Failure Analysis of the Fluorine Rubber Sealing Ring Used in Acidic Gas Fields

G Q Qi[1,2], D T Qi[1,*], H X Yan[2], B Wei[1], H B Li[1], N Ding[1], X D Shao[1], D N Zhang[1] and X H Cai[1]

[1] State Key Laboratory of Performance and Structural Safety for Petroleum Tubular Goods and Equipment Materials, CNPC Tubular Goods Research Institute, Xi'an, 710077, China
[2] School of Natural and Applied Science, Northwestern Polytechnical University, Xi'an 710129, China

Corresponding author and e-mail: D T Qi, qidt@cnpc.com.cn

Abstract. The failure of fluorine rubber sealing ring occurs when it is used in the sulfur condition after one year. By visual observation, there are some cracks and the color changed to black from brown near the location of the contact delivery medium. In order to identify the cause of the failure, the physical properties, structure and composition were tested and compared with the same batch of the rings but without using.The results showed that the hardness and density of the material were increased because of gas permeation. It is evidenced by the microstructural observation, which shows that there are holes in the material near the transport medium. The specimens were characterized by FT-IR and XPS, respectively. The results show that the three-dimensional network structure of the ring is destroyed and the peak strength of -CF_2 and -CF is weakened while the CH_3, -CH_2 and –C=O increase by the action of external stress and gas permeation. As a result of comprehensive evaluation, the reason of sealing ring failure is fatigue aging during the long-termservice life. The gas permeation leads to the destruction of the network structure, and accelerating the aging process.

1. Introduction

The gas field contained hydrogen sulfide and carbon dioxide has become an important part of the natural gas resources for exploitation in China nowadays[1,2]. Unfortunately, ordinary carbon steel pipe corrosion is very serious in such high acidic environment. In recent years, the non-metallic pipe with good corrosion resistance is researched and applied in the oil and gas field contained H_2S or CO_2, and turned into an important direction for sulfur-containing conveying pipe, gradually[3].

During the oil and gas field exploitation, sealing ring is used in non-metallic pipe as an important accessory[4]. Sealing performance and service life of rubber seal products are closely related to oil and gas field environment, such as temperature, pressure, chemical corrosion, and et al. Furthermore, with the increase of temperature and pressure in the pipeline increase and service environment becomes worse. With the deepening of the exploitation depth and increasing severe environment, the quality of rubber seal is put forward higher requirements and face enormous challenges. In the

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process of transmission, due to the high temperature, high pressure and corrosive medium[5], the seal products often failure caused by performance degradation, which lead to the contact stress release between seal products and joints. In the service environment with H_2S/CO_2, accident such as perforation or fracture often happened[6,7], usually results in oil and gas leak, even cause serious accident, which may lead to huge economic losses, casualties and ecological damage.

It has a great significance that study on the corrosion damage behavior of sealing ring serviced in corrosion environment, but there is few research report about this aspect. In this study, failure analysis of fluorine rubber sealing ring used in non-metallic pipe which anti hydrogen sulfide is investigated. For reliable operation and efficient design, the security of this engineering non-metallic pipe especially, it is urgent to investigate the failure reasons of the sealing ring and to further analyze the factors which affect the pipeline's serving ability. It will be of great benefit to prevent events which could trigger disastrous incidents, thus can reduce much loses in terms of service life and economics.

2. Material and methodologies

2.1. Background of the Failure

Non-metallic pipe (DN80 PN16MPa), as is shown in Figure 1, was used for oil gathering and transportation in sour oil and gas field. The transmission medium is mostly gas, with a small amount of oil and water. The pressure and temperature of transmission medium are 8.9MPa and 35 °C, respectively. The content of H_2S is 51800mg/m^3 while CO_2 of 3.80mol%. The whole construction project had been completed on April 2015, while the pipeline had been started to use on May 2015. After running for half a year, the inspection of pipeline application effect was carried out. The result shows that the fluorine rubber sealing rings have failed with cracks and color changed shown in Figure 2. Meanwhile, new sealing rings produced in the same batch were also collected for comparison.

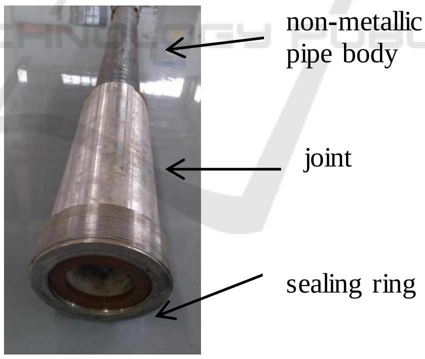

Figure 1. Structure of non-metallic pipe.

