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SEM/EDS analysis of corrosion products from the interior of a crude oil pipeline

Within the framework of environmental protection, internal corrosion risk assessment is one of the most important activities of modern pipeline corrosion management. In order to assess the risk of internal corrosion of pipelines, it is important to understand corrosion mechanisms and be able to predict whether localised corrosion will be initiated and how it can be prevented. In the present work we investigated corrosion products from the interior of the of carbon steel crude oil pipeline sampled at a low-lying dead-leg where wall perforation due to corrosion has already occurred. Morphological and compositional studies were conducted by SEM-EDS and microbiological analysis was done by using growth assay. Application of a combination of the two complementary analytical techniques enabled root cause analysis revealing a pattern specific to the corrosive action of biotic corrosive media and indicating bacterial activity and scale formation as the main root cause of the observed corrosion failure.

Key words: *SEM/EDS analysis of corrosion,*

1. INTRODUCTION

Crude oils consist of a variety of chemical substances, the majority of which are various organic compounds [1]. For corrosion to occur in a pipeline there must be liquid water present and the water must be in a form that can wet the wall of the pipe [2]. Oil transmission pipelines typically contain only small amounts of water, from <0.1% to as high as 1-2% from offshore operations. Water vapours may ingress into oil during storage, transportation, and some other operations and it is not uncommon that a substantial amount of seawater enters the system directly during the tanker load-off operations [3, 4].

The extent of internal corrosion in crude oil carrying pipelines is generally influenced by the content of water, temperature, CO_2, H_2S and O_2 content, chlorides, water chemistry, flow velocity, oil or water wetting and composition and surface condition of the steel. Sour gases and organic acids from organic phase undergo extraction into the aqueous phase and may cause a decrease in the pH and increase in the water corrosivity [1]. Some of these species are typically separated from crude during production operations performed at low pressure (atmospheric up to 1 bar gauge pressure) or in various technological processes such as desalting and rectification of crude. In the absence of main abiotic corrosive factors, the bacteria are known to cause severe internal corrosion problems in crude oil storage and transport [2-5]. Microbiologically influenced corrosion, or MIC, with very high corrosion rates of several millimetres per year is one of the most feared types of corrosion attack. Most critical locations for internal corrosion in oil pipelines are in low-spot and dead-leg areas. In these areas water stratifies at the bottom and promotes formation of deposits and MIC. Physicochemical characterization of sludge obtained from transmission pipelines is often done in order to find out the root cause of corrosion [6].

In the present work we investigate deposits from the interior of a low-laying dead-leg of a carbon steel crude oil pipeline sampled at the location where wall perforation due to corrosion has already occurred. The corrosion product sample was analysed by SEM-EDS and a microbiological growth assay.

2. EXPERIMENTAL

Heterogeneous corrosion products were collected from the location of perforation.

Four distinct types of samples were identified: red and black corrosion product samples, white flakes and black flakes. The samples were separated from the bulk of the collected deposits and dried in a desiccator.

SEM-EDS analysis was conducted on a scanning electron microscope with field emission (FE-SEM,

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Field Emission Scanning Electron Microscope FEI Quanta ™).

A swab from the deposits was taken to determine whether microbial activity contributes to the corrosion effect. The presence and number of aerobic bacteria (AERO), anaerobic (ANA) acid-producing (APB) and sulphate-reducing bacteria (SRB) was determined from growth assay (BTI MICkit 3).

3. RESULTS

3.1 SEM/EDS analysis

Figure 1 shows SEM micrographs of the four types of samples. Results of the EDS analysis are shown in Table 1. Presence of a large number of rod-shaped bacteria was also observed by SEM (Figure 2).

Table 1 - Elemental composition of four types of samples separated from the deposit collected from the interior of the corroded pipeline.

