the corrosion scale samples were removed from pipe section reactors and milled at once in anaerobic glove box to avoid spontaneous oxidation by oxygen. Then the wet powder samples and small scale pieces were freeze-drying and analyzed by X-ray powder diffraction (XRD) and free and amorphous iron extraction, respectively. A RIGAKU (D/max-rA) X-ray powder diffractometer (Rigaku, USA Inc., Danvers, MA) with a Cu Kα radiation at 40 KV and 100 mA, was used for XRD studies. Crystalline phase identification and composition were determined by the Jade XRD software and Contrasted parameters of intensity method [6]. Dithionite-citrate-bicarbonate (DCB) technique described by Tan [7] was used to determine free and amorphous iron concentration and the total iron was pre-treated by microwave digestion and determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Perkin-Elmer Optima 2000, USA).

## 3. Results and discussion

*3.1 Pipe corrosion scale morphology*
The groundwater was less corrosive and thus PipeB-GW3 corrosion scales were very smooth and much thin (only few millimeters or less than a millimeter), had no tubercles or very few tubercles but many hollow tubercles sporadically distributed on inner pipe surface [1].

*3.2 Iron release investigation using response surface methodology*

*3.2.1 Iron release in RSM experiment*
Table 3 showed the coded value of the variables together with the average iron release. $Cl_2R$ of E1 had the highest iron release while $Cl_2R$ of E4 had the lowest iron release. The relationship between the effluent total iron concentrations of tested days (1d, 3d, 5d, 8d and 11d) and LR for $Cl_2R$ was revealed in figure 2. After switching to experimental water, the iron release of pipe section reactors had positive relation with their appointed LR. The effluent total iron concentrations for $Cl_2R$ of 1d, 3d and 5d were gradually increasing, but those of 8d and 11d had a decreasing trend, and some detected data in the LR value range of 0.73 to 2.04 still exceeded the drinking water standard (0.3 $mg \cdot L^{-1}$) (figure 2).

### 3.2.2 RSM experiment analysis

The application of the RSM based on the estimates of the parameters and the experimental results indicated an empirical relationship between the response and the input variables expressed by the following fitted regression model, which is a first-order polynomial equation (2):

$$C_{totaliron} = 0.09 - 1.25e^{-3}C_{alkalinity} + 1.74e^{-3}C_{sulfate} + 0.09C_{freechlorine}$$

(2)

Both the statistical significance of the ratio of mean square due to regression model and mean square due to residual were tested using ANOVA. The ANOVA revealed that equation (2) suitably represent the actual relationship between the response and the variables. A very low probability value (p-value) of 0.0003 ($Cl_2R$) obtained from the Fisher $F$-test demonstrated a very high significance for the first-order equations in this study.

**Table 3.** Box Behnken design matrix for three variables together with the observed response (units: alkalinity in mg·L$^{-1}$ as $CaCO_3$; others in mg·L$^{-1}$).

| No. | Variables | | | LR | Total iron | No. | Variables | | | LR | Total iron |
|-----|-----------|--|--|----|-----------|-----|-----------|--|--|----|-----------|
| | Alka-linity | SO$_4^{2-}$ | Free chlorine | | | | Alka-linity | SO$_4^{2-}$ | Free chlorine | | |
| E1 | 190 | 200 | 2.0 | 1.40 | 0.417 | E9 | 130 | 120 | 2.0 | 1.40 | 0.371 |
| E2 | 190 | 40 | 2.0 | 0.52 | 0.003 | E10 | 190 | 120 | 1.0 | 0.96 | 0.258 |
| E3 | 190 | 120 | 1.0 | 0.96 | 0.172 | E11 | 130 | 120 | 0 | 1.40 | 0.016 |
| E4 | 250 | 120 | 0 | 0.73 | -0.100$^a$ | E12 | 190 | 200 | 0 | 1.40 | 0.293 |
| E5 | 130 | 200 | 1.0 | 2.04 | 0.335 | E13 | 250 | 40 | 1.0 | 0.39 | 0.006 |
| E6 | 250 | 200 | 1.0 | 1.06 | 0.127 | E14 | 190 | 40 | 0 | 0.52 | -0.010 |
| E7 | 190 | 120 | 1.0 | 0.96 | 0.259 | E15 | 250 | 120 | 2.0 | 0.73 | 0.149 |
| E8 | 130 | 40 | 1.0 | 0.76 | 0.058 | | | | | | |

$^a$ The total iron was average values tested in 11d-experiment minus their corresponding blank values in 3d-baseline. So there may appear negative values.

