Synergistic Effect of the Total Acid Number, S, Cl, and H₂O on the Corrosion of AISI 1020 in Acidic Environments

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ABSTRACT: The corrosive environment in sulfur-containing equipment is often complicated and changeable. This study adopted the Taguchi method to optimize the immersion test, and the L₂(3¹³) orthogonal table was used to design an immersion corrosion experiment. The influence of four factors, namely, the total acid number (TAN), sulfur, chlorine, and water, on the corrosion of AISI 1020 in the oil phase was studied. It showed that the effect of chlorine is the most pronounced and that of sulfur is second followed by that of the TAN and H₂O. It was also found that the effect of H₂O exceeds that of the TAN after 336 h; meanwhile, the interaction between the four factors varies over time and stabilizes after 336 h. Moreover, corrosion rate curves reveal that the stable corrosion product film formed on the metal surface gradually slows down the corrosion process. Analysis of corrosion morphology and product composition was done by scanning electron microscopy and energy-dispersive X-ray spectroscopy. Overall, the synergistic effect of the corrosion rate changing with time provides a certain reference for the corrosion protection of sulfur-containing storage equipment.

1. INTRODUCTION

The rise in sulfur content in crude oil is a global trend, and this situation has led to an increase in the corrosion rate of sulfur-containing equipment. Furthermore, clean energy, such as solar energy and lithium batteries, has begun to replace fossil fuels in some fields. The demand for crude oil in the energy market has decreased. Consequently, refineries are more inclined to purchase acidic crude oil with low prices and high sulfur content to reduce operating costs. The increase in the content of sulfur, acid, and other impurities has severely corroded some oil storage tanks in active service, and the situation has led to an increase in the corrosion rate of sulfur-containing equipment.  

Gaseous hydrogen sulfide mainly exists in the gas-phase part of petrochemical storage and transportation equipment. The presence of hydrogen sulfide causes sulfide stress cracking (SSC) and hydrogen-induced cracking (HIC) regularly. When steel equipment is not sufficiently quenched and tempered during casting, it would offer poor resistance to HIC and SSC. The inner wall of the oil storage tank is frequently immersed in the oil phase. Though the crude oil itself has no corrosive effect on metals, the active components, such as hydrogen sulfide, mercaptans, thiophenes, and elemental sulfur, in crude oil can cause direct or oblique corrosion to the inner metal wall. A study found that oils with different impurity contents have certain differences in the corrosion rule of metals in the oil phase and gas phase of equipment. With increasing equipment usage time, the corrosion area gradually developed from the surface to the inside. X-ray diffraction test results of the corrosion products from the invading iron sulfides show that the products are mainly Mackinawite and cubic FeS. Furthermore, the sulfide in oil products is not the only factor affecting equipment corrosion. Organic chlorides and water produced by natural geological processes during exploration, transportation, and storage also affect the corrosion process. These impurities in sour oil are present at various stages of refining, and they affect the normal operation of the equipment simultaneously. Naphthenic acid existing in the oil phase is a slightly stronger acid than carbonic acid, and its presence can cause naphthenic acid corrosion (NAC) in refinery equipment and transportation facilities. Through earlier study, it is known that undissociated acetic acid is the main reason for the change in the corrosion process of low carbon steel. Moreover, high temperatures will accelerate the corrosion process, including electrochemical, chemical, and molecular movement. Meanwhile, the chlorides in crude oil are hydrolyzed to form naphthenate at high temperature, and gaseous hydrochloric acid is also released, promoting the corrosion of refinery equipment and intermediate tanks and vessels. Even 316 L stainless steels with strong corrosion resistance will undergo local and pitting corrosion.
leading to equipment failure under a sulfur deposition environment containing chloride. However, with environmental conditions that are conducive to the production of iron scale materials, such as a neutral pH, the corrosion rate will decrease. Evidently, crude and processed oils are complex mixtures, their sulfide, chloride, and naphthenic acid contents as well as other factors affect the nature and degree of the equipment corrosion process collectively.

