# Effects of bull serum albumin on corrosion of carbon steel under water with different Larson ratio

Yajun Zhang[1], Lingfeng Yao[2], Lihua Sun[1*], Tingting Du[2]

[1] *Key Laboratory of Urban Stormwater System & Water Environment, Beijing University of Civil Engineering and Architecture, Beijing 100044, China*

[2] *School of Environment and Energy Engineering, Beijing University of Civil Engineering and Architecture, Beijing 100044, China*

The corrosion of metal material has brought great harm to energy, economy and water quality. Corrosion scales formed by the accumulation of corrosion products would be disturbed and release microbes, heavy metals and other contaminants into water which would seriously influence the use of people, even pose a threat to human health. Comparison of corrosion of carbon steel between with and without BSA (Bull Serum Albumin) under water with different Larson ratio would be provided in this work. The comparison was around corrosion rate, rate of iron release, morphology of corrosion scales, composition changes of corrosion scales and so on. Compared to the work condition without BSA, the one with BSA had lower corrosion rate. The mechanism of corrosion without BSA mostly matched electro-chemical corrosion and was around redox reaction of iron. The corrosion scales had few $CaCO_3$ in the early period due to BSA. In the last period, the composition of corrosion scales with BSA was similar to the one without BSA and mainly included $\gamma$-FeOOH, $\alpha$-FeOOH and $CaCO_3$. The effect of proteins mainly included the adsorption film and microbial action which inhibited corrosion. Though proteins have obvious inhibition effect, it does not work when LR is high. The use of BSA as inhibitor should be after considering the water quality especially with high or low LR (Larson ratio).

**Keywords:** Corrosion scale, BSA, LR, Adsorption film, Microbial action, Inhibition.

## INTRODUCTION

Metal material is still holding a large proportion in water distribution systems in many countries, such as 56.6% in USA, 67.2% in Italy [1] and 75.5% in China [2]. The corrosion of metal material has brought great harm including energy waste due to corrosion scales limit the flow area and reduce the flow velocity and economic losses due to the replacement and reparation of the systems resulted from the faster pipe ageing, especially the threat for the water quality [3-4].Formed by the accumulation of corrosion products, corrosion scales act as the breeding ground for microbes and sinks for heavy metals or other contaminants [5]. Corrosion scales would be disturbed and biofilms would be damaged resulted by the changes of water quality or hydraulic condition, so that microbes, heavy metals and other contaminants would be released into the water, which would result in quality problems of water such as "Red water". Those problems would seriously influence the use of people, even pose a threat to human health [4,6]

The formation process and structure of corrosion scales in water distribution systems are always complex. According to the most popular model called dissolved oxygen (DO) model [7], the corrosion scales always consists of four layers: a surface layer, a hard shell-like layer, a porous core layer and a corroding floor [8-9]. The structure and characteristics of corrosion scales always depend on the metallic materials of pipes, the contacted water quality, and possibly the hydraulic conditions, etc. Compared to materials and hydraulic conditions which are easily controlled, the water quality changed more frequently. The water quality parameters related to corrosion include pH, alkalinity, dissolved oxygen (DO), temperature, natural organic matter (NOM), microorganisms, Larson ratio and so on [10-14]. Among them, the anionic groups represented by Larson ratio in water obviously affect corrosion [11]. It was found that chlorine and sulfate could promote the corrosion of iron while alkalinity slowed down the corrosion [12]. It was proposed that Larson ratio (LR) could be used to distinguish the corrosiveness of water which was widely accepted [13-15]. A lot of studies concentrated on how Larson ratio influenced corrosiveness of water, but few studies paid attention to the effects on corrosion scales due to different Larson ratio.

To ease and solve corrosion problems of water distribution systems, a lot of strategies have been

To whom all correspondence should be sent:
E-mail: sunlihuashd@163.com

used and worked to some extent. Among them, corrosion inhibitor is one of the most convenient and effective method. However, lots of the traditional corrosion inhibitors have been abandoned due to the environmental impact and health risk issues. It is urgent that new corrosion inhibitors which are "green", safe and multifunctional should be developed [13-15].As one kind of new inhibitors, protein was attracted much attention due to its characteristics of safe, green and abundance. Lots of studies were conducted around its detection, modification and action mechanism [13-14], but studies combined with water quality in real water distribution systems were still less.

The aim of this work is to provide comparison of corrosion of carbon steel between with and without BSA (Bull Serum Albumin) under water with different Larson ratio. The comparison was around corrosion rate, rate of iron release, morphology of corrosion scales, composition changes of corrosion scales and so on. The mechanism of effect by BSA on corrosion was studied and probable explanation of different effects under different Larson ratio was given. The findings of this work would help to complete the mechanisms of proteins inhibition and provide reference for effects by proteins.