### 3.2.3 Response surface estimations for minimum iron release

Figure 3(a), (b) and (c) shows the response surface contour plot depicting the iron release surface over independent variables of sulfate concentration or alkalinity or free chlorine when one of these three parameters is fixed at three levels. The effluent iron release increased with the increasing sulfate, free chlorine concentration and decreasing alkalinity concentration. This finding agreed with the above analysis that LR (i.e. sulfate, alkalinity) and free chlorine concentration had positive relation with iron release (in figure 2 and equation (2)).



(a)                                    (b)                                    (c)
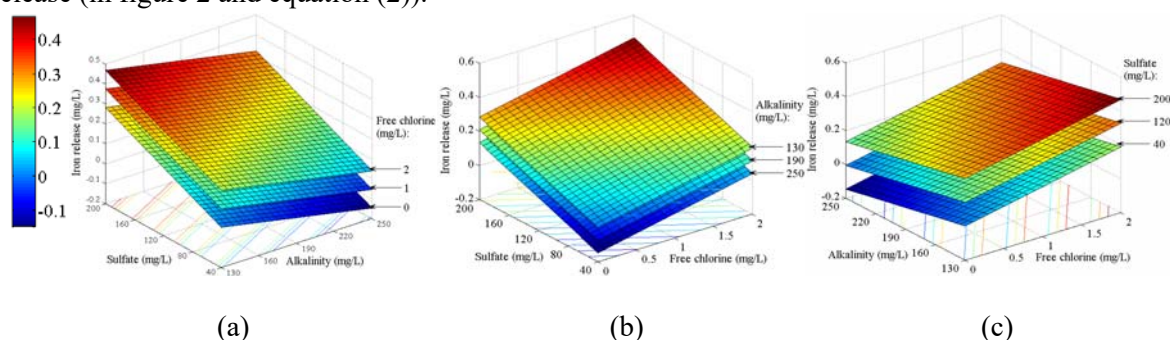
**Figure 3.** Response surface plots for the iron release versus variables of free chlorine pipe section reactor: (a) free chlorine: 0-2 mg·L$^{-1}$, (b) alkalinity: 130-250 mg·L$^{-1}$, (c) sulfate: 40-200 mg·L$^{-1}$.

## 3.3 Chemical composition and microstructure analysis of the corrosion scales

### 3.3.1 X-ray diffraction (XRD) statistical analysis

According to effluent total iron concentration, the pipe section reactors tested can be classified into three different levels: E5, E12 (high iron release reactors), E6 and E15 (medium iron release reactors),

E2, E4 and E14 (low iron release reactors). At soon as the RSM experiments were finished, scale samples from the above $Cl_2Rs$ were collected for composition and structure analysis, respectively.

The box figures (figure 4) were illustrated to make clear the chemical and structural differences for scale of site collection samples and experimented pipe reactors samples. Aforementioned the pipe section reactors were ranged into three categories by their iron release and iron oxide percentage used below was average values of multi-samples in box figures.

Freshly obtained corrosion scales of PipeB-GW3 on collection site contained $Fe_3O_4$ (18%), $\alpha$-FeOOH (64%), $FeCO_3$ (9%), $\beta$-FeOOH (8%) and $\gamma$-FeOOH (5%) (average percentage), besides their averaged amorphous iron oxide content was 13.6%. After changing the water quality, the $Fe_3O_4$ percentages of corrosion scale for listed $Cl_2Rs$ increased while the $\alpha$-FeOOH percentages of scale for those reactors all decreased. The scale of high and low iron release $Cl_2Rs$ had the highest $Fe_3O_4$ contents (41%). The $\alpha$-FeOOH contents of high, medium and low iron release $Cl_2Rs$ were decreased from the original 64% to 34%, 10% and 42%, respectively. From figure 4 the high-iron-release $Cl_2Rs$ had the highest $FeCO_3$ (20%) and amorphous iron oxide (42%) contents, while the low-iron-release $Cl_2Rs$ had higher GR (6.5%), the amorphous iron oxide (23.7%), higher $Fe_3O_4$ (41%) and $\alpha$-FeOOH (42%) contents.

