

Inhibiting corrosion in crude oil distillation units by heterocyclic compounds^a

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ABSTRACT

The behaviour of 3-amino-1,2,4-triazole (ATR) 2-amino-thiazole (ATH) and one commercial mixture (H₁) as corrosion inhibitors for carbon steel exposed to export grade Kuwaiti crude oil was studied in a crude oil distillation pilot plant (DISTOP 100) using ammonia gas as a neutralizing agent. The results show that the presence of 10 ppm of (ATR) or (ATH) decreased the corrosion rate of carbon steel by >90%. However, the commercial inhibitor (H₁) inhibited the corrosion of carbon steel by 84% under the same experimental conditions. X-ray photoelectron spectroscopy showed that the corrosion inhibition of carbon steel by (ATR) or (ATH) is attributed to the formation of iron complex layer compounds on the metal surface. SEM micrograph of the surfaces of the specimens tested in the presence of (ATR) or (ATH) showed the formation of a relatively smooth thin film, free from localized areas of attack compared to the blank specimen.

INTRODUCTION

Corrosion problems in crude oil distillation units and their overhead systems have been extensively studied (Hashimoto 1979; Forouils 1980; French & Fahey 1983; Merrica & Auerbach 1983). There are five main impurities in crude oil that contribute to the corrosion of these systems: inorganic chloride salts, organic-nitrogen and sulphur compounds, naphthenic acids and organic chlorides. Corrosion in these systems is primarily caused by hydrochloric acid produced during the hydrolysis in the heating furnace of water-soluble magnesium and calcium chloride salts in the crude oil. The situation is aggravated by the presence of hydrogen sulphide as dissolved gas in oils or its evolution from the thermal decomposition of sulphur compounds in the crude. Corrosion in the overhead system occurs whenever water condenses and absorbs the hydrogen chloride and hydrogen sulphide from the overhead atmosphere, forming a particularly aggressive environment.

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In crude oil distillation units, effective corrosion control requires not only the use of corrosion-resistant material, but also a set of chemical engineering measures, including thorough desalting of the crude, introduction of a neutralizing agent and various organic inhibitors (Ross & Pedran 1977; Al-Farkh *et al.* 1980). Nitrogen compounds such as quaternary ammonium compounds, amines, amine salts and heterocyclic compounds are well-known corrosion inhibitors used for crude oil distillation units (Ross & Pedran 1977; Al-Farkh *et al.* 1980; Merrica & Auerbech 1983). Ross & Pedran (1977) studied the corrosion rate of carbon steel exposed to a kerosene-water mixture containing different concentrations of HCl and H₂S in the presence of ammonia and morpholine in addition to other compounds as a neutralizing agent and inhibitors. Vaskkart (1985) constructed a simple apparatus as a pilot plant distillation unit to evaluate the performance of film commercial inhibitors for the overhead system. Al-Farkh *et al.* (1980) evaluated the effect of eight different compounds as corrosion inhibitors for carbon steel exposed to a continuously refluxing kerosene-water mixture containing 3 ppm HCl and 800 ppm H₂S/day over 1,000 h.

The aim of this study was to evaluate the behaviour of 3-amino-1,2,4-triazole (ATR), and 2-amino-thiazole (ATH) and the commercial inhibitor (H₁) as corrosion inhibitors for carbon steel exposed to export grade Kuwaiti crude oil in a crude oil distillation pilot plant (DISTOP 100) using ammonia gas as a neutralizing agent.

EXPERIMENTAL METHOD

3-Amino-1,2,4-triazole (98%: m.p. 153–155°) (ATR) and 2-amino-thiazole (95%: m.p. 85–88°) (ATH) (10 ppm each) were evaluated separately as corrosion inhibitors for carbon steel exposed to export Kuwaiti crude oil. These compounds were obtained from Fluka AG Chemical Company and used without purification. They are soluble in aromatic and aliphatic hydrocarbons and alcohols. They do not contribute significantly to emulsification at the dosages used. The commercial inhibitor (H₁) is recommended by the supplier to be added in quantities of 5–10 ppm as corrosion inhibitor for crude oil overhead systems.

Carbon Steel (C, 0.2%, Si, 0.5%, Mn, 0.7%, P, 0.04%, S, 0.04%, Fe, balance) with a diameter of 0.60 cm and a length of 3 cm was used in the form of rods having screw threads on both ends. Only the cylindrical body of the test specimens was exposed (see Fig. 2). The exposed surface area of each rod was 5.652 cm².