## MATERIALS AND METHODS

### *Experiment planning*

The experiment was run in six rotary coupon reactors. The reactor mainly consists of 4 parts including rotary barrel, constant temperature equipment, pump, water tank. There were 21 coupons of carbon steel in every reactor. The water was stored in the tank and got into the barrel through the pump. The barrel was cylindrical with capacity of 6L. The temperature was maintained at $25\pm1\,^{\circ}\mathrm{C}$. The motor speed was 80r/min. The reactor was placed in the dark to prevent the growth of phototrophic organisms. The experiment cycle was 16 days. Horizontal hydraulic circulation was used to simulate water flow in the real systems. The water flowed into the barrel continuously and the average hydraulic retention time (HRT) was 24h.

The size of coupon is 50mm×25mm×2mm. The chemical composition (wt.%) of the coupons was as follows: C (0.07-0.13%), Si (0.17-0.37%), Mn (0.35-0.65%), P (<0.035%), S (<0.035%), with the remainder consisting of Fe.

The water was based on pure water and was prepared by adding chemical components. The main water qualities parameters are presented in Table 1.W1 to W6 represent the working conditions.

**Table 1.** Main water quality parameters in the experiment.

| Water quality parameter | W1 | W2 | W3 | W4 | W5 | W6 |
|---|---|---|---|---|---|---|
| pH | 8.1 | 8.1 | 8.1 | 8.1 | 8.1 | 8.1 |
| Turbidity (NTU) | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 | 1.3 |
| Hardness(mg/L CaCO$_3$) | 50 | 50 | 50 | 50 | 50 | 50 |
| Cl$^-$(mg/L) | 26.6 | 106.5 | 213.0 | 26.6 | 106.5 | 213.0 |
| SO$_4^{2-}$(mg/L) | 36.0 | 144.0 | 288.0 | 36.0 | 144.0 | 288.0 |
| BSA (mg/L) | 0 | 0 | 0 | 20.0 | 20.0 | 20.0 |
| PO$_4^{3-}$(mg/L) | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| HCO$_3^-$(mg/L) | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 | 180.0 |
| LR | 0.5 | 2.0 | 4.0 | 0.5 | 2.0 | 4.0 |

Larson ration (LR)=([Cl$^-$]+2[SO$_4^{2-}$])/[ HCO$_3^-$], units of [Cl$^-$], [SO$_4^{2-}$] and [HCO$_3^-$] in mol/L.

### *Coupon treatment*

Before experiment, the coupon was treated as following steps: (1) soaked in acetone and wiped by cotton 2 times; (2) put on the clean filter paper and dried by cold wind; (3) washed by distilled water for 10s and put into anhydrous ethanol; (4) put on the clean filter paper and dried by cold wind; (5) wrapped in clean filter paper, then put into dryer and weighed after 24 hours.

During experiment, 3 coupons were taken from each reactor each time. One was put into 80mL pure water and ultrasonic oscillation was used for 5min. Then took it out and put into ultra-low temperature freezer (50℃) for 2h with other two coupons. After

that, 3 coupons were put into vacuum cooling dryer for 12h. At last, put them into dryer.

After experiment, 3coupons were washed by cleaning fluid (10%HCl and 0.5%HMTA (hexamethylenetetramine)). Then washed by pure water for 10s and put into Sodium hydroxide solution (60g/L) for 1min. Then washed by pure water for 10s and soaked in anhydrous ethanol for 1min. At last, put them into dryer and weighed after 24h.

### *SEM-EDX*

The microphotographs of corrosion scales on the coupon were taken by Scanning Electronic

Microscope (SEM, Quanta 200 FEG, Holland) and the relevant elemental composition of targeted area was measured by using Energy Dispersive X-ray Spectrum (EDX).

### XRD

The composition of corrosion scales on the coupon were tested by X-Ray Diffraction (XRD, X'PERT-PRO MPD, Holland )and the operation parameters were: Cu radiation at 40 kV and 40 mA, the 2θ ranged from 5°to 90°with a 0.04°step, and a 0.4s count time at each step.

### ICP-OES

The concentration of total iron was determined by the Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES, PerkinElmer Optima 8300, USA) after joining 1mol/LHNO₃.The concentration of dissolved iron was determined by ICP-OES after filtered through 0.45μm microfiltration membrane.

In the experiment, water flowed out from the top of the reactor so that the insoluble iron was intercepted and accumulated. The release rate of the insoluble iron was calculated as follows:

$$R = \frac{(c-c')-(c_0-c_0')}{T-T_0} \qquad (1)$$

Where R is the release rate(mg/(L·d)); $C_0$ is the concentration of total iron in last time(mg/L); $C_0'$ is the concentration of dissolved iron in last time (mg/L); C is the concentration of total iron in this time (mg/L); C' is the concentration of dissolved iron in this time (mg/L); $T_0$is the last sampling time (d); T is this sampling time (d).

