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INFLUENCE OF SULPHUR ON HIGH TEMPERATURE DEGRADATION OF STEEL STRUCTURES IN THE REFINERY INDUSTRY

ABSTRACT

This paper reviews sulphidation behaviour of steel structures in the refinery industry. The data presented are related to two aspects of the corrosion. One aspect refers to external degradation of the structures due to formation of sulphide scales on the steel surface and metal losses; another is connected with internal degradation, i.e. changes of steel microstructure and formation of internal corrosion products. The so-called modified McConomy curves, and the Couper-Gorman curves used to predict corrosion rates of steels in hydrogen-free refinery streams, and hydrogen-containing environments are shown. Decreased stability of carbides in steel due to the presence of sulphur on the steel surface is considered, and a role of hydrogen in this process is outlined.

Key words: refinery industry, steel structures, sulphide corrosion, microstructure degradation

INTRODUCTION

Sulphur is one of the foremost corrodents which causes problems in the refinery industry. It occurs in crude petroleum at various concentrations, and forms a variety of chemical compounds, including hydrogen sulphide, mercaptans, sulphides, polysulphides, thiophenes and elemental sulphur [1,2]. The cruds that are processed nowadays contain 1-3 wt. % of sulphur on average.

The most common material of refinery structures is carbon steel, followed by chromium-molybdenum (Cr-Mo) steels, such as 9Cr-1Mo, 5Cr-0.5Mo, 2.25Cr-1Mo, 1.25Cr-0.5Mo, and 18Cr-10Ni stainless steels. The main forms of damage caused by sulphur to the steel structures include weight loss corrosion and sulphide stress cracking in low temperature aqueous environments, and high temperature sulphide corrosion in non aqueous environments at 200 – 500°C [1,2].

High temperature sulphide corrosion proceeds by conversion of steels to sulphide scales due to a reaction of sulphur bearing compounds with metal elements from the steels. Corrosion rates are dependent upon temperature, sulphur concentration and the form in which the sulphur exists [1-5]. Hydrogen sulphide is the most active compound from a corrosion standpoint [6-7]. Most other sulphur forms can be considered almost inert until petroleum reaches the refinery. During refinery operations, due to catalytic

influence of steel surface, less active sulphur compounds are converted into hydrogen sulphide. The amount of hydrogen sulphide evolved increases with temperature. The conversion rate of mercaptans is particularly high, due to great ability of these compounds to adsorb on the steel surface [8-9]. In some refinery operations at hydrogen and catalyst present, sulphur compounds react with hydrogen to form the aggressive hydrogen sulphide, and the rate of sulphide corrosion becomes dependent on hydrogen sulphide concentration [9-11].

Apart from the scaling and metal losses, sulphur action results in internal damage to steel elements. Sulphur causes a degradation of steel microstructure and may form corrosion products beneath the steel surface [12].

The above-mentioned aspects of high temperature degradation of steel structures under the influence of sulphur have been presented in this paper. Based on refinery experience, sulphide corrosion rates of steels have been shown, and mechanisms of steel microstructure degradation due to sulphur action have been outlined. Because of great influence of hydrogen sulphide on the corrosion behaviour of the steels, two forms of sulphide corrosion are distinguished: without hydrogen present and with hydrogen present.

CORROSION RATES

Sulphide corrosion without hydrogen present

Sulphur contained in hydrocarbon fractions in atmospheric and vacuum distillation units, catalytic cracking units, and hydrotreating and hydrocracking units upstream of the hydrogen injection line destroys steel structures, mainly according to own concentration and process temperature. Only few corrosion problems are experienced in atmospheric and vacuum distillation units, provided that cruds contain traces of hydrogen sulphide, and total sulphur is less than 0.6 wt.%. Heat exchangers tubes, furnace tubes and piping are generally made of carbon steel. Elements of distillation columns, where temperature is above 250ºC and turbulent flow conditions are encountered, are usually lined with steel containing 12 % of chromium. At higher sulphur contents, chromium-molybdenum steels are applied. Steels containing a minimum 5 % of chromium are required for furnace tubes, headers, U-bends, elbows and pipes at service temperature 300-400ºC. In vacuum furnaces, where the temperature is higher than 400ºC, tubes made of 9Cr-1Mo steel are often used. In catalytic cracking units, at temperatures up to 540ºC in reaction section, and up to 760ºC in catalyst regeneration section, equipment and piping are protected against sulphide corrosion by using 5Cr-0,5Mo steel, 9Cr-1Mo steel or 18Cr-8/10Ni steel. Carbon steel components are protected by refractory linings. When there are some erosion problems, hard stellite linings are applied [1,2].

