International Journal of ELECTROCHEMICAL SCIENCE www.electrochemsci.org

# Electrochemical Corrosion Behavior of X70 Steel in Sand Soil Contaminated by Copper(II)

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Received: 11 July 2016 / Accepted: 2 September 2016 / Published: 10 October 2016

X70 steel, a common pipeline material for the long distance transport, has been extensively used in many domestic and overseas underground projects, for example "West-East" project of P. R. China. In order to study the effect of heavy metal copper(II) on the corrosion performance of X70 steel, electrochemical corrosion tests were conducted on X70 steel in sand soil for 35 d. The macro-/micromorphology, surface composition, polarization curve, electrochemical impedance spectroscopy (EIS)of X70 steel were characterized by scanning electron microscope (SEM), energy dispersive spectrometer (EDS), and electrochemical workstation, respectively. Five different concentrations of copper(II) were added into the sand soil simulated medium. The macro-/micro- morphology acquired by Canon 6D SLR cameras and SEM. The testing results showed that the copper(II) significantly affected the corrosion performance of X70 steel in sand soil. And corrosion products of X70 steel in sand soil contaminated by copper(II) exhibited colors such as yellow, red-brown, brown, black etc. It was the mixture of compound with Fe, Cu and pure Cu and sand particles. And with the increase of concentration of copper(II) in sand soil, corrosion current density, corrosion rate of X70 steel in sand soil contaminated by copper(II) dramatically increased firstly and then decreased by two orders of magnitude and 0.340% was the threshold, while the corrosion potential positively shifted. At low concentration of copper(II) in sand soil (0.034% and 0.068%), electrochemical impedance spectroscopy (EIS) of X70 steel presented the smaller incomplete capacitive arc in high frequency and the flat capacitive arcs in low frequency. With the concentration sequentially increase of copper(II), the smaller incomplete capacitive arc in high frequency disappeared gradually and the diffusion phenomenon also emerged. Besides, the sum of Rs, Rt and W decreased first and then increased and the minimum value (267.6  $\Omega$ ) acquired at copper(II) of 0.340%. In general, the addition of increased the corrosion degree of X70 steel in sand soil due to the formation of Cu/Fe micro cell.

Keywords: X70 steel; sand soil; copper(II); corrosion performance; corrosion degree; EIS

## **1. INTRODUCTION**

Pipeline transportation, rapidly developed in the world, is conceived as one of the most economical, convenient, reasonable methods due to series of merits such as low energy consumption, safety, reliability etc[1]. X70 steel, as the mainly pipeline materials for the long distance, has been used in "West-East" project of P. R. China and other domestic and overseas programs[2-4]. However, several catastrophic failures, mainly spills and telecommunications failures, have occurred due to corrosion of pipeline steel. It has been pointed out that the corrosion of pipeline steel is an inevitable problem due to the complicated conditions in soil medium including pH value, temperature, ions, particle size distributions etc[5-8]. Besides, the contamination of heavy metals (Cu, Cd, Zn, Hg etc.) in sand soil have transformed the physical structure and chemical properties of soil (void ratio, compressibility, strength properties etc.) and damaged the soil structure[9-11]. More recently, many scholars have appropriately researched the soil corrosion of X70 steel. From the point of experiment method, outdoor site embed and laboratory rapid simulating are the commonly two methods[12]. The outdoor site embed is close to the actual conditions, but the test is difficult due to the too long test period and too many variables. While the corrosion tendency, corrosion resistance of materials and the erosion of medium are able to acquire in a short period by the laboratory rapid simulating, but the difference to actual soil erosion is too larger[13,14]. In addition, electrochemical impedance spectroscopy (EIS) with small perturbation to test system is an effective method for the research on metal/soil system[15].