In this research, a Taguchi test, including four influencing factors with three levels, was designed to evaluate the synergistic effect of the total acid number (TAN), mercaptans, carbon tetrachloride, and water on the corrosion of AISI 1020 in the oil phase. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on some representative specimens after a weight loss test. This article presents the corrosion behavior of tank materials in liquid oil products under various influencing factors over time and the corresponding corrosion rate changes.

2. RESULTS AND DISCUSSION

2.1. Characterization of Oil Properties. Commonly, crude oil with a sulfur content of less than 0.5% is called a low-sulfur oil, oil with a sulfur content of 0.5–2% is called a sulfur-containing oil, and oil with a sulfur content above 2% is called a high-sulfur oil. As shown in Table 1, the test oil is for a sulfur-containing oil, the chloride and water contents in the oil are not high, and the oil is weakly acidic. The sulfur content of oil products is mainly attributed to the originally refined crude oil being Middle East high-sulfur crude oil. Due to the low removal rate of organic sulfides in the alkaline washing process of desulfurization in refineries, the sulfur content remains at a high level. Compared with low-sulfur oil, this type of acidic oil is more likely to cause sulfur corrosion leakage in storage and transportation equipment.

Table 1. Characterization and Detection of Oil Properties

| impurity | detection method | results |
|----------|------------------|---------|
| TAN      | acid-base neutralization titration | 0.03 mg KOHg⁻¹ |
| S        | organic element analysis (Elementar Vario microcube) | 1.56 wt % |
| Cl       | ion chromatography (ICS 1100) | 0.02 wt % |
| H₂O      | distillation     | 0.03 wt % |

After the corrosion products on the surface of samples were removed by a rust remover, the results of the weight loss method were used to calculate the corrosion rate of each group. The value of R is the difference between the sum of the corrosion rates at the three levels of the corresponding factor and the average value. The larger the value of R, the more obvious is the influence of this factor. The range analysis was performed by direct-viewing analysis, and the R values were ranked to evaluate the influence of main factors and first-order interaction factors on the corrosion rate at different periods. The R value ranking and corrosion rate results for the six periods can be seen in Table 2.

The influence of chlorine on the corrosion rate is always dominant in the six periods of 168 to 1008 h (Table 2) and second by the sulfur content. In addition, the impact of the TAN is higher than the effect of water content on corrosion in the initial stage. After 168 h, the effect of water content on the extent of corrosion gradually increases until it exceeds that of the TAN. From the corrosion rate results, it can be seen that, from 168 to 336 h, the experimental group no. 1223 has the fastest corrosion rate and, from 672 to 1008 h, the experimental group no. 1332

Fe(HS⁺)ads → FeS³⁻ + xHS⁻ + (1 − x)H⁺ (5)

Fe(HS⁻)ads + HS⁻ → FeS + H₂S (6)

It can be seen that the scale consists of two different iron sulfide layers (eqs 1–6). The thermal dissociation of iron sulfide at the interface between the inner and outer layers transports the S element to the inside to form fine particles and a porous inner layer and leads to the bubble-like appearance of the corrosion products. It can be clearly seen in Figure 1-10–27 that, when the levels of the TAN are 2 and 3, the corrosion products on the surface are much more complicated than those in Figure 1-1–9 when the level of the TAN is 1. Due to the presence of organic acids and chlorides, the corrosion appearance varies greatly at different impurity concentrations. As shown in Figure 1-13,16,19, there are loose flaky black films on the surface of the samples; meanwhile, fluffy and fragile tan scales can be observed in Figure 1-17,18,21. This is mainly due to the compressive stresses generated by FeS formation within the scale so that the outer layer gradually peels off from the inner layer. It shows that, under different concentrations of each impurity, there are some differences in the corrosion process and results.

