External Damage by Corrosion on Steel Gas Pipeline

A. Benmoussat[1*], H. Hadjiat[1] and M. Hadjel[2]

[1]Faculty of Engineering Sciences, Laboratory of Material Sciences, University of Tlemcen, BP 230 chetouan 13000, Tlemcen, Algeria

[2]Faculty of Sciences, Industrial Chemistry Department, University of Sciences and Technology, BP 1505 Oran, 31000, Algeria

Abstract

Under degraded coatings and inadequate cathodic protection (CP) steel gas pipelines exposed to environmentally assisted multiple corrosion. In electrochemical process corrosion, dissolution of the iron is an anodic reaction. The nature of the cathodic process depends on the availability of oxygen and implies aerobics or anaerobics conditions. The most severe corrosion process is that of microbiologically influenced corrosion. Damage can be a localized corrosion or SCC corrosion (Stress corrosion cracking). Microstructural damage is intergranular type at low stress intensity and implies the interaction of the material with the corrosive environment characterized by the apparition of corrosion microcracks.

Introduction

The search for always-increasing gas pipeline profitability has led to the development of high-strength and high-toughness pipelines steels [1]. More than 90% of pipeline steels are currently High Strength Low Alloys Steels (HSLA). Different metallurgical ways (TMCP process) or Thermo Mechanical Controlled Process may obtain such materials. Two kinds of microstructure have been chosen: pearlitic-ferritic steels or bainitic-ferritic steels [2].

X60 improved steel gas pipeline presents pearlitic-ferritic microstructure for tube diameter 40 inches. The tubes have been exploited for thirty years in Algeria but they present today several anomalies on steel surface: disbonded coating, loss of matter, reduction of the thickness of more 50%, external localized corrosion in large surface, multiple stress-corrosion crack colonies…

To protect against externally induced corrosion and cracking, X60 steel gas pipelines are used different materials coatings which include coal tar, polyolefin, polyethylene tapes, polyvinyl chloride (PVC) or fusion bonded epoxies and they constitute a passive protection. Gas pipeline is further protected by an active protection constituted by an impressed current cathodic protection (CP) system with a minimum specified potential of – 850 mV ($Cu/CuSO_4$).

Unfortunately, corrosion and fissuration problems still can occur in the system under certain conditions. External damage of X60 steel in environmentally assisted multiple corrosion motivates our research. Corrosive environment and cracking are main threats for buried pipelines in sparsely settled geological areas, where the soil aggressiveness (High clay) and bacterial activity appear.

Field excavations indicate that the loss of thermoplastic is quite localized and causes the coatings to crack and fall apart in service. The coatings based on coal tar are more or less subject to oxidation. The next generation of coatings systems is based on epoxy painting intended gunpowder on a hot support and polyurethanne paintings gunned on a cold support. The anticorrosion efficiency of materials coatings has been improved. They will be used for the next renovation systems of Algerian gas pipeline.

SCC occurs in many structures, generally without expectation that a specific combination of material and environment would produce such damage [3]. SCC involves mechanics through the role of stress and the material through its interaction with the corrosive environment.

In zones where steel gas pipeline are damaged, the samples of corroded X60 steel and non-corroded one have been taken and have been studied using microanalytical techniques. Micrographic analysis has

*corresponding author. E-mail: a_benmoussat@mail.univ-Tlemcen.dz

been done by optical microscopy and electronic microscopy (MEB). Corrosion deposits are analyzed by EDAX microanalysis and X-rays diffraction (DRX).

Electrochemical and microbial process

The nature of a corrosion process is often deduced by observing the corrosion products at the particular site. Field excavations indicate that the cathodic protection is failing under degraded coating (Fig. 1) and increases CP current demand and allows corrosion cells to propagate on the pipe's surface. It has been found for many tubes, that a localized corrosion has a tendency to be developed in surface as a consequence of the cathodic protection. Increased permeability allows effective CP potentials to develop on the underlying steel surface. The level is controlled by the generation of ions from the pipe's surface, these solutions have a pH in the region of 8, which promotes the formation of hydroxyl ions that, in turn, facilitate the absorption of carbon dioxide derived from decaying organic matter in the soil.