### HPC

The microorganism was counted for by Heterotrophy Plate Counts (HPC).

## RESULTS
### Corrosion rate

BSA inhibited corrosion because the corrosion rate with BSA was always below the one without BSA according to Figure 1-a, b and c. When LR was 0.5 and 2.0, the rate got the peak at the 2nd day, then decreased quickly and decreased slowly after 8 days. The inhibition ratios of BSA were 22.9% and 22.2%. When LR was 4.0, the rate got the peak at the 1st day, then decreased quickly and decreased slowly after 8 days. The inhibition ratio of BSA was only 9.1% and the effect of BSA became very little especially after 4 days. Compared to the inhibition ratios of which LR was 0.5 and 2.0, the inhibition ratio of which LR being 4.0 was smaller so that the inhibition effect reduced significantly with BSA and LR being 4.0.

Overall, the corrosion rates of W4, W5 and W6

were ranked as W4<W5<W6 which was consistent with LR according to Figure 1-d. The phenomenon showed that the inhibition effect of BSA was poor under the condition of LR being high.
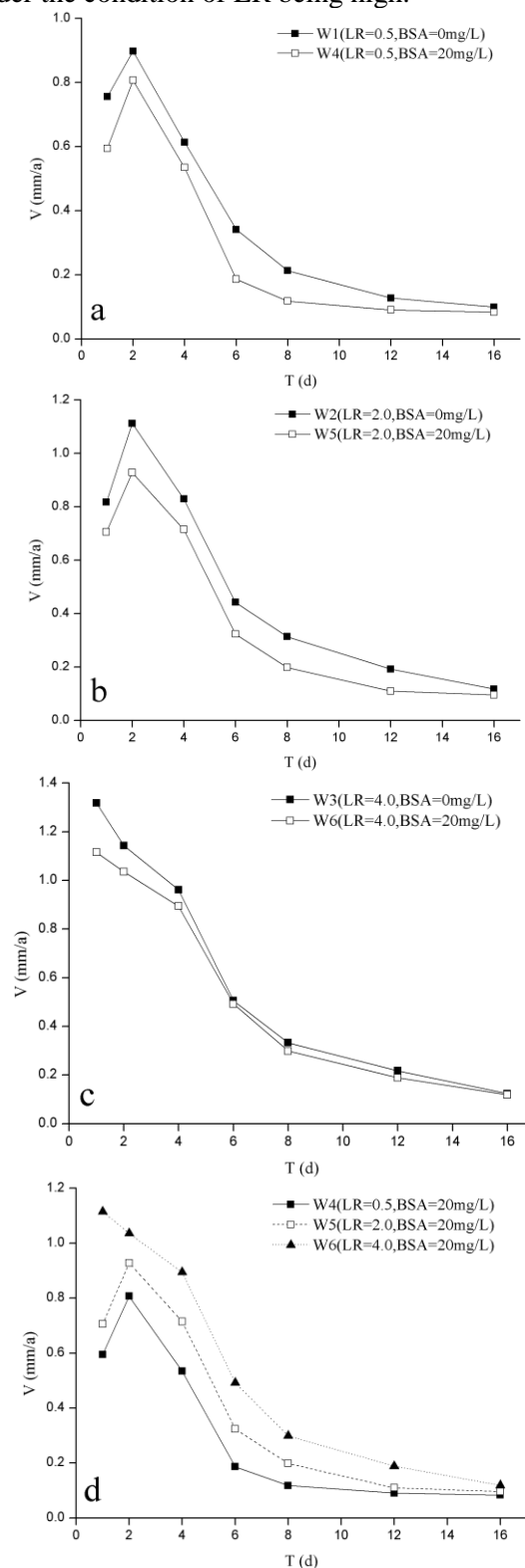


**Fig. 1.** Corrosion rate of coupons in 16 days. (a) LR=0.5, (b) LR=2.0, (c) LR=4.0, (d) BSA=20mg/L.

### *Morphology of corrosion scales*

Based on SEM analysis, the calcium oxide which

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had regular shape formed much with the thin iron oxide on the surface of corrosion scales in the 1st day without BSA (Figure 2-a).The size of calcium oxide became bigger and some areas became bare due to the scales fell off in the 4th day (Figure 2-b). The calcium oxide became bigger and more and the scales became thicker in the 16th day (Figure 2-c).