In terms of laboratory rapid simulating, wang et al[16] found that the corrosion resistance of X70 steel better than that of  $A_3$  in acidic medium with  $SO_4^{2-}$ , Cl<sup>-</sup> and alkaline systems with pH of 10. While the corrosion resistance of  $A_3$  steel better than that of X70 steel in strongly alkaline systems containing CO<sub>3</sub><sup>2-</sup> and weak alkaline systems containing HCO<sub>3</sub><sup>-</sup> (pH=8). Cui et al[17] also studied the stress corrosion cracking behavior of X70 steel in dilute bicarbonate solutions and the results show that when the solution pH changed from 6.8 to 5.5, SCC susceptibility decreases due to the enhancement of anodic dissolution and when the solution pH changed from 5.5 to 4.0, SCC susceptibility increases due to the acceleration of cathode reactions. El-Sayed M. Sherif et al also studied the anodic dissolution of API X70 steel in Arabian gulf seawater and found that the general corrosion decreases and pitting corrosion increased with the increase of immersion time[18]. Liu et al analyzed the relationship between corrosion rate of X70 steel and index of NaOH polluted soil and found that the corrosion rate of X70 steel decreased with the increase of NaOH in soil, void ratio and pH of soil[19]. Zhang et al found that the corrosion rate of X70 steel increased with the increase of NaCl in soil and built a multiple regression equation between resistivity, saturation and corrosion rate[20] and Hao et al discovered that the mass loss rate of X70 steel sample increased with the increase of the content of  $H_2SO_4$  in soils[21].

From a study content point of view, the researches were mainly about the aggressive ions and processed in solution containing chloride ions, carbonate/bicarbonate etc. and the corrosion evaluation of X70 steel in sand soil contaminated by NaCl and H<sub>2</sub>SO<sub>4</sub> has also been studied by the most

promising approaches based on the electrochemical impedance spectroscopy (EIS) theory for the research of soil corrosion and established the multiple regression equation about corrosive rate[20,21]. With the rapid development of industrialization and urbanization, the increasing number of heavy metal pollution incident has caused the concern and attention of scientists and experts in the ecological and agricultural field. The heavy metal pollution is a threat to the environment and human health due to the properties of resistant to degradation and toxicity. Thereinto, copper(II) mainly from antivirus agent and additive agent contained copper in agriculture is one of the most polluted heavy metals[22-23]. In addition, relevant theoretical and experimental researches contribute the pipeline protection in area polluted by heavy metal. In order to establish the complete theoretical system of corrosion behavior of X70 steel in soil medium contaminated by copper(II), the effect of the copper(II) on the corrosion performance of X70 in simulated sand soil for 35 d was studied by the method based on the electrochemical impedance spectroscopy (EIS) theory in this paper. And the corrosion mechanism was analyzed through the characterization results of morphology, corrosion composition, polarization and impedance. All of these could provide a theoretical basis for material selection and the application of X70 steel in engineering.

# 2. EXPERIMENTAL PROCEDURE

# 2.1 Experimental materials and pre-treatment

X70 steel was the experimental material and the composition of it was listed in Table 1. The test coupons with dimensions of  $15 \times 15 \times 2$  mm was cut from the X70 steel plate and then subsequently polished with sand paper to 2000 grit size submerged in water, cleaned immediately with alcohol, dried and set aside.

С	Cr	Si	Mn	Р	Ni	Mo	Cu	Co	V	S	Fe
0.0645	0.021	0.201	1.906	0.011 9	0.021	0.234	0.012	0.013	0.011	< 0.0005	Bal.

 Table 1. Chemical composition of X70 steel (wt.%)

Table 2. Mix proportion of sand soil contaminated by copper(II)

$C_{copper(II)}$ (%)	$m_{sand}(g)$	$Cu(NO_3)_2 \cdot 3H_2O(g)$	$m_{w}(g)$	$\rho_{s}\left(\Omega\cdot m\right)$
0.000	500	0.00	75.00	245.96
0.034	500	0.64	74.86	15.83
0.068	500	1.28	74.72	8.15
0.170	500	3.21	74.30	3.32
0.340	500	6.41	73.60	2.04
0.680	500	12.82	72.20	1.14

