Efficiency of Applying Inhibitor to Control Internal Corrosion in Gas Pipeline Systems

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Abstract

Utilization of film-former corrosion inhibitors is one of the most reliable and economical ways of controlling internal corrosion of oil and gas pipeline systems. The current study sheds light on the feasibility range of the success of the application of corrosion inhibitor "amines base filming inhibitor" in the gas pipeline 34" BMK "Brega-Misurata-Khoms" by utilizing various ways such as monitoring techniques, test and analysis methods, injection rate of inhibitor and efficiency of corrosion inhabitation. Internal corrosion is monitored by different techniques such as electrical resistance (E/R) probe using cosasco corrocometer model CK-3, direct specimens of dry gas and intelligent pig surveys. The samples of the last two methods of monitoring are achieved by chemical analysis in laboratory of Sirte Oil Company. This chemical analysis is accomplished to determine the content of compounds in the gas, for instance iron/iron oxide, sulphur, carbon dioxide and hydrogen sulphide, etc. In reality, the internal corrosion rate of the inner surface of the pipeline system is negligible in comparison with standard criteria of corrosion. Furthermore, assessment of the film-forming corrosion inhibitor was found roughly sufficient to provide an excellent internal corrosion inhabitation because of the environmentally friendly properties of the gas, as a dry and sweet gas.

Keywords: *Efficiency, Corrosion, Inhibitor, Film, Protection and Gas pipeline systems.*

1. Introduction

All over the world, maintaining facilities and extending their lifespan is essential by paying attention to the materials involved in the installation of these facilities e.g. oil and

gas complexes, petrochemical industries, pipeline systems, power generation and water desalination plants, various industrial utilities, as well as engines and structures for aircraft, cars and ships. Corrosion is one of the main challenges facing the world for this reason, unremitting efforts have been made and are still being made to confront corrosion by studying its mechanism and causes, and working to apply the most effective and modern methods of protection to preserve them.

 The search for safe and economical methods to transport fluids is a top priority for companies operating in the oil and gas sector. Oil and gas companies often focus on pipelines system to transport their productions of fluids, but pipelines usually suffer from two types of damage; First, the internal damage[1,2] that is targeted in this investigation, resulting from the corrosion between the inner tube wall and the transported material. Secondly, the external damage[3] that usually occurs when the pipelines pass through aggressive environment such as wet and marshy areas.

The internal corrosion can be governed by addition of small amounts of substances to the environment inside the structures. These substances may be liquid or powder and known as inhibitors. Corrosion inhibitor provides a protective film between the environment and the internal surface. In general, inhibitors should be added by specific concentration with good circulation to ensure keeping a dense protective layer for long time. Inhibitors can be divided into several types according to their mechanism and composition such as adsorption-type inhibitor, hydrogen-evolution poisons, scavengers, oxidizers and vapor-phase inhibitors. Objective of this study is to investigate the corrosion of inner surface of gas pipeline system and applying specific inhibitor to control corrosion damage, and assesse its performance.

2. Field work

The construction of the gas pipeline system 34" BMK (Brega-Misurata-Khoms) is completed in 1981, after that it is hydrostatically tested and started operating immediately in 1983. The process of continuous corrosion inhibitor injection began in 1990. The gas pipeline system has been operated by gas transmission and supply department in Sirte Oil Company[4,5].

The gas pipeline system 34" BMK (Brega-Misurata-Khoms) is injected by inhibitor "1053 S" based on amine as a liquid to provide a premium dense protective film-former against internal corrosion, isolating internal surface wall of the pipeline from the pumped gas[4,5]. The rate of required dosage is 0.25 Pint of inhibitor/MMSCF (million standard cubic feet per day) of gas continuously.

2.1. The injection method of inhibitor "1053 S" in the gas pipeline system

The injection process is accomplished by electrical and piston pumps according to the pressure of the flowing gas in the system. The pressure produced by the two pumps must be greater than the pressure of the gas flowing in the system in order to allow the chemical inhibitor to flow. In fact, the pressure of the gas flowing into the pipeline system is 700 psi, while the chemical inhibitor pressure is approximately 750 psi. To avoid the collapse of the system, the pressure inside it must be adjusted so that, it does not reach the explosion pressure, this can be obtained by means of safety valves that adjust the pressure of the two pumps. Since the amount of gas flow in the system is not fixed and variable, the inhibitor flow must be adjusted accordingly to ensure that the required protection is achieved.