Compared to the scales without BSA, there were some iron oxide and less calcium oxide in the first 4 days (Figure 2-d,e). The phenomenon of scales fell off still occurred (Figure 2-e). However, much calcium oxide appeared on the scales in the 16th day (Figure 2-f).
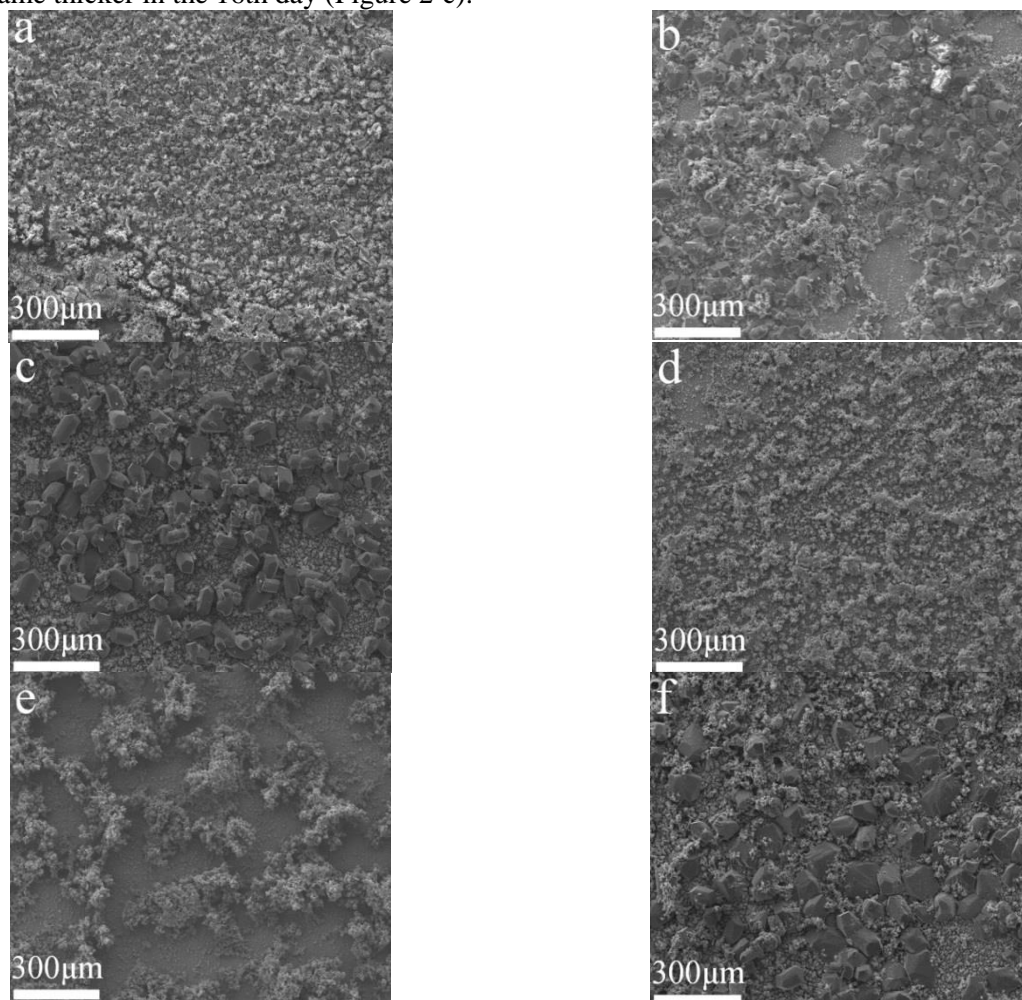


**Fig. 2.** SEM images of corrosion scales without (W1) and with (W4) BSA.
(a) W1 in 1st day; (b) W1 in 4th day; (c) W1 in 16th day; (d) W4 in 1st day; (e) W4 in 4th day; (f) W4 in 16th day.

### *Composition of corrosion scales*

Composition of corrosion scales changed with time in W1(without BSA) (Figure 3-a).In the 1st day, the corrosion scales were comprised mainly of $\gamma$-FeOOH (41.8%), $CaCO_3$ (16.9%) and $Fe(OH)_3$(22.4%). The proportion of $\gamma$-FeOOH and $Fe(OH)_3$ decreased much, but the proportion of $\alpha$-FeOOH and $CaCO_3$ increased while the remainder changed little. In the 16th day, the corrosion scales were comprised mainly of $\gamma$-FeOOH (16.8%), $\alpha$-FeOOH(23.6%) and $CaCO_3$ (24.2%) while each remain composition was about 9%.

