



# Synergy effect of naphthenic acid corrosion and sulfur corrosion in crude oil distillation unit

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## ABSTRACT

The synergy effect of naphthenic acid corrosion and sulfur corrosion at high temperature in crude oil distillation unit was studied using Q235 carbon-manganese steel and 316 stainless steel. The corrosion of Q235 and 316 in corrosion media containing sulfur and/or naphthenic acid at 280 °C was investigated by weight loss, scanning electron microscope (SEM), EDS and X-ray diffractometer (XRD) analysis. The results showed that in corrosion media containing only sulfur, the corrosion rate of Q235 and 316 first increased and then decreased with the increase of sulfur content. In corrosion media containing naphthenic acid and sulfur, with the variations of acid value or sulfur content, the synergy effect of naphthenic acid corrosion and sulfur corrosion has a great influence on the corrosion rate of Q235 and 316. It was indicated that the sulfur accelerated naphthenic acid corrosion below a certain sulfur content but prevented naphthenic acid corrosion above that. The corrosion products on two steels after exposure to corrosion media were investigated. The stable Cr<sub>5</sub>S<sub>8</sub> phases detected in the corrosion products film of 316 were considered as the reason why 316 has greater corrosion resistance to that of Q235.

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## 1. Introduction

Naphthenic acid and sulfides often exist simultaneously in crude oil during the refining process, so naphthenic acid corrosion [1–4] and sulfur corrosion [5–8] occur concurrently and react upon each other in the whole crude oil distillation units. This problem has not yet been completely investigated and it had a serious influence on the production activity of the oil refinery enterprises. The naphthenic acid corrosion and sulfur corrosion have been studied mostly separately by other investigators. Research on the synergy corrosion behavior of naphthenic acid and sulfur at high temperatures, however, is scarce.

Craig [9] showed that hydrogen sulfide possesses a quite strong inhibitory effect on naphthenic acid corrosion at 260 °C and there exists an acid critical value. Through iron powder experiment, Yépez [10] found that FeS cannot form until H<sub>2</sub>S content exceed a certain value. However H<sub>2</sub>S can react with iron naphthenate first so that it destroys the chemical equilibrium between naphthenic acid and metal, accelerating the naphthenic acid corrosion. Cooper [11] suggested that sulfides react more vigorously with metal material by decomposing into H<sub>2</sub>S above 288 °C. Through his research, Kane and Cayard [12] demonstrated that the sulfur and naphthenic

acid corrosion is a continuum. With the continuous variation of sulfur content the naphthenic acid presents different corrosivity. H<sub>2</sub>S could inhibit naphthenic acid corrosion only when H<sub>2</sub>S content is in the appropriate range. However, when H<sub>2</sub>S content exceeded a certain value, the protective sulfides scales were eroded by high velocity liquid causing erosion–corrosion and the naphthenic acid accelerated corrosion. Zheng and co-workers [13] at Metal Research Institute of Academia Sinica carried out successive researches of naphthenic acid corrosion and sulfur corrosion. They only studied synergy corrosion behavior of naphthenic acid in corrosion media with 1% sulfur content and different acid value at 270 °C.

In this study, the synergy effect of naphthenic acid corrosion and sulfur corrosion in simulated field environmental condition has been investigated. The corrosion rate of Q235 carbon–manganese steel and 316 stainless steel in high temperature corrosion media with different acid value and sulfur content was obtained; the influence of acid value and sulfur content on the synergy effect of acid corrosion and sulfur corrosion was analyzed. The results of this study provide insight into how to control the synergy corrosion of naphthenic acid and sulfur for oil refinery enterprises.

## 2. Experimental

### 2.1. Materials and media

Two steels, Q235 carbon-manganese steel and 316 stainless steel were selected. The chemical composition of Q235 and 316

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**Table 1**  
Chemical composition of Q235 and 316 steel (mass fraction/%).

Steel	C	Mn	Si	S	P	Ni	Cr	Mo	Fe
Q235	0.14–0.22	0.30–0.65	≤0.30	≤0.050	≤0.045				Bal
316	≤0.030	≤2.00	≤1.00	≤0.030	≤0.035	12.0–15.0	16.0–17.0	2.0–3.0	Bal

steel is shown in Table 1. All specimens were machined as rectangle coupons with dimension of 50 mm × 10 mm × 3 mm. All coupon surfaces were ground to 600-grit by sand paper, cleaned and degreased in acetone, dried immediately and weighed before corrosion tests.

Five Q235 coupons and five 316 coupons were used in each experiment. Three coupons of each steel were used to measure the weight change, i.e. to determine the corrosion rate, while the other two coupons were used for morphology observation and phase analysis respectively.

