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Passivation of the Zinc Anode of a Crude Oil Vertical Separator Resulting in Corrosion

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Abstract: This paper presents the results of chemical analysis and laboratory tests to evaluate the performance of zinc anodes in the internal chambers of a crude oil vertical separator. Frequently, sediments and saline water are co-produced with crude oil and the basic function of a tri-phase separator is to separate the oil and gas from the saline water and natural contaminants. It has been observed that corrosion has taken place in the internal chamber due to the failure of the zinc anodes. This anode failure is associated with scale deposition on the anode surface and the high temperature used in oil-water separation. Chemical analysis indicated that this deposit is composed of basic zinc chloride, zinc carbonae and oily materials. On the basis of the laboratory tests, a mechanism to explain the failure of the zinc anode is proposed.

Key words: Corrosion, failures, zinc anode, crude oil vertical separator, passivation.

1. Introduction

Crude oil from the production fields is associated with formation water, sediment and natural gas. The composition and concentration of these constituents vary depending on the geological diversities and reservoir rock. Water from reservoir rock is a saline solution that can reach values of 30% by mass of soluble salts, mainly found in the form of chlorides (Cl^-) and in smaller quantities in sulphates (SO_4^{2-}), carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-). The most common cations are sodium, potassium, calcium and magnesium. The sediments consist of microscopic particles, such as clays, silica sand, silicates, iron sulphide, iron oxide, and so forth, from reservoir rock or originating in the corrosion of pipes. The natural gas produced in Brazil is made up of methane and generally associated with the humidity, carbon dioxide (CO_2) and hydrogen sulphide (H_2S) most often causing corrosive conditions.

The efficient separation of crude oil, water and natural gas is carried out by a vertical or horizontal separator, where the saline water-in-oil emulsions are broken, separating the oily phase of the water through temperature and adding a demulsifier. Fig. 1 shows a simplified diagram of a vertical separator that processes crude oil separating it into three distinct phases: oil, natural gas and water with high salinity. The dimensions and characteristics of the separator and the operating conditions (temperature, pressure) are dependent on flow and on the relations among crude oil, water and natural gas [1-3].

Generally, the emulsion must be separated by the addition of a chemical demulsifier before the crude oil can be accepted for transportation. The quality criteria for a delivered crude oil are the residual salt content and the water content. For the oil to have pipeline quality, it is necessary to reduce the water content to less than approximately 0.50% [1]. The temperature of the separator is maintained in the range of 60 to 70 ºC by burning natural gas as shown in Fig. 1 (fire tube and chimney).

Considering the high corrosiveness of saline water, the internal chamber and bottom of the separator where these saline waters are processed are coated with an epoxy-phenolic coating and anticorrosion is aided with

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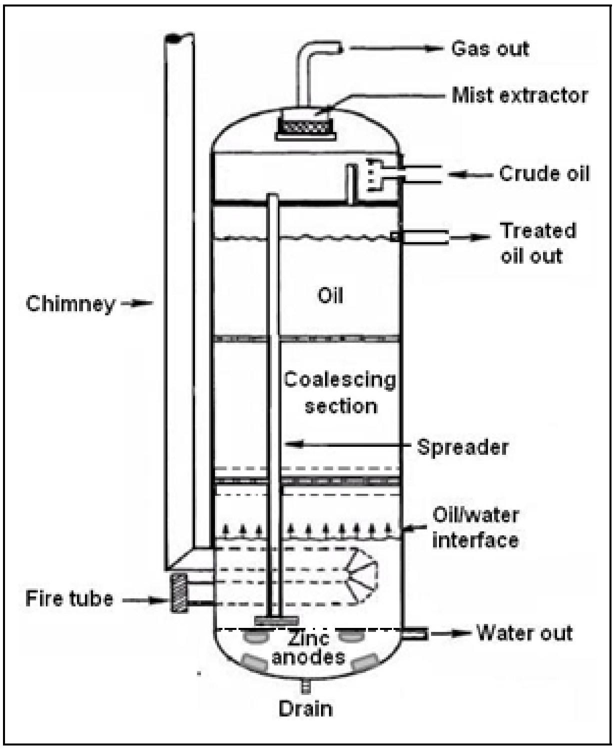

Fig. 1 Representation of a vertical separator evidencing the zinc anodes on the bottom.

the protection of galvanic anodes (zinc or aluminium). The galvanic anodes function is to increase the anticorrosive protection to act in the event of organic coating porosity or coating failure, which puts the carbon steel in contact with the corrosive medium. The project should prevent the contact of the oily part with the anodes because its operation is based on the conductivity of the corrosive medium.

The inspection carried out on the vertical separator to evaluate the failure of the zinc anodes, after 4 months of continuous operation, operating with temperatures ranging from 60 to 70 ºC, found that the anodes exhibited an adherent deposit on the surface preventing the normal wear and tear for the supply of electrons necessary for cathodic protection.

2. Materials

The laboratory methodology used to evaluate the failure or malfunction of the zinc anodes consisted, essentially, of the following steps: preparation of coupons of carbon steel and zinc anodes; preparation of the emulsion; assembling a laboratory test to evaluate the functioning of the zinc anode operating conditions of the separator and indication of the chemical analysis used in samples from the zinc anodes that operated in the separator during the 4 months.