2.2. Techniques and methods for monitoring the rate of internal corrosion

I-   The electrical resistance (E/R) probes

The technique works, depending on Ohm law. It obviously depends upon the wire resistance of the probe. Cosasco corrosometer model CK-3 provides the readings via its probes located on three positions along the gas pipeline system.

The electrical resistance of a conducting wire can be expressed by the following formula:

$$R = \rho L / A \qquad\qquad (1)$$

Where: ρ is the intrinsic electrical resistivity of the wire.

L is the length of the wire.

A is the cross-sectional area of the wire section.

The intrinsic electrical resistivity changes from alloy to alloy and depends on temperature. For a specific alloy at constant temperature, the electrical resistance of a fixed-length sample rises as the cross-sectional area reduces. Consequently, the measurement of electrical resistance might be used to determine metal loss[5]. However, the probe sometimes provides fake reading since the sensor wire may be thicken by electrical conductive impurities, therefore readings refer to no corrosion obtains contrary to the reality.

II-   Chromatography technique for analysis of dry gas specimen

The gas is sampled from the pipeline and analysed for corrosion inhibitor residuals and other compounds counts. The specimen is achieved from valves on gas pipeline system. The gas sample is analysed by gas chromatography technique[6].

Chromatography is an important biophysical technique that enables the separation, identification, and purification of mixture components for qualitative and quantitative analysis. In chemical analysis, this technique works on the principle of mixture separation, where the mixture dissolves into a fluid, namely gas or solvent known as am mobile phase. The mobile phase passes through a system that has a stationary phase installed. The constituents of the mixture have different responses to the stationary phase, i.e. these molecules remain on stationary phase for different periods, long or short, depending on their interactions with its surface sites, leading to their separation from each other[7,8].

III-   Intelligent pig surveys

It is a device utilizes to perform various operations including, cleaning and inspecting for the purpose of detecting defects and consequently preventing leaks by achieving required maintenance in the pipeline system. The pig inserts into the pipeline system via launching station, and it is pushed by the pressure-driven flow of the product until it reaches the receiving trap[9,10,11].

The gas pipeline in Sirte Oil Company is pigged twice per a year. The resultant deposit from the pigging process is sampled for chemical analysis in the laboratory[4].

3. Results

3.1. Corrosion monitoring by cosasco corrosometer model CK-3
3.1.1. Readings of electrical resistance (E/R) probe

The readings are recorded from approximately the end of July to the end of September in 2005 along the gas pipeline system at three sites as revealed in table 1.

Table 1. Readings of E/R probe which are collected at three positions along the gas pipeline.

Position of E/R probe	Previous E/R probe readings Dial/Check	Date of previous E/R probe readings	Recent E/R probe readings Dial/Check	Date of recent E/R probe readings
11.9 Km	70/779	02-08-2005	68/799	27-09-2005
268 Km	61.5/800	31-07-2005	55/801	29-09-2005
405 Km	67/843	31-07-2005	65/845	28-09-2005

Corrosion rate may be calculated for the previous results in table 1 by the following relationship:-

MPY = 0.365 x Multiplier x Δ Dial / Δ Day   (2)

 The calculations of corrosion rate are performed as seen in table 2.

Table 2. Calculation of corrosion rate is obtained by equation 2.

Position of E/R probe	Previous dial (Ω) reading	Recent dial (Ω) reading	Δ Dial (Ω)	Δ Days (Ω)	Multiplier (mill/ Ω)	MPY	Notes
11.9 Km	70	68	2	56	10	0.130357142	Protected
268 Km	61.5	55	6.5	60	10	0.395416666	Protected
405 Km	67	65	2	59	10	0.123728813	Protected

Table 3 shows further readings were reported roughly from the end of September to the end of November in 2005 at the same three locations.

Table 3. Readings of E/R probe which are collected at three sites along the gas pipeline.

Position of E/R probe	Previous E/R probe readings Dial/Check	Date of previous E/R probe readings	Recent E/R probe readings Dial/Check	Date of recent E/R probe readings
11.9 Km	68/779	27-09-2005	67/798	28-11-2005
268 Km	55/801	29-09-2005	53/800	22-11-2005
405 Km	65/845	28-09-2005	59/800	22-11-2005

Also calculation of the corrosion rate from the results for the end of September to the end of November in 2005 at the same locations in table 3, using the equation 2. See table 4.

