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# Difference in the characteristics of the rust layers on carbon steel and their corrosion behavior in an acidic medium: Limiting factors for cleaner pickling

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# ABSTRACT

This work aims at revealing the key factors that limit the cleaner production level of a pickling process. By comparing the difference in their characteristics and the corrosion behaviors in an acidic medium, three kinds of sample, including the matrix steel (AS), the naturally-corroded carbon steel (NR) and the carbon steel treated under high temperature oxidation (OR), after immersed in the experimental solutions with or without hexamethylenetetramine (HA), were characterized with the methods, such as, electrochemical polarization, X-ray diffraction (XRD) and scanning electron microscopy (SEM). Results indicated, no matter which kind of rust layers, the adsorption of HA on their surface all accorded with the same adsorption isotherm. Although the rust layers did not change the adsorption pattern of HA directly, but their steric effect would influence the adsorption potential of HA; the forming process of rust layers (under different environmental conditions) heavily influenced their composition, structure, and the interface roughness between the rust layer and the metal matrix, and also influenced the corrosion behavior of samples in an acidic medium, which were the key factors that limited the cleaner production level of a pickling process. These results indicated that an object-oriented pickling strategy should be adopted for a practical pickling process.

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1. Introduction

Due to the highly active nature of iron, formation of rust layers on the surface of steel and iron materials is a common phenomenon during the processes of transportation, hot rolling, surface treatment, and storage. The formed rust layers generally present a loose structure, which cannot effectively prevent the oxygen in air from penetrating inside the metal matrix; on the contrary, they may absorb moisture and dissolve more oxygen, and accelerate the corrosion of steel and iron materials in the open air (Tamura, 2008). For the purposes of achieving an effective corrosion protection and surface decoration, a commonly used method is removing the rust layers first, and then creating a stable protective coating on the surface by the methods of coating (Hwang et al., 2005), hot dipping (Graeve et al., 2013), and electroplating (Wang et al., 2007). Rust removing from the surface of steel and iron materials is so far a routine step to get a clean surface for the convenience of subsequent surface treatment and protection. The methods for rust removing now have diversified options.

The methods for fust removing now have diversified options, which include sand blasting, shot blasting, manual polishing, and acid pickling (Magdalena, 2010; Archana and Sahu, 2009). In a large-scale plant for the surface-treatment of steel and iron materials, acid pickling is generally the primary option, and also is commonly-adopted for its flexibilities and adaptabilities in a continuous production to clean work-pieces with complex shape and structure. A routine industrial pickling process generally uses some strong acids as pickling liquors, in which a corrosion reaction of removing the rust layers occurs between the rusts on the surface and the hydrogen ions in acidic solutions. The reasons leading to the formation of rust layers are very complex and diverse (Singh





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et al., 2008), which make the formed rust layers exhibiting quite a considerable difference in their physical-chemical characteristics, such as composition, density, phase, structure and morphology (Castaño et al., 2010; Li et al., 2008). These characteristics are very essential for their dominant influence on the corrosion behavior in pickling liquors, which totally determines the effectiveness and acid consumption of a pickling process.

The purpose of an industrial acid pickling process is mainly to remove the rust layers on the surface. However, owing to the strong, aggressive property of the used pickling liquor and the rather thin thickness of the rust layers on the surface (Cornu et al., 2014), the corrosion reaction between the metal matrix and the corrosive medium occurs naturally after the rust layers having been totally removed. This is so-called a phenomenon of over-pickling, which is very common in an industrial pickling process. The phenomenon of over-pickling is the direct reason leading to the over consumption of metal material and pickling liquors as well as creating excessive spent pickling liquor. Moreover, spent pickling liquors are classified as hazardous wastes in the list of the Environmental Protection Agency (EPA) of USA. Traditional methods of treating spent pickling liquors are mainly pipe-end approaches, which do not accord with the requirement of cleaner pickling. To sum up, controlling the over-pickling, minimizing the over consumption of metal material and the creation of spent pickling liquors are of primary importance for the wastes management in the relevant fields (Tang et al., 2012a). For retarding the over-pickling in an industrial pickling process, adding a corrosion inhibitor in a pickling process is an effective method, which is adopted by most surface treatment plants. However, the occurrence of rust lavers has a negative impact on the effective utilization of a corrosion inhibitor and may prolong the pickling process, which may be a limiting factor for cleaner pickling (Tang et al., 2012b). It should be noted that the diversified characteristics of rust layers determine their special corrosion behaviors even in the same pickling medium and need a suitable pickling strategy to obtain an optimal pickling result. The concept of cleaner production refers to controlling the creation of pollutants by maximally utilizing raw materials and energy from a whole process, not just treating the pollutants from the end-pipe. In this regard, the characteristics of rust layers actually play important roles in determining the cleaner production level of an acid pickling process.

