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Material Selection Strategy for Corrosion Control in Iranian Upstream Oil and Gas Industry

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ABSTRACT

Annually, a huge amount of money is lost due to corrosion problems in upstream and downstream oil and gas industries. To control the corrosion costs, recently, corrosion control/corrosion management concept is developed. The aim of corrosion management philosophy is to reduce corrosion costs and increase safety by re-evaluation process in different stages of the project. The material selection process is one of the key stages in integration assurance of the system, which plays important role in the overall corrosion control process. Some important parameters in selecting suitable materials for use in a given working and environmental condition includes design pressure and temperature, weldability, costs and corrosion concerns. Nowadays, the last one attracted the attention of the both researchers and owners. Codes like ISO 21457 necessitate providing Material Selection Procedure Report before proceeding executive steps of the project. Without any specific material selection procedure; the material selection process will be a complex and confusing task because of the diversity in codes and fluid service conditions. This study aims to introduce researchers and engineering with corrosion concerns especially in CO_2, H_2S, and salt contained services and the solutions which are normally employed in the upstream oil industry to deal with associated problems. Towards, environmental deterioration problems the oil and gas fields of Iran are discussed and the related treatments are presented.

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1. Introduction

Pipes, fitting, valves, and the other products which are used in oil and gas well-head and production lines shall be selected in a way that withstands internal pressures due to service fluids, besides the external loads by bending, tension and/or temperature expansion/contraction. ASME SEC VIII describes the rules for construction of the pressurized products (ASME BPVC, 1998). In addition to mechanical strength evaluation, these products should assure the integrity of the system for the whole design life. It means that they should be selected enough strong to eliminate corrosion attacks by the environmental conditions and to resist the internal and external corrosive environment. The importance of corrosion control in oil and gas industry is very clear and many studies dedicate to investigating different aspects of corrosion phenomena in energy transportation systems via pipes (Eskandarzade et al., 2018). There are plenty of steel materials with different corrosion resistance characteristics. The material composition and even the fabrication method of the product are very important in corrosion rate during the service. The effects of Chromium on corrosion behavior of Low-alloy Steel has been studied by Zhou et al. (2015). According to their report, the increase of chromium content results in the improvement of corrosion resistance of the Low-alloy Steel. The assessment of localized corrosion in carbon steel is reported by Nasirpouri et al. (2014). Effects of chloride content on CO_2 corrosion of the carbon steel in simulated oil and gas well environments are investigated by Liu et al. (2014).

Several researchers who have used theoretical models to investigate the effects of influencing parameters in the integrity of the pipeline/piping systems. Shabarchin and Tesfamariam (2017) have assessed the risk of seismicity and the internal corrosion on the oil and gas pipeline infrastructure. Zhou et al. (2016) have tried to estimate the probability of the corrosion failure in petroleum industry using the fuzzy logic method.

Choosing among materials to manage the corrosion rate needs a very careful understanding of the working conditions especially the severity of the service fluid. In Iran to calculate the severity of the service fluid, Drill Stem Test (DST) (Bredehoeft,1965) is normally used to identify the fluid composition of the reservoir. The result of these tests usually lists the H_2O, CO_2, salt, and other fluid content of the crude oil or gas.

In addition to the fluid service severity, other criteria such as the safety and easy-to-repair level should be considered in the material selection process. As a rule of thumb, it should be taken extra attentions to products that are used in hard- to- repair locations.

Corrosion management in oil and gas industry is a continuous process from design and construction to operations (Dawson, 2010). It is also a team effort that involves a range of expertise from corrosion engineers, materials specialists, reservoir engineers, and process engineers. This study concentrated on the corrosion measures which are taken in Iranian Oil and Gas fields during material selection process. These measures are normally taken based on the international codes as well as the long-term experience of the Iranian National Oil Company. The focus of this study is on low carbon steel alloys and their internal corrosion problems. Towards, the most frequent aggressive environments in Iranian Oil and Gas wells; such as H_2S, CO_2, chloride contents and their corrosion mechanisms will be discussed and the related treatments will be described.

