PRJ, Vol. 2, (January 1990); P. 63–66, 5 FIGS, 1 TABLE.

Short Note

H_2S INDUCED LOCALIZED CORROSION OF AUSTENITIC STAINLESS STEEL BELLOW: A CASE STUDY

M.L. Mehta* and A.T. Hassan*

دراسة ظاهرة تآكل صمامات التهوية الفولاذية تحت تأثير غاز يد$_2$كب

د. م. ل. مهتا وعبدالفتاح حسن

أجريت الإختبارات الميكانيكية والميتالوغرافية اللازمة لإيجاد أسباب تآكل صمامات التهوية لخزانات النفط بحقل الحمادة ، ومن خلال فحص هذه الإختبارات وتحليل نواتج التآكل المتواجدة على سطح الصمام بواسطة الأشعة السينية ، إتضح بأن غازكبريتيد الهيدروجين المبلل هو السبب الرئيسي في تآكل هذه الصمامات المصنوعة من الحديد الفولاذي نوع 321.

INTRODUCTION

Bellow is the component of pilot operated relief valve on surge crude oil tanks. Material of the bellow as per specification is austenitic stainless steel, type 321. Environment inside the bellow is that of the tank gases entering the bellow through pilot valve.

Since flange of the relief valve is connected to the flare line, external surface of bellow is exposed to the gases of the flare line. Operational pressure within the bellow is maintained in the range from 0.02 to 0.06 kg/cm^2 above atm pressure and temperature about 38°C. Bellow was observed to suffer from localized corrosion, causing perforations (Fig. 1) resulting in gas leaks making it difficult to maintain desired pressure within the bellow for operation of the valve.

METALLOGRAPHIC STUDIES

Macroscopic Examination

Extensive pitting were observed both on internal and external surfaces of the bellow. Some of the pits have propagated through wall thickness (0.3 mm) of the bellow. Fig. 2 shows pitting on the external surface of the bellow in their different stages of developments. Some pits had initiated revealing that pitting can start from outer surface and environment surrounding the external surface of the bellow is also corrosive enough to cause pit initiation and their propagation. Deposit

FIG. 1. Localized corrosion causing perforation.

*Petroleum Research Centre, Tripoli, G.S.P.L.A.J.

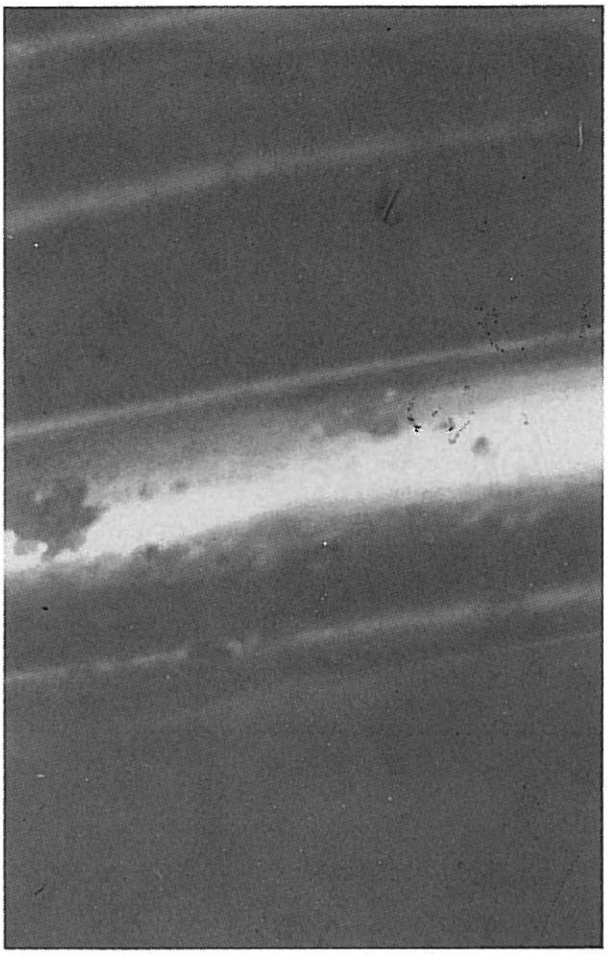

FIG. 2. Pitting on external surface of the bellow showing different stages of their growth X6.

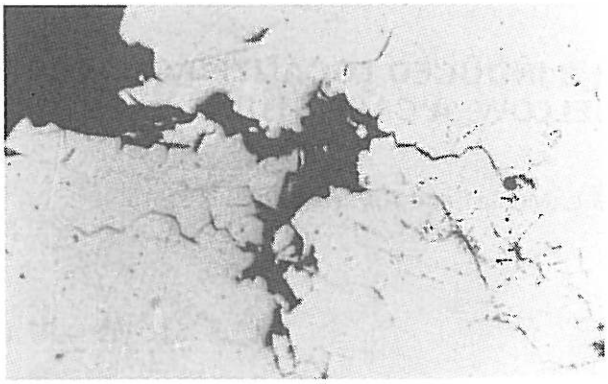

FIG. 3. Intercrystalline cracking and pitting (unetched) X500.

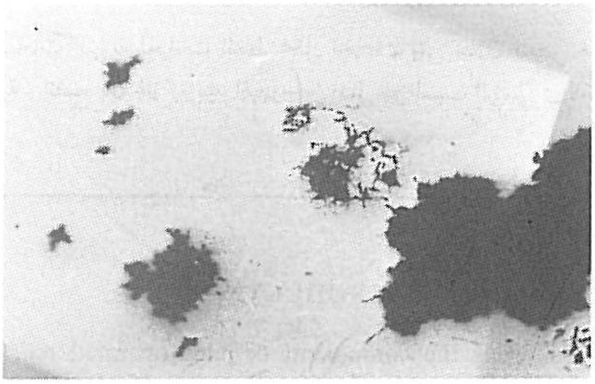

FIG. 4(a). Showing pits in their different stages X125.