To the best of our knowledge, the reported literature involving in the investigation of an acid pickling process mainly focused on the corrosion inhibition mechanism of various inhibitors (Shubina et al., 2016; Gao et al., 2015; Pandarinathan et al., 2014; Hmamou et al., 2013), and in the most experiments about corrosion inhibition, the rust layers were generally abraded completely in advance, and only the corrosion inhibition behavior of inhibitor on the surface of the metal matrix was explained (Umoren et al., 2013; Gerengi and Sahin, 2012; Asipita et al., 2014). There is little information available to explain the corrosion behavior of different rust layers in an acidic medium. In a practical acid pickling process, a pickling formula is almost adopted only based on the information from a corrosion inhibition experiment without considering the impact of rust layers. Actually, relevant investigation is of primary importance in choosing a suitable pickling strategy, since the various rust layers may have quite diversified characteristics, which may exhibit quite different corrosion behavior in an acidic medium and is a key factor to determine the corrosion reaction and the consumption of pickling liquor. In this meaning, a detailed insight into the rust layers is essential in making an optimal decision for cleaner pickling. The present work focuses on a comparative investigation of two common rust layers, that is, one is the rust layer formed in a natural condition, the other is the oxidation layer formed under high temperature, in which, two close aspects were mainly considered: (1) characterizing the two different rust layers with the methods of scanning electron microscopy (SEM), X-ray diffraction (XRD), surface roughness measurement, and comparing their characteristics with a bare iron sample without any rust layers; (2) illustrating their corrosion behaviors in the same acidic medium with the methods of polarization curves, calculating and analyzing the thermodynamic parameters on the surface. We hope the presented results would provide a useful reference to promote the cleaner production level of industrial pickling.

## 2. Materials and methods

#### 2.1. Materials and reagents

The used samples were all standard A3 carbon steel and purchased from Xinyou instrument factory of Jiangsu Province (China) with the size  $40 \times 13 \times 2$  mm. Their basic composition was: Fe: 98.53% (wt.), C: 0.27% (wt.), Cr: 0.10% (wt.), Ni: 0.05% (wt.), Mn: 0.61% (wt.), Si: 0.22% (wt.), Cu: 0.05% (wt.), Mo: 0.02% (wt.), S: 0.15% (wt.). All the samples, after purchased, were abraded with a series of emery paper from #200 to #1200, washed three times with distilled water, degreased with acetone, and then dried with a stream of cold air. After accurately weighing, one third of the abraded samples were hung vertically outside of our laboratory (located at the Guangzhou Higher Education Mega Center, Panyu District, Guangzhou, China) for 3 months. The rust layer so-formed was very similar to the corrosion products in a natural state. The other one third of the abraded samples were put in a muffle furnace and heated to 600 °C for 3 h. With the above procedures, three kinds of sample were prepared, which were the abraded samples without any rust layers (AS), the samples with a natural corroded rust layer (NR), and the samples with an oxidation layer produced under high temperature (OR). The experimental solution was prepared by diluting A.R. grade hydrochloric acid (Guangzhou Donghong Chemical Reagent Factory, Guangzhou, China) with distilled water. Hexamethylenetetramine (HA), a C.P. grade reagent (Aladdin Industrial Corporation, Shanghai, China), was used as a corrosion inhibitor to compare the corrosion behavior of different steel samples (Volovitch et al., 2011). A.R. grade acetone, purchased from Tianjin Chemical Reagent Factory (Tianjin, China), was used as a degreasing agent.

#### 2.2. Apparatus

An SEM (S-3700N, Hitachi, Japan) was used to observe the morphology of all the samples' surface before and after being immersed in the experimental solutions with or without the presence of HA. The composition phase on the surface of the samples was analyzed by an XRD (D/MAX-Ultima IV, Rigaku, Japan). The cross section of the samples was also observed with the same SEM. All the polarization experiments were carried out with a CHI660E electrochemical analyzer (Shanghai Operation Instrument Co. Ltd., China). A surface roughness tester (LEST OLS4000, Olympus, Japan) was used to measure the surface roughness of the samples.