2. Corrosion Study

Corrosion study is an inevitable part of the material selection process. It usually considers both erosion and corrosion mechanisms. Production of sand and other solids are common in the most of oil and gas wells. Therefore, the presence of the simultaneous erosion and corrosion mechanisms during the service life is very common. The aim of corrosion study is to find that how much the fluid in service is corrosive and aggressive to the materials. Corrosion evaluations and calculations can be based on the well-known corrosion models (such as Sell model, Norsok) (Olsen, 2003), laboratory tests or field experiences. Using last method requires the well-documented successful experience of the material usage at the specific service fluid condition for at least two years. According to NACE MR0175, if it is the case, the usage of the same material at the similar service condition is acceptable. Most of the crude oil and gas production lines in Iran can be categorized as wet hydrocarbons. For this type of fluid services the possible corrosion mechanisms for carbon steels are listed in Table 1 which should be considered in corrosion evaluations. To do so, firstly the composition of the production fluid should be understood. Table 3 indicates a typical composition of the production fluid in Central Oil Fields of Iran.

Table 2 has been obtained from DST results. Normally, fluid samples, reservoir pressure, formation properties, productivity estimates including flow rate and hydrodynamic information are the data can be obtained from a DST. According to the results from this test, the oil and gas fields can be categorized as sour or sweet services. In next sections corrosive compounds in oil and gas fields are described and the fundamental for material selection in Iranian Companies are presented.

Table 1. Corrosion Mechanisms which are possible in Oil and Gas industry

Corrosion Mechanism	Corrosion Mechanism (Continue)
General Corrosion due to CO_2 & H_2S	Pitting
SSC/SCC caused by H_2S	Dissolved Oxygen corrosion
HIC/SWC	ASCC
MIC	

3. H_2S Corrosion

3.1. Wet-H_2S Content Fluids

If the water exists at the service fluid, then the H_2S damage can be observed at the carbon steel; but the dry H_2S is not deteriorative. In general, the damage rate of the wet-H_2S is depending on the amount of liquid water and the partial pressure (PP) of the H_2S. Since, the partial pressure of the H_2S is directly related to the total pressure of the fluid (Eq. 1); then, it can be concluded that as the working pressure increases, the corrosion rate due to the H_2S increases, dependently.

$$P_{H_2S} = P_{total} \ Mole\% \ H_2S \qquad (1)$$

Other important factors in corrosion rate of the H_2S compound are including: in situ pH, H_2S level, contaminants, temperature. Standard NACE MR0175-P2 has categorized H_2S content fluids into four regions including Region zero (sweet service), Region 1 (Mild sour service), Region 2 (Medium sour service) and Region 3 (severe sour service) based on in situ pH and H_2S partial pressure (Figure 1).

Table 2. Typical reservoir fluid composition for a gas well located in Iranian Central Gas Fields

Component	Partial Pressure (Bar)
H_2S	4.34
CO_2	5.40
N_2	26
C_1	127
C_2	8.40
C_3	3.47
ISO-C_4	0.78
N-C_4	1.50
ISO-C_5	0.70
N-C_5	0.62
C_6	1.05
C_{7+}	3.44
Total	100
C_{7+} Properties	
Specific gravity	0.76
Molecular weight	121.02
Fluid Properties	
API	
TEMP (°F)	170
GOR (SCF/STB)	29.82

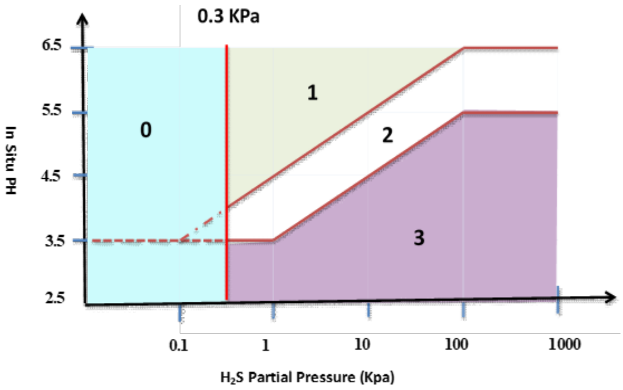

Figure 1. H_2S environment severity for SSC cracking in carbon steels (NACE MR0175, 2001)

3.2. Wet-H_2S Induced Damages

The deterioration of metal due to contact with hydrogen sulfide (H_2S) is called sour corrosion. Hydrogen sulfide when dissolved in water produces a weak acid, its general corrosion is rare a problem (Kane and Cayard, 1999); but it is the source of atomic hydrogen and known to be the main reason for the occurrence of the several types of cracks. Major defects induced by hydrogen sulfide are illustrated in (Figure 2). Among all defects, SSC is the most crucial crack type. SSC is the combined influence of hydrogen sulfide and tensile stress. It propagates over the ranges of velocities from 10^{-3} to 10mm/h depending upon combination of alloy and the environment involved (Popoola, 2013). Then, this type of crack can grow very fast and catastrophic failure can occur in hours/days. SSC is also less likely to be founded during the periodic inspections.