To predict the relative corrosivity of crud petroleum and its various fractions without hydrogen present, sulphide corrosion rates vs temperature data have been elaborated on the basis of industrial experience. First data were provided by a survey conducted by the American Petroleum Institute (API) Subcommittee on Corrosion in 1961. Although the data given by respondents were incomplete and scattered

considerably, they were combined with earlier reported corrosion rates and presented as the so-called original McConomy curves [5].

Further experience has proved that the original McConomy curves should be decreased by factor 2.5, and in 1986 the modified curves were reported [4]. The modified McConomy curves suitable for hydrocarbon fractions containing 0.6 wt % of sulphur are shown in Fig.1a, and correction factors for the fractions with various total sulphur content are presented in Fig. 1b. Beneficial effects of alloying steels with chromium may be seen. Corrosion rates are roughly tenfold reduced when ferritic 9Cr steel instead of carbon steel is applied. Lowest corrosion rates are noted for austenitic 18Cr-8/10Ni steel.
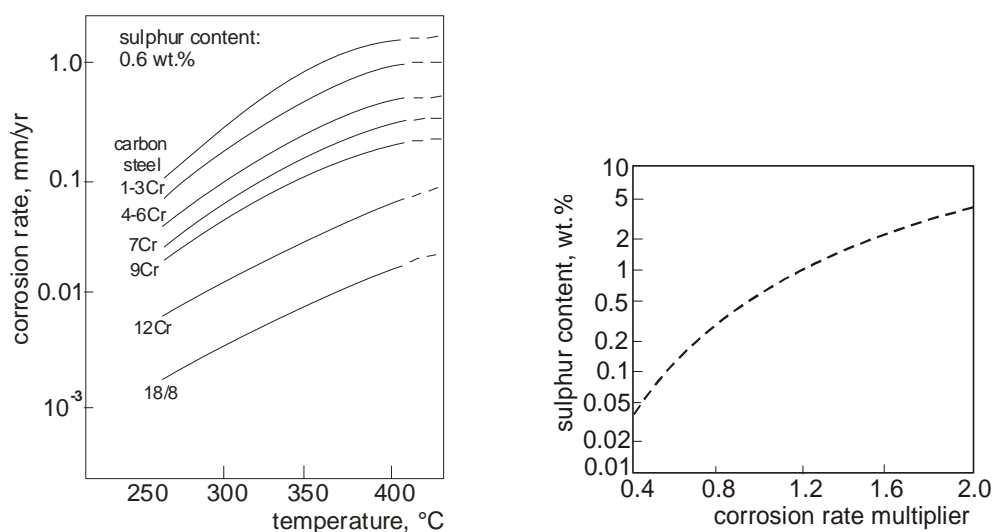

Fig. 1. Modified McConomy curves showing the influence of temperature on sulphide corrosion rates of steels (a) and effects of sulphur content on the corrosion rates in 290-400ºC (b) [4]

In certain circumstances these modified McConomy curves have been proven unreliable, particularly in hot distillation section of hydrocracker units. In some conditions they underpredict the observed corrosion rates, and very low sulphur levels (< 30 wppm total sulphur) are beyond the parameters of the curves. Further data are needed to be collected in order to review and assess the existing sulphide corrosion prediction curves used by the refinery industry [12,13].

Sulphide corrosion with hydrogen present

The presence of hydrogen in some refinery operations, for example hydrotreating, hydrocracking an catalytic reforming, increases the severity of sulphide corrosion. In this case the corrosion is detrimental not only because of metal loss but also because of volume of sulphide scale formed that can lead to reactor plugging.

Reactors, piping, and elements of furnaces and heat exchangers downstream the hydrogen injection line are particularly exposed to the corrosion. Reactors are usually made of 2.25Cr-1Mo/3Cr-1Mo steels, and vanadium modified grades 2.25Cr-1Mo-0.25V, 3Cr-1Mo-0.25V-Ti-B, 3Cr-1Mo-0.25V-Nb-Ca. The protection against sulphide corrosion in thick wall reactors is provided by an internal lining or weld overlay over the base metal, using 18Cr-8/10Ni steels stabilized with niobium or tantalum [14,15]. Internal parts of the reactors are made of stabilized 18Cr-8/10Ni steels, and catalyst screens may be additionally protected by means of aluminium diffusion layer [16].