Table 4. Calculation of corrosion rate is achieved by equation 2.

Position of E/R probe	Previous dial (Ω) reading	Recent dial (Ω) reading	Δ Dial (Ω)	Δ Days (Ω)	Multiplier (mill/ Ω)	MPY	Notes
11.9 Km	68	67	1	62	10	0.058870967	Protected
268 Km	55	53	2	54	10	0.135185185	Protected
405 Km	65	59	6	55	10	0.398181818	Protected

The calculations of corrosion rate in tables 2 and 4 obviously refer the gas pipeline system does not suffer from any internal corrosion comparing to a criterion for corrosion classification[12,13] as seen in table 5.

Table 5. Criteria of corrosion rate.

Relative corrosion resistance	MPY
Outstanding	< 1
Excellent	1 – 5
Good	5 – 20
Fair	20 – 50
Poor	50 – 200
Unacceptable	> 200

The corrosion rate of the results taken from the end of July to the end of September "table 2", as shown in figure 1. It rises sharply from the first to the second position (268 Km) by 67 %. Then it drops rapidly by 69 % to the last position (405 Km) approximately as same as the first position.

However, for the corrosion rate in the period from the end of September to the end of November "table 4", as in figure 1, it gives an increasing behavior with the increase in the distance of the sites. This an increment was recorded from the first site to the second and from the second to the third by 56 % and 66 % respectively.

Ultimately, the gas pipeline system appears to be perfectly protected because the overall corrosion rate is less than 0.4 mil/year according to the criteria of corrosion rate in table 5.
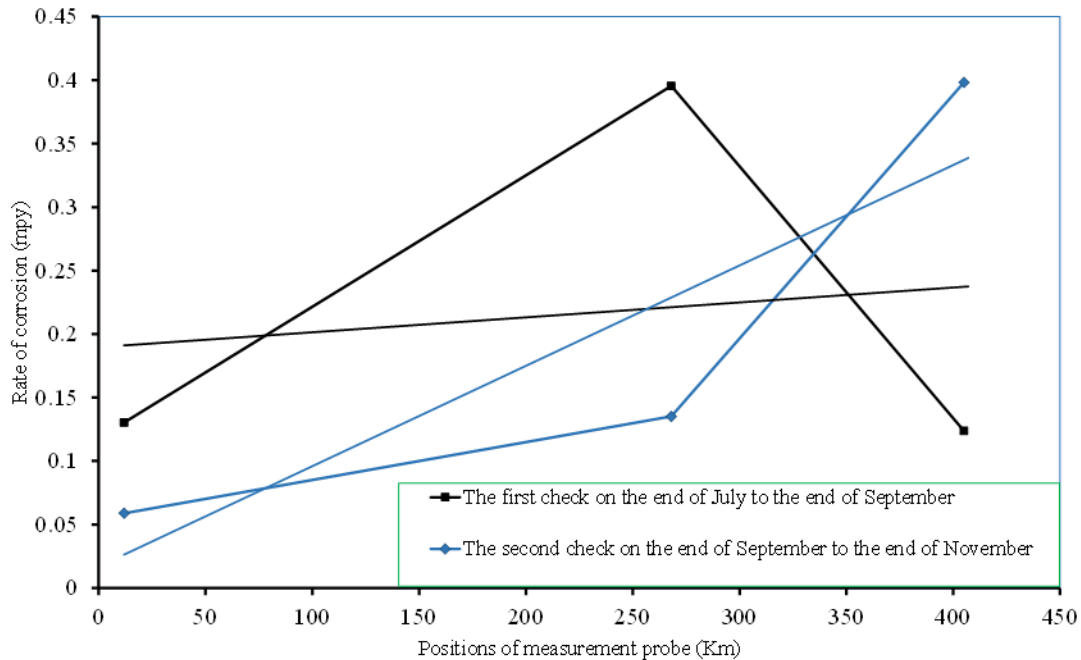

Figure 1. Rate of corrosion measured by E/R probe on various times at the same locations

3.2. Monthly chemical inhibitor injection average

The table 6 shows the monthly target amount of inhibitor injection that must be provided to control the internal corrosion in the gas pipeline system[4]. Moreover the figures 2 and 3 are represented the behavior of the found dosage of chemical inhibitor according to required dosage at the first check and at the second check respectively.