Differ from W1, the composition of corrosion scales W4 (with BSA) was mainly $\gamma$-FeOOH

(46.7%), $\alpha$-FeOOH (11.9%) and $Fe(OH)_3$ (21.7%) with few $CaCO_3$ (2.3%) in the 1st day (Figure 3b). Similarly, the proportion of $\gamma$-FeOOH decreased much and $\alpha$-FeOOH and $CaCO_3$ increased while the remainder changed little. In the 16th day, the corrosion scales were comprised mainly of $\gamma$-FeOOH (16.9%), $\alpha$-FeOOH (34.5%) and $CaCO_3$ (19.4%) while each remain composition was about 6%.

Overall, composition of corrosion scales after 16 days was similar and mainly contained $\gamma$-FeOOH, $\alpha$-FeOOH and $CaCO_3$. However, the formation of $CaCO_3$ was inhibited in the water with BSA while $\alpha$-FeOOH increased and became main part of scales.

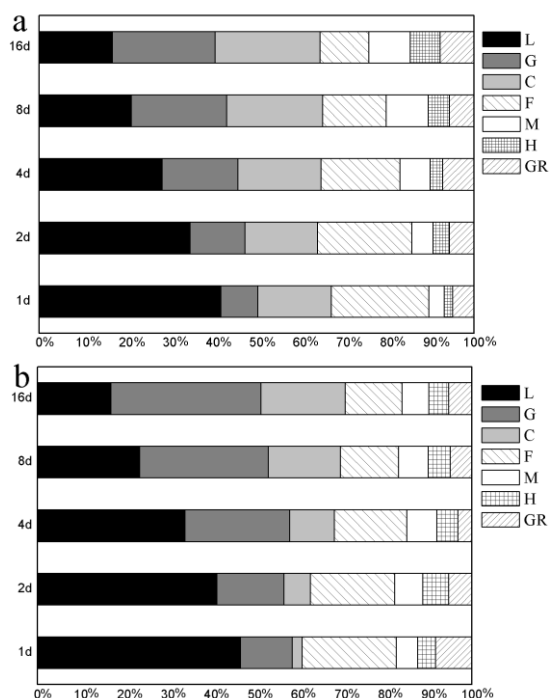The effect of inhibition worked in the first 4 days and weakened in the following days.



**Fig. 3.** Crystalline composition variation of corrosion scales. (a) W1, (b) W4.

[L: Lepidocrocite, γ-FeOOH; G:Goethite, α-FeOOH; C: Calcite, $CaCO_3$; F: $Fe(OH)_3$; M: Magnetite, $Fe_3O_4$; H: Hematite, $Fe_2O_3$; GR: green rust ($CO_3$, $SO_4$, or $PO_4$)]

*Rate of insoluble iron release*

The rate of insoluble iron release in the water with BSA was below the one without BSA in the first 6 days was shown as Figure 4. But the condition after the 6th day was opposite and rate of insoluble iron release in the water with BSA was above.

Figure 4-d shows that the changes of rate of insoluble iron release were similar even LR was different. The rate of insoluble iron release decreased fast in first 4 days, then increased and got the peak in the 8th day. Overall, the rates of insoluble iron release were ranked as W4 < W5 < W6 which was consistent with LR increasing. The phenomenon was similar to the corrosion rate.

*The total number of microorganism*

Compared to the condition with BSA, the total number of microorganism was too small. Figure 5 shows that the changes of total numbers of microorganism of W4, W5 and W6 was similar even they had different LR. The total number of microorganism of them decreased in first 2 days then increased. W5 and W6 reached the peak value as8.64××$10^8$CFU/L and 12.56×$10^8$CFU/L in the 6th day, and then decreased fast. But W4 reached the peak value as13.08××$10^8$CFU/L in the 8th day and