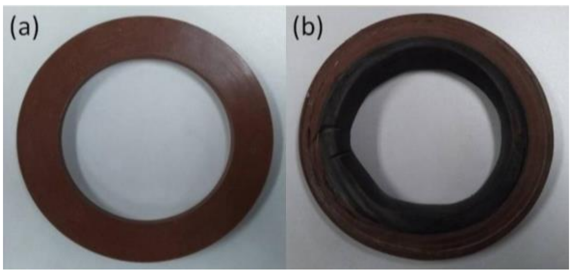

Figure 2. Macro morphology of (a) the new sealing ring and (b) used one.

2.2. Failure description

It can be seen from Figure 2 that the color of the used sealing inside changes from brown to dark obviously, while the outer color is not changed. Compared with the new one, the color changed border of the used sealing ring is at a third place from inside to outside. Moreover, we can easily find by visual observation that the color changed border have some cracks, also in the black area. We can also find that it has an obvious squeeze traces in the sealing ring surface, and the thickness decreases from 7.72mm to 6.54mm, approximately.

2.3. Methodologies

Many factors may cause the failure of sealing ring and more studies are needed. Firstly, the background information and the operation conditions that might lead to failures of the ring were investigated in detail. Secondly, probable causes for failure of ring were systematically analyzed by various measurements, such as Shore hardness, density, morphology observations, composition analysis, etc.

The specimens of sealing ring were cut from the same failed one which was taken from the pipeline after running for half a year. By comparison, specimens for above tests were also taken from a new ring which produced from the same batch with the failed one. At least three specimens taken along the circumference of the ring were tested for each measurement to evaluate the results statistically. The "used" samples were collected from the area close to the damage region of the failed ring (as seen in Figure 2b). The "new" samples were taken from the new ring (as seen in Figure 2a).

Surface morphologies of rings were detected bydigital microscope (KH-7700, Hirox, Japan)and scanning electron microscope (SEM, JEOL-6700F, Tokyo, Japan). To check any significant chemical modification of the fiber, the specimens were characterized by Fourier transform infrared spectroscopy (FT-IR) and X-ray photoelectron spectroscopy (XPS), respectively, which were obtained by using a Nicolet Avator 360 Spectrometer (Wisconsin, USA) and a PHI5300 X-ray photoelectron spectrometer (PE Corp., USA).

3. Results and analysis

Analysis contain morphology and structure will be conducted as follows to study the actual reason for such gradual failure of the sealing ring.

3.1. Analysis of physical properties

Firstly, the physical properties of the new sealing ring and used one were investigated, can be seen in table 1, the Shore hardness value of the used sealing ring are increasing compared to the new one's (the value of Shore hardness is 27.6). For the old sealing ring, of particular note is Shore hardness value of the black part is bigger than the brown part's. That is to say, the part of the sealing ring to be exposed to fluid change to harden gradually.

Table 1. the physical properties of the new sealing ring and used one.

Types	Shore Hardness	Density (g/cm^3)
The new ring	27.6	2.1296
The brown part of the old one	29.2	1.8391
The black part of the old one	33.6	1.7539

The density of old sealing ring is smaller than the new one, and the black part of the sealing ring even smaller than the brown part. The reason due to the density decline after the sealing ring used in acidic gas fields together with the non-mental pipe is corrosion medium, such as H_2S, CO_2, permeate into the body of sealing ring, and then the pores become more and more bigger with the service time increasing. The pressure difference between inside and outside of the pipe lead to the occurrence of gas permeation.

3.2. Analysis of microstructure

For researching the microstructure of the invalid sealing ring, the optical microscope was used to characterize the structure. From the Figure 3, we can find that the color of the sealing ring used for half year changed from brown to black partially and obviously.

For further research, scanning electron microscope was used to characterize the microstructure. There are some micrometer grade pore in the used sealing ring(seen in Figure 4 b) , compared to the new one (seen in Figure 4 a). The arising pores are resulted from gas permeation.