The figure 2 shows the required and found atomization of chemical inhibitor dosage versus flow rate of gas response at the first check. Typically, the required dose reveals a regular linear rise with an increment of gas flow rate. Initially, at the first three flows of the gas, the found dose transient increases in parallel to the behavior of the required dose, with an average rise of approximately 8 % higher. Then it drops significantly by 22

% compared to the required dose. This means that the gas pipeline system is protected with chemical inhibitor film with an over dose of 10 %, 7 % and 6 % at the first three flow rates of gas production of 143, 166 and 210 MMSCFD respectively, but it is unprotected at flow rate of 245 MMSCFD, showing a reduction of 22 % for found dosage. Namely, in this particular flow rate, there is no sufficient protective film of inhibitor to build up.
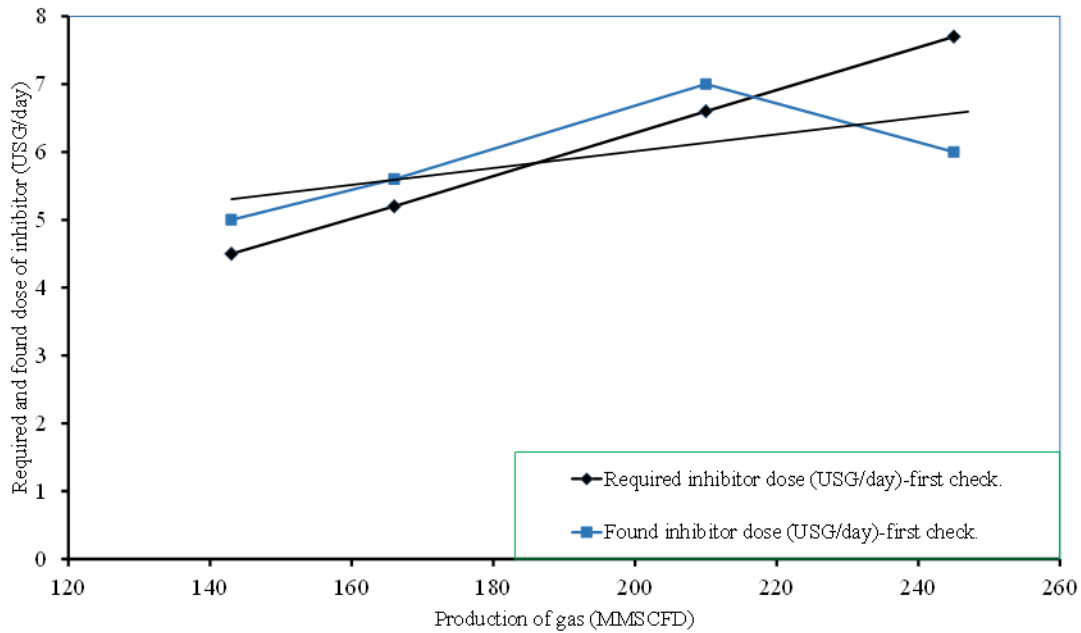

Figure 2. Production of gas (MMSCFD) versus required and found injection dose of inhibitor (USG/day) in first check.