then decreased fast. The total numbers of microorganism of three work conditions have little differences with same concentration of BSA and do not straightly related to changes of LR
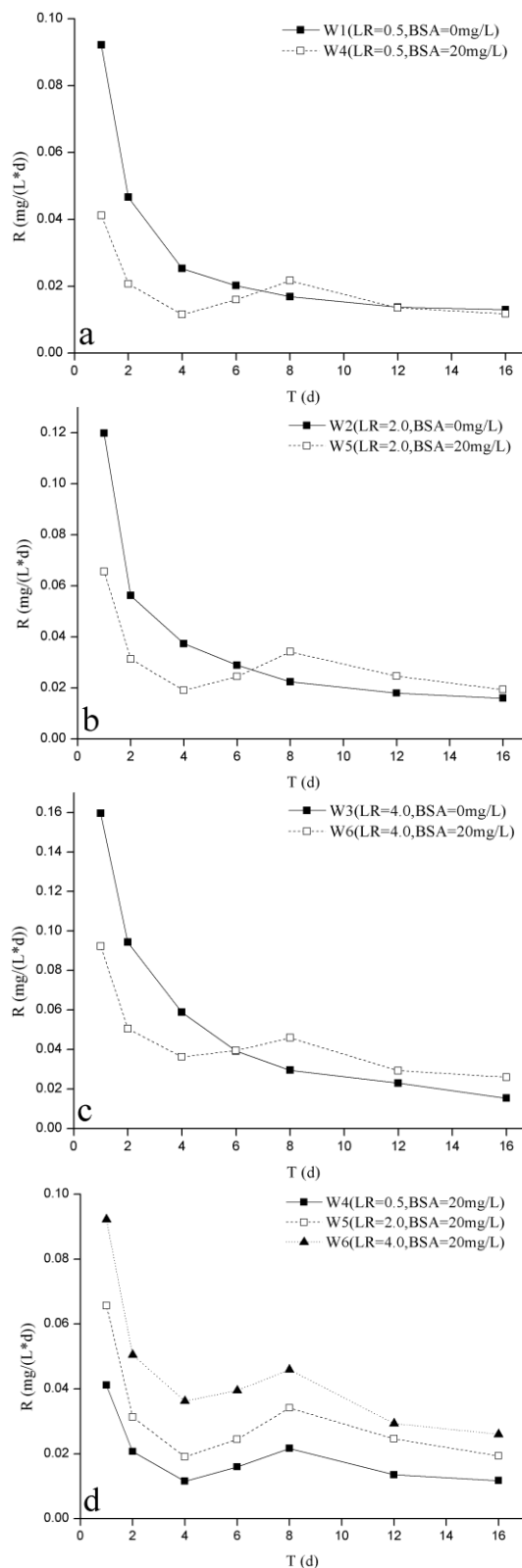


**Fig. 4.** The insoluble iron concentration under different conditions.(a) LR=0.5, (b) LR=2.0, (3) LR=4.0, (d)  BSA=20mg/L.
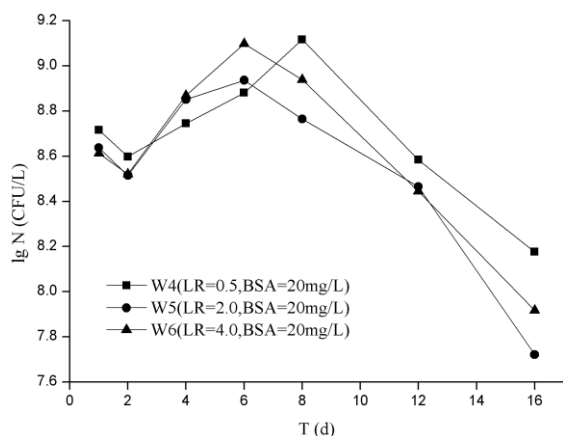
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**Fig. 5.** The total number of microorganism under different conditions.

## DISCUSSION
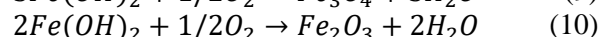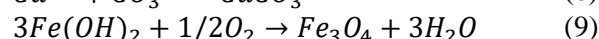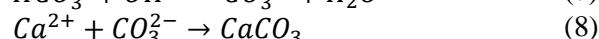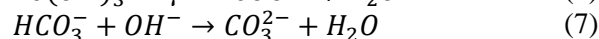
*Corrosion mechanism under water without BSA*

In this experiment, the main type of corrosion is electrochemical corrosion without BSA (W1, W2, W3) due to low concentration of microorganism.

The electrochemical corrosion of carbon steel was mainly about the iron-based redox reaction [15] which was in accordance with dissolved 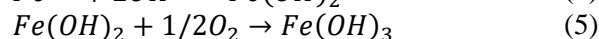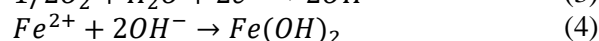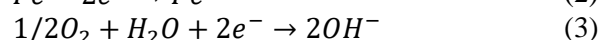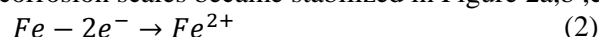oxygen model theory. In the early, steel exposed to water, which develops galvanic effect under the condition of water and dissolved oxygen. Iron in anode was oxidized into $Fe^{2+}$ and dissolved into the water (Eqs.2). Dissolved oxygen at the cathode was reduced to $OH^-$(Eqs.3)which combined with $Fe^{2+}$ to form $Fe(OH)_2$(Eqs.4).$Fe(OH)_2$ was easy to be further oxidized to form $Fe(OH)_3$in the presence of high concentration of DO (Eqs.5). Some $Fe(OH)_3$were easily occurred to dehydration and formed $\gamma$-FeOOH (Eqs.6). And the local concentration of $OH^-$ increased which would lead to move balance to the right in Eqs.7 and form $CO_3^{2-}$,then further formed $CaCO_3$(Eqs.8). These reactions happened when the iron directly contacted with water and sufficient DO, so these reactions mainly happened at the beginning of the corrosion or the top layer of corrosion scale. This also explained the formation of calcium scale and iron oxide layer in Figure 3-a and the product was mainly composed of $\gamma$-FeOOH, $Fe(OH)_3$ and $CaCO_3$ in Figure 4-a in the 1st and 4th day.