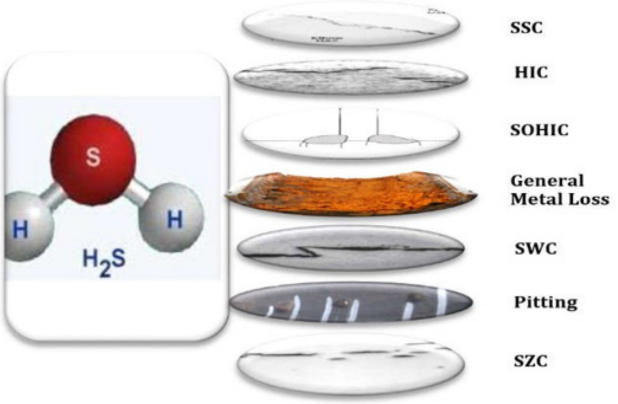

Figure 2. The hydrogen sulfide induced major defects

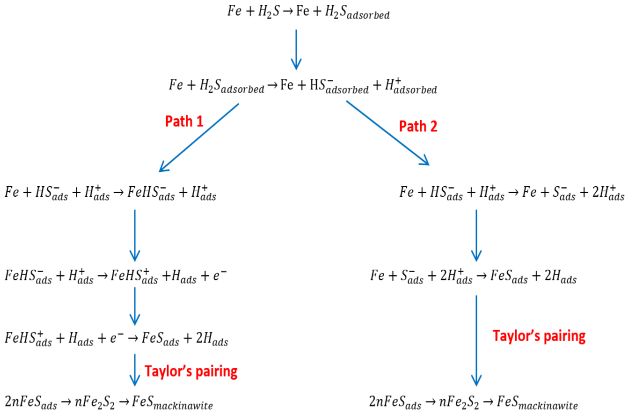

Figure 3. The Proposed mechanism for H_2S corrosion on steel (Koteeswaran, 2010)

For this reason, where the SSC is the probable defect type; choosing SSC resistance materials is priority in the material selection process.

3.3. Mechanism of H_2S- Induced Defects

The internal corrosion of carbon steel in the presence of hydrogen sulfide represents a significant problem for both oil refineries and natural gas treatment facilities. Surface scale formation is one of the important factors governing the corrosion rate. The scale growth depends primarily on the kinetics of scale formation. In contrast to relatively straightforward iron carbonate precipitation in pure CO_2 corrosion, in an H_2S environment many types of iron sulfide may form such as amorphous ferrous sulfide, mackinawite, cubic ferrous sulfide, smythite, greigte, pyrrhotite, troilite and pyrite, among which mackinawite is considered to form first on the steel surface by a direct surface reaction (Sun and Nesic, 2007). The poorly known mechanism of H_2S corrosion makes it difficult to quantify the kinetics of iron sulfide scale formation. A probable mechanism for Iron dissolution in aqueous solutions containing H_2S based on the formation of mackinawite film, as proposed by Sun et al (2008) is shown in (Figure 3).

4. CO_2 Content Fluids

Similar to H_2S, CO_2 can lead to metal corrosion just at the presence of the liquid water. The comprehensive study of the CO_2 corrosion has been done by the European Federation of Corrosion (EFC) and reported as EFC-23. It causes both general and localized corrosion types. Steels are very unstable when exposed to dissolved CO_2 in water; but after a first layer corrosion, stable protective scale of $FeCO_2$ is produced which hinders the corrosion of internal layers of the metal.

4.1. CO_2 Induced Corrosions (Sweet Corrosion)

CO_2 related problems are widely described in publication of European Federation of corrosion (Kermani and Smith, 1997). Major corrosion types due to CO_2 are illustrated in (Figure 4).

