Study on the Sulfide Corrosion to the Internal Surface of Transportation Pipeline

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This article briefly tests and analyzes the sulfur content and the distribution of active sulfur in the crude oil of Kurkow Kazakhstan and Siberian Russian, and discusses the relationship between active sulfur content and total sulfur content, active sulfur and corrosion. At the same time, it measures the open circuit potential of X70 steel and X60 steel witch have been immerged in the above two kind of crude oil for a period of time, discusses the sulfur corrosion to metal.

Keywords : active sulfur, sulfur, alkyl sulfhydrate, corrosion, open circuit potential

1. Introduction

In order to keep the balance of supply and demand of Chinese power market, China imports a large amount of crude oil from the south Siberian Russian and Kurkow Kazakhstan. Compared with the Chinese crude oil, crude oil from south Siberian Russian and Kurkow Kazakhstan have higher percentage of sulfide, while their content of wax and acid value are lower. It has been proved that the crude oil with higher concentration of sulfide will result in sulfur corrosion in the interior surface of pipeline and equipment used to transport and store the crude oil.¹⁾ So it is important to analyze the being's manner and study the corrosion performance of sulfide in the crude oil of Siberian Russian and kurkow Kazakhstan.

2. Experiment procedures

2.1 Crude oil sample

There are four crude oil sample for experiment, oil I of Kurkow Kazakhstan and oil I of Siberian Russian that was from the loading siding of Dushanzi petroleum refinery in Mar of 2003; oil II of Kurkow Kazakhstan and oil II of Siberian Russian that was from the loading siding of Dushanzi petroleum refinery in Sep of 2004.

2.2 Measurement of total sulfur and corrosive sulfur content in the petroleum $^{3)}$

First all kinds of sulfides are digested into SO_4^{2-} based on the technology of microwave digestion; then take titration with barium chloride solution, according to the mass of barium sulfate the total sulfur content is calculated. Copper powder is added into the petroleum sample that the total sulfur has been tested and react with it at a determined heating temperature in continue stirring process, then filtrate the sample and test the sulfur content of the filter liquor after the reaction last 2.5 hour. According to the principle of copper strip corrosion the active sulfur content is the difference of sulfur content before and after reaction.

2.3 Measurement of alkyl sulfhydrate in the petroleum

The detection methods is according to the methods for determination of alkyl sulfhydrate in jet fuel.

The solvent for potentiometric titration: 0.2 mol/L 2-propanol solvent of sodium acetate.

The Potentiometric titration solution: 0.0025N 2-propanol solvent of silver nitrate.

Titration tube: 2 mL(0.01).

Indicator electrode - glass electrode ;

Reference electrode - silver _ silver sulfide electrode

2.4 Electrochemical experiment

In order to find whether there is sulfur corrosion when steel put into the crude oil of south Siberian Russian and Kurkow Kazakhsta. X60 and X70 is selected to take the electrochemical experiment. The test sample is made into

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25 mm×15 mm×2 mm and the surface is ground and polished by P60 brown corundum, then the waterproof abrasive paper of $150 \pm ,280 \pm ,400 \pm ,600 \pm ,800 \pm ,1000 \pm$ are used to polished the test sample, to ensure the effective area is 10 mm×10 mm and the other area is sealed by epoxy resin. In order to study the influence of different crude oil to the open circuit potential the chemical characteristics of steel in the crude oil is tested by automatic electric potential scanning technique, and the speed is 1 mV/s. there are 3 same sample every test group and the test use three electrode, the auxiliary electrode is platinum electrode and the reference electrode is saturated calomel electrode (SCE).

3. Results

3.1 The experimental results analysis of measurement of sulfide and total sulfur content in the petroleum

The test data is listed in the Table 1.

a. It can be found from the experiment result that the sulfur content is much different in the test petroleum at the different sampling time.

b. It can be found from the experiment results that the order of potential corrosive of four kinds test petroleum to steel is: oil I of Kurkow Kazakhstan>oil I of Siberian Russian>oil II of Kurkow Kazakhstan>oil II of Siberian Russian.

c. the amount of active sulfur in the petroleum determines the potential corrosive; the higher, the stronger.

The sulfide corrosion to the steel is closely related to the water content, there are no corrosion to the facility if there is no water for the sulfide can not decomposition when the temperature is below 120°C. But during the petroleum transported by pipeline, the trace water vapor will transform into liquid water and form water film on the inner surface of pipeline when temperature is decreased.