Along with the corrosion layer growing, the transmission of DO was restrained and would be insufficient. New formation of $Fe(OH)_2$was transformed to $Fe_3O_4$ or $Fe_2O_3$ through intermediate products (green rust) (Eqs.9,10). At the same time, some $\gamma$-FeOOH became $\alpha$-FeOOH while corrosion going on. It can be found in Figure 4a that $\gamma$-FeOOH was dominant in the early period, then would became $\alpha$-FeOOH due to particle-particle interactions[16].Therefore, shortage of DO would

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happen when corrosion layer became thicker. The proportion of $Fe_3O_4$, $Fe_2O_3$, green rust and $\alpha$-FeOOH would rise while the proportion of $Fe(OH)_3$ and $\gamma$-FeOOH reduced, which was consistent with the change of proportion in Figure 4-a.

The thick corrosion scale formed in the last period and the corrosion layer becomes a hinder to the transmission of DO so that anaerobic circumstance was created. The oxidation of $Fe(OH)_2$ became slow and made the balance in Eqs.6 tend to move left which made the concentration of $Fe^{2+}$ too high near the corrosion floor. Therefore, the iron dissolution of carbon steel was inhibited which was the reason why the corrosion tended to be flat and the corrosion scales became stabilized in Figure 2a,b ,c.

$$Fe - 2e^- \rightarrow Fe^{2+} \tag{2}$$
$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \tag{3}$$
$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{4}$$
$$Fe(OH)_2 + 1/2O_2 \rightarrow Fe(OH)_3 \tag{5}$$
$$Fe(OH)_3 \rightarrow \gamma - FeOOH + H_2O \tag{6}$$
$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \tag{7}$$
$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \tag{8}$$
$$3Fe(OH)_2 + 1/2O_2 \rightarrow Fe_3O_4 + 3H_2O \tag{9}$$
$$2Fe(OH)_2 + 1/2O_2 \rightarrow Fe_2O_3 + 2H_2O \tag{10}$$
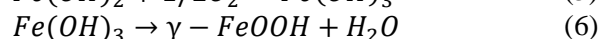
*Effect on corrosion by BSA*

In this experiment, compared with W1, W2 and W3, more protein was added to W4, W5 and W6, which had obvious influence on the corrosion of carbon steel. The effect of protein can be divided into two parts: (1) the effect of film formed of the protein on carbon steel surface by adsorption; (2) the effect of the microorganism produced by the protein on the corrosion.

*The adsorption film*

After the contacting of protein and carbon steel, a thin layer of protein formed by adsorption would be attached to the surface of the carbon steel within a few minutes [17]. The adsorption of the protein on surface was mainly affected by three kinds of effects, electrostatic force, hydrogen bond and dispersion force. Among them, the electrostatic force produced by the electric field between the protein and the surface of material was the strongest, and then the electrostatic force between intra molecular amino acids and surface, the weakest was dispersion force produced by instantaneous dipole [18].The adsorption process of protein was not only the process of mixingeffect of both physical adsorption and chemical adsorption, and it was a complex physiological process. It was related to the surface hydrophilic/hydrophobic property, chemical composition and microstructure, and also related to the size, charge and structure stability of the protein

molecule [19].

It can be seen from Figure 3 and Figure 4, compared to condition W1, W2 and W3 which without BSA, the corrosion fouling layer of the condition W4, W5, W6 which with protein did not form a significant layer of calcium scale layer in the early stage and it was mainly composed of ordinary iron oxide. However, Figure 2 and Figure 5 showed that the conditions with protein inhibited the corrosion and iron release in the early stage, showing that the protein in the early stage does have the effect of inhibiting corrosion. Researchers showed that [20-21] water of hydration and the opposite charged ions which were released by contact between proteins and surface would increase the entropy. With the promotion of increase of the entropy, the adsorption of proteins began by active patch on the groups in the microcell riveting with material surface. As the extension of time, some chemical bond in the molecule of adsorbed proteins opened and formed more locus combination with surface. Consequently, molecular conformation of proteins changed. This change may be the reason resulting in calcium scale layer difficult to form greatly in the early stage, and the formed part can be also loose off due to the effect of protein film.
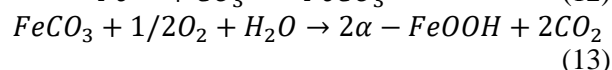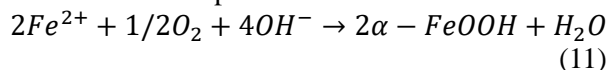
At the same time, protein film in the one hand could fill the pores formed during the formation of iron oxide layers, making the scale layer more compact, thus having good corrosion inhibition effect in the early stage; on the other hand, due to the mobility and the vulnerability of protein film, along with the corrosion process more corrosion products formed, the protein film gradually cracking and parts of iron oxide coming into the water, resulting in an increase in iron release. This can explain that the release of iron have a short period of rise after 6 days in Figure 5-d. This was a kind of original balance broken between protein film and iron scale layer, and new corrosion scale forming process, and the calcium scale could also be well adhered to on the scale layer, as can be seen in Figure 3-f.