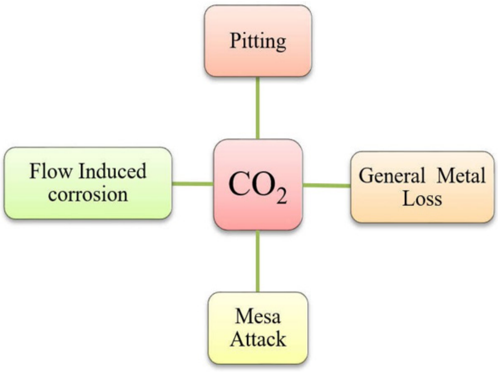

Figure 4. Major corrosion mechanisms due to CO_2

General Corrosion: Dissolved CO_2 in water reacts with metal and produces Iron Carbonates. This type of corrosion is one of the most critical considerations in calculation of Corrosion Allowances.

Pitting: In low speed flows this type of corrosion can occur in any temperature. However, the rate of pitting increases by increasing temperature and the partial pressure of the CO_2. Depending on chemical composition of the material, there is a given temperature which the rate of the pitting is highest in this temperature; for carbon steels used in oil and gas industry the range of critical temperature is 80-90 Celsius.

Mesa attack: Mesa is the name of a mountain in USA and also the special type of pitting is named Mesa because of the shape similarity of this type of pitting with Mesa Mountain. In a special condition (flow speed: 0.1-7 m/sec; temperature: 40-80 degrees; partial pressure of CO_2 greater than 1.5 bars) the Iron Carbonate scale can be removed due to the contact of solids and the produced locally bare steel surface is corroded and this phenomenon is repeated until the localized Mesa attack with flat bottom and clear edges occurred.

Flow induced localized corrosion: This type of corrosion is the result of removing of protective scale in a region of previously produced localized corrosions. Hence, a bigger area of the metal is exposed to corrosion.

Most influencing parameters in CO_2 corrosion are including water-cut, water analysis, fugacity of CO_2. Fugacity of CO_2 is influenced by total pressure and temperature and can be found from Table 2.B13.2 of standard API-RP580 (2016). Also, the calculating of CO_2 corrosion rate can be done using the relations offered in this standard (Eq. 2):

$$CR_{base} = f(T, pH).f_{CO_2}^{0.62}.(\frac{S}{19})^{0.146+0.0324 f_{CO_2}} \tag{2}$$

In this equation f is the fugacity; S is the shear stress of the fluid. The shear stress of the fluid is calculated as following [18]:

$$S = \frac{f.\rho_m.u_m^2}{2} \tag{3}$$

4.2. Mechanism of CO_2 induced defects

Dissolved CO_2 in water produces carbonic acid which is rich in atomic hydrogen. The most common chemical reactions which are common at the presence of CO_2 and H_2O folows (Kermani and Smith, 1997):

$$CO_{2(g)} + H_2O \rightarrow CO_{2(dissolved)} \tag{4}$$

$$CO_{2(dissolved)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO^-_3 \tag{5}$$

$$CO_2 + H_2O + Fe \rightarrow FeCO_{3\,(ironcarbonate)} + H_2 \tag{6}$$

However, the actual mechanisms of a localized corrosion of carbon steels in CO_2 environments are not clear, and there are no rules for its prediction. As discussed before a produced iron carbonate is very protective scale; when this protective scale is locally damaged due to contact of solid particles or the flow of the fluid; the chloride salts can touch the uncoated surface of the steel and the iron chloride is replaced with iron oxide in these regions. As the mole volume of the iron chloride is greater than the mole volume of the iron oxide; it causes the break of more protective iron carbonate scale and the corrosion extended (Davies and Burstein, 1980). Bare areas act as an anode of a galvanic cell where surrounding film- covered areas operate as the cathode. It is assumed that the repetition of this procedure constitutes the localized corrosion mechanism at the presence of wet-CO_2.

5. Combined CO_2 and H_2S Content Fluids

Corrosion mechanism and the H_2S induced cracks changes by changing in pH level of the fluid. The presence of both CO_2 and H_2S cause the reduction in pH level of the fluid and hence, increase the severity of the corrosive environment and consequently the occurrence of the crack and the other defects. The value of in situ pH can be obtained using Figure 5. It should be noted that if the fluid is containing bicarbonate ions or other influencing elements, then Figure 5 is not valid and other suitable curves should be employed. The presence of a small concentrations of H_2S can have a significant effect on the CO_2 corrosion; this is because iron sulfide can precipitate as the corrosion product in CO_2/H_2S environments. Depending on the exposure conditions, different forms of FeS can form and their specific corrosion protectiveness may be different. There are currently no generally accepted predictive algorithms for any form of H_2S corrosion. There are also still several unknowns about the corrosion reactions that lead to pitting, which is the most common mode of sour service equipment failure. To determine how much H_2S is required to turn a system from sweet to sour corrosion, different rules of thumb have been used. In the 1980s, Dunlop et al. proposed the use of a CO_2/H_2S ratio of 500 at 25 °C to determine whether the corrosion product will be $FeCO_3$ or FeS. For values geater than 500, the product will be $FeCO_3$ and for vales less than 500 the product will be FeS. Other authors proposed a ratio of CO_2/H_2S lower than 20 to have sour corrosion, while a mixed regime is considered when the ratio ranges between 20 and 500 and sweet corrosion for values higher than 500.