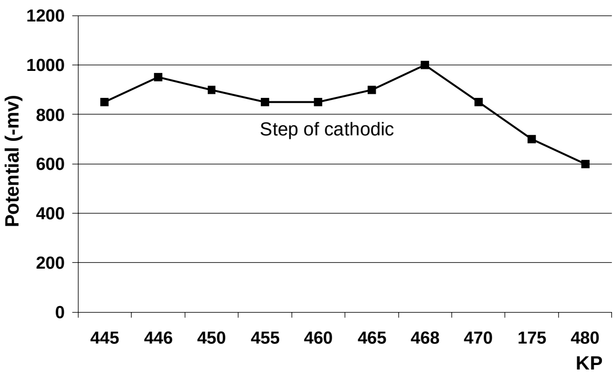

Fig. 1. CP potential values in damaged zone- KP 445 to KP 480 under coating failure (KP – Kilometric point).

Steel pipelines corrode by electrochemical process. Dissolution of the iron is an anodic reaction (1) controlled by continuous formation and a rupture of a passive film formed on steel's surface. This film is composed of Fe_3O_4 as simulated in laboratories studying. The nature of the cathodic process depends on the availability of oxygen and implies aerobics or anaerobics conditions that corresponds respectively to the equations (2) and (3).

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (3)$$

Testing of the undamaged tubes shows that the damage starts on the failing surface defects as roughness, pitting corrosion formed in zones fragilised by the free hydrogen in corrosion acidic media. The propagation is dominated by anodic dissolution at the tip of microcrack and successive fragile rupture at the joint of grains.

The nature of a corrosion process often can be deduced by observing the corrosion products at the particular site. The most severe corrosion process is the microbiologically influenced one, which accounts the corrosion deposits identified on the system. The mechanism (Fig. 2) of corrosion is based on the formation of a galvanic couple between microbiologically produced iron sulfides and the steel surface. This couple is normally short-lived because the iron sulfide matrix becomes saturated with electrons derived from the corrosion process [4]. In the presence of sulfate-reducing bacteria, however, the corrosion process is perpetuated because these organisms can remove electrons generated in the corrosion process from the iron sulfide surface. This process is assumed to involve the formation of cathodic hydrogen on the iron sulfide, but may involve direct transfer of electrons from the iron sulfide matrix to redox proteins in the bacterial cell wall. The electrons derived by the bacteria are used to reduce ground water sulfate to sulfide, a process that provides the organisms with metabolic energy and produces more iron sulfide. Iron sulfide is electrically conducting, which can have a influence on the current density required to maintain adequate CP potentials. The CP system in effect tries to protect the iron sulfide in contact with the pipe.

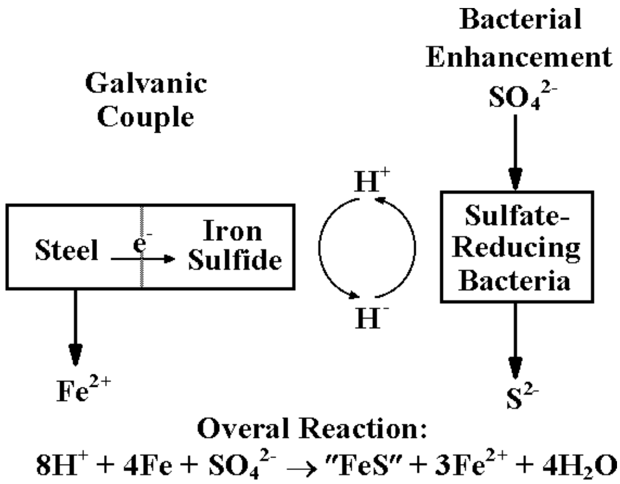

Fig. 2. Mechanism of microbiologically influenced corrosion by Sulfate Reducing Bacteria.

Corrosion rates, associated with this mechanism, are proportional to the amount of iron sulfide in the corrosion cell. Corrosion rates measured from fields observations, confirmed in laboratory studies, are 2.5 mm/year [5]. There are claims in the literature that this mechanism can lead to corrosion rates as high as 6.4 mm/year [4]. The frequency of occurrence and the possible corrosion rates of this mechanism are a serious threat for the pipeline integrity. This is the most common failure mechanism for tape wrapped pipelines in wet high clay soils where ground water has low conductivity.