In order to better reveal the influence of copper(II) contained in sand soil on the corrosion behavior of X70 steel, six kinds of sand soil with different proportions of Cu(NO<sub>3</sub>)<sub>2</sub> (the mass fraction of copper(II) accounting for dry soil c: 0.000%, 0.034%, 0.068%, 0.170%, 0.340%, 0.680%) were selected as the test soil according to the actual situation and the composition of different contaminated soil were listed in Table 2. And the resistivity of soil samples tested by digital bridge of TH2828A was also listed in Table 2. The moisture content of sand soil is also important factors affecting the soil corrosion of steel. Sand soil with too low water content is a high-impedance medium system resulting in the reduction of electrochemical measurement precision, while there is a gap between simulation soil with too high content and actual soil corrosion. Taking the crystal water in the drug into account, water content of 15% was selected as the parameter value in this work. Under this water content X70 steel in soil contaminated by NaCl presented the lower corrosion rate[24]. A certain amount of thoroughly dissolving Cu(NO<sub>3</sub>)<sub>2</sub> solution was sufficiently mixed with determined amount of standard soil and placed in sealed bag for 24 h, which subsequently removed into the labeled soil cell for the next tests. Besides, in order to reduce the influence factors in experiment the compact degree of the soil samples controlled by the height was the same and the pure quartz sand (CHINA ISO STANDARD SAND CO., LTD.) was applied.

## 2.2 Test device

In the indoor electrochemical measurement device, the dimension of every soil sample cell is  $70.7 \times 70.7 \times 70.7 \text{ mm}^3$  and the copper sheet of  $70.7 \times 70.7 \times 0.2 \text{ mm}^3$  used to test the electrical resistivity ( $\rho_s$ ) of soil sample was fixed onto the inner wall of sample cell. The X70 steel samples with work area of  $1 \text{ cm}^2$  were buried at the same position in the prepared sand soil for 35 d and plastic wrap was covered on the sample cell to prevent the evaporation of moisture. And then the electrochemical behavior of X70 steel were tested.

## 2.3 Test and characterization

The corrosion of the X70 steel with age of 35 d in copper(II) contaminated sand soil were tested by CS350 electrochemical workstation produced by Wuhan Corrtest Instrument Co., Ltd in China under temperature of  $20\pm1$  °C and humidity of  $45\pm2\%$ . During the testing, X70 steel working electrode, saturated calomel reference (SCE) electrode and platinum auxiliary electrode formed three-electrode test system. Polarization curves were measured at scanning speed of 0.5 mV/s, scanning range of  $\pm300$  mV (relative to corrosion potential). Electrochemical impedance spectroscopy (EIS) was measured under  $10^{-2}$ ~ $10^{5}$  Hz and sinusoidal AC excitation signal amplitude of 5 mV. The micro-/macro- corrosion morphology before and after rust cleaning acquired through scanning electron microscopy (Hitachi-TM 3000) and Canon 6D SLR cameras respectively. Besides, Bruker Model QUANTAX energy dispersive spectrometer (EDS) for the corrosion products was tested by TM-3000 combined spectrum analyzer.

#### 3.1 Macro corrosion morphology

Figure 1 and Figure 2 are the macro corrosion morphology of X70 embedded in contaminated sand soil with different copper(II) (for 35 d) after cleaning the loose sand and rust cleaning. Obviously, the corrosion degree of X70 steel in copper(II) contaminated sand soil is larger than that in sand soil without contamination and it increase with the increase of copper(II) content. While the corrosion degree of X70 in soil contaminated by copper(II) for 35 d generally is more serious than that in soil contaminated by NaCl, NaOH for nearly the same time (28 d). And with the increase of contaminated by copper(II) are consistent with that in soil contaminated by NaCl and H<sub>2</sub>SO<sub>4</sub>, but contrast to that in soil contaminated by NaOH [19-21]. Overall invagination at 0.170% and even partial deletion at 0.340%, 0.680% appeared on the X70 samples. In addition, the hard compound of corrosion products and sand exhibited various colors such as yellow, red brown, brown, black etc. and was closely combined with the substrates. In terms of the sand soil, the sand particles in the vicinity of sample (range of a few centimeters) presented red-brown and the color of them became darker with the decrease of distance to sample and the increase of copper(II) content. And with the increased.