Reactor effluent piping operating above 250ºC, depending on the environmental parameters and expected corrosion rates, is made of carbon steel, Cr-Mo steels or stabilized 18Cr-8/10Ni steels [2,3,17]. For furnace tubes 9Cr-1Mo steel, aluminized Cr-Mo steels, or stabilized 18Cr-8/10Ni steels are applied [2,17,18].

Basic information for material selection for refinery hydrogen units is provided by the so-called Couper-Gorman curves. The curves were elaborated on the bases of a survey conducted by National Association of Corrosion Engineers (NACE) Comitee T-8 on Refining Industry [11]. They present the influence of temperature and hydrogen sulphide concentration on corrosion rates of carbon steel, 5Cr-0.5Mo steel, 9Cr-1Mo and 18Cr-8Ni steel. For ferritic steels two sets of curves apply, depending on whether the environment is gas oil or naphtha. It was indicated that no corrosion occurs at low hydrogen sulphide concentration and temperature exceeding 320ºC. Total process pressure of 1 – 18 MPa was found to have no meaningful influence on the corrosion rates.

Some of the Couper-Gorman curves are presented on Fig. 2. Original parts of the curves are solid, and the dashed lines indicate probable corrosion rates in conditions beyond the NACE survey. It may be seen that the corrosion rates of carbon steel and 5Cr-0.5Mo steel are similar. Addition of 9% of chromium improves the corrosion resistance only in a small degree, and a distinct improvement is provided by 18 % of chromium in austenitic steel.

MECHANISM OF STEEL MICROSTRUCTURE DEGRADATION

Mechanisms of high temperature sulphide corrosion of steels has been studied by several investigators in laboratory environments, including H_2-H_2S atmospheres that are closest equivalents of refinery streams. Carbon steels, Cr-Mo steels and Cr-Ni austenitic steels were under studies [19-23]. Chemical composition and morphology of sulphide scales were examined to explain corrosion kinetics of the steels and mechanisms of the process. Despite the lack of complete understanding of the sulphidation mechanism in these systems, there was a general agreement as to significance of chromium on the sulphide corrosion resistance. It should be noted however, that the sulphide corrosion mechanism was considered from the point of partial processes connected with growth of sulphide scales, and a role of hydrogen in the corrosion progress was not taken into account.

To better understand the sulphidation mechanism, partial processes inside the steels under influence of sulphur and hydrogen were considered. Some metallographic examinations of refinery furnace tubes after prolonged service in refinery units were carried out to reveal mechanisms of steel microstructure degradation [12,24,25]. Carbon steel, 5Cr-0.5Mo steel and 9Cr-1Mo steel in hydrocarbon fractions without hydrogen were examined, as well as 9Cr-1Mo steel in hydrocarbons with hydrogen present. Regardless steel grade and environmental parameters, sulphur was found to change carbon concentration profiles in the steels and to co-operate with hydrogen action. Characteristics of damage caused by sulphur to microstructure of 9Cr-1Mo steel in hydrogen-free and hydrogen containing hydrocarbon streams are presented underneath.
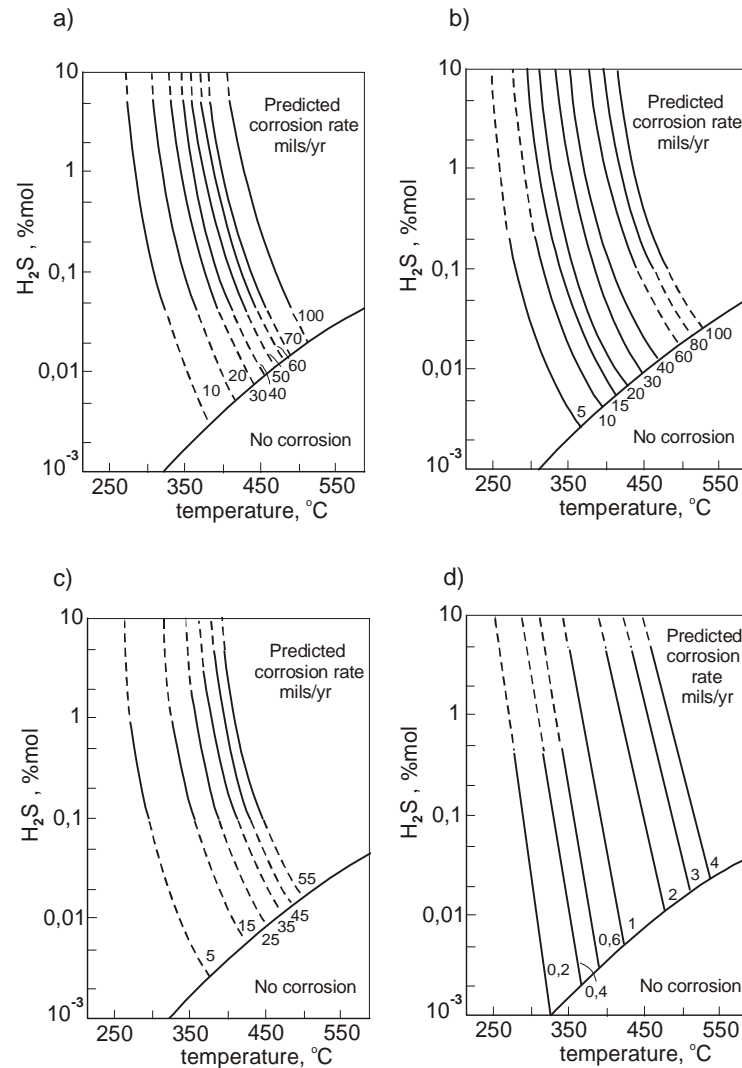
Fig. 2. Effect of temperature and hydrogen sulphide concentration on corrosion rates in H_2-H_2S environment: a) carbon steel (gas oil), b) 5Cr-0.5Mo steel (gas oil), c) 9Cr-1Mo steel (gas oil), d) 18Cr-8Ni steel [11]