Structural damage by SCC corrosion

Unprotected steel surfaces exposed to the soil corrosive environment are susceptible to stress corrosion cracking (SCC) [6]. It involves the interaction between stress and environment to cause damage in situations, where independently their effect would be lower. Micrography analysis of X60 corroded samples (Fig. 3) indicates that the structural damage is one of intergranular type, and predominant growth in surface implies the interaction of the material with the environment under stress effect. Corrosion microcracks are formed as a consequence of the structural damage by corrosion and stress effect at X60 steel surface. The behavior of X60 steel is a critical aspect. The microcraks can propagate under the stress interaction by loading effect and the interaction of the material with the environment.

Microhardness analysis (Fig. 4) indicates that the values decrease along the thickness from the internal to the external corroded surface. The brusque fall of microhardness inside towards outside X60 corroded steel tube could be explained by predominant growth of corrosion microcracks longitudinally the long of the surface. The step of SCC cracking is not determined. Using B31G criterion, established by NACE Company, can rehabilitate corroded pipes.

External damage by SCC in steel surface can be explained by dissolution and strain phenomenon. Dissolution speed is expressed as a penetration rate, calculated and then compared to experimental values, according to Faraday's second law:

$$\frac{da}{dt} = i_0 \frac{M}{\rho z F} \quad (4)$$

where da/dt = corrosion speed, M = atomic weight of iron, z = valence of the solvated species, ρ = density and F = Faraday's constant, i_0 = maximum anodic

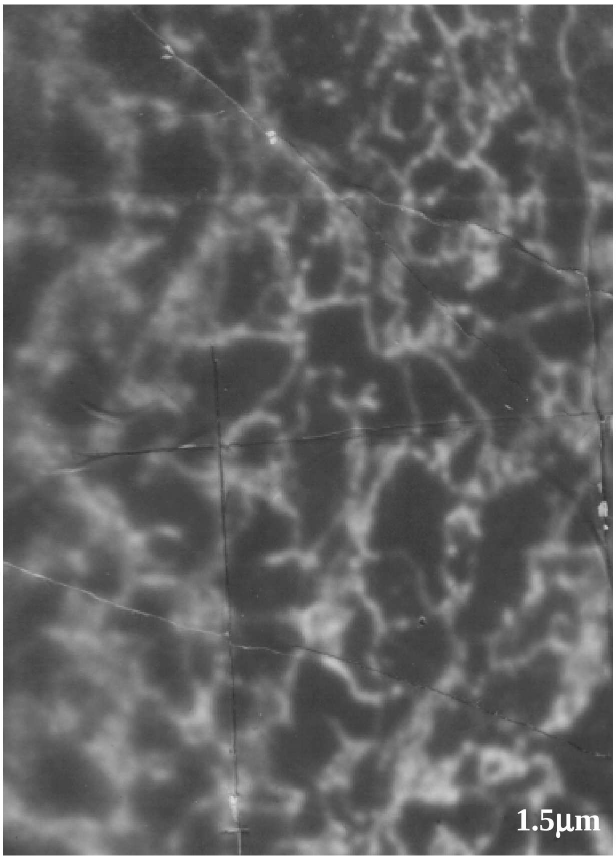

Fig. 3. Micrography of X60 steel, showing microstructural damage of the type intergranular view on optical microscope Reichert MeF_2.

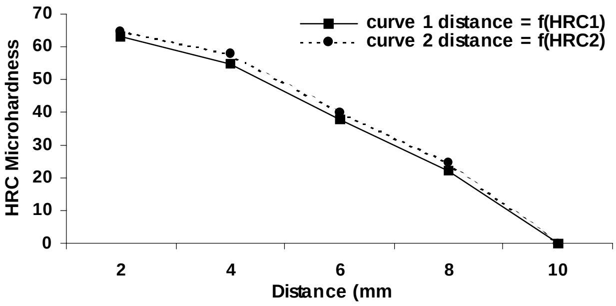

Fig. 4. Decreasing values of HRC Microhardness in X60 steel corroded along the thickness.

current density.