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| trial no. | A | B | C | E<sub>1</sub> | A×B | A×C | E<sub>2</sub> | E<sub>3</sub> | A×D | B×C | B×D | C×D | corrosion rate (mm y<sup>-1</sup>) |
|----------|---|---|---|---------|------|------|---------|---------|------|------|------|------|-----------------------------|
| 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0.0254 | 0.0324 | 0.0230 | 0.016 | 0.0190 | 0.0178 |
| 2 | 1 | 1 | 1 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 2 | 0.1547 | 0.1058 | 0.0766 | 0.0478 | 0.0494 | 0.0466 |
| 3 | 1 | 1 | 1 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 0.0651 | 0.0500 | 0.0685 | 0.0674 | 0.0731 | 0.0616 |
| 4 | 1 | 2 | 2 | 2 | 1 | 1 | 2 | 2 | 2 | 3 | 3 | 3 | 0.0193 | 0.0143 | 0.0110 | 0.0089 | 0.0091 | 0.0098 |
| 5 | 1 | 2 | 2 | 2 | 2 | 2 | 2 | 3 | 3 | 3 | 1 | 1 | 0.4122 | 0.4925 | 0.3360 | 0.2771 | 0.2935 | 0.2535 |
| 6 | 1 | 2 | 2 | 2 | 3 | 3 | 3 | 1 | 1 | 2 | 2 | 2 | 0.2518 | 0.1613 | 0.1053 | 0.0821 | 0.064 | 0.0662 |
| 7 | 1 | 3 | 3 | 3 | 1 | 1 | 1 | 3 | 3 | 2 | 2 | 2 | 0.3389 | 0.2664 | 0.2025 | 0.1595 | 0.1614 | 0.1950 |
| 8 | 1 | 3 | 3 | 2 | 2 | 2 | 1 | 1 | 1 | 3 | 3 | 3 | 0.3289 | 0.3509 | 0.3707 | 0.3222 | 0.3181 | 0.3069 |
| 9 | 1 | 3 | 3 | 3 | 3 | 3 | 3 | 2 | 2 | 2 | 1 | 1 | 0.3808 | 0.2793 | 0.2234 | 0.1756 | 0.1639 | 0.1475 |
| 10 | 2 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 0.2177 | 0.3307 | 0.298 | 0.1799 | 0.1544 | 0.1457 |
| 11 | 2 | 1 | 2 | 3 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 0.3080 | 0.2793 | 0.2234 | 0.1756 | 0.1639 | 0.1475 |
| 12 | 2 | 1 | 2 | 3 | 3 | 3 | 2 | 3 | 1 | 2 | 3 | 1 | 0.2177 | 0.3307 | 0.298 | 0.1799 | 0.1544 | 0.1457 |
| 13 | 2 | 1 | 2 | 3 | 1 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 0.3080 | 0.2793 | 0.2234 | 0.1756 | 0.1639 | 0.1475 |
| 14 | 2 | 2 | 2 | 3 | 1 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 0.2055 | 0.1606 | 0.1106 | 0.1573 | 0.1446 | 0.1490 |
| 15 | 2 | 2 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 0.2055 | 0.1606 | 0.1106 | 0.1573 | 0.1446 | 0.1490 |
| 16 | 2 | 2 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 0.2055 | 0.1606 | 0.1106 | 0.1573 | 0.1446 | 0.1490 |
| 17 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 0.3038 | 0.1923 | 0.1416 | 0.1665 | 0.1201 | 0.1375 |
| 18 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 0.2492 | 0.1489 | 0.1172 | 0.153 | 0.1331 | 0.1225 |
| 19 | 3 | 1 | 3 | 2 | 1 | 2 | 3 | 1 | 2 | 3 | 1 | 2 | 0.2257 | 0.1258 | 0.1048 | 0.0839 | 0.0646 | 0.0711 |

Where A, B, C, and D represent the TAN, S, Cl, and H<sub>2</sub>O, and E₁–E₃ are error terms.
has the fastest corrosion rate. The presence of sulfur and chloride results in faster corrosion rates obviously.