#### 2.3. Polarization measurement

All the polarization measurements were conducted in a conventional three-electrode cell assembly. For comparing the surface characteristics of various rust layers, the working electrodes were embedded in a PVC holder with paraffin seal, exposed area of  $1 \text{ cm}^2$  (0.155 in<sup>2</sup>) of AS, NR and OR. The platinum foil was used as an auxiliary electrode, while a saturated calomel electrode (SCE) was chosen as a reference electrode. Between the working electrode

and the auxiliary electrode, a Luggin capillary was settled. After the working electrode immersed into the experimental solutions for 2 h to reach a steady state, the polarization curves were measured using a CHI660E apparatus between  $30 \pm 0.5$  °C and  $60 \pm 0.5$  °C. With a 5 mV/s scanning rate, the polarization curves were recorded ranging from -300 mV to 300 mV relative to the self-corrosion potential versus SCE (Tang et al., 2012b). The relevant corrosion current density (*I*, A · cm<sup>-2</sup>) and the corrosion potential (*E*, V) could be obtained from the polarization curves. With the data of corrosion current density, the inhibition efficiency (*IE* (%)) can be calculated with the following equation:

$$IE = (I_0 - I)/I_0 \times 100\%$$
(1)

where  $I_0$  (A·cm<sup>-2</sup>) and I (A·cm<sup>-2</sup>) are the corrosion current density without and with the inhibitor based on the data of the polarization measurements.

#### 2.4. Surface roughness measurement

A chemical method was adopted to remove the rust layer by immersing the samples into an experimental solution (500 mL 37% (wt.) HCl + 500 mL distilled water + 3.5 g HA). After vigorously stirred the experimental solution for about 10 min at 15  $\pm$  0.5 °C till the rust layers were totally removed, the samples were rinsed with distilled water, dried with a cold air blower. After that, the surface roughness was measured with a surface roughness tester. High concentration of HA was assumed to be able to protect the metal matrix from acid corrosion (Castaño et al., 2010).

#### 3. Results and discussion

#### 3.1. XRD pattern

The XRD patterns of the surface layers on the samples are shown in Fig. 1, which indicate the surface composition of AS, NR, and OR. By comparing the observed XRD results with the Joint Committee on Powder Diffraction Standards (JCPDS) files, the surface composition of the three kinds of sample can be determined. The material parameters of the samples are listed in Table 1.

After comparing with the standard patterns, the surface layer of AS was mainly composed of Fe and Fe<sub>3</sub>O<sub>4</sub> (Fig. 1(a)). The surface composition of NR was mainly Fe and Fe<sub>2</sub>O<sub>3</sub>, and other minor compositions were also observed, which showed very small peak values in the XRD image (Fig. 1(b)). While, the composition on the surface of OR was more diversified, which was mainly contained of Fe, Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> (Fig. 1(c)).

# 3.2. SEM results

The results of SEM observation generally give a visual description to the morphology of the sample's surface, which can make a qualitative evaluation to the corrosion behavior of the steel surface. The samples under different conditions were observed by an SEM with the images shown in Fig. 2.

As shown in Fig. 2(a), the surface scratch on AS was homogeneous after being abraded by a series of emery papers, while for NR and OR, the morphology of the samples' surface was quite different from that of AS. The rust layer of NR was formed under natural conditions, whose forming mechanism was mainly the pitting corrosion with the corrosion products mainly composing with

Table	1		
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Lattice parameter obtained from the XRD measurement of the three kinds of sample.

Samples	Phase constitution	JCPDS files	a	b	с
AS	Fe	50-1275	2.42700	2.42700	7.66603
	Fe <sub>3</sub> O <sub>4</sub>	75-1609	5.91196	5.94503	8.38799
NR	Fe	50-1275	2.42700	2.42700	7.66603
	Fe <sub>2</sub> O <sub>3</sub>	89-7047	5.09447	8.78869	9.43523
	γ-FeOOH	44-1415	12.52000	3.87300	3.07100
OR	Fe	34-0529	2.45001	2.45001	3.93003
	Fe <sub>2</sub> O <sub>3</sub>	88-2359	5.11199	5.11199	13.82001
	Fe <sub>3</sub> O <sub>4</sub>	76-0956	5.93202	5.91983	16.74562





**Fig. 2.** SEM images of the samples at different conditions. (a) AS before immersion; (b) AS immersed in the blank experimental solution (10% (wt.) HCl); (c) AS immersed in the experimental solution with 1.00 g/L HA; (d) NR before immersion; (e) NR immersed in the blank experimental solution (10% (wt.) HCl); (f) NR immersed in the experimental solution with 1.00 g/L HA; (g) OR before immersion; (h) OR immersed in the blank experimental solution (10% (wt.) HCl); (i) OR immersed in the experimental solution with 1.00 g/L HA; (g) OR before immersion; (h) OR immersed in the blank experimental solution (10% (wt.) HCl); (i) OR immersed in the experimental solution with 1.00 g/L HA; (j) OR before immersion; (h) OR immersed in the blank experimental solution (10% (wt.) HCl); (i) OR immersed in the experimental solution with 1.00 g/L HA; (j) OR before immersion; (h) OR immersed in the blank experimental solution (10% (wt.) HCl); (i) OR immersed in the experimental solution with 1.00 g/L HA; (j) OR before immersion; (h) OR immersed in the blank experimental solution (10% (wt.) HCl); (i) OR immersed in the experimental solution with 1.00 g/L HA; (j) OR before immersion (×10000).