Sulphide corrosion without hydrogen present

Sulphur from hydrocarbon fractions can be transported across a protective mill oxide scale on 9Cr-1Mo steel surface and react with metal elements to form sulphides beneath the scale. Depending on the process particulars, mainly temperature and sulphur content, the oxide scale may be replaced by a sulphide scale, or the oxides may stay on the surface for a long time [12,24].

In Fig. 3 an oxide scale on the inside surface of 9Cr-1Mo steel tube after 22 years of service in a vacuum distillation furnace is presented. In this tube, residuum from atmospheric distillation unit of high sulphur content 1.7 wt.% was preheated up to 390°C. It may be seen that the scale was only partly destroyed by sulphur and between the scale and the steel surface a very thin layer of sulphide scale formed.

Sulphur diffused deeper into the steel interior that resulted in disappearance of $M_{23}C_6$ carbides. A carbide-free, chromium and molybdenum depleted layer beneath the steel surface formed (Fig. 3, 4a,b). Within the layer, fine chromium/iron sulphides

situated along grain boundaries of the metal matrix may be seen. Beneath the decarburised layer, a zone of increased carbon content developed (Fig. 4b).
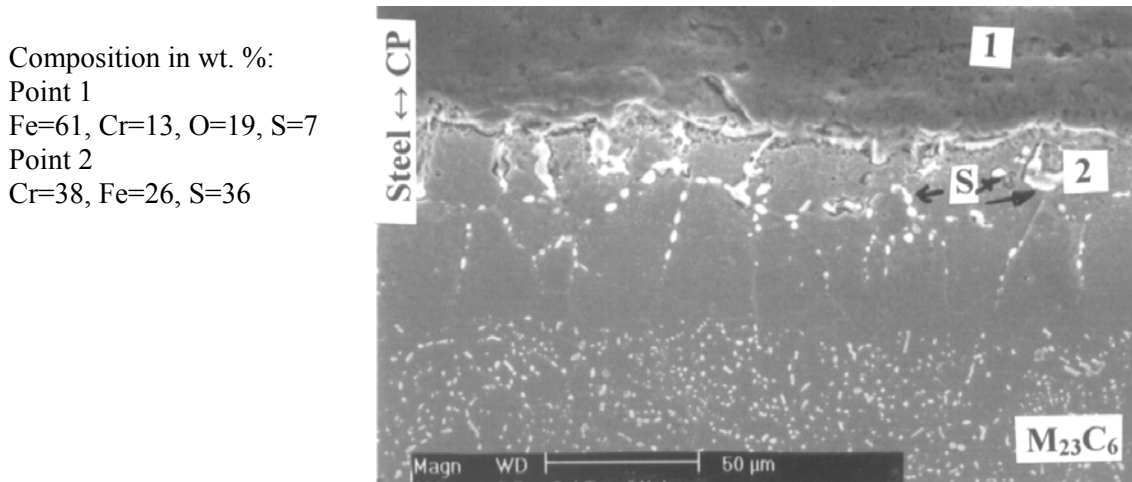
Composition in wt. %:
Point 1
Fe=61, Cr=13, O=19, S=7
Point 2
Cr=38, Fe=26, S=36