Element At% / Point No.	Red corrosion sample			Black corrosion sample			White flake			Black flake		
	1	2	3	4	5	6	7	8	9	10	11	12
O	70.95	30.88	34.07	45.04	41.49	44.98	46.17	62.63	49.32	45.93	46.26	57.76
C	8.12	19.83	55.33	48.19	30.97	27.95	38.25	13.45	33.85	48.44	21.34	16.27
Fe	2.96	26.21	7.17	1.77	21.09	15.36	0.33	-	9.11	1.35	21.99	1.29
S	9.23	18.63	2.93	2.37	4.94	7.86	-	-	1.56	2.78	9.66	12.58
Ca	8.73	3.92	0.51	0.41	1.52	2.41	-	-	0.40	0.28	0.75	12.10
Si	-	0.52	-	-	-	1.42	-	13.47	0.28	1.22	-	
Ti	-	-	-	-	-	-	14.07	2.55	4.39	-	-	
Bal.	-	-	-	Na, Cl, K	-	-	-	-	Na, Al	-	-	

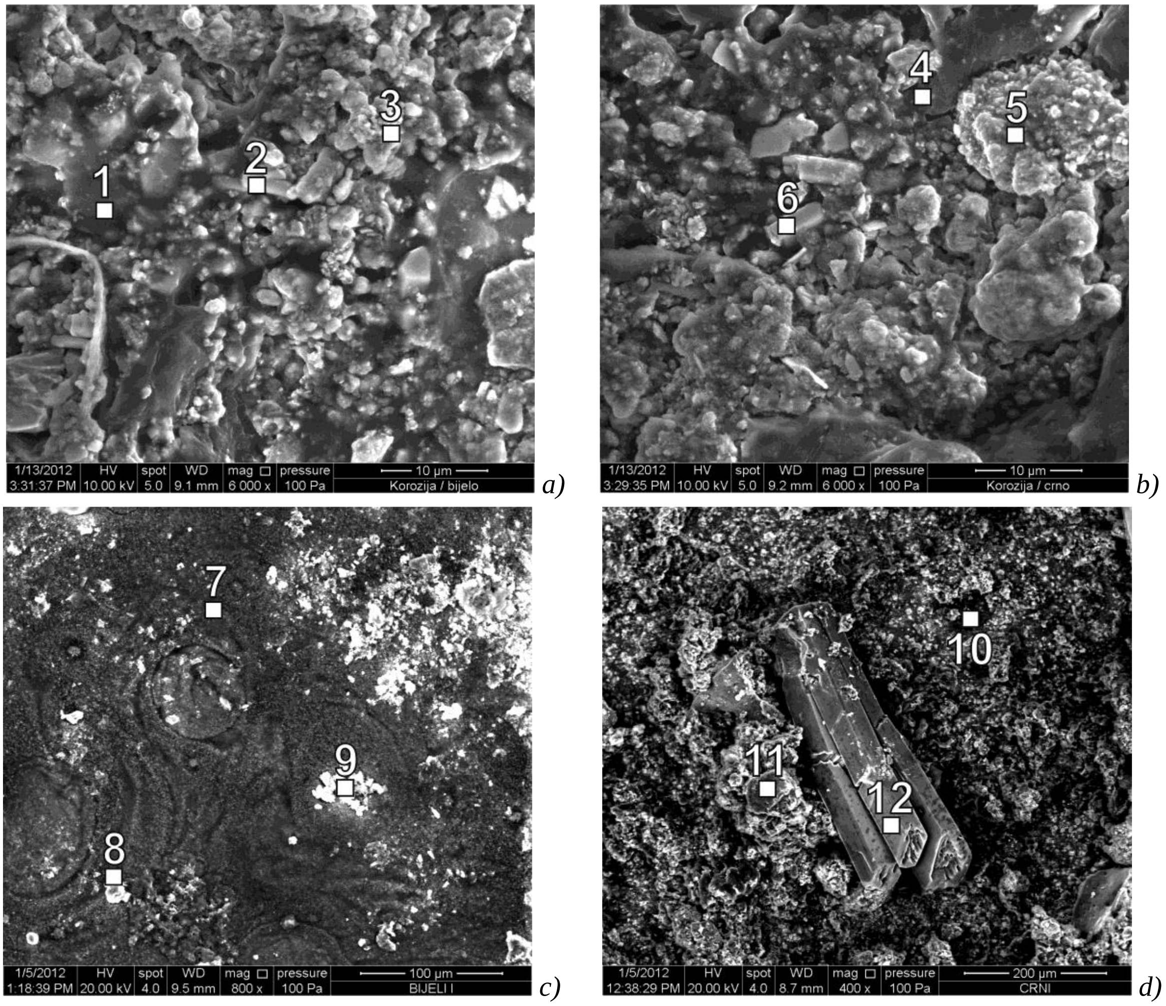

Figure 1 - SEM micrograph of: a) red corrosion sample, b) black corrosion sample, c) white flake and c) back flake separated from the deposit collected from the interior of the corroded pipeline.

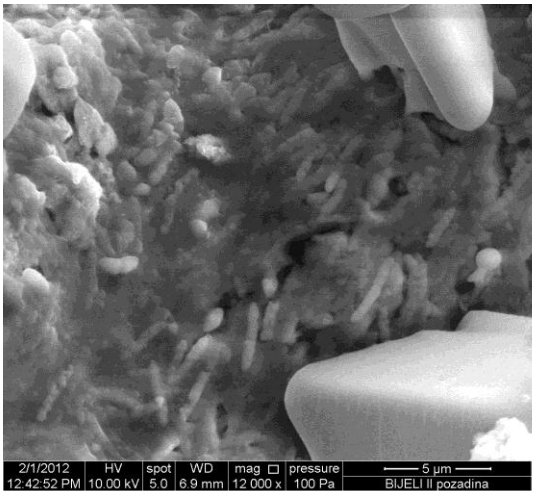

Figure 2 - SEM micrograph of the bacteria present in the corrosion sample.

3.2. Bacterial tests

Microbiological analysis confirmed the presence of aerobic (>10^6 cells/ml), anaerobic (>10^6 cells/ml), organic acid-producing bacteria (>10^6 cells/ml) and sulphate-reducing bacteria (10^3 -10^4 cells/ml).

4. DISCUSSION

SEM/EDS is perhaps one of the most popular technique used for examining and analysing elemental surface component of corrosion-related samples [7]. The SEM examination provides information about the result of the interaction between the corrosive environment and steel pipe, specifically with regard to the morphology of the metal surface, deposits and corrosion products. Deposits may be crystalline or amorphous. In the present case SEM micrographs in Figure 1 show that the samples from the pipeline interior are only partially crystallized.

In corrosion studies EDS is used to provide chemical information about the features being examined by SEM. Often, the relative amounts of elements detected are categorized as major, minor or trace values. Major elements in red and black samples of corrosion products are C, Fe and O. Minor elements are Ca and Si, while the traces of Na, Cl, K and Al were also found. White flakes additionally contain significant amount of Ti confirming the assumption that the flakes are delaminated chips of paint from some area of the pipe interior. Debris found on white flakes contains Si. Black flakes are constituted mostly of C and O, which is in accordance with the assumption that these flakes are made of plastic. Crystallized forms found on the surface of black flakes contained significant amounts of Fe, Ca and S.

Although EDS indicates only elemental composition, it is possible to postulate the probable nature of the corrosion products and scales. Deposits in pipelines can consist of iron oxide, iron carbonate, iron sulphide, sand, clay and mud [8]. Often, paraffins and asphaltenes are included in the deposits. Due to its extreme insolubility barium sulphate is also likely to form scales. These scales often contain some strontium sulphate. In the present analysis no barium or strontium were detected by EDS. However, the analysis shows probable presence of Fe, Si and Ca scales.

