Eng. & Tech. Journal, Vol.28, No.9, 2010

Corrosion and Hydrogen Attack of Pipelines in Oil and Gas Fields

Dr. Sami I. J. AL-Rubaiey*

Received on: 4/11/2009
Accepted on: 16/2/2010

Abstract

Conditions for hydrogen sulfide and carbon dioxide corrosion of pipeline in oil, gas, and gas-condensate fields are discussed. Various factors are shown to affect the **CO_2** and **H_2S** corrosion rate of steel in oil and gas field media. Protective properties of sulfide film as a function of partial pressures of **H_2S** and **CO_2**, **pH** and temperatures are studied.

التاكل والهجوم الهيدروجيني في خطوط انابيب حقول النفط والغاز

الخلاصة

يتركز البحث الحالي على التاكل الذي يسببه كل من غاز كبريتيد الهيدروجين وغاز ثاني اوكسيد الكربون لخطوط انابيب النفط والغاز وانابيب المكثفات في حقول النفط والغاز العراقية حيث لاتوجد بحوث علمية منشورة سابقا على التاكل في الحقول العراقية . لقد تبين وجود عوامل مختلفة تؤثر على معدلات تاكل الفولاذ التي تصنع منها الانابيب العاملة في هذه الحقول .يهدف البحث الى دراسة تاثير كل من الضغط الجزيئي لغاز كبريتيد الهيدروجين وغاز ثاني اوكسيد الكربون والداله الحامضية للمحاليل المستخدمة ودرجة الحرارة على خواص الطبقة الواقية على سطوح الانابيب.

Introduction

In the field of mining or oil and gas development, oil corrosion, and pipeline corrosion in the casing is a very serious, especially in a number of years of continuous exploitation of old oil fields, scrapped a tube directly attributed to corrosion of the ratio of 60% (1) .

The areas of major corrosion and hydrogen attack related problems for oil and gas field environments are universal. **CO_2** and **H_2S** gases in combination with water are responsible for most of the corrosion problems associated with processing oil and gas. The internals of pipeline become complicated when **CO_2** acts in conjunction with **H_2S,** deposited solids and other environments (2-4) .

In the recent years, the gases **H_2S** and **CO_2** in fluids encountered in various phases of oil and gas fields necessitate the suitable steel products and pipeline, for sour gas application.

The problems of steel pipeline in oil and gas environments can be divided into the two categories: (5-8) I- General corrosion and II- Hydrogen attack.

In order to clarity the controlling factors in corrosion and hydrogen entry in to steel pipelines , this work had been made to analyze the protective properties of sulfide film as a function of partial pressures of H2S and **CO_2** ,

***Production Engineering & Metallurgy Department, University of Technology / Baghdad**

https://doi.org/10.30684/etj.28.9.11
2412-0758/University of Technology-Iraq, Baghdad, Iraq

pH and temperatures .The detailed influence of these parameters are still poorly understood especially in Iraqi fields of oil and gas.

In work (5,6) reported that at P**H2S** below 0.1 psi a protective sulfide film was formed , which consists of FeS2 (Pyrite) , FeS (Troilite) and some Fe3S4 (Kansite) .providing low corrosion rate, but a nonproductive film was formed composited primarily of Kansite in region of 0.1-4.0 psi .

This condition makes the hydrogen entry increased inducing hydrogen blistering. The no protective nature of Kansite as it grown was firstly mentioned by Mayer Riggs McGlasson and Sudbury (9)

They were also pointed that, the presence of **CO_2** and salts influences the corrosion forms and its rates.

Experimental Work

Specimens used in this work were prepared from commercially produced X-60 grade pipeline steel whose chemical composion illustrated in **Table (1).** They were supplied by Iraqi North Oil Company.

The dimension of the specimens are 4* 15* 30 , 0.5* 50*50 and 10*20*100 mm for the measurements of corrosion rate , hydrogen permeation rate and internal blistering tests respectively. The specimens were mechanically polished with emery paper and degreased in a cotton under ultrasonic vibration.

Corrosion tests were carried out for five days in the cell simply illustrated in **Figure 1**. Using mainly synthetic sea water saturated with mixed gas of various composions of **H_2S** and **CO_2** after deaeration with deoxygenated N_2 as listed in **Table (2).**

Fig. 2. Schematic illustration of the experimental apparatus for hydrogen permeation measurements.

The partial pressures of gases employed were extended to 5 and 30 atm. for H_2S and **CO_2** respectively for limited study in an autoclave.

Results and Discussion

CO_2 - Brine System

The corrosion rate of pipeline steel in this system increases with **PCO2** as expected from the lower pressure experiments. The expression for the corrosion rate as a function of **PCO2** was found and represented in to equation (1) . This equation finding in coincided with work(8) :

$$\text{Log IC} = \text{Log } \mathbf{P_{CO_2}} + 1.18$$

Where IC is the corrosion rate.