As shown in Figure 2, there were only some small localized corrosion pits and tiny loosen of original metallic luster on the steel samples in the sand soil without copper(II) contamination. When the content of copper(II) was 0.034% and 0.068%, the corrosion degree of samples significantly increased and showed typical localized corrosion. Etch pits mainly distributed at the edges of sample, while the pits of 0.068% were deeper than that of 0.034% and a long around "tunnel" formed. Besides, in the central part there was large un-corroded areas at 0.034%, but only many tiny corrosion pits, not as a whole, existed in the central part at 0.068%. When the content of copper(II) was 0.170%, the corrosion of samples was further increased. Dull surface, integrally collapsed corrosion pits with uneven interior and even two penetrated regions of  $2 \text{ mm}^2$  formed on the samples. This phenomenon was caused by the increasingly large and connection of corrosion pits and the growing increase of anode dissolution caused by the autocatalytic effect in individual region. When the content of copper( II) was 0.340% and 0.680%, the corrosion is considerably serious. The perforated regions connected into a whole and there were a large area and more than half deletion appeared at 0.340% and 0.680% respectively. Compared to the corrosion of X70 in other contaminated soil, pitting is the mainly corrosion form of X70 in soil contaminated by NaCl of 18.0 g/kg and all concentration of NaOH. Comprehensive non-uniform corrosion is the corrosion form of X70 in soil contaminated by low concentration of H<sub>2</sub>SO<sub>4</sub> (1.5, 4.5 g/kg) and non-uniform corrosion is that in soil contaminated by high concentration of H<sub>2</sub>SO<sub>4</sub> (9.0, 18.0 g/kg) for 112 d[19-21].



Figure 1. Macro corrosion morphology of X70 steel in sand soil contaminated by different concentration of copper(II) for 35d (Before rust cleaning):(a)0.000%, (b)0.034%, (c)0.068%, (d)0.170%, (e)0.340%, (f)0.680%.



Figure 2. Macro corrosion morphology of X70 steel in sand soil contaminated by different concentration of copper(II) for 35d (After rust cleaning):(a)0.000%, (b)0.034%, (c)0.068%, (d)0.170%, (e)0.340%, (f)0.680%.

These colorized corrosion products (Figure 1) adhered to the sample can be inferred as iron oxides and pure copper simple substance. On the one hand, the adhesive effect of corrosion products on loose sand lead to the formation of compound firmly stuck on the surface of the specimen. On the another hand, the various ions generated through electrode reaction spread into the depths of sand medium by diffusion, thus there were  $Fe^{2+}$  and  $Fe^{3+}$  even at the depths away from the electrodes. The corrosion products formed by the reaction of ions deposited on the surface of sand particles and hydroxide also covered on the sand particles. All of the above affect the formation of color sand products which is different from that of X70 steel formed in soil without copper(II) contamination and contaminated by NaCl and H<sub>2</sub>SO<sub>4</sub>[20,21]. And the corrosion products with different colors are difficultly removed from the substrate by mechanical means. While small amount of sand particles adhesion to the samples was very easy to remove and the sand nearby the samples presents the original pale yellow. That also show that the corrosion degree of the X70 steel in sand soil without copper(II) contamination was light and the corrosion products were less. In contrast, the corrosion products of X70 steel formed in soil contaminated by H<sub>2</sub>SO<sub>4</sub> of low contents were difficultly removed from substrate by cotton swab, while the corrosion products of X70 steel formed in soil contaminated by H<sub>2</sub>SO<sub>4</sub> of high contents fall off automatically[21].