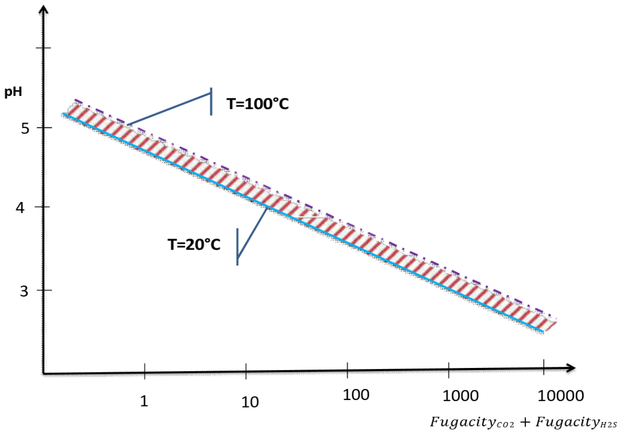

Figure 5. In situ pH of the condensed water under the CO_2 and H_2S pressure (NACE MR0175, 2001)

Table 3. Material Selection Rules for Different Fluid Condition

Corrosive Media	Possible Failure Type	Actions
H_2S (Partial pressure lower than 0.05 bar)	General Corrosion	Generally, no action needed for H2S content, however, the following should be noted: – Design should be based on other corrosive element types. – Avoid using materials susceptible for SSC and HSC. – Avoid using steels with yield strength greater than 965 MPa; if is inevitable, SSC and HSC tests are required. – Extra attention should be made for crack possibility in high concentrated load points.
H_2S (Partial pressure greater than 0.05 bar)	SSC, Pitting, HIC, SOHIC, SWC, SZC, General corrosion.	– Selection of material based on Appendix A of Standard NACE MR0175 P2 or using other methods of material selections in this standard. – Hardness in welding zone should be controlled according to NACE MR0175 P2; Table A.1. In general, the hardness of the heat affected zone and other sections should not be greater than 22 RC; otherwise Post Weld Heat Treatment is required.
CO_2 partial pressure less than 0.5 bar (Low risk)	General corrosion	No special action is needed

Table 3. Material Selection Rules for Different Fluid Condition (Cont'd)

Corrosive Media	Possible Failure Type	Actions
CO_2 partial pressure in the range of 0.5 to 2 bars (Medium risk)	General corrosion	– Higher Corrosion allowance should be considered. – Maximum weld metal penetration should be 0.5mm. – It is recommended using cupper content filler metals for root welding (e.g. AWS-7018-G) – Using of suitable inhibitors
CO_2 partial pressure greater than 2 bar (High Risk)	General Corrosion, Pitting, Mesa attack, flow induced attack.	– Corrosion Resistant Alloys should be used – Maximum weld metal penetration should be 0.5mm. – t is recommended using cupper content filler metals for root welding (e.g. AWS-7018-G) – Using of suitable inhibitors
Combined H_2S and CO_2 ($CO_2/H_2S<20$) Combined H_2S and CO_2 ($CO_2/H_2S>20$)	Depends on H_2S partial pressure Depends on CO_2 partial pressure	– Related H_2S partial pressure measures should be considered. – Related CO_2 partial pressure measures should be considered

A review of a wide number of field cases reports quantitative information about sour weight loss corrosion and proposes possible mechanisms. Fluid corrosiveness is classified into three categories, from a negligible corrosiveness which constitutes about 40%-50% of the cases (both in oil and gas production), to a moderate one (typically within 1 mm/year) in the most of other cases, and lastly to a very severe corrosion (10 mm/year, even in apparently mild conditions) in a few cases. The flow velocity and flow regime are shown to be the most leading factors of the transition between negligible and intermediate and severe corrosion categories. Very severe corrosion cases require "pit promoters" (sulfur, oxygen, and bacteria) and a "galvanic effect" with surrounding non-corroding surfaces. On the other hand, the H_2S and CO_2 partial pressure as well as the pH or the H_2S/CO_2 ratio not influence the corrosion likelihood if the CO_2/H_2S ratio is lower than 20.