A crude oil distillation pilot plant (DISTOP 100) was used in this study (Fig. 1). It is a 100 L batch pilot distillation unit that was custom-built to carry out the true boiling point (TBP) distillation of crude oils and products in compliance with current ASTM/CEN norms. It can process stabilized crude oil of density range 0.82–0.95 kg/L. It comprises: (i) a 100 L capacity still pot with an electric thermosiphon heater to reduce the possibility of hot spots and cracking, (ii) a 3 m packed multi-knit adiabatic column giving a high yield throughout, high efficiency and low pressure drop, and (iii) a reflux divider and a jacketed condenser take-off system that can be cooled for volatile components, or heated when waxy or viscous material is distilled. The unit can be operated at atmospheric pressure or under vacuum down to about 267 pa. Dynamic retention during distillation can be maintained at between 2% and 4% by adjustment of the column pressure drop. The refluxing system was provided with a continuous stream of ammonia as a neutral-

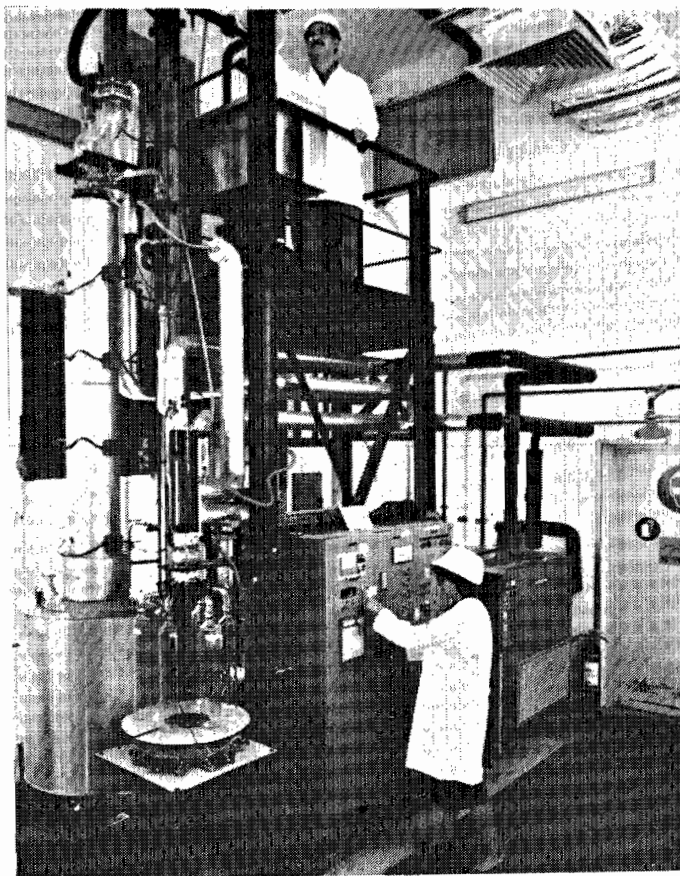


Fig. 1. Crude oil distribution pilot plant (DISTOP 100).

izing agent. The amount of ammonia needed to adjust the pH of the testing mixture between 6.0 and 6.5 was obtained by passing nitrogen through an ammonia solution (25 ml of ammonia solution, 25% wt/v, diluted with distilled water to 200 ml). Four carbon steel specimens were fixed inside the overhead system of the pilot plant which was modified to accommodate the special teflon holder for carbon steel specimens (Fig. 2). The pilot plant was operated for about 8 h per day on six consecutive days (50 h total) at atmospheric pressure using export grade Kuwaiti crude oil (50 kg). During shutdown, the system was kept under nitrogen to avoid oxidation of the specimen. The temperature inside the overhead system ranged from 20°C to 100°C around the carbon steel specimens.

A Mcpherson ESCA-36 spectrometer with a MgK_{α} -source (1253.6 eV) was used for measuring X-ray photoelectron spectra. The microscopic examination of the carbon steel specimen after exposure to the crude oil was carried out using a scanning electron microscope (Model MBI, CAMEBAX). The elemental analyses for the exposed surfaces were determined by EDS (KEVEX) attached to the CAMEBAX.