# 3.2 Microscopic corrosion morphology

Low and high magnification ( $\times 30 \sim \times 1000$ ) of microscopic corrosion morphology of the samples in contaminated sand soil with different copper(II) before and after the rust cleaning were as shown in Figure 3 and Figure 4. Seen from the low magnification morphology, the corrosion product layers present different degrees of cracking. This will be the diffusion channel of corrosive media to the under of corrosion product layer and the effect of "blocking corrosion battery" further promoted the pitting. In addition, microcracks in pitting pits connected to each other and extended to the internal of metal. And then stress corrosion cracking (SCC) appeared on the surface of X70 steel in a large scale[25]. Many corrosion products deposited on the sand particles and there were also thin layer of corrosion products on the samples as see in Figure 3. In addition, local cracks and peeling of the products layer appeared. And the forms of corrosion products, such as grainy, coral, irregular polyhedral, flaky etc., became increasingly complex with the increase of copper(II) concentration.

And seen from Figure 4, there was a large area of thin peeling layer on the samples when the content of copper(II) was 0.034%. And the corrosion morphology was uneven and layered, but the organization characteristics of surface substrate still retained as a whole. When the content of copper(II) in soil medium was 0.068%, the peeling layer is thick. And a large number of small dissolved pits and big etch pits formed by the connection of small dissolved pits both appeared on the surface of samples. In addition, organization characteristics of surface substrate stufface substrate had changed but still shown a certain regularity. When the content of copper(II) in soil medium was 0.170%, corrosion perforation emerged and many particulate matter, cracks and porous structure formed nearby it which will constantly accelerate corrosion process.



**Figure 3.** Typical micro corrosion morphology of X70 steel in different copper(II) contaminated sand: (a)0.034%, (b)0.170%, (c)0.680%. (Before rust cleaning)

When the content of copper(II) in soil medium increased to 0.680%, the structure of unmissing part with large of pore is more loose and the surface structure presented worm-like, which was related to the formation of more and more oxide layer with loose structure. In contrast, the corrosion forms of X70 steel in soil contaminated by NaCl and  $H_2SO_4$  is mainly lacal pitting with irregular round or oval[20,21]. This is consistent with the results of macro corrosion morphology. With the increase of copper(II) in sand soil medium, the corrosion degree of X70 steel increased significantly.



Figure 4. Micro corrosion morphology of X70 steel in different copper(II) contaminated sand: (a)0.034%, (b)0.068%, (c)0.170%, (d)0.680%. (After rust cleaning)

#### 3.3 EDS characterization

EDS test results of X70 steel in different copper(II) (0.034%, 0.068%, 0.170%, 0.680%) contaminated sand for 35d were shown in Figure 5. Obviously the corrosion product layer is mainly composed of Fe, C, O, Cu, Si. Wherein, Fe mainly existed in the form of oxide. While in terms of O, except for the amount contained in the compound, it also remained in cracks and porous, loose surface structure. Besides, with the increase of copper(II) content in the soil medium, the atomic concentration ratio of Fe/O presented the trend of decrease. Namely, there was the transition trend from low valence to high valence for Fe, which is consist with the deepening of color for the corrosion products. Results show that the cation (Na<sup>+</sup>) in solution can penetrate the corrosion product layer in sandy soil corrosive environments[26]. Similarly, the cation (Cu<sup>2+</sup>) in solution can also penetrate the

corrosion product layer reach to the metal surface in sandy soil corrosive environments. Thus less amount of solid pure Cu and copper oxide formed on the surface of sample electrode spread difficultly into the depths of soil medium, while the Fe ions generated on the sample surface can be dissolved in water and easily diffused into the soil medium.





Figure 5. Atom percent of the X70 steel surface in sand soil contaminated by different copper(II): (a)0.034%, (b)0.068%, (c)0.170%, (d)0.680%.

Thus surface layered structure of corrosion products on samples was formed and it included inner layer of pure Cu and outer layer of compound contained Fe and copper oxide. In addition, Si is mainly from quartz sand and X70 steel and C with atomic concentration of substantially 20% was also mainly from X70 steel, which is similar to that of soil contaminated by NaCl[26,27].