The coupons to represent the inner chamber of the separator were made from 15 cm × 10 cm × 0.2 cm AISI 1020 steel sheets with the following composition: 0.21% carbon, 0.32% Mn, 0.035% Si, 0.011% S and 0.009% P. They were prepared with three different sandpapers 150, 320 and 400 in that order. Then they were degreased with acetone, washed with deionized water and anhydrous alcohol, and were finally dried with hot air and stored in desiccators for use in the tests [4].

The 5 cm × 2 cm × 2 cm coupons, representing the zinc anode, were made from the anode itself used in the vertical separator, the analysis of which is presented in Table 1 [5]. Then they were degreased with acetone, washed with deionized water and anhydrous alcohol, and were finally dried with hot air and stored in desiccators for use in the tests.

The emulsion to represent the operational conditions of the separator was prepared from the mixture of 40% (by mass) of crude oil and 60% (by mass) of synthetic formation water with high saline, as shown in Table 2. Also added were 20 mL of a commercial demulsifier based substance di (2-ethyhexil) phthalate. Demulsifiers are frequently injected to the emulsion at the wellhead to take advantage of the high temperature of the freshly raised emulsion to accelerate the demulsification step [1].

The laboratory tests were performed in order to explain the failure of the cathodic protection of the

Table 1 Composition (wt.%) of zinc anode.

Elements	Composition (wt.%)
Fe	0.0005
Cd	0.062
Pb	0.00
Si	0.0045
Cu	0.00
Al	0.35
Zn	Remainder

Table 2 Chemical composition of saline water.

Constituents	Composition (mg/L)
Sodium (Na^+)	29,400
Potassium (K^+)	630
Calcium (Ca^{2+})	2,500
Magnesium (Mg^{2+})	420
Chloride (Cl^-)	55,000
Bromide (Br^-)	122
Sulphate (SO_4^{2-})	60
Bicarbonate (HCO_3^-)	653

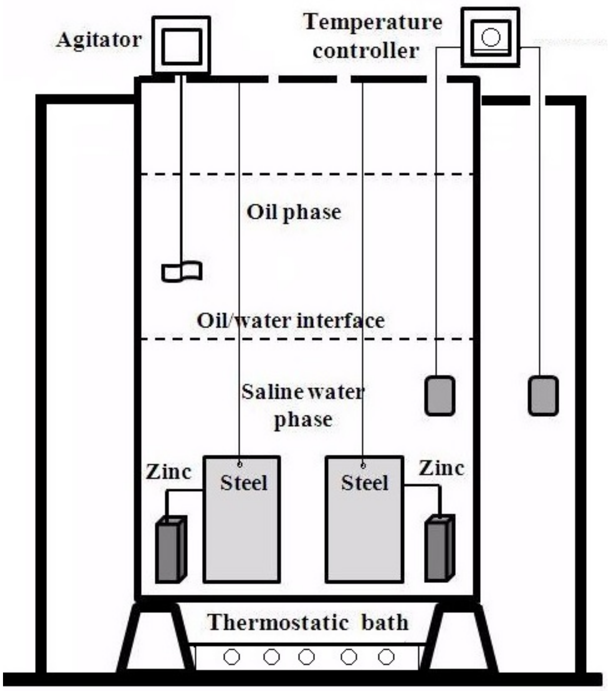

Fig. 2 Laboratory experiment for evaluating the performance of the zinc anode.

zinc anode installed in the three-phase separator and to propose a mechanism to explain this anomaly.

The experiment consisted essentially of a glass vessel resistant to temperature variation with 3 L of capacity as shown in the diagram in Fig. 2. Two carbon steel plates were mounted in the container and electrically coupled to zinc anodes. Then, carefully placed on saline solution was the volume of crude oil without mixing. Later this set was placed in a thermostatic bath with the temperature maintained at 65 ºC. The exposure time was 30 days (720 hours). The tests followed the three experimental programming: without agitation; with alternating agitation daily for 2 hours; with continuous agitation.

Chemical analyses for identification of chemical species of the adherent deposit on the anode were carried out using the X-ray diffractometry and infrared (IR) analysis.

3. Results and Discussion

Chemical analysis of the anodes, presented in Table 1, indicates that the results are included and are satisfactory in the standard ASTM B 418 Type I [5].

The analysis by x-ray diffractometry revealed that the adherent deposit on the anode installed in the three-phase separator consists of basic zinc chloride ($4Zn(OH)_2 \cdot ZnCl_2$) and traces of zinc carbonate ($ZnCO_3$). The oily mass adherent to the anode was analysed by infrared (IR) and was revealed to be constituted of high molecular weight hydrocarbon and a di(2-ethyhexil)phthalate, DEHP, substance normally found in commercial demulsifiers.