Fig. 3. Cross-section of 9Cr-1Mo steel tube after service in vacuum distillation furnace: corrosion products (CP) composed of partly destroyed oxide scale and thin sulphide scale on the inside surface of the tube, carbide-free layer with sulphides (S) beneath the steel surface followed by $M_{23}C_6$ carbide containing zone. Scanning electron microscope [12,24]
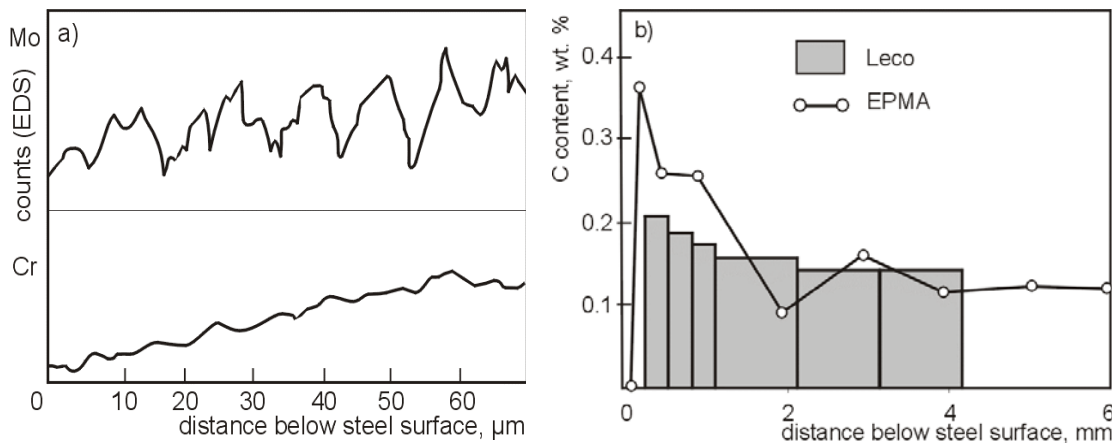

Fig. 4. Cross-section of 9Cr-1Mo steel tube after service in vacuum distillation furnace. Profiles of chromium/molybdenum (a) and carbon (b) beneath the inside surface of the tube. Scanning electron microscope (a), Leco aparatus and electron probe microanalyser EPMA (b) [12,24]

It was concluded that in hydrogen-free refinery environments, damage caused by sulphur to steel microstructure may be linked with a decreased stability of carbides. There is an antagonism between the two elements, sulphur and carbon [26,27]. The presence of sulphur on the steel surface causes the activity of carbon in the steel to increase, the thermal stability of the carbides to decrease, and the carbon that is released from the carbides to diffuse inside the steel. In 9Cr-1Mo steel the carbon loss in $M_{23}C_6$ carbides causes their transformation into ferrite [28]. Diffusion of sulphur inside the steel results in a progressive failure of carbides situated at the front of the diffusion. The carbon profile in the steels differentiates, namely, a layer of low carbon content forms beneath the surface, followed by a zone of higher carbon content. In the decarburised layer chromium/iron sulphides form.

A low corrosion rate of this steel, of hundred parts of millimetre per year, may be referred to a quite high stability of $M_{23}C_6$ carbides at the presence of sulphur. In this example, processes connected with growth of the sulphide scale were practically meaningless.

Sulphide corrosion with hydrogen present

Sulphur contained in hydrocarbon fractions exerts much more destructive influence on steels when hydrogen is present. After some time of service, an original mill oxide scale on steel surface is replaced by brittle, low-adherent sulphide scale [12,24].