6. Discussion

Different types of corrosion environments need different measures in order to mitigate the metal loss phenomena and consequent failures. Both the material composition of the product and the product fabrication method are important in corrosion behavior of the metals. For example, for flat-rolled carbon steel the inclusion places can be the HIC/SWC initiation points. Hence, for this type of material when used in sour service related HIC/SWC evaluation tests should be done (NACE MR0175, 2001). Chrome is very important element for CO_2corrosion control and about 0.5-1% Chrome can substantially improve the CO_2 corrosion rate of the material. Other elements which can enhance the resistance of material against CO_2 attacks are including Nickel, Molybdenum and Cobalt. However, the optimum selection of the material is not enough for corrosion control. There are other supplementary methods that can mitigate different types of corrosion. Using inhibitors such as glycol and methanol can reduce the rate of corrosion up to 90%. However, inhibitors cannot relief the SSC type failures. Table 3 indicates the actions which normally are taken against the most common corrosive media. In addition to information provided in Table 3; these rules also should be considered in material selection for different situations.

- Metallic coatings (electroplated and electroless plated), conversion coatings, plastic coatings and linings are not acceptable for preventing SSC (MR0175, N.S., 2002).
- Overlays applied by thermal processes such as welding, silver brazing, or spray metalizing

systems are acceptable if they comply with one of the following requirements (MR0175, N.S., 2002).

- Quenched and Tempered and Tempered products have better SSC resistance (EFC-16., 2009).

7. Conclusion

In this paper, the most common corrosion problems in upstream facilities of Iranian Central Oil Fields (I.C.O.F) are discussed. The corrosion mechanisms are described and the special strategies which experts in the I.C.O.F are using during material selection process are elaborated. According to the above discussion H_2S and CO_2 are the most corrosive media in oil and gas fields. While H_2S leads to localized damages; CO_2 causes a variety of problems such as localized or general corrosion. However; H_2S induced cracks are very dangerous and mitigation is much critical for this type of corrosive media.

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استراتژی انتخاب مواد برای کنترل خوردگی در صنایع بالادستی نفت و گاز ایران

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چکیده

سالانه مبالغ بالایی به خاطر مشکلات ناشی از وقوع خوردگی در صنایع بالادستی و پایین‌دستی نفت و گاز، از دست می‌رود. به‌منظور کنترل هزینه‌های خوردگی، اخیراً مفاهیم کنترل خوردگی و مدیریت خوردگی توسعه‌یافته‌اند. هدف از فلسفه مدیریت خوردگی کاهش هزینه‌های خوردگی و افزایش ایمنی با فرآیند ارزیابی مجدد در مراحل مختلف پروژه است. فرآیند انتخاب مواد یکی از مراحل کلیدی در تضمین یکپارچگی سیستم بوده و نقش مهمی در سیستم جامع کنترل خوردگی ایفا می‌کند. برخی از پارامترهای مهم در انتخاب مواد مناسب برای کاربردهای مختلف شامل: فشار و دمای طراحی، جوش‌پذیری، مسائل مالی و سایر ملاحظات خوردگی می‌باشند. استانداردهایی مانند ISO 21457 تهیه سند رویه انتخاب مواد قبل از مراحل اجرایی پروژه را الزامی نموده است. بدون داشتن رویه‌ای مشخص برای انتخاب مواد، فرآیند انتخاب مواد به دلیل تنوع در کدها و شرایط سیال سرویس، کاری بسیار پیچیده و گیج‌کننده به شمار می‌آید. هدف از این مطالعه ارائه خلاصه فرآیندها و رویه‌های مرسوم در شرکت‌های بالادستی نفت و گاز برای انتخاب مواد در شرایط وجود خوردگی درنتیجه CO_2، H_2S و نمک می‌باشد. همچنین تدابیری برای رفع معضل آلودگی محیط‌زیست درنتیجه نشت فرآورده‌های هیدروکربنی به محیط‌زیست با رویکرد انتخاب صحیح مواد موردبحث قرار گرفته است.

واژگان کلیدی: انتخاب مواد، خوردگی، صنعت نفت و گاز، مدیریت خوردگی