The corrosion media used in the test included various mixtures of 7# technical white oil (a high-boiling petroleum distillate consisted of different kinds of C16–C31 isoparaffin), analytical pure naphthenic acid (acid value is 169 mg KOH/g) and analytical pure dimethyl disulfide. The test media were prepared by spiking the white oil with pure naphthenic acid and dimethyl disulfide to achieve the desired total sulfur content and total acid value.

Crude oils often contain sulfur from 0.5 wt% to 5 wt% and acid from 0.1 mg KOH/g to 3.5 mg KOH/g [12]. But particularly in some severe situations the acid values of crude oils exceed 10 mg KOH/g [14]. So the preparation of the test media was based on this actual situation.

## 2.2. Apparatus and procedures

The corrosion tests were carried out in a high temperature reaction kettle by immersion method. The specimens was hold by a heat-resistant and anti-corrosion ceramic scaffold in this reaction kettle.

For calculating the corrosion rate, before each test the specimens were degreased by acetone, dried in drying oven and weighed immediately. After each test, the corrosion products film of specimens which were used to measure the weight change were ultrasonically removed in a special solvent for 5 min, and specimens were rinsed by running water, rinsed by distilled water, ultrasonically degreased in acetone, dried in a drying oven and weighed. The solvent was prepared according to GB/T 16545-1996, a Chinese national standard for corrosion product removal, by adding 3.5 g methenamine to 500 mL hydrochloric acid (1.19 g/mL), and then diluting it with distilled water to 1000 mL solution.

The corrosion media used in the previous test was refreshed before each new test started so as to ensure the accuracy of experimental data. The duration of each corrosion test was 24 h and the test temperature was 280 °C.

The corrosion rate  $V$  (mm/y), was calculated as follows:

$$V = \frac{\Delta w}{\rho_{st}} \times 24 \times 365$$

where  $\rho$  is the material density (g/mm<sup>3</sup>),  $s$  denotes the corrosion area (mm<sup>2</sup>),  $t$  is the test duration (h), and  $\Delta w$  (g) denotes the weight differences of specimens before corrosion tests and after tests with corrosion films being removed.

After the corrosion tests, a JEOL/JSM-6490LV scanning electron microscope (SEM) with an X-ray diffractometer (XRD) was used for morphology observation and composition analyses of corrosion product film on specimen surfaces.

## 3. Results and discussion

### 3.1. The influence of sulfur content on the sulfur corrosion

Table 2 shows the corrosion rates of Q235 and 316 in corrosion media with different sulfur contents at 280 °C. It was found that the corrosion rate of Q235 increased little with sulfur content increasing from 1% to 2% but increased sharply with sulfur content increasing from 2% to 3% and reached the peak value when the sulfur content is 3% then decreased sharply with the sulfur content increasing from 3% to 5%. The corrosion rate of 316 has the same changing tendency as that of Q235 with the sulfur content increasing. The difference was that the corrosion rate of 316 reached the peak value when the sulfur content was 4% while the corrosion rate of Q235 reached the peak value when the sulfur content was 3%. It was concluded that the corrosion rate of both steel reached peak value when the sulfur content reached a certain level and above the level the corrosion rate decreased.

Figs. 1 and 2 show the morphologies of 316 and Q235 after 24 h corrosion tests in corrosion media with different content sulfur at 280 °C. When the sulfur content was 2% (Fig. 1a) Q235 steel was corroded seriously. The corrosion products film was loose and local peeling; when the sulfur content was 3% (Fig. 1b), many crevices and some white spheres appeared on the corrosion products film; when the sulfur content was 4% (Fig. 1c), there were few crevices on the corrosion products film and the structure of corrosion products film was uniform. This was attributed to the increased thickness of the corrosion product film with the increase of sulfur content. When the sulfur content was 5% (Fig. 1d), the corrosion products film was dense and uniform without any crevice on it and it entirely covered the surface of specimens. The 316 specimens in corrosion media with different sulfur content from 1% to 5% presented almost the same corrosion morphology, as shown in Fig. 2. Apparent and smooth corrosion products film covered the 316 specimens was observed. The corrosion characteristic of both Q235 and 316 in corrosion media only containing sulfur with different sulfur content was uniform corrosion.

The influence of sulfur content on the corrosion rates of Q235 and 316 indicates that protective corrosion product film played an important role in the sulfur corrosion. The high corrosion rate in low sulfur content corrosion media was attributed to the thin protective corrosion product film which offered no protection to the metal substrate. Though the protective corrosion product film grows faster with the sulfur content increasing under a certain level, the sulfur corrosion became more severely accordingly, the corrosion rate increased. When the sulfur content increased above

**Table 2**  
Corrosion rates of two steels in corrosion media with different sulfur contents.

w (Sulfur content)/%	$\bar{v}$ (Corrosion rate)/(mm per year)	
	316	Q235
1	0.0602	3.2917
2	0.1491	3.5463
3	0.1835	5.8597
4	0.3296	5.4468
5	0.0309	1.6837

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