All the corroded specimen were cleaned by dipping in Clark's solution (ASTM 1981). After 30 min, the specimens were washed with water, then cleaned with a

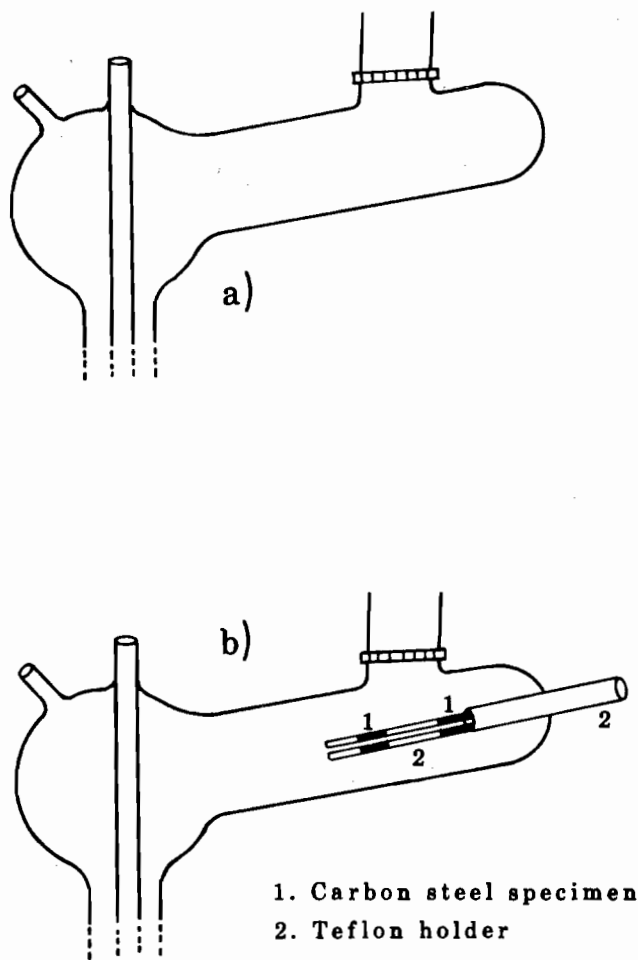


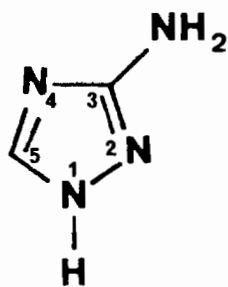
Fig. 2. (a) DISTOP 100 elbow before modification. (b) DISTOP 100 elbow after the teflon specimen holder was added.

plastic brush, washed again with distilled water and, finally, with acetone. The specimens were then dried and weighed. The average mass losses were used to calculate the corrosion rates from the mass-loss method as mil/yr (mpy) according to ASTM G1-81 (1981).

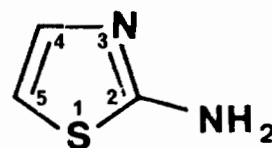
Each tested organic compound was previously dissolved in ethanol to give 0.2% w/v solution and then added to the refluxing crude oil as a single volume based on the initial weight of the crude oil. The inhibitor efficiencies were calculated relative to the corrosion rates obtained in the presence of ammonia alone.

RESULTS AND DISCUSSIONS

3-Amino-1,2,4-triazole (ATR) and 2-amino-thiazole (ATH) are strongly basic materials in comparison with other heterocyclic organic compounds such as azoles and imidazoles.



(ATR)



(ATH)

They are thermally stable at high temperature (300°C) and have the ability to form complexes with carbon steel surface as indicated by XPS studies.

Experiments were conducted to investigate the behaviour of different concentrations of 3-amino-1,2,4-triazole (ATR) and 2-amino-thiazole (ATH) (10, 20, 30 and 40 ppm) as corrosion inhibitors for carbon steel exposed to a kerosene-water mixture (10% water) containing 3 ppm of HCl and 800 ppm of hydrogen sulphide/day at 55–60°C and pH 6.0–6.5 for 50 h exposure time, using ammonia as neutralizing agent. Screening tests showed that 10 ppm of the compounds ATR and ATH gave good inhibitor efficiencies (>84%) (Table 1) among all the tested concentrations, (Al-Kharafi & Al-Hajjar 1990). The behaviour of this concentration for the two organic compounds (ATR and ATH) and the commercial inhibitor (H_1) (10 ppm) was studied in a crude oil distillation pilot plant (DISTOP 100) using export grade Kuwaiti crude oil.