*Microbial action*

Figure 6 shows that there were lots of microorganisms in the corrosion scales in W4, W5andW6. But the total numbers of microorganism of three work conditions did not straightly related to changes of LR. The total numbers of microorganism of work conditions without BSA were too small which indicated that microbial action was the important reason for corrosion scales differences between with and without BSA.

Different microorganisms had different effects during the formation of corrosion scales. It was

found that anaerobic bacteria groups in the deposit sediment would induce the formation of $Fe_3O_4$withhigh pH and low redox potential [22]. Genin et al. [23]found similar phenomenon in their study. It was indicated that there was microbial mechanism which could induce the formation of products such as $Fe_3O_4$and affect with the electrochemical corrosion. Bonneville et al. [24]found the iron-reducing bacteria was related to the reduction reaction of $Fe^{3+}$ and controlled release of iron. Yang et al. [25] and Wang et al. found the iron-reducing bacteria could promote to form protective layer and control the release of iron so that the corrosion would be inhibited. Jin et al. [26] found that density of iron-reducing bacteria directly influenced the formation of green rust in the core layer. Under the effects of iron-oxidation bacteria, $Fe^{2+}$ would be directly oxidized to $\alpha$-FeOOH (Eqs.11, 12 and 13) [27]. Additional explanation for the proportion of $\alpha$-FeOOH was higher than the one without BSA was provided.

$$2Fe^{2+} + 1/2O_2 + 4OH^- \rightarrow 2\alpha - FeOOH + H_2O \quad (11)$$

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \quad (12)$$

$$FeCO_3 + 1/2O_2 + H_2O \rightarrow 2\alpha - FeOOH + 2CO_2 \quad (13)$$

*Influence on corrosion under BSA by Larson ratio*

Based on Figure 1-d and Figure 5-d, corrosion rate and rate of insoluble iron release were ranked as W4 < W5 < W6 which was consistent with LR. It is indicated that corrosiveness of water which is characterized by LR obviously influences the corrosion of carbon steel. In the early period, the inhibition effect of BSA due to the formation of film and the microbial action slowed down the electrochemical corrosion and inhibited the total corrosion. In the last period, the inhibition effect of BSA weakened and the corrosion condition gradually close to the one without BSA until steady due to the main electrochemical corrosion.

The inhibition ratio of corrosion rates were ranked as W6 (9.1%) < W5 (22.1%) < W4 (22.9%). The inhibition ratio of corrosion rate decreased fast when the LR increased. It indicates that the electrochemical corrosion always dominates the corrosion.

CONCLUSIONS

This work was aimed at trying to find effect mechanism of proteins and give probable explanation of different effects under different Larson ratio by comparing the corrosion of carb on steel between with and without BSA.

Compared to the work condition without BSA,

the one with BSA had lower corrosion rate. The corrosion scales had few $CaCO_3$ in the early period due to BSA. In the last period, the composition of corrosion scales with BSA was similar to the one without BSA and mainly included $\gamma$-FeOOH (16.8%), $\alpha$-FeOOH (23.6%) and $CaCO_3$ (19.4%). The rate of insoluble iron release with BSA was lower in first 6 days and higher in last days. The total numbers of microorganism of three work conditions had little differences with same concentration of BSA and did not straightly related to changes of LR.

The mechanism of corrosion without BSA mostly matched electrochemical corrosion and was about redox reaction of iron. The effect of proteins mainly included two aspects: (1) the adsorption film which was mainly composed of proteins changed the surface properties of corrosion scales and made the scales denser to inhibition corrosion. It also could make calcium oxide easier to fall off so that calcium scale layer could not form; (2) microbial action might accelerate corrosion by promoting the redox reaction of iron or inhibit corrosion by promoting to form a protective layer and reducing release of iron. At last, the electrochemical corrosion dominates the corrosion. Though proteins have obvious inhibition effect, it does not work when LR is high. The use of BSA as inhibitor should be after considering the water quality especially LR.

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