Obviously, at the second check that is shown in the figure 3, the gas pipeline system lacks for the optimum dosage because of the found dosage of chemical inhibitor is lower than the required level, recording the worst failure at flow rates of 245 and 300 MMSCFD with respective values of 35 % and 36 %. In fact, the gas pipeline system suffers from severe condition i.e. absence of reliable dense protective film-forming corrosion inhibitor.
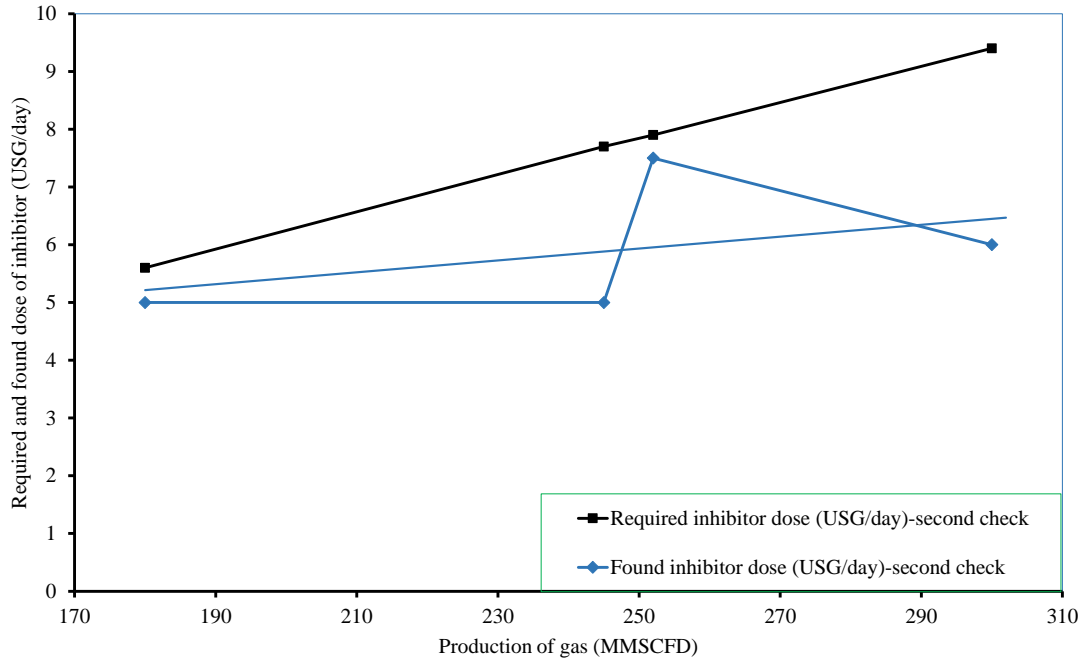
Figure 3. Production of gas (MMSCFD) versus required and found injection dose of inhibitor (USG/day) in second check.

Table 6. The target amount of the chemical inhibitor injection for each flow rate of gas.   * Pump is out of order.

Time of check	Production in MMSCFD (1st check)	Required/adjusted injection dose in USG/Day	Found injection dose on 1st check	Production in MMSCFD (2nd check)	Required/adjusted injection dose in USG/Day	Found injection dose on 2nd check	Monthly average injection dose	Injection dose adjustment
July 2007	338	10.6	Off*	330	10.3	Off*	0.0	
Nov. 2007	245	7.7	6.0	300	9.4	6.0	6.0	As required on the basis of production of that particular day
July 2008	210	6.6	7.0	252	7.9	7.5	7.3	
Aug. 2008	166	5.2	5.6	245	7.7	5.0	5.3	
Nov. 2008	143	4.5	5.0	180	5.6	5.0	5.0	

3.3. Results of deposits analysis from gas pipeline by intelligent pig surveys

Scale and deposit specimens were collected from several sites along the pipeline system via intelligent pig surveys. The chemical analysis tests were performed for samples by chemical laboratory in Sirte Oil Company and the results, reporting as seen in following tables (7-12)[4-6].

Table 7. Compounds by weight percentage as present in the deposit specimen.

Test / 17-04-2006	Results	Locations of specimen collection
Loss on ignition (wt %)	11.79	
Acid insoluble (wt %)	03.81	600 Km (near Misurata city)
Iron as iron oxide (wt %)	83.97	
inhibitor	Present	

Table 8. Compounds by weight percentage as present in the deposit specimen.

Test / 21-04-2006	Results	Locations of specimen collection
Loss on ignition (wt %)	13.5	
Acid insoluble (wt %)	03.62	430 Km (near Alwashka area)
Iron as iron oxide (wt %)	82.88	
inhibitor	Present	

Table 9. Compounds by weight percentage as present in the deposit specimen.

Test / 20-04-2006	Results	Locations of specimen collection
Loss on ignition (wt %)	15.20	
Acid insoluble (wt %)	02.84	350 Km (near Sirte city)
Iron as iron oxide (wt %)	81.96	
inhibitor	Present	

Table 10. Compounds by weight percentage as present in the deposit specimen.

Test / 17-05-2006	Results	Locations of specimen collection
Loss on ignition (wt %)	10.60	
Acid insoluble (wt %)	03.74	600 Km (near Misurata city)
Iron as iron oxide (wt %)	85.10	
inhibitor	Present	

Table 11. Compounds by weight percentage as present in the deposit specimen.