Table 1. Corrosion rates and inhibitor efficiencies for carbon steel in kerosene-water mixture (10% water) containing different concentrations of ATR and ATH using nitrogen as a carrier gas for ammonia and hydrogen sulphide after 50 h exposure

Experiment no.	Material added	3-Amino-1,2,4-triazole (ATR)		2-Amino-thiazole (ATH)	
		Corrosion rate (mpy)	Inhibitor efficiency (%)	Corrosion rate (mpy)	Inhibitor efficiency (%)
1	None	11.80	—	11.80	—
2	Ammonia	4.50	—	4.50	—
3	Ammonia + 10 ppm	0.69	84.7	0.53	88.2
4	Ammonia + 20 ppm	0.72	84.0	1.01	77.6
5	Ammonia + 30 ppm	1.31	70.9	0.94	79.1
6	Ammonia + 40 ppm	1.93	57.1	1.14	74.7

The calculation of inhibitor efficiency for experiments 3–6 is based on the results of experiment 2.

Table 2. Corrosion rates and inhibitor efficiencies in DISTOP 100 after 50 h of exposure using export grade Kuwaiti crude oil in the presence of ammonia as a neutralizing agent

Experiment no.	Material added	Corrosion rate (mpy)	Inhibitor efficiency (%)
1	Crude oil alone	71.50	—
2	Crude oil neutralized with ammonia	48.32	—
3	Crude oil neutralized with ammonia + 10 ppm of ATR	2.96	93.7
4	Crude oil neutralized with ammonia + 10 ppm of ATH	3.17	93.4
5	Crude oil neutralized with ammonia + 10 ppm of H ₁	7.72	84.0

The calculation of inhibitor efficiency for experiments 3–5 is based on the results of experiment 2.

Table 2 presents the corrosion rate and inhibitor efficiencies of 10 ppm of ATR and ATH collected from the pilot plant (DISTOP 100) after 50 h of exposure using ammonia as a neutralizing agent. The results show that the presence of 10 ppm of (ATR) or (ATH) increased the inhibitor efficiency of the crude oil to >90%. However, in the presence of 10 ppm of (H₁), the inhibitor efficiency was 84%. These results indicated that the organic compounds (ATR and ATH) had a good performance as corrosion inhibitors for carbon steel under the tested conditions compared to the commercial inhibitor (H₁). This may be attributed to the ability of the organic compounds to form a film or complex layer on the metal surface and protect it from further attack. This conclusion resulted from XPS studies on carbon steel samples exposed to crude oil for 50 h at pH 6.0–6.5. The XPS spectra of carbon steel surface shows that the surface is composed mainly of Fe₃O₄ and possibly FeO, where two maxima of the (2p_{2/3}) spin-orbit component are observed at ~711.0 and 710.7 eV. The bombardment of the surface by Argon ions for more than 10 min did not remove the oxide (Fe₃O₄) layer from the surface. The XPS of the metal plate exposed for 50 h in the pilot plant (DISTOP 100) using crude oil containing 10 ppm of (ATR) shows a medium Fe(2p) spectral line at 709.2 eV, beside a stronger line at 710.7 eV associated with nitrogen. This indicates the possibility of complex formation between ATR and iron, besides the presence of Fe₃O₄ structure. The XPS of 2-amino-thiazole (ATH) shows a broad line of the N(1s) at 400.6 eV and S(2p) at 164.2 eV. When a carbon steel plate is exposed in the pilot plant containing the crude oil and 10 ppm of ATH, the Fe(2p_{2/3}) energy region shows the presence of two maxima for Fe(2p_{3/2}) at 710.8 and 713.1 eV which is attributed to the presence of Fe₃O₄ and Fe^{III}-N or Fe^{III}-N,S complex layer, as can be deduced from the relatively strong O(1s) and medium N(1s) and S(2p) spectral lines. These N(1s), O(1s) and S(2p) spectral lines were no longer observed after the surface had been bombarded with Argon ions for 4 min.

Some insight into the mechanism of inhibition by the two organic compounds (ATR and ATH) can be deduced from the morphological examination of the surface of the samples by the SEM and EDS (Energy Dispersive Spectroscopy) analysis which show the composition and the role of the protective film formed. Plates 1–4 show the SEM micrographs of typical surface condition of specimens exposed for