Usually chlorine and sulfur are the main causes of equipment corrosion in the petroleum refining industry. From eqs 1–6, it is known that a layer of an adhesive protective film is formed on the surface of the metal within a certain period of time after the active sulfur contacts the metal.24 Due to the fact that the FeS\(_{1-x}\) crystal structure is different from the surface structure of the steel, FeS\(_{1-x}\) is loose and falls off easily. This causes the fresh metal substrate to be brought into further contact with the corrosive medium, which increases the corrosion rate.

Most organic chlorides in crude oil are derived from chlorine-containing chemical additives added to prevent asphaltenes and waxes from blocking oil wells during the initial extraction process, and organic chlorides are not easily removed in subsequent processing.27 Such chlorides are not corrosive in the pure state, but acidic substances such as hydrochloric acid and chloride salts are easily produced on the surface of ferrous metals when they decompose or come into contact with water.28

Due to the destruction of the FeS film by chemically unstable organic chlorides, the two different types of corrosion product films of FeS and ferrocyanide alternately evolve, gradually deepening the erosion depth, which also makes chlorine the dominant cause of corrosion. However, some scholars have recently discovered that HS\(^-\) is more corrosive than Cl\(^-\) in and alkaline environment.29

Compared with sulfides and chlorides, the effect of NAC in oil products is more complicated. Generally, carbon steel and organic acids form oil-soluble corrosion products (eq 7), but due to the presence of active sulfur, the formed FeS protective film hinders the corrosion of steels by naphthenic acid to some extent (eq 8).17,23,30,31

\[
\text{Fe} + 2\text{RCOOH} \rightarrow \text{Fe(RCOO)\(_2\)} + \text{H}_2
\] (7)
Acetic acid is a weaker acid than hydrochloric acid, and its corrosive effect is less than that of chloride and sulfide. However, when the organic acid content is high and FeS has not been formed on the surface of the sample, the effect of organic acid on the metal is higher than that of other acidic materials.

The average corrosion rate curve of the four factors with three levels was determined from the corrosion results (Figure 2). The corrosion rates at the three levels corresponding to the TAN, S, Cl, and H$_2$O all gradually decreased over time. After the protective corrosion products are formed on the metal surface, Cl can effectively penetrate with oxygen or sulfur and form a metal salt, which causes the surface film to crack and accelerates the progress of corrosion.$^{15,30}$ Obviously, chlorine will not only corrode the equipment but also influence the effect of the corrosion product protection film and destroy the integrity of the anticorrosive protection film.$^{29}$ In the process of removing organic chlorine from oil products, a more selective dechlorination method should be used.

**2.3. Surface Morphology and Corrosion Product Analysis.** The microstructure of the AISI 1020 specimen after immersion in heavy diesel oil for 1008 h is given in Figure 3. The surface of the specimen was covered with a layer of iron oxide, and a certain amount of S and Cl was detected in the corrosion products.

Active sulfur reacts with carbon steel to produce a sulfur iron compound (eq 1). Subsequently, the sulfur iron compound is susceptible to oxidation after contacting oxygen in the oil phase. If the pyrite is less oxidized, the electrons accumulated on the surface of the ferrite will further reduce the polysulfide and continue to produce H$_2$S.$^{32}$

In view of the corrosion analysis in the immersion experiment, the influence of Cl on corrosion is always dominant. Therefore, in the micro morphology and composition analysis, SEM and EDS were performed for nine experimental groups with a Cl level of 3. Figure 4 shows the SEM morphology of the corresponding experimental group sample with a Cl level of 3 immersed for 1008 h. It can be seen from the micro morphology of each group of samples that the corrosion morphology is quite different due to the differences in the contents of TAN, S, Cl, and H$_2$O. Needle-shaped corrosion products can be found on the sample surface in Figure 4a–c. The study found that the iron sulfides on the surface of the metal substrate are finally converted into chemically stable pyrite, which can stably exist in a neutral environment.