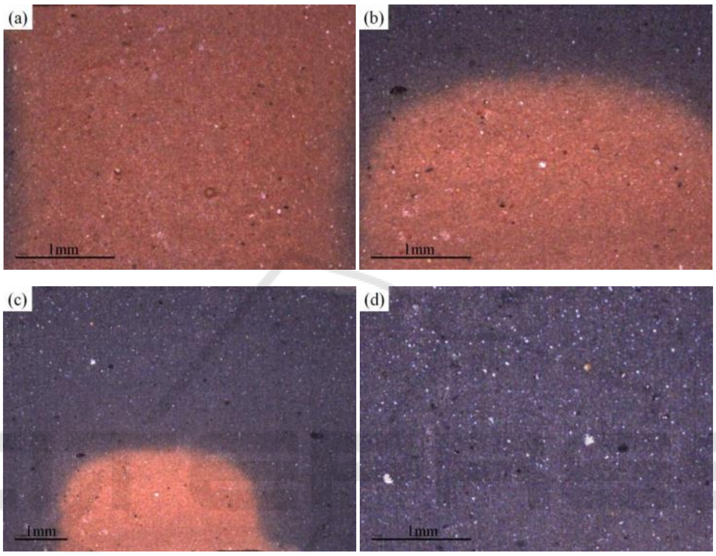

Figure 3. Optical microscope of the sealing ring used for half year.

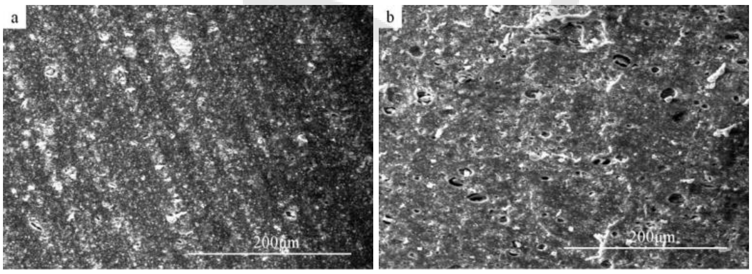

Figure 4. SEM of the sealing ring (a) the new one; (b) the used one.

3.3. FT-IR analysis

Due to service in acidic gas fields, the sealing ring, along with the time increasing, with some aging, which have the characteristics of the physical properties deterioration, some cracks and color change. For understanding what have changed for compositions of the sealing ring with aging, The structures of the sealing ring were characterized by Fourier transform infrared spectroscopy. Figure 5 compares the FT-IR spectrum of the used sealing ring with the spectra of new one. The peaks at around 884 cm^{-1}, 2852 cm^{-1} and 2922 cm^{-1} are assigned to =CH, $-CH_2$ and $-CH_3$ vibration, respectively, bending stretching. The absorption peaks at 1742cm-1 is due to –C=O stretching. Moreover, -CF and $-CF_2$

bending stretching at 1078 cm^{-1}, 1125 cm^{-1}, and 1181 cm^{-1} respectively, reveals the existence of fluorine in the sealing ring.

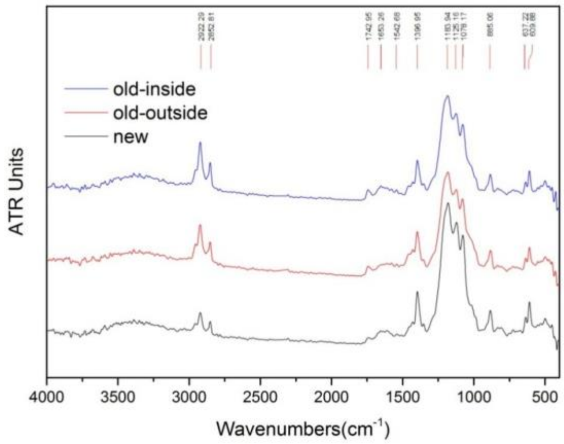

Figure 5. FTIR of sealing ring.

Through the tests (Figure 5), the results show that the old ring absorption peak is close to the new one, but the absorption intensity is different. It can be seen from Figure 5 that the absorption intensity of -CF and -CF_2 decreases while the absorption intensities of CH, CH_2, CH_3 and C=O increase with the service life of the fluorine rubber seal ring increasing. During the aging of the sealing ring, the position of the unsaturated bond in the rubber molecule is oxygenated to C=O structure. On the contrary, -CF and -CF_2 bond strength decreased, indicating that -CF and -CF_2 bond breakage and recombination, which lead to the degree of branching increase, eventually. That is the reasons why the -CH group absorption intensity increase. Therefore, the cause of failure of fluorine rubber seals is due to molecular breakage and cross linking.

3.4. XPS analysis

Elemental ID and Quantification of the new and the used sealing ring are shown in Figure 6. It is seen obviously that the element exist in the rubber mainly include Si, S, O, C and F. The trace additives such as Na, Ca, Cl and N not be investigated in this study. By comparing the elemental quantification of two rings (in table 2), the content of O and C element increase, with the percent content of atomic (at. %) from 13.82 to 19.25, 59.91 to 64.94, respectively. Contrarily, the content of F element decrease with the percent content of atomic from 14.34 to 7.11, the elemental F peak of both used and new rings counts to binding energy relation is shown in Figure 7.