### 3.4 Polarization curve analysis

Figure 6 is the polarization curves and Table 3 is the fitted results of the polarization curves for X70 steel embedded in different sand soil with copper(II) for 35 d through Tafel extrapolation. Similar to that in NaCl contaminated soil with the same water content of 15%, the anodic polarization of X70 steel in sand soil with copper(II) is large[26,27]. It can be concluded the copper(II) in sand medium affected significantly the corrosion property of X70 and with the increase of copper(II) content, the polarization curves presented a certain regularity. Generally speaking, the addition of copper(II) in sand soil made the corrosion potential shift positively and the shift amount increased with the increase of copper(II) content. Compared to the corrosion potential of X70 steel in sand soil without copper(II) (799 mV), the shift amount was small(0.034% of 64 mV, 0.068% of 80 mV) when the concentration of copper(II) is 0.034%, 0.068%. The shift amount drastically increased to 244 mV, 597 mV at copper(II) of 0.170%, 0.340% respectively. And the shift amount slowly increased to maximum value of 615 mV at copper(II) of 2%. In contrast, the corrosion potential of X70 steel in soil contaminated by NaCl present continuously positive shift with the increase of NaCl in sand soil and the effect is not significant[26,27].



**Figure 6.** Polarization curves of X70 steel in contaminated sand with different copper(II) content (35 d) of 0.000%, 0.034%, 0.068%, 0.170%, 0.340%, 0.680%.

$C_{copper(II)}$ (%)	$I_{corr}(\mu A/cm^2)$	$E_{corr}(V)$	r <sub>corr</sub> (mm/a)
0.000	2.774	-0.799	0.033
0.034	19.409	-0.735	0.228
0.068	24.895	-0.719	0.293
0.170	261.470	-0.555	3.076
0.340	309.670	-0.202	3.642
0.680	31.519	-0.184	0.371

Table 3. Fitted results for polarization curves of X70 steel in sand contaminated by copper(II) (35 d)

Besides, the addition of copper(II) in sand soil also significantly impact the corrosion current density and made the corrosion current density move positively compared to the X70 in sand soil without copper(II) (2.774  $\mu$ A/cm<sup>2</sup>). When the addition of copper(II) in soil medium was 0.034%, 0.068%, the corrosion current density dramatically increased by nearly 7, 9 times respectively. When the addition of copper(II) in soil medium reached to 0.170%, the corrosion current density(261.47  $\mu$ A/cm<sup>2</sup>) of X70 steel even increased by two orders of magnitude compared to that in sand soil without copper(II). When the addition of copper(II) in soil medium increased to 0.340%, corrosion current density of X70 steel further increased to the maximum value of 309.67  $\mu$ A/cm<sup>2</sup>. While when the addition of copper(II) in soil medium was 0.680%, the corrosion current density sharply decreased by

nearly 10 times compared to that at 0.340%, but it still above that at 0.034%. According to the standard, the addition of changed the corrosion grade of X70 steel from slight corrosion (I) into serious (III) and severe corrosion (IV)[28,29]. In terms of instantaneous corrosion rate, it increased firstly and then decreased with the increase of copper(II) concentration and the maximum value(3.642 mm/a) acquired at  $Cu^{2+}$  of 0.340%. The decrease of corrosion rate under  $Cu^{2+}$  of 0.680% is caused by the increase of anodic polarization resistance. And that may been explained by that during the anodic process, cohesive composite layer of corrosion products and sands particles formed quickly on the surface of electrode under high concentration of copper(II) blocked the transmission channel of matter between samples and soil medium[28,29]. That is to say the corrosion product layer plays protective effect, which is similar to that in soil leachate[30].

In general, the formation of numerous corrosion micro-cell caused by the precipitation of pure Cu on sample increased corrosion degree. In short, the corrosion resistance of X70 steel reduced firstly and then increased with the increase of copper(II) in soil. While the corrosion rate of X70 in soil contaminated by NaCl continuously increase with the increase of NaCl in soil and the decrease of soil resistivity[26,27].