Table 3. Composition of Corrosion Products of AISI 1020 Immersed for 1008 h at a Chlorine Level of 3

| arrangement no. | C wt % | O wt % | Al wt % | Si wt % | S wt % | Cl wt % | Mn wt % | Fe wt % |
|----------------|--------|--------|---------|---------|--------|---------|---------|---------|
| 1133           | 8.78   | 16.84  | 0.09    | 0.17    | 22.98  | 0.17    | 50.97   |         |
| 1231           | 6.37   | 25.22  | 0.57    | 0.15    | 0.72   | 5.90    | 0.12    | 60.94   |
| 1332           | 5.56   | 24.61  | 0.19    | 1.53    | 6.84   | 0.19    | 61.08   |         |
| 2131           | 23.07  | 24.88  | 0.25    | 0.06    | 0.40   | 0.22    | 51.11   |         |
| 2232           | 14.34  | 24.92  | 0.07    | 0.57    | 1.50   | 4.51    | 0.39    | 53.70   |
| 2333           | 14.11  | 20.60  | 0.12    | 0.67    | 2.94   | 3.75    | 57.81   |         |
| 3132           | 18.58  | 25.09  | 0.13    | 0.34    | 1.07   | 0.33    | 77.96   |         |
| 3233           | 10.63  | 9.67   | 6.87    | 0.13    | 1.13   | 0.29    | 54.56   |         |
| 3331           | 7.85   | 15.84  | 0.34    | 1.31    | 0.94   | 74.06   |         |
environment. After the level increased, in Figure 4d−i, pyrite was hardly observed on the surface, and the corrosion products on the surface were more compact with general corrosion accompanied by partial pitting.

The EDS area analysis results of the above nine groups of samples are given in Table 3. The corrosion products are mainly composed of C, O, Si, Cl, Mn, and Fe. It is worth noting that the C content is relatively high when the TAN level is high and the S level is low. Moreover, when the TAN level is 3, there is no S in the corrosion product and the content of chlorine is low. The abovementioned was because, under high acetic acid concentrations, the oxide scale formed during the corrosion process

Figure 5. 168 h interaction diagram of TAN, S, Cl, and H₂O.

Figure 6. 336 h interaction-effect diagram of TAN, S, Cl, and H₂O.

Figure 7. 504 h interaction-effect diagram of the TAN, S, Cl, and H₂O.
effectively prevents active sulfur and organic chlorine, as shown in Figure 4g–i.\(^3\)

2.4. Interaction Effects. In this study, Minitab software was used to analyze the synergistic effects of the corrosion rates in the above tests, and interaction diagrams of the four factors in six periods were made, as shown in Figures 5–10. The interaction plot can show the interaction between several factors in synergy and reveal the effect of the factor on the response. In the interaction plot, intersecting lines indicate that there is an interaction effect, while parallel lines are the opposite. The change in the corrosion rate can be known from the trend of the line chart.

In Figure 5, initially, the corrosion rate increased at elevated TANs, attributed to undissociated acetic acid affecting the

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Figure 8. 672 h interaction-effect diagram of the TAN, S, Cl, and H\(_2\)O.

Figure 9. 840 h interaction-effect diagram of the TAN, S, Cl, and H\(_2\)O.

Figure 10. 1008 h interaction-effect diagram of the TAN, S, Cl, and H\(_2\)O.
corrosion of carbon steel. At higher sulfur content, the corrosion rate tends to decrease. According to previous studies, the presence of active sulfur may lead to the formation of FeS on the metal surface to limit the corrosion rate. The interaction between chlorine and other factors is not obvious after the chloride concentration increases, and the same is true for the increased water content.

Active sulfur and sulfur ions react with carbon steel directly to form iron sulfides in an anoxic environment (eq 2). Under the influence of various impurities, the surface film is converted into other secondary corrosion products. The corrosion rate decreases after the formation of various corrosion product films on the surface of the metal. Therefore, the interaction among the TAN, S, and Cl is more obvious (Figure 6).