In Fig. 5 a part of sulphide scale on the inside surface of 9Cr-1Mo steel tube after 10 years' service in a furnace in desulphurisation unit is shown. In this furnace, mixture of petrol fractions with low sulphur content of 200-350 wppm, and hydrogen of 2 MPa partial pressure were preheated up to 305ºC. The scale was composed of several alternate, not very compact chromium/iron/sulphur and iron/sulphur layers.
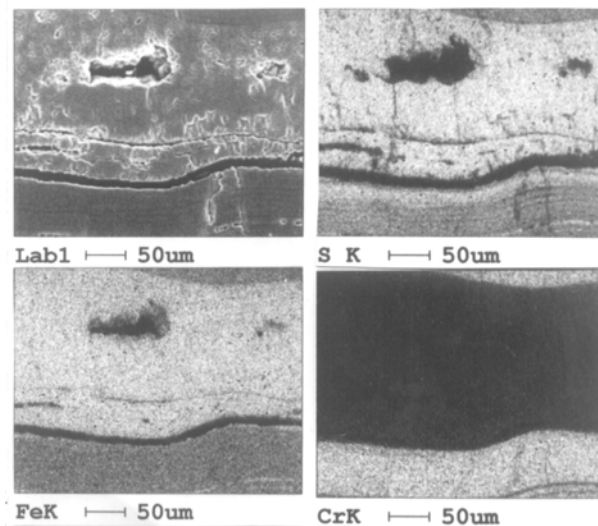

Fig. 5. Cross-section of multi-layer sulphide scale on the inside surface of 9Cr-1Mo steel tube after service in a furnace in desulphurisation unit: micrograph and distribution of sulphur, iron and chromium. Scanning electron microscope [12,24]

In Fig. 6a,b an increased volume fraction of $M_{23}C_6$ carbides in the subsurface steel layer (a) compared to the inside of the steel (b) is shown. This is confirmed by the carbon concentration profile in Fig. 6c: the greatest carbon content is noted close to the steel surface.

As in the hydrogen-free renvironment, decreased stability of carbides in steel at the presence of sulphur plays a role. Because of antagonism between sulphur and carbon, the sulphur on the steel surface causes the carbon activity in the steel to increase, and the stability of the carbides to decrease. Moreover, hydrogen accelerates the process of carbide decomposition. Elevated temperature and increased hydrogen partial pressure allow for hydrogen particles to dissociate and hydrogen atoms to adsorb on steel surface, and diffuse inside the steel. At temperatures and pressures below the Nelson curves, hydrogen alone is not able to react with the carbon contained in the carbides. However, under parallel influence of the sulphur and the hydrogen, the carbides are more prone to decompose than under the sulphur action alone. The carbon that is released from the carbides diffuses inside the steel. Damage to the carbides proceeds on

the surface and just beneath the surface that results in a steep carbon concentration profile.
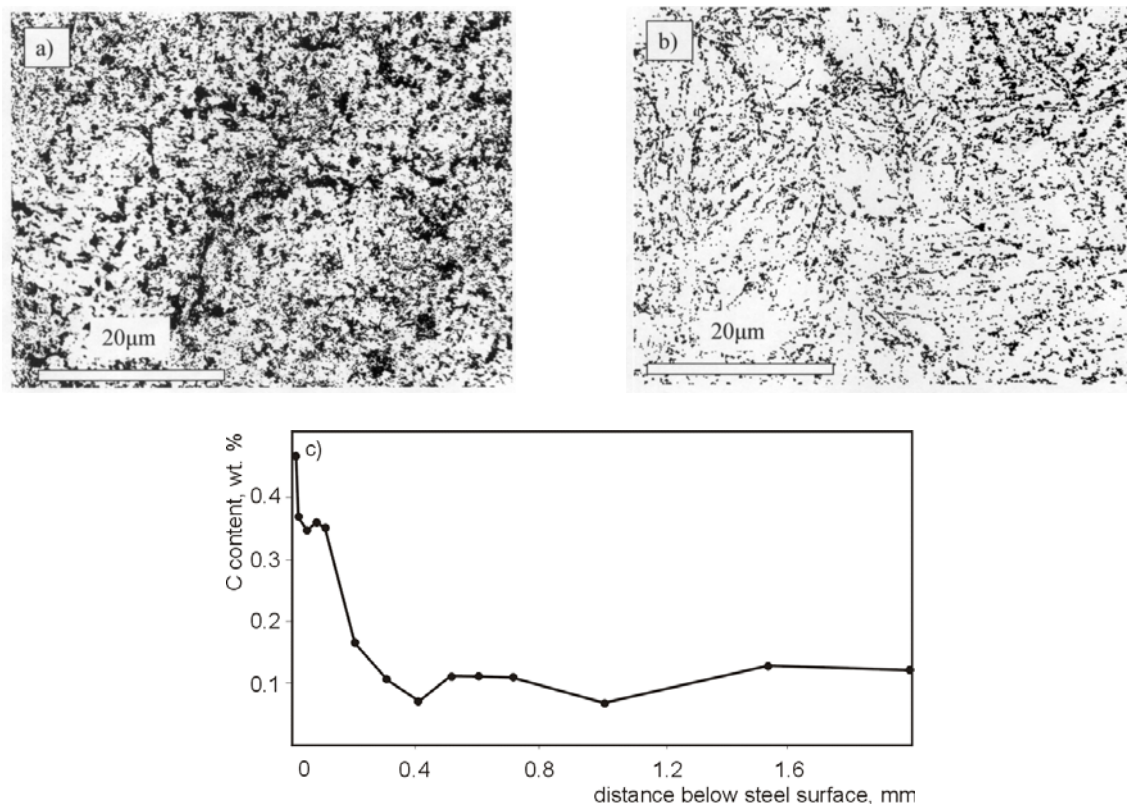