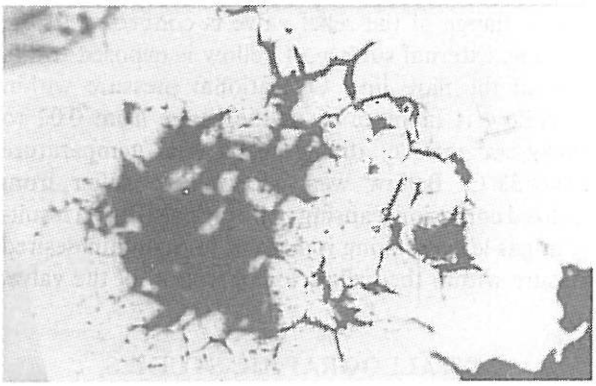

FIG. 4(b). Encircled area in Fig. 4a showing intergranular attack leading to formation of pits X500.

of particles on surfaces of bellow was also observed. Sites of pit formation had presence of thin black film.

Microscopic examination

Samples having different degrees of pitting were cut from bellow. Morphology of localized corrosion in the form of intercrystalline cracking, intercrystalline corrosion as well as pitting corrosion were detected as seen in Fig. 3. Figs. (4a, 4b) show early stages of localized attack which started from grain boundaries and progressed into grains to form pits.

X-RAY DIFFRACTION ANALYSIS

Material deposited on the surface of bellow was scrapped. Corrosion product film on pit sites was thin and adherent. Material coming from those sites was only a very small fraction of material collected.

Table 1 gives results of X-ray diffraction analysis. The main component of the material are kaolinite and quartz. The rest of the components (Iron sulphide and siderite) are present in very small quantities as revealed by very weak intensity of reflections due to these substances.

Analysis of environment

Gas stream from the tank entering pilot valve had

Table 1. Results of X-Ray Diffraction Analysis of materials from the surfaces of the bellow

Compound	Relative peak Intensity	Remarks
Kaolinite, $Al_2Si_2O_5(OH)_4$	Very strong	Major component
Quartz, SiO_2	Strong	Major component
Siderite, $FeCo_2$	Weak	Minor component
Marcasite, FeS_2	Very weak	Very small amount
Greigite, Fe_3S_4	Very weak	Very small amount

pungent odour indicating the presence of H_2S and carried with it water vapour. Gas sample was taken from the side tube connecting tank and pilot valve and the condensate was found to contain 8.11 ppm of H_2S.

LABORATORY INVESTIGATIONS

In order to ascertain that wet H_2S gas can cause pitting corrosion of bellow material, small samples from bellow after cleaning were exposed to wet H_2S gas as described here. Distilled water, (75 ml), was taken in 250 ml Duran glass bottle with a tight cap. It was first purged with high purity Nitrogen gas for 10 minutes and then H_2S gas for 15 minutes. One sample was fully immersed in the solution and the other one was exposed above the solution level. The bottle was sealed to prevent entry of air and to generate wet H_2S gas environment above solution level. Temperature was maintained at 38°C. After two days small black spots appeared on the sample above solution level which grew with time. Solution was observed to turn milky. Samples were removed from the bottle after seven days and solution was analysed to contain 0.8 ppm H_2S. Fully immersed sample did not show any corrosion. Fig. 5 shows localized corrosion on the sample exposed to wet H_2S gas above water level. Solution had turned milky indicating that there was presence of residual oxygen in the solution reacting with H_2S to form sulphur.

FIG. 5. Pitting caused by exposure to wet H_2S above solution level X6.

DISCUSSION

The observation that bellow has also suffered from intercrystalline cracking is difficult to explain as they could be caused by either corrosion fatigue or stress corrosion cracking. Since bellow is subject to pressure variation due to its nature of operation, corrosion fatigue appears to be more probable. It is also observed that initially intergranular attack occurs as illustrated in Fig. 4 and this spreads leading to formation of pits.

Pitting of austenitic stainless steel, of which the bellow is made, is the cause of its failure. Results of present studies attribute pitting corrosion to the presence of wet H_2S gas in the environment to which the bellow is exposed during its service. In the available literature there are only few references to pitting corrosion of stainless steel in chloride free solutions [1]. Ijzermans and Vander Krogt [2] observed pitting corrosion on 18 Cr-2 Mo Stainless steel in 0.5 M $H_2SO_4+H_2S$ gas solution and reported that the presence of H_2S gas is essential because H_2SO_4 does not cause pitting corrosion. Recent investigations [3–4] show that austenitic stainless steels like other iron base alloys are susceptible to microbial corrosion in the presence of sulfate reducing bacteria (SRB). The resultant corrosion manifests in the form of pitting. It is attributed to H_2S produced by SRB which leads to break down of passive film on the stainless steel followed by pitting corrosion. However, mechanism of localized corrosion of austenitic stainless steel in the presence of H_2S in the environment is far from clear.

In the present case, the environment entering bellow is essentially gaseous containing water vapours and solid particles. For corrosion to start and continue, there has to be a water film on bellow surface i.e. surface has to remain wet which would result from condensation of water vapour. This film would readily absorb H_2S from the environment and would also contain various species such as clay, deposited from the environment and those originating from the corroding metal. Presence of such species helps to keep metal surface wet by lowering critical humidity required to form moisture film on the metal surface [5] and also makes it corrosive.

CONCLUSION

1 Pitting corrosion starts both from internal and external surfaces of the bellow and is caused by the presence of wet H_2S gas in the environment.

2 Propagation of pits to form perforations in the bellow wall is responsible for failure of the bellow.

ACKNOWLEDGEMENT

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