In the four periods beyond 504 h, the interaction between the four factors is basically the same (Figures 7–10). Contrary to the previous periods, an increase in the TAN leads to a decrease in the corrosion rate. The main reason is that the Fe(RCOO)₂ film generated by the organic acid was gradually replaced by FeS, Fe₂O₃, and FeCl₃, and the latter are more stable and insoluble in the oil phase. Meanwhile, the presence of water provides ionization conditions for multiple impurities and generally promotes the corrosion process and eventually reaches a stable state of the film thickness. Overall, while chlorine and sulfur promote the corrosion of carbon steel, their corrosion products protect it from other impurities in sour oil as well.

3. CONCLUSIONS

In this study, the Taguchi design was used to optimize the weight loss experiment to calculate the corrosion rate over multiple periods and obtain the most critical influencing factors. Before 336 h, the initial order of corrosion influence capability is Cl > S > TAN > H₂O. After 336 h, this changed to Cl > S > H₂O > TAN, and the interaction between factors became stable. This research found that, during the entire process, the synergistic effect of S and Cl impurities can significantly enhance the corrosion ability of acidic environments to AISI 1020. However, if the corrosion product film exists stably for a long time, it could alleviate the corrosion of the carbon steel partly. In practice, as crude oil is gradually acidified, protecting the initial corrosion scale has a positive effect on the anti-corrosion of sulfur-containing equipment. Furthermore, the synergistic effect of chlorine and sulfur in acid oils should be prevented during crude oil refining particularly.

4. METHODS AND MATERIALS

4.1. Oil Impurity Detection. The oil used in the experiment was sampled from the heavy diesel oil of a refinery production line in Jiangsu. The initial boiling point of the diesel oil was 244 °C, and the 95% distillation temperature was 365 °C. By acid–base neutralization titration, organic element analysis, ion chromatography, and distillation, the contents of several components of heavy diesel oil were determined, namely, the TAN and sulfur, chloride ion, and water contents. In this test, a simulated corrosion medium under different conditions was used to study the influence of various factors on oil-induced corrosion.

4.2. Orthogonal Design. In this research, we compared the effects on corrosion of four main factors: TAN (0–12 mg KOHg⁻¹), S (0–0.5 wt %), Cl (0–0.5 wt %), and H₂O (0–4 wt %). These are the main factors affecting the internal corrosion of petrochemical storage tanks. The target impurity concentration was changed by increasing acetic acid, butanethiol, carbon tetrachloride, and H₂O. The factors and levels of the orthogonal experimental design are shown in Table 4.

Table 4. Factors and Levels of the Orthogonal Experiment

| level | TAN (mg KOHg⁻¹) | S wt % | Cl wt % | H₂O wt % |
|-------|----------------|--------|---------|---------|
| 1     | 0              | 0      | 0       | 0       |
| 2     | 6              | 0.25   | 0.25    | 2       |
| 3     | 12             | 0.5    | 0.5     | 4       |
| 4     | 0              | 0      | 0       | 0       |
| 5     | 0              | 0.25   | 0.25    | 2       |
| 6     | 0              | 0.5    | 0.5     | 4       |
| 7     | 0              | 0.25   | 0.25    | 2       |
| 8     | 0              | 0.5    | 0.5     | 4       |
| 9     | 0              | 0.25   | 0.25    | 2       |
| 10    | 0              | 0.5    | 0.5     | 4       |
| 11    | 0              | 0.25   | 0.25    | 2       |
| 12    | 0              | 0.5    | 0.5     | 4       |
| 13    | 0              | 0.25   | 0.25    | 2       |
| 14    | 0              | 0.5    | 0.5     | 4       |
| 15    | 0              | 0.25   | 0.25    | 2       |
| 16    | 0              | 0.5    | 0.5     | 4       |
| 17    | 0              | 0.25   | 0.25    | 2       |
| 18    | 0              | 0.5    | 0.5     | 4       |
| 19    | 0              | 0.25   | 0.25    | 2       |
| 20    | 0              | 0.5    | 0.5     | 4       |
| 21    | 0              | 0.25   | 0.25    | 2       |
| 22    | 0              | 0.5    | 0.5     | 4       |
| 23    | 0              | 0.25   | 0.25    | 2       |
| 24    | 0              | 0.5    | 0.5     | 4       |
| 25    | 0              | 0.25   | 0.25    | 2       |
| 26    | 0              | 0.5    | 0.5     | 4       |
| 27    | 0              | 0.25   | 0.25    | 2       |