Fig. 6. Cross-section of 9Cr-1Mo steel tube after service in a furnace in desulphurisation unit.: $M_{23}C_6$ carbides 50 μm beneath the inside surface of 9Cr-1Mo steel tube (a) and $M_{23}C_6$ carbides inside the steel (b), carbon extraction replicas, transmission electron microscope. Carbon profile beneath the inside surface of the tube, electron probe microanalyser (c), [12,24]

Higher corrosion rate of 9Cr-1Mo steel 0.1 mm/year in the hydrogen containing environment, despite very low sulphur content and temperature, indicates that decreased stability of $M_{23}C_6$ carbides under joined action of sulphur and hydrogen is an important factor that determines the corrosion rate. Partial processes connected with the growth of brittle, low adherent sulphide scale, which was continuously removed from the steel surface during service, were of lesser importance.

SUMMARY

The sulphidation behaviour of steel structures in the refinery industry was reviewed. The data presented are related to two aspects of the corrosion. One aspect refers to external degradation of the structures due to formation of sulphide scales on steel surfaces and metal losses; another is connected with internal degradation, i.e. changes of steel microstructure and formation of internal corrosion products.

The characteristics and degree of steel degradation strongly depend on temperature, sulphur concentration and type of refinery environments. Sulphide corrosion rate generally increases with temperature and sulphur content. In hydrogen-free

environments corrosion rates depend on chromium content and type of steel. Corrosion rates of ferritic Cr-Mo steels decrease with chromium content. Lowest corrosion rates are noted for austenitic 18Cr-8/10Ni steel. The presence of hydrogen increases the severity of sulphide corrosion. In hydrogen containing environments corrosion rates of carbon steel and 5Cr-0.5Mo steel are similar. Addition of 9% of chromium improves the corrosion resistance only in a small degree, and a distinct improvement is provided by 18 % of chromium in austenitic steel. In the both environments the corrosion rates can be predicted using some curves elaborated on the basis of long-term refinery experiences. The so-called modified McConomy curves can be applied when the hydrogen-free environments are considered, and the Couper-Gorman curves are used to predict corrosion rates in the hydrogen-containing environments. Results of laboratory examinations generally are not taken into account in refinery practice.

Internal degradation of steels is limited to subsurface areas mainly and in most practical applications have insignificant influence on properties of the steel structures. However, it is an important factor that should be taken into account when mechanism of sulphur attack and sulphidation resistance of steels is considered. Antagonism between sulphur in refinery environment and carbon in steel exists. The sulphur on the steel surface causes the carbon activity in the steel to increase, and the stability of the carbides to decrease. The carbon that is released from the carbides diffuses inside the steel. Hydrogen supports the process of carbide destabilisation. This is why an increased sulphide corrosion rate of the steel at the presence of hydrogen can be expected.

REFERENCES

1.   Corrosion in the Petrochemical Industry. (Ed. L. Garverick). ASM International, Materials Park OH, 1995.

2.   White R.A., Ehmke E.F.: Materials Selection for Refineries and Associated Facilities. National Association of Corrosion Engineers, Houston, Texas, 1991.

3.   Foroulis Z.A.: High temperature degradation of structural materials in environments encountered in the petroleum and petrochemical industries: Some mechanistic observations. Anti-Corrosion 32 (1985), pp. 4-9.

4.   Gutzeit J.: High temperature sulfidic corrosion of steels, in Process Industry Corrosion – The Theory and Practice. National Association of Corrosion Engineers 1986.