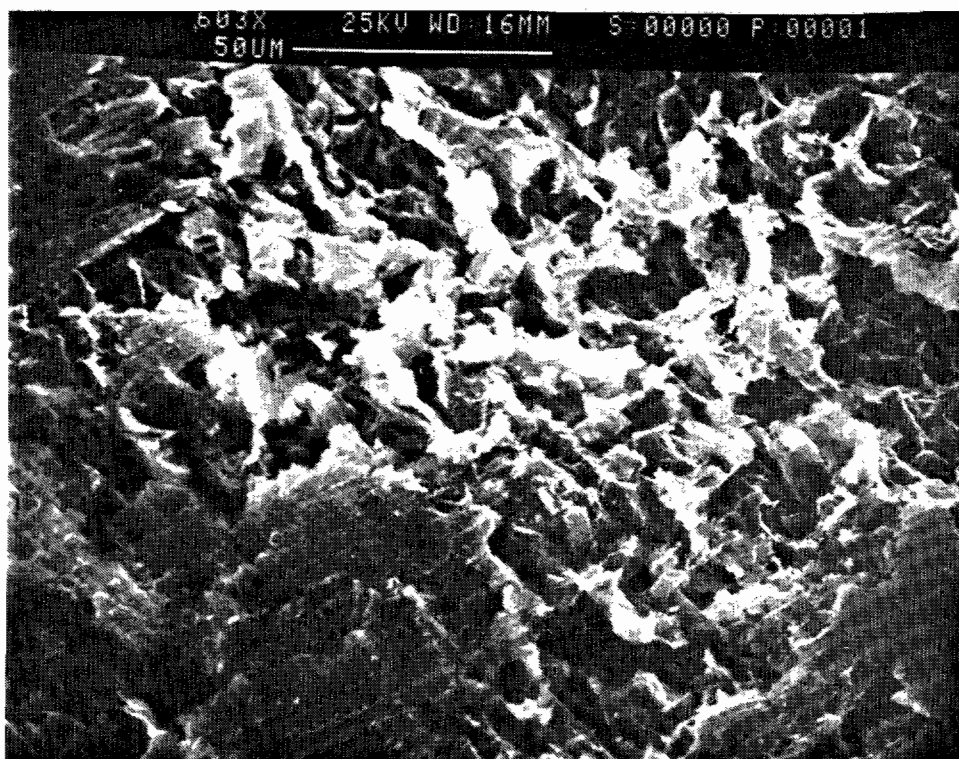


Plate 1. Scanning electron micrograph (603 X) showing the morphological features of the surface of carbon steel after exposure for 50 h in export grade Kuwaiti crude oil with no inhibitor.

50 h at pH 6.0–6.5 to the export Kuwaiti crude oil with and without inhibitor in the crude oil distillation pilot plant (DISTOP 100). In general, the conditions of the tested specimens bear a marked relationship to the corrosion rate determined by measuring the weight loss (cf. Table 2). A high corrosion rate corresponds to the development of large amounts of corrosion products on the specimen surface, as is shown in Plate 1 for a specimen exposed to the crude oil with no inhibitor added. The mode of attack is general, as expected with carbon steel but there are localized areas of heavy corrosion attack. EDS analysis revealed that the corrosion products formed on the surface of a specimen exposed to the crude oil with no inhibitor gave strong peaks related to Fe, Cl and S (Fig. 3). Plates 2 and 3 show the surface condition of specimens exposed to crude oil containing 10 ppm of (ATR) and (ATH), respectively. The results indicate that the samples exposed to the inhibited crude oil (Plates 2 and 3) show a coherent protective surface film. In both cases, the effect of the two organic compounds (ATR and ATH) has resulted in stifling of the initiation of corrosion by formation of a uniform and translucent inhibitor film. The more protective nature of the film formed upon addition of the two organic compounds (ATR and ATH) is reflected by the corrosion rate determinations (cf. Table 2). EDS analyses showed the presence of Fe (presumably from the substrate materials) with traces of S and/or Cl on the samples surface of Fe (Figs 4–5). Plate 4 shows the corrosion products on the specimen surface exposed to the crude oil in the presence of 10 ppm of the commercial inhibitor (H_1). EDS analysis indicated that the corro-