In the laboratory test without agitation, the anodes behaved as the corrosion protection for the carbon steel plate, although the temperature favoured the formation of a white film on the surface of the zinc anodes. This film, partly, prevents contact with the electrolyte and consequently reduces the passage of electrons for carbon steel plate. At the beginning of the test, the value of the potential measured with a saturated calomel electrode reference (SCE) was of -1100 mV. After 380 hours exposure the value was -900 mV and at the end of the test the potential was void, showing a passivation on the surface of the anodes.

X-ray diffractometry analysis revealed that it consists of basic zinc chloride ($4\ Zn(OH)_2 \cdot ZnCl_2$), and traces of zinc carbonate ($ZnCO_3$), similar to that found in the anodes of the three-phase separator.

With alternating or continuous agitation, the test highlights contamination of the oily phase with saline water. This fact causes a reduction in the conductivity of the medium and the formation of an oily film on the anode. The association of oily mass with temperature and time favour the formation of an oily film on the anode favouring the loss of the anticorrosive protection on the carbon steel sheets. The beginning of the essay presented a potential protection of -795 mV (saturated calomel electrode reference) and at the end this potential reduced to -600 mV, thus favouring the corrosion of the steel sheet.

In order to explain and to propose a mechanism for deposits occurring on the zinc anodes and consequently the failure of the anodes leading to the increased probability of corrosion on the bottom of the vertical separator, where there is the highest concentration of saline water, the following were considered:

Treating the bottom of the vertical separator with two coats of epoxy-phenolic with a medium thickness ranging from 450 to 500 µm;

Placing zinc anodes, required to increase the resistance of the epoxy-phenolic coating as shown in the diagram in Fig. 3;

The chemical analysis and the measure of the potential with the saturated calomel electrode reference of the anode showed that they were in accordance with ASTM B 418 Type I [5]; Chemical analyses of the deposit on the surface of the anode showed that it consists of basic zinc chloride (4 $Zn(OH)_2 \cdot ZnCl_2$), traces of zinc carbonate ($ZnCO_3$) [6] and an oily layer from the crude oil; Temperatures above 65 ºC contribute to deterioration of the zinc anodes at high salinity solutions [6-8]; Increasing the temperature favors the reduction of the viscosity of the crude oil, which leads to a better separation of the emulsion; however, the highest temperature benefits the impregnation of the oil on the surface, increasing its anode passivation; It was found that, during the operational process, the oily phase can migrate to the saline water and consequently reach the zinc anodes.

This fact was noted during the demonstration in the laboratory with the corrosive medium agitation; The deposit formed on the anode surface prevents its performance in providing electrons to the carbon steel plate and thus providing the corrosive attack from the saline water.

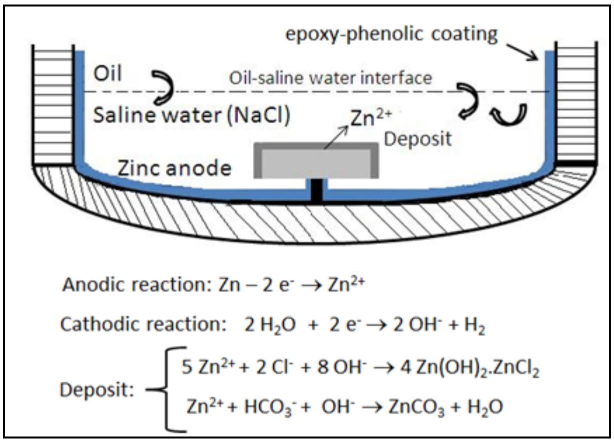

Fig. 3 Schematic showing the occurrence of anode passivation at the bottom of the vertical separator.

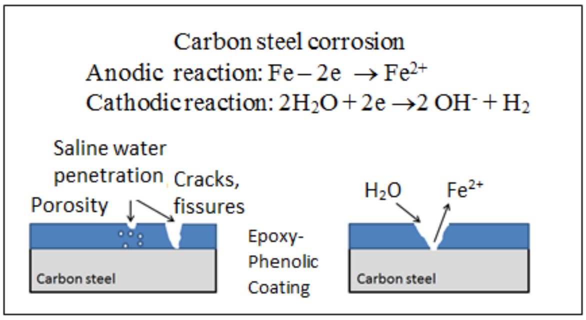

Fig. 4 Schematic showing the occurrence of localized corrosion in the vertical separator.

The possible cracks, fissures or porosity in epoxy-phenolic coating together with the zinc anode passivation are valid considering the occurrence of localized corrosion in carbon steel [9, 10] as shown in diagram in Fig. 4.

5. Conclusions

On the basis of the chemical analyses, laboratory tests and inspections are carried out on the vertical separator. It was concluded that:

The anode was in accordance with the technical specifications suggesting a good performance in corrosion protection.

The deposit on the surface of the anode consists of zinc hydroxide ($Zn(OH)_3$) basic zinc chloride (4 $Zn(OH)_2 \cdot ZnCl_2$), traces of zinc carbonate ($ZnCO_3$) and an oily layer from the crude oil.

The oil that migrated from the oily phase to the aqueous phase (saline), which associated with high temperatures in the vertical separator, was responsible for the deposit formed on the surface of the anode. Therefore, the passivation of zinc anode will not protect the carbon steel from localized corrosion.

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