We all know that the temperature of the crude oil trans

Table 1. percentage of sulfur and active sulfur in the test petroleum

sample	Total sulfur content(%)	alkyl sulfhydrate content(%)	Active sulfur content	Water content
oil I of Kurkow Kazakhstan	0.0720	0.0034	0.0597	trace
oil Ⅱ of Kurkow Kazakhstan	0.0222	0.0017	0.0140	trace
oil I of Siberian Russian	0.0196	0.0055	0.0104	trace
oil II of Siberian Russian	0.1464	0.0027	0.1293	trace

ported by pipeline is always below 60° C, the sulfur , thioether and disulfide in the petroleum all keep stable, so they will not cause the corrosion to the steel. But only the alkyl sulfhydrate has the higher active at this temperature and maybe cause sulfur corrosion, so the sulfur corrosion can been judged by alkyl sulfhydrate content.

3.2 Experiment results analysis of electrochemical experiment

The experiment results of the open circuit potential of the X60 steel is shown in the first and second carve drawn and of the X70 steel is shown in the third and fourth carve drawn.

The following results are drown from above the figures.

a. there are a little fluctuation of open circuit potential because that a little change take place on the electrodes when they were put into the petroleum. But the chemical characteristics of two kinds of steel in four kinds of crude oil are almost unchanged.

b. According to the open circuit potential of the test steel, the potential corrosive risk of X60and X70 steel in four kind of crude oil is: oil I of Kurkow Kazakhstan>oil I of Siberian Russian>oil II of Kurkow Kazakhstan>oil

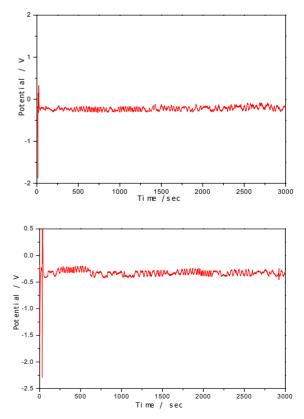


Fig. 1. The carve drawn of open circuit potential and time of X60 steel in the oil II (left) and oil I (right) of Kurkow Kazakhstan.

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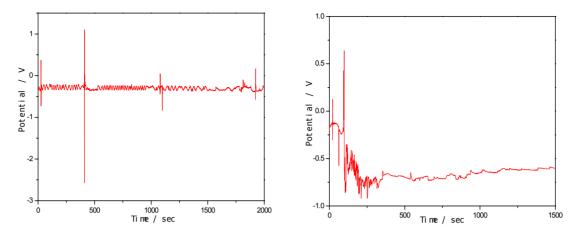


Fig. 2. The carve drawn of open circuit potential and time of X60 steel in the oil II (left) and oil I (right) of Siberian Russian.

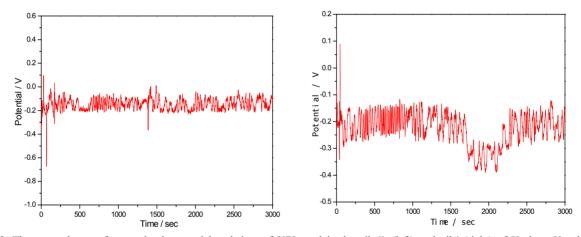


Fig. 3. The carve drawn of open circuit potential and time of X70 steel in the oil II (left) and oil I (right) of Kurkow Kazakhstan.

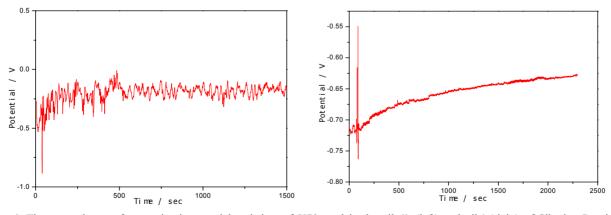


Fig. 4. The carve drawn of open circuit potential and time of X70 steel in the oil II (left) and oil I (right) of Siberian Russian.

II of Siberian Russian. This order is same as the results of the alkyl sulfhydrate content.

c. the potential corrosion of X60 is stronger than X 70

according to the open circuit potential of steel in the crude oil.

4. Conclusions

It is all known that the sulfur corrosion is a very complex problem, from this sturdy we find that: 1. the active sulfur content is not directly proportional to the sulfur content in the crude oil; the potential corrosion and corrosion strength of active sulfur to the steel is closely related to the environmental conditions; the potential corrosion of X60 is stronger than X70.

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