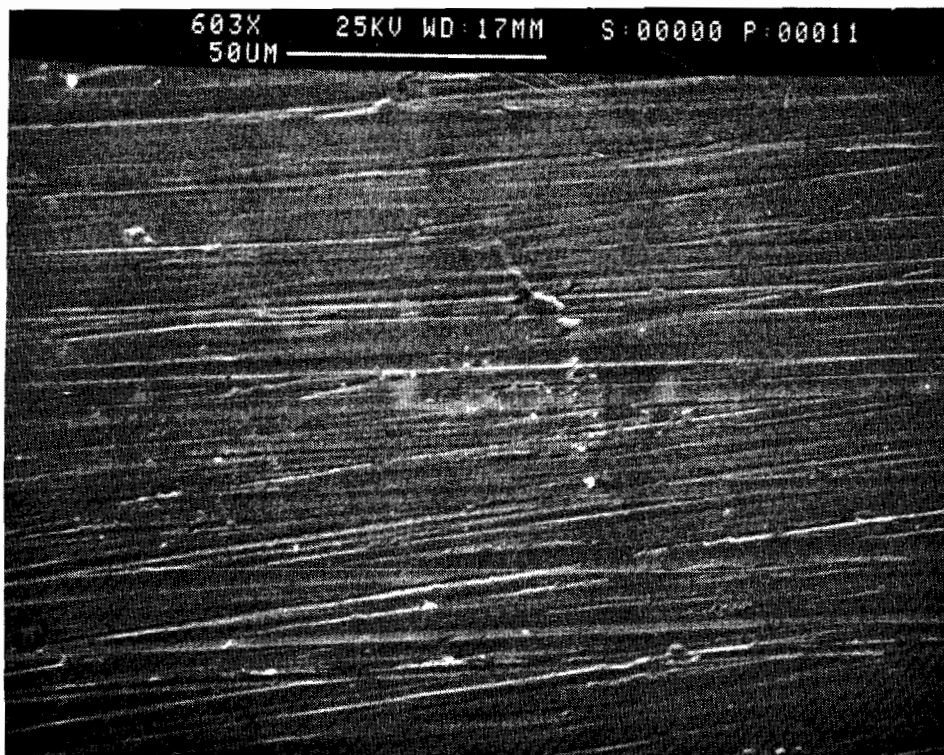


Plate 2. Scanning electron micrograph (603 X) showing the morphological features of corrosion formed on the surface of carbon steel after exposure for 50 h in export grade Kuwaiti crude oil containing 10 ppm 3-amino-1,2,4-triazole (ATR).

sion product is composed of strong peak related to Fe and two medium peaks attributed to Cl and S (Fig. 6).

CONCLUSION

1. The presence of 10 ppm of the compounds 3-amino-1,2,4-triazole (ATR) and 2-amino-thiazole (ATH) provided up to 93% inhibition of corrosion of carbon steel in export Kuwaiti crude oil in the presence of ammonia under the experimental conditions used. However, the commercial inhibitor (H_1) inhibited the corrosion of carbon steel under the same experimental conditions by 84%.
2. XPS results show the ability of ATR and ATH to form iron complexes.
3. SEM micrograph of the specimen after prolonged exposure (50 h) to an export Kuwaiti crude oil shows the formation of a uniform and translucent inhibitor film.

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Plate 3. Scanning electron micrograph (601 X) showing the morphological features of corrosion formed on the surface of carbon steel after exposure for 50 h in export grade Kuwaiti crude oil containing 10 ppm 2-amino-thiazole (ATH).

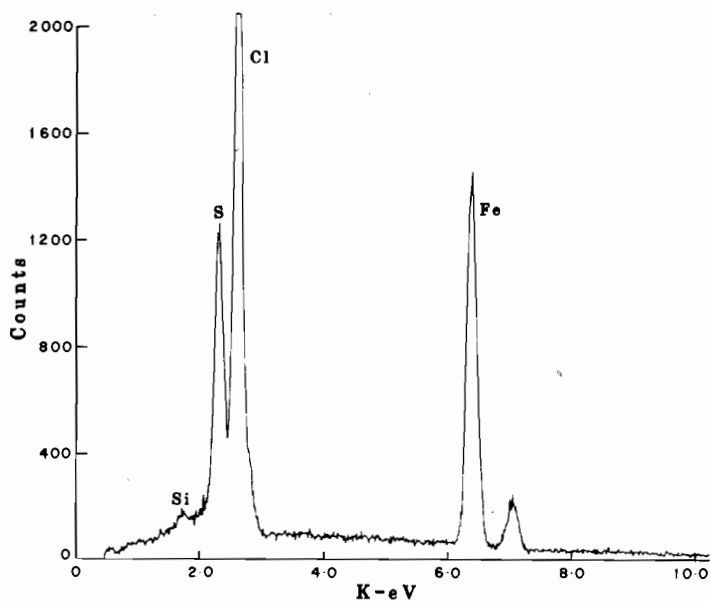


Fig. 3. EDS analysis of carbon steel exposed to export grade Kuwaiti crude oil with no inhibitor.