4. Discussion

In the actual process of service, the sealing ring need to withstand a certain compressive stress, even more alternating pressure. In this case, the aging of the sealing material is directly affected by the stress. In addition, the aging of the seal ring is also affected by the results of the rubber material, components and contact with the external environment (such as temperature, H_2S and CO_2 and other transmission medium). From the pressure gauge reading for pipe connecting, the ring by the value of compressive stress at sealing ring reach 24MPa. The macroscopic analysis of the fracture morphology shows that the occurrence of the crack due to the compressive stress is too large, and then the molecular chain of rubber is cut off by stress (Figure 5). However, the latter part of the study found that, there is not appear similar phenomenon in the air environment when applied stress at 24MPa. Through mechanical analysis, the reason is that partial molecules of the transmission with the service time increases, will be permeated into the inside of the rubber and make volume expansion. Furthermore, rubber network structure of the molecular chain will expand to three-dimensional space. The excessive deformation will cause loss of elasticity, reduce the rubber material resilience, and result in decreased sealing performance, eventually. The applied stress and gas permeation promote each other, and accelerating the aging of the sealing ring[8-10].The reason of the color of theused sealing inside changed from brown to black is that the rubber chemical additives react chemically with H_2S and CO_2 which from transmission.

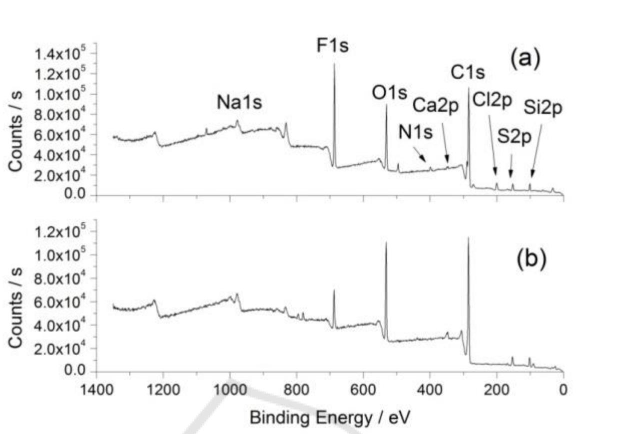

Figure 6. XPS analysis of (a) used sealing ring and (b) new one.

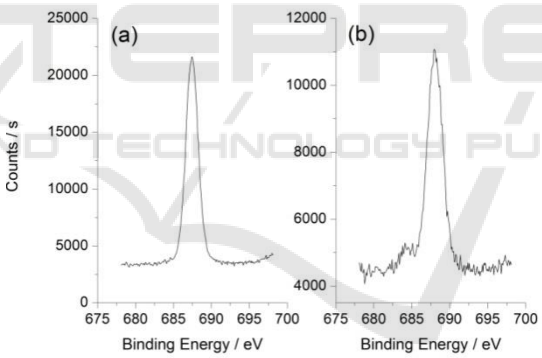

Figure 7. F1s scan in (a) the used sealing ring and (b) the new one.

Table 2. Elemental Quantification of the new sealing ring (At. %).

sample	O	F	C
New sealing ring	13.82	14.34	59.91
used sealing ring	19.25	7.11	64.94

For the fluorine rubber aging process, it can be divided into three stages[11,12]. Firstly, the rubber make an elastic deformation after loading, also known as softening. Secondly, as the stress or deformation is relatively slow and cannot be evenly distributed, it will focus and generate rupture nucleus somewhere, in the rubber surface or internal. Thirdly, the rupture nucleus increases until the rubber is destroyed as a whole.

Therefore, according to the analysis the structure, composition and related physical properties of the failure of the seal, comparison with the same batch of non-service sealing ring, it is shown that the failure of the used sealing ring is due to fatigue aging. During the process of service life, the sealing ring structure change and properties degradation due to the applied stress, and the gas permeation accelerates the fatigue aging process.

5. Conclusions

1) The reason of sealing ring failure is fatigue aging during the long-term service life.

2) The gas permeation leads to the destruction of the network structure, and accelerating the aging process.

3) This type of sealing ring is not suitable for using in acidic gas fields, high-grade sealing materials should be selected. for preventing the sealing ring failure used in theacidic gas fields, the most important strategies is evaluations and detections before using.

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