3.5 EIS analysis



**Figure 7.** EIS of X70 steel in contaminated sand with different copper(II) content (35d) of 0.000%, 0.034%, 0.068%, 0.170%, 0.340%, 0.680%.

EIS of X70 steel corroded in copper(II) contaminated sand soil for 35 d was also tested and the results shown in Figure 7. Evidently, the effect of copper(II) on the EIS of X70 steel is significant. The EIS in uncontaminated sand contains two distinct capacitive arc and the sum of polarization

resistance and solution resistance is large more than that in contaminated sand soil. It is a process jointly controlled by the charge transfer and particle adsorption on electrode surface and the main reaction is the depolarization of oxygen. While the EIS of X70 steel in contaminated soil with copper(II) of 0.034% and 0.068% consist of the smaller incomplete capacitive arc in high frequency and the flat capacitive arcs in low frequency, which is similar to that of X70 steel in salinized sandy soil at the initial stage of corrosion[26]. This shows that electrochemical polarization and concentration polarization exist simultaneously in the cathode process of metal electrode[28,29]. And with the increase of copper(II), concentration polarization enhanced and electrochemical polarization weakened. When the content of copper(II) increased sequentially, the smaller incomplete capacitive arc in high frequency disappeared gradually and the diffusion phenomenon also emerged.

Furthermore, for the X70 steel in contaminated soil, only the low frequency regions were simulated through equivalent circuit due to the too small "capacitance tail" of EIS in high frequency region. EIS of 0.034% and 0.068% simulated by equivalent circuit Figure 8a and that of 0.170%, 0.340%, 0.680% were simulated by equivalent circuit Figure 8b and the results were listed in Table 4. Four components were included in Figure 8a and Figure 8b: Rs- medium resistance,  $QPE_1$  (element with constant phase angle)-capacitor of double electric layer on the interface of samples/soil medium, Rt resistance of charge transfer and W-Warburg impedance. Besides, n represent the deviation between C and the ideal capacitance and the smaller n, the deviation of C greater.



Figure 8. Equivalent electrical circuit model used to analyze the EIS date of X70 steel in sand soil for 35 d.

**Table 4.** Fit results for low frequency range in EIS of X70 steel in sand contaminated by copper(II) (35d)

$C_{copper(II)}(\%)$	$R_{s}\left(\Omega\right)$	$QPE_1 - Y_0 (uF)$	QPE <sub>1</sub> - n	$R_{t}(\Omega)$	$R_w(\Omega)$	$R_s + R_t + R_w(\Omega)$
0.034	372.2	1.0310 <sup>-3</sup>	0.319	1202.0	-	1574.2
0.068	247.8	$2.7410^{-3}$	0.642	806.3	-	1054.1
0.170	60.1	3.1510-3	0.562	150.3	63.0	273.4
0.340	41.8	6.8710 <sup>-3</sup>	0.207	98.6	127.2	267.6
0.680	27.1	3.8510 <sup>-4</sup>	0.473	588.3	1907.0	2522.4

The addition of copper(II) made the charge transfer resistance (Rt) present significant decrease first and then increase and the minimum value (98.6  $\Omega$ ) acquired at copper(II) of 0.340%. And it is similar to the variation of charge transfer resistance to time for the short-term corrosion of X70 steel in sandy soils[26]. While the double electric layer capacitor (QPE<sub>1</sub>) change inversely with the increase of copper(II) content and the maximum value also acquired at copper(II) of 0.340%. However, the medium resistance (R<sub>s</sub>) constantly decreased with the increase of copper(II) content, which is related to gradual decreasing of the soil resistivity (Table 2) caused by the increase of ions. And the high concentrations of copper(II) decreased the outer corrosion while increased the inner corrosion. Overall, the sum of Rs, Rt and W decreased first and then increased and the minimum value(267.6  $\Omega$ ) acquired at copper(II) of 0.340%, which is consist with above results. Generally speaking, the corrosion degree of X70 increased with the increase of copper(II) concentration. In contrast, the corrosion behavior of X70 steel in sandy soils is controlled by charge transfer processes[26].