Fe<sub>2</sub>O<sub>3</sub>. Under a natural state, the corrosion on a carbon steel sample started from one pitting point and developed to the nearest surface. As demonstrated in Fig. 2(d), the rust layer of NR was a loose structure, and some cracks were found on its surface. The rust layer of OR was formed under the condition of high temperature in a muffle furnace, which mainly composed of Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>. For OR, under the atmosphere in the muffle furnace, the whole carbon steel sample can act as the acting sites to form a compact rust layer, which was different from the pitting corrosion of NR. Due to the difference of the forming process, the morphology and the interface roughness and between the rust layer and the metal matrix were different between NR and OR, which might have varying influences on their corrosion behavior. Comparing the results in Fig. 2(g), (d), and (j), the rust layer of OR had higher compactness than that of NR; while, the granularity of the rust layer on NR was larger than that on OR sample.

Fig. 2(b), (e) and (h) were the images of the three kinds of sample immersed in a 10% (wt.) HCl solution without adding HA. The rough surface indicated that the samples were heavily corroded by the used aggressive solution. Comparing these images, without the protection of HA, the surface of OR was the roughest,

while the surface of AS was the smoothest, which demonstrated that the corrosion of OR was the most drastic.

SEM images shown in Fig. 2(c), (f) and (I) provided a visual description of the three kinds of sample after immersion in the experimental solution containing 1.00 g/L HA for 2 h. The obtained images illustrated that a protecting film of HA has formed on the surface of the three kinds of sample, giving an effective protection to the iron matrix below. The surface was relatively smoother than that of the sample that had not been protected by HA, which indicated that the corrosion reaction was markedly inhibited. Although compact films had formed on the three samples, their morphology was different from each other. OR was the roughest, while AS was the smoothest among the three samples. This result was quite similar to the case without adding HA, which indicated that the corrosion rate of the samples accorded with the following sequence: OR > NR > AS.

Additionally, the cross-section images of the rust layers of NR and ORwere observed and are demonstrated in Fig. 3. In here, a resin was used to fix the samples under the SEM. Fig. 3(a) gave a visual image of the rust layer on NR, which indicated that rusting appeared in position 1 and 4, and no rusting in position 2 and 3. The



Fig. 3. Cross-section images of the rust layer of two different samples. (a) NR; (b) OR.

result revealed that the rust layer on NR was a discrete and loose structure. For OR, shown in Fig. 3(b), the rust layer was compact and could be divided into several sub-layers. Different from the traditional three sub-layers structure containing  $Fe_2O_3/Fe_3O_4/FeO$  (Chen and Yuen, 2000a), Fig. 1(c) implied that only  $Fe_2O_3$  and  $Fe_3O_4$  were found on OR. The reason for this phenomenon was that sub-layer of FeO became unstable and transformed to  $Fe_3O_4$  when the cooling process occurred below 570 °C (Chen and Yuen, 2000b).

Based on these observations, it could be concluded that the forming process of rust layers heavily influenced their composition, structure, and the interface roughness between the rust layer and the metal matrix.

## 3.3. Corrosion behavior of the samples under different conditions

Fig. 4 shows the potentiodynamic polarization curves for AS, NR and OR after being immersed in a 10% (wt.) HCl solution under different HA concentrations at 30 °C for 2 h. The electrochemical parameters such as anodic *Tafel* slope ( $\beta_a$ ), cathodic *Tafel* slope ( $\beta_c$ ), corrosion potential ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ) were recorded in a supporting software with the CHI660E electrochemical workstation. The inhibition efficiency (*IE* (%)) was calculated accordingly and is listed in Table 2.

As shown in Fig. 4, the presence of HA resulted in the shifts, of both the anodic and the cathodic branches, to more lower values of  $I_{\text{corr}}$ , which indicated a remarkable decrease in the corrosion rate. Data summarized in Table 2 demonstrated an obvious decrease in the  $I_{\text{corr}}$  in the presence of HA. For the three kinds of sample, *IE* increased with the increasing of HA concentration.

*Tafel* slopes include the values of  $\beta_a$  and  $\beta_c$ . They both decreased with the addition of HA, which demonstrated that HA mainly concentrated at the active sites on the working electrode surface, and sharply retarded the metallic dissolution on the anode and the hydrogen evolution reactions simultaneously, which inhibited the

corrosion reaction on the sample's surface.