Test / 20-05-2006	Results	Locations of specimen collection
Loss on ignition (wt %)	09.84	
Acid insoluble (wt %)	04.54	430 Km (near Alwashka area)
Iron as iron oxide (wt %)	83.50	
inhibitor	Present	

Table 12. Compounds by weight percentage as present in the deposit specimen.

Test / 21-05-2006	Results	Locations of specimen collection
Loss on ignition (wt %)	12.20	
Acid insoluble (wt %)	02.75	350 Km (near Sirte city)
Iron as iron oxide (wt %)	83.18	
inhibitor	Present	

Typical transient of positions of deposit specimen versus iron oxide reveals in figure 4 for intelligent pig surveys . The magnitude of iron oxide rises with an increment of time, i.e. the content of iron oxide at sites of 350, 430 and 600 Km on May is higher by respective values of 1.5 %, 1 % and 2 % than that at the same locations on April . This interprets that the internal corrosion rate is time dependent . Additionally, the rate of internal corrosion is proportional to the increasing distance, namely it increases as the length of pipeline raises . For instance, on April the weight percentage of iron oxide rises nearly linearly as the distance increases along the pipeline system . Namely, locations

430 and 600 Km show an increase in the amount of iron oxide with respective values of 1 % and 2 % compared to that for the initial site (350 Km). Further, the weight percentage of iron oxide in response of May tends to behave similarly to the transient of April by 0.4 % and 3 % at positions 430 and 600 Km respectively according to first location (350 Km).
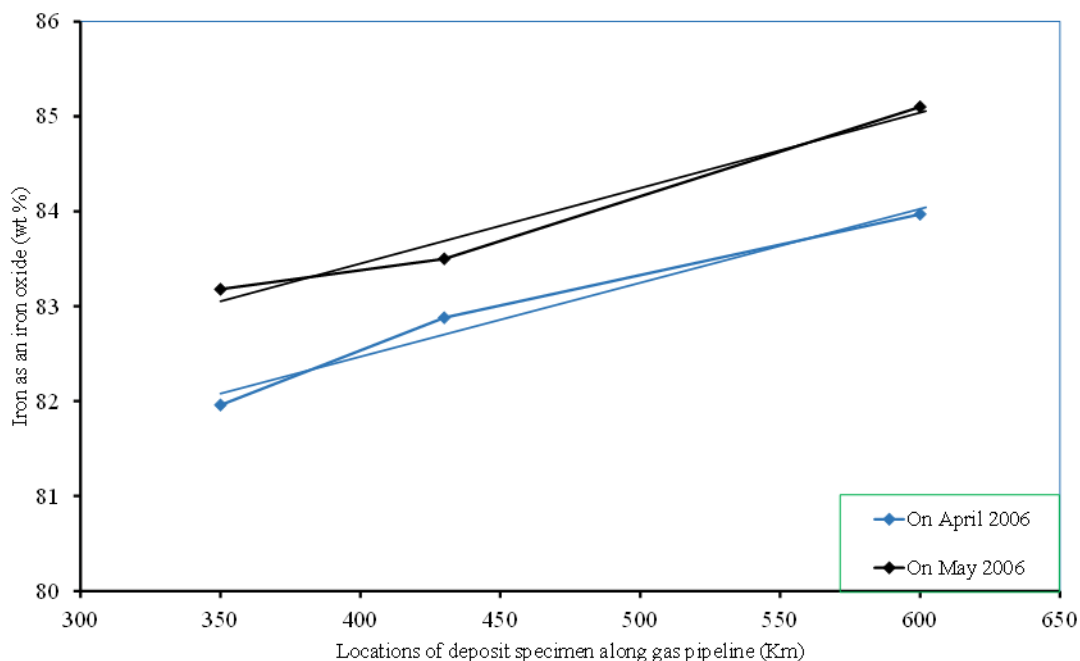

Figure 4. Locations of deposit specimen along gas pipeline (Km versusiron oxide (wt %) as percent in the deposit sample.

3.4. Results of dry gas specimen analysis from gas pipeline system

Analysis of dry gas specimen revealed existence of the following components for example, several types of gases and corrosion inhibitor residuals as in table 13.