Microbiologically influenced corrosion or MIC is responsible for most of the internal corrosion in oil transmission pipelines and storage tanks [9]. High bacteria counts obtained in serial dilution experiments in this study are strong indication of MIC. MIC can occur when microbes, nutrients and proper environmental conditions are available. Deposits, present on the pipe wall provide sites for the colonization of microbes. Role of microbial activity in under-deposit corrosion failures is known to be substantial [10]. Microbial activity may create concentration cells or produce organic acids or acid-producing gases, making the environment aggressive for carbon steel. Additionally, several corrosion mechanisms have been attributed to sulphate-reducing bacteria or SRB, including cathodic depolarization by the enzyme dehydrogenase, anodic depolarization, production of iron sulphides, release of exopolymers capable of binding metal ions, sulphide-induced stress corrosion cracking, and hydrogen-induced cracking or blistering [7].

SRB that are widely regarded as the causative agents of MIC in anaerobic environments [11]. Even in oxygen containing environment, anaerobic microorganisms survive in anaerobic microniches [7]. If the aerobic respiration rate within a biofilm is greater than the oxygen diffusion rate, the metal–biofilm interface can become anaerobic and provide a niche for sulphide production by SRB.

Oxygen can dissolve in oil during storage and filling and emptying operations. The oxygen solubility in the organic phase (60 ppm to 70 ppm) is higher than in the aqueous phase (8 ppm) [12]. Oxygen diffuses from the organic phase to the water phase according to the solubility of each phase. Since oil with water is transported through the pipeline under pressure the supply of oxygen may be sufficient for the aerobic bacteria and faculative acid producing bacteria to thrive and oxidize hydrocarbons. These bacteria accelerate corrosion by SRB trough cleaving hydrocarbon chains to a length able to be metabolized by SRB. Aromatics that are degraded trough consumption of hydrogen utilized for ATP synthesis by heterotrophic microbes may further be converted into alcohols trough the addition of oxygen by autotrophic bacteria while intermediate hydrocarbon degradation products make available energy sources for the physiological activities of SRB [13].

The results of this study confirm the above described corrosion mechanism and the observation that one of the most serious areas for internal corrosion in oil pipelines are in dead-leg areas. These areas of low or no flow, or intermittent flow promote sediment formation and intense bacterial corrosion.

5. CONSLUSION

Multiple causes of internal corrosion in transport pipelines that should be considered by corrosion investigator include: sour oil, pure welds, under-deposit corrosion, microbial corrosion, stray currents and the combinations thereof. Based on the results of SEM/EDS and bacterial analysis under-deposit corrosion aggravated by microbial action may be named as the root cause of the observed corrosion damage. It may be concluded that SEM/EDS is an investigative procedure that with knowledge of the operating environment may be extremely valuable as it helps determine the significance of probable causes of corrosion activity.

6. LITERATURE

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IZVOD

SEM/EDS ANALIZA KOROZIJE PROIZVODA IZ UNUTRAŠNJOSTI NAFTOVODA

U okviru zaštite okoliša, procjena rizika unutarnje korozije cjevovoda je jedna od najvažnijih aktivnosti suvremenog korozijskog menadžmenta cjevovoda. Da bi se procijenio rizik od korozije u cjevovodima, važno je razumjeti mehanizme reakcija korozije i biti u mogućnosti predvidjeti hoće li doći do lokalizirane korozije i kako lokaliziranu koroziju spriječiti. U ovom radu istražene su naslage iz unutrašnjosti naftovoda od ugljičnog čelika. Uzorci su prikupljeni na nisko položenom odvojku u kojem je došlo do perforacije stjenke zbog korozije. Morfološka analiza i analiza sastava provedene su SEM/EDS metodom te je napravljena i mikrobiološka analiza. Rezultati primjene dviju komplementarnih tehnika analize ukazuju na korozijsko djelovanje biološkog medija i koroziju ispod naslaga potpomognutu bakterijskom aktivnosti kao glavni uzrok korozijskog oštećenja cjevovoda.

Ključne reči: *SEM/EDS analiza korozije, unutrašnjost naftovoda, zaštita okoliša*

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