For comparing the corrosion behavior of the three kinds sample in the solution without HA. The experiments of potentiondynamic polarization were conducted in the solution10% (wt.) HCl without HA under different temperature (from 30 °C to 60 °C). The results are shown in Fig. 5, with the corresponding electrochemical parameters listed in Table 3, which indicate, under the same condition without adding HA, the magnitude of  $I_{corr}$  accords with the following sequence: OR > NR > AS, and the corrosion rate is the following sequence: OR > NR > AS.

In addition, for testing the influence of HA on the corrosion behavior of the three kinds of sample, a comparative experiment with adding HA was carried out under the same condition. The results are shown in Fig. 6, and the corresponded electrochemical parameters were calculated and are listed in Table 4. The data demonstrated that under the same condition, the reaction rate for the anodic branch of the three kinds of sample was the following sequence: AS < NR < OR, and the magnitude for  $I_{\rm corr}$  was: AS < NR < OR. Even with the protection of HA, OR has the highest corrosion potential, while the AS has the lowest.

In summary, the results in Figs. 4–6 and Tables 2–4 indicated that the sample OR generally had the highest corrosion potential under any kind of conditions, which implied the surface characteristics of rust layer was the dominant factor influencing the corrosion behavior of the samples in the experimental solutions. However, other factors, including the temperature and additive (HA), also had varying degrees of influence on the corrosion behavior, namely, adding more HA and lowering the pickling temperature, were in favor of decreasing the corrosion rate.

#### 3.4. Adsorption thermodynamics

The above results have illustrated the temperature and the concentration of HA are important factors next to the rust layers



Fig. 4. Potentiodynamic polarization curves for various concentrations of HA for the samples at 30 °C. (a) AS; (b) NR; (c) OR.

Table 2
Electrochemical parameters obtained from the polarization measurements for the three kinds of sample with various concentrations of HA at 30 °C.

Samples	Concentration of HA (g/L)	$-\beta_{c} (mV \cdot dec^{-1})$	$\beta_a (\mathrm{mV} \cdot \mathrm{dec}^{-1})$	$E_{\rm corr}$ (V)	$I_{\rm corr}~({\rm mA}{\cdot}{\rm cm}^{-2})$	IE (%)
AS	0	262.47	216.54	-0.434	35.54	0
	0.125	186.32	188.29	-0.443	13.66	72.03
	0.25	183.18	167.45	-0.478	3.849	89.17
	0.5	175.81	197.55	-0.471	3.810	89.28
	0.75	173.55	178.28	-0.476	3.550	90.01
	1	170.71	176.06	-0.474	3.494	90.17
	1.25	182.0	174.70	-0.473	3.479	90.21
NR	0	304.69	242.24	-0.445	56.7	0
	0.125	171.91	194.86	-0.456	14.30	74.78
	0.25	160.41	174.70	-0.474	4.62	91.83
	0.5	168.77	185.77	-0.478	4.53	91.99
	0.75	185.90	173.70	-0.478	3.60	93.65
	1	188.29	174.37	-0.486	3.34	94.10
	1.25	201.65	174.18	-0.486	3.07	94.58
OR	0	358.42	246.85	-0.430	68.04	0
	0.125	193.61	193.87	-0.460	23.43	65.57
	0.25	168.72	188.39	-0.476	6.19	90.89
	0.5	180.34	122.94	-0.463	5.88	91.35
	0.75	191.39	211.19	-0.482	5.81	91.46
	1	194.74	203.17	-0.483	5.40	92.05
	1.25	190.69	189.57	-0.484	5.38	92.10



Fig. 5. Potentiodynamic polarization curves for the samples without HA at different temperatures. (a) 30 °C; (b) 40 °C; (c) 50 °C; (d) 60 °C.

that influence the corrosion behavior of the samples. For further exploring the thermodynamic mechanism and giving a relevant thermodynamic explanation, an adsorption isotherm method was used here. First of all, the corrosion inhibition efficiencies were calculated according to the potentiondynamic polarization measurement with the results shown in Fig. 7, then, the thermodynamic parameters of the adsorption were calculated accordingly.

The values of *IE* generally express the inhibition efficiency of HA to retard the samples from being corroded by the corrosive liquors. The results in Fig. 7 indicated the samples had subjected to quite

different corrosive effect even under the same conditions, namely, the corrosion inhibition efficiency of HA to the samples followed the sequence: AS > NR > OR, which further verified the previous analysis.

Based on the method of Sekine and Hirakawa (1986), the degree of surface coverage ( $\theta$ , %) on the surface can be calculated with the following equation:

$$\theta = (IE_0 - IE)/IE_0 \tag{2}$$

Samples	Temperature (°C)	$-\beta_{\rm c} ({\rm mV}\cdot{\rm dec}^{-1})$	$\beta_a (\mathrm{mV} \cdot \mathrm{dec}^{-1})$	E <sub>corr</sub> (
<b>Table 3</b> Electrochemical p	arameters obtained from the polariz	ation measurements for three kir	nds of sample without HA from 3	30 °C to 60 °C.