Penetration speed is determined by the measurement of the maximum current density that can arise at a bare steel surface submitted to the same environment conditions (pH = 8).

When equation (4) is rewritten:

$$da = \frac{M}{\rho z F} i(t) dt \quad (5)$$

$$i(t) = i_0 \times (t/t_0)^{-\beta} \quad (6)$$

where t - time, t_0 - reference time and β - fitting constant which reflects the current flowing as a function of time for repassivation in the absence of external loading.

When the strain rates are high, the rate of cracking can out-pace the rate of dissolution. This means that the dissolution may continue at a rate da/dt. In contrast, when the rate of penetration is slow, the rates of film growth decreases, so that no dissolution related crack growth occurs.

A model of dissolution controlled SCC could then be developed by characterizing the rate limiting process by correlation with some measure of slip as result of strains due to microscopic slip or microplastic flow within a grain or accumulated at grain boundaries.

The transgranular SCC type of corrosion, described in [7], corresponds to high intensity of stresses, a near-neutral pH and low conductivity water conditions have not been shown.

Corrosive soil action

In zones of damaged pipeline, the soil resistivity and pH are the important characteristic to determine the soil aggressiveness. The value of a pH is in region of 8. The soil resistivity ρ [Ω. Cm] (Fig. 5) has been determined by Wenner method [8].

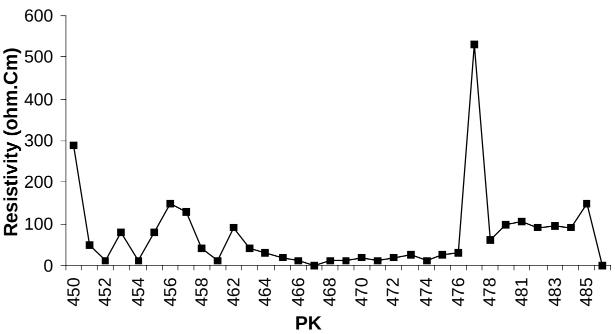

Fig. 5. Soil resistivity values ρ determined by Wenner method in damaged zone (KP 450 to KP 486) showing the corrosive nature of soil and probable geological pile formation.

$$\rho = 2\pi a(\Delta V/I) \quad (8)$$

ΔV- potential variation [V], I - current intensity [amp.]

The clayey nature of soil presents the weak values of soil resistivity and characteristic of an aggressive soil. The geological piles of corrosion are accentuated on buried steel surfaces.

Carbon Steel X60 is susceptible to the SCC corrosion in the presences of the following chemical species: CO_3^{2-}/HCO_3^-, CO/CO_2 solution, OH^-.

Conclusion

The external damage by corrosion in gas pipeline is a complex phenomenon, and the integrity of the structure is critical aspect considering the natural gas transport and the corrosion actions factors. It depends on the balance between main components: material corrosive environment and stress. Under degraded coatings and inadequate CP potentials, X60 steel surfaces are exposed to the different modes of corrosion damage threat Hydrogen induced cracking. SCC damage mode has not been a major treat to gas pipeline integrity on this system, but research in this area will enable reliable prediction of remaining life and SCC process. Steel damage that occurs on this pipeline system can be identified by careful examination of the corrosion deposits found during pipeline excavation. The most severe corrosion process is the one microbiologically influenced. The mechanism of corrosion is based on the formation of a galvanic couple between microbiologically produced iron sulfides and the steel surface. Corrosion microcracks are a consequence of the damage by corrosion and stress effect at steel surface and can propagate by loading effect, temperature effect and the interaction of the material with the environment. Corrosion microcraks damage studying will permit to promote new couples of materials and environment in order to avoid the mechanisms of corrosion occuring. Specific corrosion mechanisms where studied in the laboratory to establish corrosion rate data for the more common scenarios. The research will provide data for risk assessment models to be used for maintenance and operation of the pipeline system.

The corrosion problems raise questions as the remaining safe life of the tubes. Some of the probablistic approaches can be applied or are being developed to study the corrosion related cracking and pitting phenomena.

Future coating systems must answer the durability and reliability requirements in service and in regard with economic aspect.

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