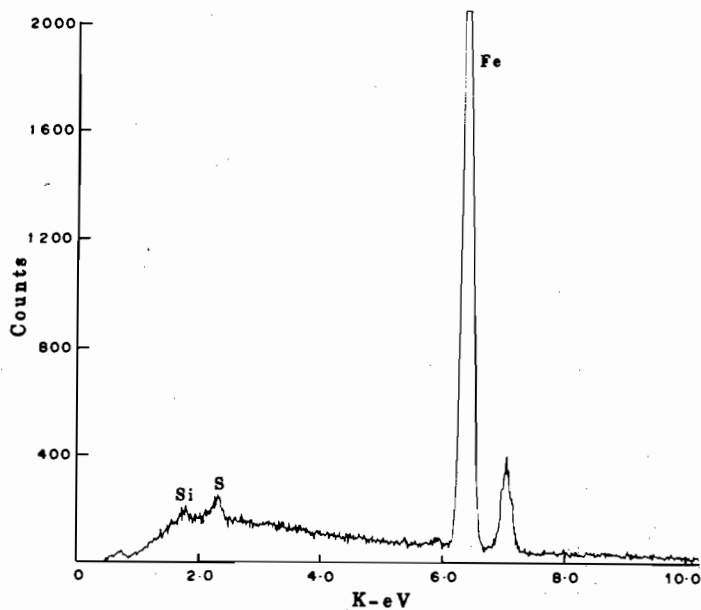


Fig. 4. EDS analysis of carbon steel exposed to export grade Kuwaiti crude oil containing 10 ppm 3-amino-1,2,4-triazole (ATR).

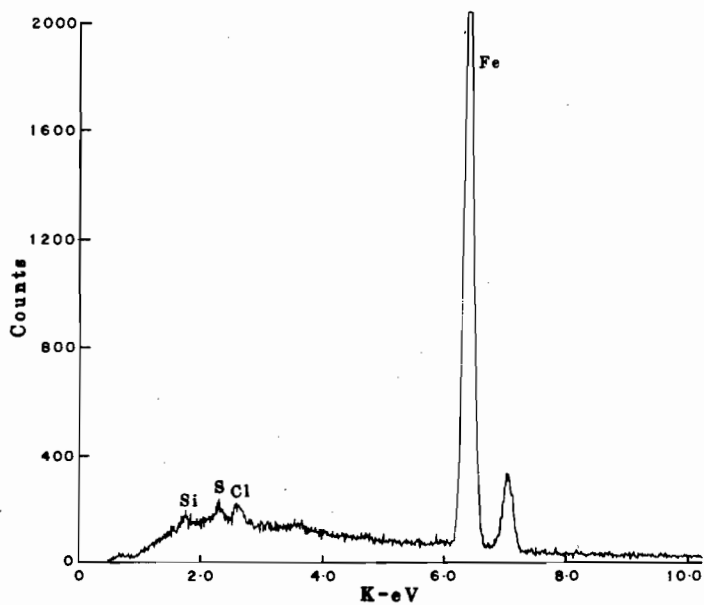


Fig. 5. EDS analysis of carbon steel exposed to export grade Kuwaiti crude oil containing 10 ppm 2-amino-thiazole (ATH).