Samples	Temperature (°C)	$-\beta_{\rm c} ({\rm mV}\cdot{\rm dec}^{-1})$	$\beta_a (mV \cdot dec^{-1})$	$E_{\rm corr}$ (V)	$I_{\rm corr}({\rm mA}\cdot{\rm cm}^{-2})$
AS	30	262.46	216.54	-0.434	35.54
NR		304.69	242.24	-0.445	56.70
OR		358.42	246.85	-0.430	68.04
AS	40	291.88	248.75	-0.423	98.89
NR		396.66	306.65	-0.439	120.0
OR		357.14	320.10	-0.429	131.9
AS	50	488.99	355.23	-0.426	150
NR		422.83	337.26	-0.432	167.6
OR		348.91	343.17	-0.413	227.9
AS	60	294.55	225.47	-0.432	198.8
NR		432.71	383.11	-0.419	211.2
OR		406.50	397.93	-0.422	284.8



Fig. 6. Potentiodynamic polarization curves for the samples with 0.25 g/L HA at different temperatures. (a) 30 °C; (b) 40 °C; (c) 50 °C; (d) 60 °C.

Tabl	e 4	
<b>F1</b>		1

Electrochemical parameters obtained from the polarization measurements for three kinds of sample with 0.25 g/L HA from 30 °C to 60 °C.

Samples	Temperature (°C)	$-\beta_{c} (mV \cdot dec^{-1})$	$\beta_a (\mathrm{mV} \cdot \mathrm{dec}^{-1})$	$E_{\rm corr}$ (V)	$I_{\rm corr}({ m mA}\cdot{ m cm}^{-2})$
AS	30	183.18	167.45	-0.478	3.849
NR		160.41	174.70	-0.474	4.62
OR		168.72	188.39	-0.476	6.19
AS	40	185.74	187.55	-0.46	13.42
NR		177.18	193.61	-0.461	14.75
OR		176.77	207.43	-0.453	23.35
AS	50	234.47	256.61	-0.456	26.82
NR		211.95	257.20	-0.451	28.16
OR		235.85	282.09	-0.446	54.22
AS	60	263.78	235.29	-0.453	49.68
NR		212.59	311.33	-0.440	50.67
OR		219.97	330.91	-0.449	87.97

where  $IE_0$  (%) and IE (%) are the inhibition efficiency without and with the inhibitor based on the data of the polarization measurements.

The obtained values of  $\theta$  for the three kinds of sample were substituted into the Langmuir, Temkin and Freundlich adsorption isotherm to precede a linear regression, respectively. The linear



Fig. 7. Corrosion inhibition of HA on the samples: (a) AS; (b) NR; (c) OR.

correlation coefficients ( $r^2$ ) are listed in Table 5. Comparing  $r^2$  for each adsorption isotherm, the results of  $r^2$  for Langmuir adsorption isotherm were very close to 1.00, which implied that the adsorption of HA was well accorded with the Langmuir isotherm for each kind of sample.

The results in Table 5 indicated that the adsorption of HA on the surface of the three kinds of sample all accorded with the same adsorption isotherm. Fitting  $c/\theta$  and the concentration of HA (c) with a linear regression method, and obtained the relationship curves shown in Fig. 8 (from 30 °C to 60 °C), the relevant thermodynamic parameter, including  $\Delta G^0$ ,  $\Delta H^0$ , and  $\Delta S^0$ , could be calculated with the results listed in Table 6.

The values of  $\Delta G^0$  were negative and located in the range of -40 to -20 kJ·mol<sup>-1</sup>, which indicated that the adsorption of HA on the samples' surface was a spontaneous, combined physical-chemical adsorption process. The values of  $\Delta H^0$  for AS, NR, OR were -7.88, -8.76, -16.30 kJ·mol<sup>-1</sup>. The negative value of  $\Delta H^0$  meant that the process of adsorption of HA was exothermic, which gave a reasonable explanation to the experimental phenomenon that the IE values decreased with the increasing of temperature (shown in Fig. 7). The adsorption on the surface was actually a process of replacing the water molecules by HA. Lower temperature was more favorable for the adsorption of HA. Moreover, the value of  $\Delta H^0$  for AS was the largest, while, the value of  $\Delta H^0$  for OR was the smallest, which demonstrated that with the increasing of temperature, the adsorption potential was the following sequence: OR < NR < AS. All of the values of  $\Delta S^0$  were positive and increased with the increase of the temperature, which demonstrated the replacing process leading to the increasing of disorder of the whole system, and the system became more disordered when the temperature increased. Furthermore, under the same experimental temperature, the value of  $\Delta S^0$  showed the following sequence: AS > NR > OR. which implied that the system was the most disordered for AS and the adsorption process was the most likely to occur. This conclusion also gave a reasonable explanation to the

Table 5Linear correlation coefficient of different samples at different temperatures.