The interaction mechanism of X70 steel in sand soil contaminated by different copper(II) content including one anodic reaction and three cathodic reactions just as follows:

anodic reactions

	$Fe+H_2O\rightarrow (FeOH)_{ad}+H^++e$	(1)
	(FeOH) <sub>ad</sub> →FeOH <sup>+</sup> +e [RDS]	(2)
	$FeOH^++H^+\rightarrow Fe^{2+}+H_2O$	(3)
cathodic reactions		
	$O_2 + e \rightarrow O_2^-$	(4)
	$O_2^+H_2O^+e \rightarrow HO_2^+OH^-$ [RDS]	(5)
	$HO_2^+H_2O^+2e \rightarrow 3OH^-$	(6)
	$2H^++2e \rightarrow H_2$	(7)
	Cu <sup>2+</sup> +2e→Cu	(8)

During three cathodic reactions, the reduction of  $Cu^{2+}$  played the major role, the next is the reduction of oxygen and the role of hydrogen evolution reaction is weakest. And the pure Cu was further oxidized to the copper oxide, i.e. part of the color corrosion products [31].

#### **4. CONCLUSIONS**

This work shows that copper(II) in sand soil has significantly affect the corrosion behavior of X70 steel in sand soil contaminated by copper(II) for 35 d, which is different from that in the chloride ions and carbonate/bicarbonate contaminated soil. In generally, the corrosion rate and degree increase with the increase of copper(II) for 35 d, which is similar with that of X70 steel in NaCl contaminated soil. According to the experiment and characterizations, we can draw the following conclusions:

(1). The corrosion products of X70 steel in sand soil contaminated by copper(II) exhibited colors such as yellow, red-brown, brown, black etc. It is the mixture of compound with Fe, Cu and pure Cu and sand particles, among them there was the transition trend from low valence to high valence for Fe. Besides, that firmly adhered to the sample surface especially for the X70 steel in sand soil with high concentration of copper(II).

(2). The corrosion degree of X70 steel in sand soil contaminated by copper(II) significantly increased with the increase of copper(II) concentration. Local corrosion appeared for the X70 steel in sand soil with low concentration (0.034%, 0.068%) of copper(II) and uneven general corrosion and a large area deletion occurred on the X70 steel in sand soil with high concentration (0.170%, 0.340%, 0.680%) of copper(II).

(3). The corrosion current density, corrosion rate of X70 steel in sand soil contaminated by copper(II) dramatically increased firstly and then decreased by two orders of magnitude with the increase of concentration of copper(II) in sand soil and 0.340% is the threshold, while the corrosion potential sharp -positively shifted.

(4). The EIS of X70 steel in sand soil with low concentration (0.034%, 0.068%) of copper(II) included the incomplete capacitive arc in high frequency region and flat capacitive arc in low frequency region. While the EIS of X70 steel in sand soil with high concentration (0.170%, 0.340%, 2.0) of copper(II) included capacitive arc in high frequency region and Warburg impedance in low frequency region. In general, "Rs+ Rt + W" decreased first and then increased and the minimum value (267.6  $\Omega$ ) acquired at copper(II) of 0.340%, which was consist with above polarization curve results.

In terms of the corrosion mechanism of X70 steel in sand soil contaminated by copper(II), Cu/Fe micro cell generally replaced the dominated oxygen depolarization and hydrogen evolution reaction is weakest. And this work is benefit to the control of soil corrosion for X70 steel and provide the theoretical basis for future research.

## **ACKNOWLEDGEMENTS**

This work was supported by the National Natural Science Foundation of China (No. 51208333 and 51501125), the China Postdoctoral Science Foundation (No.2012M520604 and No. 2016M591415), the Natural Science Foundation for Young Scientists of Shanxi Province (No.2013021013-2, No.2014011036-1 No.2014011015-7) the Science and Technology Programs for Research and Development of Shaanxi Province (No. 2013KJXX-08).

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