Furthermore, to study the interaction between factors, a four-factor, three-level orthogonal experiment design was adopted. A total of 27 groups of experiments was planned by using the L₂₇(3⁴) orthogonal table to arrange process variables, as shown in Table 5. The effect of synergy was analyzed by the L₂₇(3⁴)-type orthogonal table. Corrosion rate analysis was used to determine the variables that most affected the corrosion of the specimen under multiple factors and their interactions. In this study, the interaction between four single factors (TAN, S, Cl, and H₂O) was considered through the L₂₇(3⁴)-type orthogonal table. The design also included six interactions between two factors and three error terms to study the interaction effects between variables.

4.3. Immersion Test. The test material type was AISI 1020, a heavy diesel storage tank material from a refinery in Jiangsu. The main components of this type of carbon steel are 0.20% C, 0.035% S, 0.35% Mn, 0.035% P, 0.15% N, 0.25% Cu, and Fe balance. The specimen size was 50 mm × 25 mm × 2 mm. The

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surface of the hanging piece was dry-polished with 800-mesh sandpaper to remove the oxide layer before weighing. After preliminary grinding, the residual metal debris and oil stains on the surface were cleaned with anhydrous ethanol, and the sample was then dried with a hot air gun.

A Teflon-coated metal wire was used to hang and fix the washed and dried sample under the oil phase in the wide-mouthed flask. To reduce the leakage of gaseous hydrogen sulfide from the container, the rubber stopper of the wide-mouthed flask was sealed with Teflon tape. Finally, the wide-mouthed flask containing the sample and oil was placed in a constant-temperature oil bath. The constant-temperature oil bath used glycerine as a heat transfer medium, and the heating temperature was set to 35 °C. To analyze the influence of the corrosive media on the corrosion of the specimens in different periods, sample corrosion was studied at six periods (168, 336, 504, 672, 840, and 1008 h). Each test group consists of 19 specimens for the immersion test in six periods and component analysis.

In this experiment, the weight loss method was used to calculate the corrosion rate. A rust remover was formulated and used to remove the corrosion products attached to the sample surface. The samples were then washed with absolute ethanol and distilled water, dried in a drying cabinet, and weighed with an electronic balance. The corrosion depth change of the immersed sample was obtained by the following equation.36

\[ R = \frac{K(M - M_i)}{STD} \]  

(9)

where \( R \) is the corrosion rate (mm y\(^{-1}\)), \( K \) is a constant, \( 8.76 \times 10^{-7} \), \( M \) is the mass of the sample before the test (g), \( M_i \) is the mass of the sample after the test (g), \( S \) is the total area of the sample (cm\(^2\)), \( T \) is the immersion time (h), and \( D \) is the material density (kg m\(^{-3}\)).

### 4.4. Micromorphology and Composition Analysis

To study the corrosion microstructure and corrosion product composition under the influence of multiple interacting factors, the surface corrosion morphology of the sample was observed by SEM analysis (Apollo 300 equipment, ODUcat Camscan Ltd., U.K.). Max 20 equipment (Oxford Instruments Analytical Ltd., U.K.) for EDS analysis combined with Aztec Energy software was used to analyze the composition of corrosion products and the influence of different factors and levels on product composition. This combined analysis method is more convenient to avoiding inaccurate results due to sample oxidation. Meanwhile, it is capable of confirming the presence of the special constituents effectively.37

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