		Adsorption isotherm equation <sup>a</sup>	Linear correlat	ion coefficient $(r^2)$		
			30 °C	40 °C	50 °C	60 °C
Langmuir	AS	c/ heta = 1/K + c	0.9998	0.9997	0.9997	0.9998
-	NR		0.9999	0.9998	0.9997	0.9999
	OR		0.9995	0.9997	0.9997	0.9996
Temkin	AS	$\theta = -\ln K/2a - \ln c/2a$	0.5521	0.5819	0.5532	0.5567
	NR		0.6512	0.6287	0.5733	0.6102
	OR		0.5329	0.5811	0.5445	0.5695
Freundlich	AS	$\ln\theta = \ln K + n \ln c$	0.5429	0.5788	0.5416	0.5492
	NR		0.9826	0.9265	0.9812	0.9521
	OR		0.5291	0.5728	0.5411	0.5502

<sup>a</sup> *c*: concentration of HA ( $g \cdot L^{-1}$ ); *K*: adsorption constant ( $L \cdot g^{-1}$ ); -1/2a: Temkin constant ( $J \cdot g^{-1}$ ); *n*: Freundlich constant.



Fig. 8. Langmuir isotherm at different temperatures: (a) AS; (b) NR; (c) OR.

Table 6

Inermodynamic	parameters of	the adsorption	at different	temperatures.	

T (K)	Samples	$\Delta G^0 (kJ \cdot mol^{-1})$	$\Delta H^0 (kJ \cdot mol^{-1})$	$\Delta S^0 (\mathbf{J} \cdot \mathbf{mol}^{-1} \cdot \mathbf{K}^{-1})$
303.15	AS	-32.49	-7.88	81.21
313.15		-33.30	-7.88	83.87
323.15		-34.10	-7.88	86.54
333.15		-34.93	-7.88	89.25
303.15	NR	-32.98	-8.76	79.91
313.15		-33.85	-8.76	82.78
323.15		-34.65	-8.76	85.39
333.15		-35.38	-8.76	87.81
303.15	OR	-32.26	-16.30	52.67
313.15		-32.83	-16.30	52.79
323.15		-33.41	-16.30	52.98
333.15		-33.82	-16.30	53.02

experimental phenomenon that OR had the highest corrosion potential and AS had the lowest.

# 3.5. Effect of the surface roughness of metal matrix on the corrosion reaction

In order to illustrate the effect of the surface roughness after the removal of the rust layers on the corrosion reaction for different samples, the differential polarization curves were plotted out according to the relevant potentiondynamic polarization measurement and compared under different surface roughness.

Fig. 9 shows the differential polarization curves of AS, NR and OR in the 10% (wt.) HCl and 0.25 g/L HA at 30 °C, and Fig. 10 demonstrates the differential polarization curves of AS, NR and OR in the 20% (wt.) HCl and 0.25 g/L HA at 30 °C to further illustrate the corrosion inhibition in a stronger acidic environment. The Y-axis of Figs. 9 and 10 are indicated as a semi-logarithmic slope (S, V<sup>-1</sup>) of the polarization curve, which is defined as follows:

$$s = \frac{d \log I}{dE}$$
(3)

where  $I(A \cdot cm^{-2})$  is the current density, E(V) is the potential of the electrode.

In an acidic medium, the rust layer would be dissolved and the corrosion reaction in an acid pickling process can be generally expressed by the following equations:

$$Fe_2O_3 + 6H^+ \rightarrow 2Fe^{3+} + 3H_2O$$
 (4)

$$Fe_{3}O_{4} + 8H^{+} \rightarrow Fe^{2+} + 2Fe^{3+} + 4H_{2}O$$
(5)

$$Fe + 2H^+ \to Fe^{2+} + H_2 \uparrow \tag{6}$$

After the samples were immersed in the experimental solutions for a while, the corrosion reaction resulted in a quite different morphology on the surface of the samples, and also caused variation in their surface roughness. Due to the surface roughness has a strong effect on the corrosion behavior of the samples, for comparing their difference after pickling, a surface roughness  $(R_a)$ measurement was carried out. Under the same testing conditions,  $R_a$  of NR was found to be 8.503  $\mu$ m, while the  $R_a$  of OR was 10.028 µm. Moreover, after immersion in the same experimental solution, R<sub>a</sub> of AS was found to be 1.256 µm. These data and the results of SEM observation revealed that the rust layers formed under different conditions would cause a major difference in the surface roughness of the metal matrix, which was an essential factor to influence the subsequent corrosion reaction on the surface of metal matrix. Generally, the corrosion potential has a close relationship with the energy required to move an electron on the surface, and less requirement of energy to move an electron would lead to a higher corrosion potential. The electron work function



Fig. 9. Differential polarization curves in the 10% (wt.) HCl and 0.25 g/L HA medium at 30 °C. (a) AS; (b) NR; (c) OR.