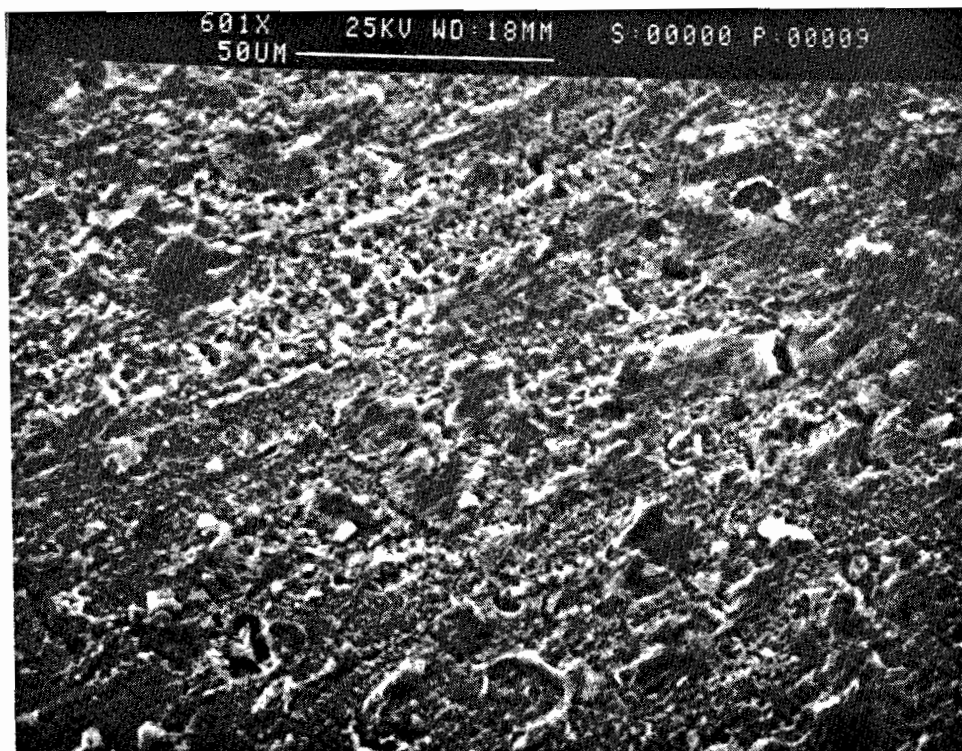


Plate 4. Scanning electron micrograph (601 X) showing the morphological features of corrosion formed on the surface of carbon steel after exposure for 50 h in export grade Kuwaiti crude oil containing 10 ppm of the commercial inhibitor (H_1).

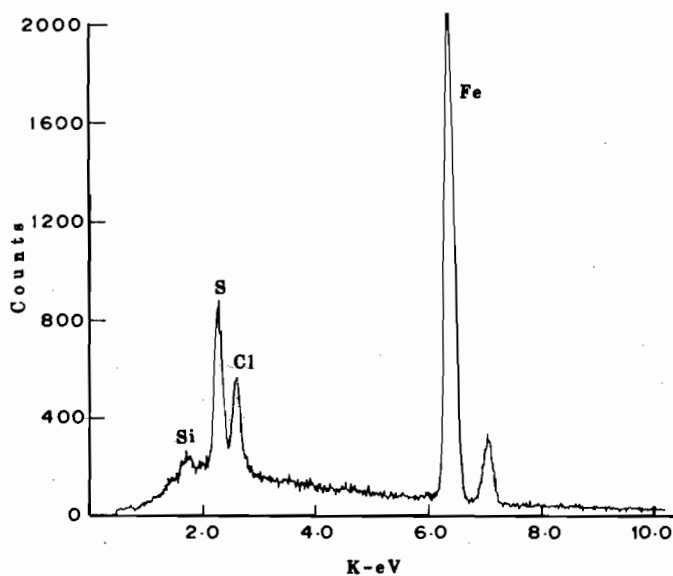


Fig. 6. EDS analysis of carbon steel exposed to export grade Kuwaiti crude oil containing 10 ppm of the commercial inhibitor (H_1).

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منع التآكل الحادث في وحدات تقطير الزيت الخام بواسطة مركبات عضوية غير متجانسة

فايزة الخرافي* و فاروق الحجار
إدارة البترول والبتروكيماويات وعلوم المواد ،
معهد الكويت للابحاث العلمية ، ص . ب ٢٤٨٨٥ ،
الصفاء ١٣١٠٩ ، الكويت

خلاصة

لقد تم دراسة سلوك كل من ٣ - أمينو - ١ ، ٢ ، ٤ - ترايازول (*ATR*) و ٢ - أمينو ثيازول (*ATH*) والمخلوط التجاري (*H₁*) كمثبطات لتآكل الحديد الكربوني المعرض للزيت الخام الكويتي المصدر ، وذلك في وحدة تقطير الزيت الخام (*DISTOP 100*) في وجود غاز الأمونيا كعامل للتبادل .

ولقد أوضحت النتائج ان وجود ١٠ جزء في المليون من (*ATR*) أو (*ATH*) في الزيت الخام يقلل سرعة تآكل الحديد الكربوني بنسبة اعلى من ٩٠٪ ، في حين ان المخلوط التجاري (*H₁*) يخفضه بنسبة ٨٤٪ تحت نفس الظروف . ولقد أظهرت دراسة أشعة اكس للتحليل الكيميائي (*ESCA*) ان منع أو تقليل تآكل الحديد الكربوني يعزى إلى تكوين طبقة معقدة من الحديد مع المركبات (*ATR*) أو (*ATH*) على سطح المعدن تحميه من التآكل .

ولقد دلت الدراسة بالمجهر الإلكتروني الماسح لأسطح عينات الحديد الكربوني في وجود المركبات (*ATR*) أو (*ATH*) على وجود طبقة رقيقة وناعمة خالية من مناطق التآكل الموضعي مقارنة بالعينة المعرضة للزيت الخام فقط .

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