The $\beta$-FeOOH once existed in PipeB-GW3 scale samples were not detected in $Cl_2Rs$ corrosion scale samples at the end of 11d-experiment which indicated that $\beta$-FeOOH might change into GR [8], $Fe_3O_4$ and $FeCO_3$ [9, 10] under high sulfate water. Because of the increased DO, sulfate concentration of new experimental water, corrosion scale on $Cl_2Rs$ had more $FeCO_3$ and GR formation and then $FeCO_3$ were oxidized into $Fe_3O_4$ according to Siderite model [11]. Previous studies had shown that $Fe_3O_4$ were the thermodynamically stable Fe-oxides phase and the dense magnetite tightly fixed on the metal surface possesses protective and anticorrosive properties [12]. But the scale layer in $Cl_2Rs$ was very thin and Fe(II) of newly formed $Fe_3O_4$ was still unstable and could be transformed in Fe(III) which resulted to red water case.

The high iron release $Cl_2Rs$ had higher amorphous iron oxide, Fe(II) derived from new produced $Fe_3O_4$ or $FeCO_3$ and their thin, non-protective scale was easy for oxidants and sulfate ions penetration. In addition the water filled in high iron release $Cl_2Rs$ with high LR (>0.73) were more corrosive, so these $Cl_2Rs$ had higher iron release during 11d-experiment. Though the low iron release $Cl_2Rs$ had higher GR and some amorphous iron oxide, they didn't have much iron release in low LR water ($\leq$0.73). As the thin corrosion scale had many unstable iron oxides or intermediate iron products, its iron release had close relationship with water quality.
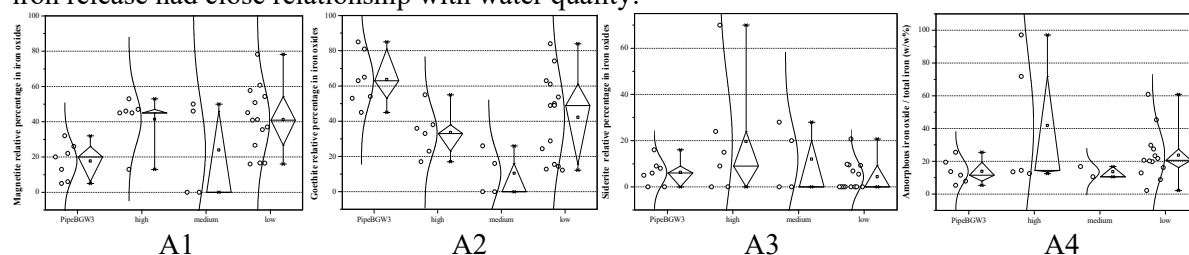


**Figure 4.** Corrosion scale chemical composition variation of free chlorine pipe section reactor (A1-A4) under water quality changing. PipeBGW3 represented corrosion scale samples on collection site, while "high", "medium" and "low" represented scale samples on high iron release reactors, medium iron release reactors, or low iron release reactors.

## 4. Conclusions

The influence of several key water quality parameters on the iron release of the pipes historically transporting treated groundwater and their thin corrosion scale stability was investigated through RSM water quality change experiment. RSM experiment results indicated that the iron release of pipe section reactors was positively related with LR viz. sulfate concentration positively related with iron release and alkalinity negatively related with iron release. And iron release was positively related with free

chlorine. After RSM experiment, the high iron released $Cl_2Rs$ receiving new water with LR in the range of 1.40-2.04 had highest $FeCO_3$ and amorphous iron oxide amount; while the low iron released $Cl_2Rs$ receiving new water with LR in the range of 0.52-0.73 had higher GR and amorphous iron oxide amount. In high LR water (>0.73), the thin and non-protective corrosion scale containing higher amorphous iron oxide, Fe(II) derived from new produced $Fe_3O_4$ or $FeCO_3$ or GR was easy for oxidants and sulfate ions penetration, and had higher iron release. Though the low iron release pipe reactors had higher $Fe_3O_4$, $FeCO_3$, GR and amorphous iron oxide, they didn't have much iron release in low LR water (≤0.73).

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