Fig. 10. Differential polarization curves in the 20% (wt.) HCl and 0.25 g/L HA medium at 30 °C. (a) AS; (b) NR; (c) OR.

(EWF), the minimum energy required to move electrons, is heavily influenced by the surface roughness. Rougher surface means a lower EWF, which implies more electrons would be easily released and results in a higher corrosion rate (Chui et al., 2011; Li and Li, 2006; Qiao et al., 2009).

The main difference among the samples of AS, NR and OR was the rust layer on their surface, which may have an obvious influence on the adsorption potential of the molecules of HA. The XRD images in Fig. 1 showed that the composition of the rust layer for the two kinds of sample (NR, OR) were Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>. After hybridization of Fe atoms of the rust laver and combination with oxygen atoms, no lone pair electrons of Fe atoms left to form a coordinate bond with the lone pair electrons of N atoms on the amidogen of HA, which implied that the rust layer would not adsorb HA, but it would sterically hinder the adsorption of HA. Only until the original rust-covered iron matrix became bared out, the molecule of HA could be adsorbed to form a protective film. As it was shown in the SEM images, cracks could be observed on the surface of NR, and the rust layer on the NR samples was a discrete and loose structure. During the pickling process to remove the rust layer, the molecules of HA could pass through the cracks and adsorb onto the metal matrix of the sample. After the rust layer was removed, and the original rust-covered iron matrix now became exposed, then HA was absorbed on its surface to form a compact film to inhibit a further corrosion. However, due to the compact structure of the rust layer on the OR sample, HA could not form a protective film on the rust layer's surface, the corrosion reaction generally occurred very quickly to remove the rust layer. After the rust layer was totally stripped off from the surface of OR, the molecule of HA could be absorbed onto the surface of the matrix, and as a result, the adsorption potential of HA accorded with the sequence: AS > NR > OR, which implied that easier adsorption would result in more effective protection to the sample. However, as shown in Figs. 9 and 10, no desorption peaks were found in the differential polarization curves in the experimental solution, which demonstrated that the inhibitor had a strong adsorption on the anode part of the electrode and the adsorption film were stable on the surface of metal matrix. Although a stable film had been formed, due to the different surface roughness, the corrosion densities were different, they followed the sequence: OR > NR > AS, which implied that, for the higher rough surface, the subsequent corrosion reaction rate was still higher than that of the other two samples, even with the protection of HA.

High concentration of pickling liquors can accelerate the pickling process, while high concentrations of inhibitor can reduce the over-pickling. For maintaining a suitable pickling speed and at the same time to avoid the over-pickling phenomenon, an optimal pickling formula should be adopted on the basis of the characteristics of rust layers. For OR, low-concentration of pickling liquor and high-concentration of inhibitor are favored, and for NR, highconcentration of pickling liquor and low-concentration of inhibitor are more suitable.

# 4. Conclusions

In the present investigation, the surface characteristics of AS, NR and OR, as well as their corrosion behavior in the experimental solutions were compared under the same conditions. According to our experimental results, the following conclusions were drawn:

- 1. The rust layer of NR was mainly composed of Fe<sub>2</sub>O<sub>3</sub>, while for OR, the composition of the rust layer included Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub>, and the rust layer on OR was more compact than that on NR.
- 2. The rust layer on NR exhibited a discrete and loose structure, while, the rust layer on OR was compact and continuous. No matter which kind of rust layers, the adsorption of HA on their surface all accorded with the same adsorption isotherm. Although the rust layers did not change the adsorption pattern of HA directly, but their steric effect would influence the adsorption potential of HA.
- 3. The forming process of rust layers heavily influenced their composition, structure, and the interface roughness between

the rust layer and the metal matrix, and also influenced the corrosion behavior of samples, which was the key factor that limited the cleaner production level of a pickling process. After the rust layer was removed, the surface roughness of the OR sample was higher than that of the NR sample, and the rate of over-pickling accorded with the following sequence: OR > NR > AS. Rougher surface led to a higher corrosion potential and accelerated the corrosion reaction, but easier adsorption of inhibitor resulted in more effective protection to the metal matrix and less requirement of pickling liquor, which consisted with the objectives for cleaner production.

4. For ensuring a suitable pickling rate and avoiding the overpickling phenomenon, an object-oriented pickling strategy should be adopted according to the characteristics of rust layers.

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