5.   McConomy H.F.: High-temperature sulfidic corrosion in hydrogen-free environment. Proceedings API Vol. 43 (III). Washington D.C.: API 1963, pp. 78-96.

6.   Phiel R.L.: Correlation of corrosion in a crude distillation unit with chemistry of the crudes. Corrosion 16 (1960), pp. 139-141.

7.   Couper A.S., Dravnieks A.: High temperature corrosion by catalytically formed hydrogen sulfide. Corrosion 18 (1962), pp. 291t-298t.

8.   Couper A.S.: High temperature mercaptan corrosion of steels. Corrosion 19 (1963), pp. 396t-401t.

9.   NACE Technical Committee Reports, Publication 56-7: Collection and correlation of high temperature hydrogen sulfide corrosion data. Sorrel G., Hoyt W.B. Corrosion 12 (1956), pp. 213t-234t.

10. NACE Technical Committee Reports, Publication 57-3: High temperature sulfide corrosion in catalytic reforming of light naphthas. Corrosion 13 (1957), pp. 37t-42t.

11. Couper A.S., Gorman J.W.: Computer correlations to estimate high temperature H_2S corrosion in refinery streams. Materials Protection and Performance 10 (1971), pp. 31-37.

12. Hucińska J.: Degradation of steels in refinery furnace environments. Politechnika Gdańska, Gdańsk, 2003.

13. Baker K.C.: Prediction tools for sulfidic corrosion.. Materials Performance 40 (2001), pp. 62-65.

14. Detemple I., Hanus F., Luxenburger G.: Advanced steels for hydrogen reactors. Hydrocarbon Engineering 4 (1999), pp. 1-8.

15. Antalfy L.P., Chaku P.N.: US perspective of modern hydroprocessing reactor metallurgy. Hydrocarbon Technology International, Quaterly. Spring 1996, pp. 39-48.

16. Bayer G.T.: Vapor aluminum diffused steels for high-temperature corrosion resistance. Materials Performance 34 (1995), pp. 34-38.

17. Weinbaum M.J., McGill W.A.: Alonizing to prevent corrosion in the HPI sulfur recovery plant. Proc. International Conference Sulfur 87, Houston, Texas 1987. British Sulphur 1987.

18. Hucińska J., Wilczewski L.: Dobór materiału na rury modernizowanego pieca 500-F1 w instalacji hydroodsiarczania olejów napędowych Rafinerii Gdańskiej SA..Gdańsk, Politechnika Gdańska, Wydz. Mechaniczny 1997.

19. Gesmundo F., Viani F., Znamirowski W., Godlewski K., Bregani F.: The corrosion of iron and of three commercial steels in H_2-H_2S and H_2-H_2S-CO_2 gas mixtures at 400-700°C. Werkstoffe und Korrosion 43 (1992), pp. 83-95.

20. Haycock E.: High-temperature sulfiding of iron alloys in hydrogen sulfide-hydrogen mixtures. Journal of the Electrochemical Society 106 (1959), pp. 764-771.

21. McCoy J..D., Hamel F.B.: Effect of hydrodesulfurizing process variables on corrosion rates. Materials Protection and Performance 10 (1971), pp. 17-22.

22. McCoy J.D.: Corrosion rates for H_2S et elevated temperatures in refinery hydrodesulfurization process. Materials performance 14 (1974), pp. 19-25.

23. Schulte M., Rahmel A., Schutze M.: The sulfidation behavior of several commercial ferritic and austenitic steels. Oxidation of Metals 41 (1998), pp. 33-70.

24. Hucińska J.: In-service degradation of refinery furnace tubes. The European Corrosion Congress Eurocorr 2003, European Federation of Corrosion. Budapest, Hungary 2003. Proc. CD-ROM.

25. Hucińska J., Dampc J.: Effects of coking and decoking on characteristics of 5Cr-0,5Mo steel in refinery furnace environment. The European Corrosion Congress Eurocorr 2003, European Federation of Corrosion. Lisbon, 2005. Proc. CD-ROM.

26. Grabke H. J.: Metal dusting of low- and high-alloy steels. Corrosion 51 (1995), pp. 711-720.

27. Schneider A., Viefhaus H., Inden G., Grabke H. J., Muler-Lorenz E. M.: Influence of H_2S on metal dusting. Materials and Corrosion 49 (1998), pp. 336-339.

28. Goldschmidt H. J.: Interstitial alloys. Butterworths, London, 1967.