Table 13. Content of compounds in the dry specimen of gas

| Components name	Mole (%)
Nitrogen	0.7
Carbon dioxide	3.11
Hydrogen sulphide	0.32
Methane	82.97
Ethane	9.22
Propane	2.56
Iso-Butane	0.45
N-Butane	0.53
Iso-Pentane	0.21
N-Pentane	0.14
Hexane	0.11

4. Discussion

As it is known, natural gas is a homogeneous gaseous mixture consisting mostly of hydrocarbons, nitrogen, carbon dioxide, hydrogen sulfide, water, traces of mercury, organic acids and noble gases. Among these compounds are carbon dioxide, hydrogen sulfide, water, traces of mercury and organic acids that can corrode the inner tube wall. Natural gas usually contains pure water, contrary to crude oil, in which water often contains salts. This water in the gas dissolves carbon dioxide and hydrogen sulfide and becomes acidic and corrosive. The corrosion caused by carbon dioxide is called sweet corrosion, whereas the corrosion by hydrogen sulfide is known as acidic corrosion, and oxygen corrosion is the corrosion caused by oxygen gas. Corrosion rates and intensity are dependent upon the type and concentration of aggressive ingredients, temperature,

flow regime, and velocity. The presence of sulfur compounds determines the acidity of natural gas (sour gas) where the sweet gas should be less than 4 ppmv H_2S[14].

This value considers the maximum approved quality of natural gas while using the pipeline as a means of transportation.

The presence of hydrogen sulfide causes regular and pit corrosion as well as hydrogen attack. The latter is often in the form of cracks or blisters, causing the emission of hydrogen sulfide from them to the environment. Accordingly, standards and special requirements were determined for the use of certain corrosion-resistant alloys to reduce the corrosion phenomenon during the transportation of hydrogen sulfide-polluted gas[15-17]. Hydrogen attack or sulfide stress cracking might be stopped via controlling the pH by caustic injection, adding hydrogen sulfide corrosion inhibitors and scavengers, using cement and organic layers or choosing suitable alloys that have a great ability to resist this type of corrosion[15].

Dry carbon dioxide is non-corrosive environment. Nevertheless, when it dissolves in water, it forms carbonic acid (H_2CO_3), corroding the wall of the pipe, which is usually made of carbon steel. This type of corrosion (sweet corrosion) is common in natural gas transmission pipelines, where a protective black ($FeCO_3$) layer of corrosion forms on the pipe surface of the carbon steel and low-alloy steels (to 9 % Cr). The passive layer extremely forms under certain conditions, but it usually breaks down due to the high stream velocity and stresses causing, localized corrosion. Sweet corrosion can be inhibited by several ways: use of martensitic stainless steels (>12% Cr), control pH by caustic injection and injection of corrosion inhibitors, which are not effective at high temperatures.

$$Fe + CO_2 + H_2O \rightarrow FeCO_3 + H_2$$
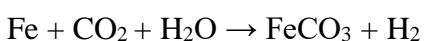
The only element that is absent from natural gas reserves is oxygen gas, but due to gas collection systems sometimes operating under the atmospheric pressure, it is possible to enter air through open valves, causing pitting corrosion.

In addition to being corrosive, oxygen in large concentrations greater than 50 ppmv can oxidize amines and glycol, forming corrosive substances. Oxygen can also reacts with hydrocarbons during regeneration at high-temperature adsorption bed to form water, reducing the resistance of the stainless steels to stress corrosion cracking and galvanic corrosion. Finally, the existence of oxygen is necessity, provided that not exceed 10 ppmv to maintain protective oxide layers on stainless steels, titanium, and aluminum.

Temperature has a complex effect on the corrosion process. High temperature usually leads to acceleration of electrochemical reactions and the transfer of corrosion products from the metal surface to the environment and aggressive substances to the surface. Up to a certain temperature, the increase in the corrosion rate is directly proportional to an increment of temperature, but after a specific temperature, the corrosion rate reduces due to the decrease in the solubility of aggressive gases in aqueous solutions. Usually maximum is at 60-80 ^{o}C depending on the chemical composition of the liquid phase [18, 19]. Moreover, temperature enhances to precipitate and form protective film of $FeCO_3$.

The increased flow rate allows aggressive substances to reach the surface of the metal to remove corrosion products and protective layers such as inhibitor and iron carbonate. Consequently, corrosion rate increases. At lower flow rates, aggressive materials exposes to the metal surface for a longer time causing corrosion, and sediments can easily accumulate causing localized corrosion[20].

Inorganic materials can be removed by cleaning with acids. As well as deposits of organic matters are often scraped off by pigs. Gas hydrates are formed as a result of the trapped molecules of methane or other gases such as nitrogen, oxygen or hydrogen sulfide in the cage structure formed by the water molecules. The formation of hydrates can be prevented in three ways: dehydration of the gas from water or injection of inhibitors to prevent their formation such as methanol and ethylene glycol by 50 %[18,21] or keeping the temperature and pressure outside the range of its formation, but the latter is not practically possible.

Organic acids, for instance acetic acid, which might cause dissolution of protective iron carbonate scale accelerating internal corrosion. This acid can contribute to the Top-of-Line corrosion, when the gas inside the pipeline cools, the water vapor condenses forming fine film of water on the inner surface of the upper part of pipeline, leading to localized corrosion[18,22]. Mercury often exists in little amounts in natural gas causing stress corrosion cracking, specifically liquid metal embrittlement. Therefore, it must be removed from natural gas to a lower concentration than $0.01 \text{ mg/Nm}^{3[14, 23-27]}$.

The protection against corrosion of the inner steel surface of the gas pipeline system is precipitation of corrosion products layer dependent. If the layer of corrosion products is not deposited, the occurrence of corrosion is confirmed. The protection of internal corrosion promotes more easily at high pH in the water phase or at high temperature by fabricating iron carbonate ($FeCO_3$) that precipitates on the inner steel surface of the gas pipeline as a dense protective corrosion products film. At low temperatures, hydrogen sulfide can combine with carbon dioxide to form iron sulfide (FeS) in lieu of the iron carbonate layer. The iron sulfide layer has a faster precipitation characteristic than its iron carbonate counterpart, as it precipitates quickly on the inner surface of the tube providing almost perfect protection. However, insufficient internal protection can occur if protective corrosion products layer is not dense enough, causing sever corrosion problems i.e. localized corrosion attack in the form of pitting.

As stated before the corrosion rate in gas condensate pipeline might be considerably reduced by increment the pH of the water phase via pH stabilization technique[28-30], even in existence of carbon dioxide. The precipitation of protective corrosion products scale on the inner carbon steel surface of the gas pipeline is enhanced by the rise of pH. However unfortunately, stabilization technique cannot work at presence of large quantities of water in gas pipeline systems. Therefore the addition of corrosion inhibitor is the most common and successful method used for such pipeline systems, controlling internal corrosion. Moreover, another type of corrosion often happens, which is the erosion corrosion, which occurs because of wear between the gas particles and the inner surface of the pipe wall particularly during transportation of dry gas.

The erosion corrosion considers the main source of corrosion products that might accumulate later on the inner surface of the pipeline wall as a protective layer. Nevertheless, the protective film may subjected to localized attack such as pitting corrosion as a result of presence of flaws in the layer e.g. spallings or cracks.

Conclusions

Obviously, the carbon dioxide, hydrogen sulphide and water are all responsible for internal corrosion phenomenon in oil and gas pipeline systems. The concentration of these elements, and extra factors e.g. velocity, flow regime, temperature, chemistry of water, oil or water wetting and, composition and surface condition of the pipeline metal, the whole governs the internal corrosion. The rate of internal corrosion might change markedly with fine alteration of any one of these factors. The properties of thin protective film of corrosion products accumulating on the inner steel surface of the pipeline are influenced by any a bit change in the previous factors. In this particular case of dry gas, no internal corrosion occurs since initial products might be easily deposited on the inner surface of gas pipeline forming a reliable dense protective layer. However, utilization of inhibitor should be involved because no grantee of water absence even in dry gas transportation. Sometimes the rate of inhibitor injection was found insufficient i.e. the found dosage rate is lower than the required dosage rate. Certainly, the electrical resistance (E/R) probe is unreliable monitoring instrument because of the fake readings may be provided. Therefore highly recommended the corrosion coupon (weight loss method) should be involved in the monitoring process. Coupon test is of great importance to the corrosion monitoring, since it does not only introduce an indicator about the presence of corrosion but it can also reveal precisely the type of corrosion contrary to other methods of monitoring.

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