This equation, however, may not have application since the role of **PCO_2** can not simply be translated into pH. The corrosion rate in synthetic sea water with various pH are much smaller compared with those in high pressure **CO_2** tests.

CO_2 corrosion of carbon steel used in oil production and transportation (when a liquid water phase is present) is influenced by a large number of parameters, some of which are:

Temperature, **CO_2** partial pressure, pH, Concentration of dissolved corrosion product (**$FeCO_3$**), water wetting and metal microstructure.

The detailed influence of these parameters is still poorly understood and some of them are closely linked to each other. A small change in one of them may influence the corrosion rate considerably.

The temperature dependences on pH and the corrosion rate disagree each other as shown in **Figure 3**. This is attributed to changes in the properties of the thin layer of corrosion products and scale which always accumulate on the steel surface. The morphology and the composition of this layer determine whether the attack is worst case corrosion, low corrosion under protective films, or mesa corrosion. The layer also seems to interact with the inhibitor transport to the surface and therefore plays an important role for the performance.

The relative abundance of surface layer, as determined by XRD (**Figure** 4) are given in **Table** 3 . $FeCO_3$ was the main constituent of the surface layer. The iron oxides also constituted a sizeable portion on the surface layer.

The fluid contained Ca^{+2}, which can form calcium carbonate. CaCO3 precipitated in competition with siderite ($FeCO_3$).

When very small amounts of corrosion product deposit on the surface, or a porous film, generally very high uniform corrosion rates are obtained, even at low temperature and high pH.

Experiments have shown that precipitation rate of FeCO**3** is a slow , temperature- dependent, process, and at that a high degree of supersaturating can be maintained in a corroding system.

It has been shown also that, increased pH has a large impact on protective film formation and the corrosion rates. At high pH (6-7), protective films are more easily formed because the solubility of Fe^{++} is reduced by several orders of magnitude (<< 1ppm) below the solubility in pure water and CO_2 when the pH is increased. The low solubility also implies that protective films will not be easily dissolved. Protective films, once formed, can therefore only be removed mechanically, or by erosion. This is important to realize in order to understand the different mechanisms taking place when carbon steel corrodes(10) .

The higher corrosion rate at higher temperature can be explained only by the accelerated cathodic reaction at salt compounds represented by CaCO3 deposited onto steel surface at higher temperatures(2) .

CO_2 - H_2S Brine System

Hydrogen sulfide is the main corrosive gas in the oil and gas industry(3) . Facilities and equipment for metal corrosion damage has been particularly severe. In the oil and gas field facilities and equipment corrosion of the many factors, hydrogen sulfide is the most dangerous(7) .

Sweet corrosion occurred when a very small partial pressure of $\mathbf{H_2S}$ was added. At this condition, uniform corrosion was found. The added $\mathbf{H_2S}$ only accelerated the general corrosion rate.

As shown from **Figure** 5, the corrosion rate and hydrogen content have high values. As the partial pressure of H2S increased, the general corrosion rate decreased quickly, but corrosion tends to be localized. Severe pitting was found because of dewdrop formation, where heterogeneous concentration of dissolved gases is expected followed by the localized corrosion with acidification due to hydration of metallic ions. If acidification occurs, different sulfide is considered to be preferable, which is no more protective.

The corrosion scale mainly composed of coarse grains of **FeS & FeS_2**., which were loose and brittle. (6) In sour corrosion, general corrosion rate decreases slowly and pitting became slight with increasing partial pressure of **H_2S.** The primary corrosion product had fine grains of **Fe_3S_4** , made the scale more compact and continuous(6) . The hydrogen permeation data for various pH shown in **Figure 6**. suggest that pH is critical below which bulk sulfide identified as **Fe_3S_4 a**nd **FeS_2** are more predominant than **FeS.** This explanation is illustrated in **Figure 7.** The arrhenios plot of data in **Figure 3** provides, the apparent a activation energies for **CO_2** saturated solution: 4.9 Kcal/mole, whereas almost 15.3 Kcal/mole obtained in the case of **H_2S** saturated solutions.

The retardation of hydrogen entry into steel at higher temperature can be attributed to the formation of more protective films, which may take the order of ten hours to be formed. It is, however, true that the most hydrogen dissolved in lattices, or trapped at defects in steel will diffuse out at 60 C ° when injection of hydrogen is stopped. Additionally, the decrease in solubility found through permeation experiments at higher temperature is suggesting that, hydrogen entry process is certainly disturbed due to the decrease in adsorbed hydrogen concentration at higher temperature stable film formation and hydrogen volition may also be involved.(7, 8)

Conclusions

1- CO_2 - Brine System:

-High corrosion rate is the problem to be solved especially at high temperatures under ambient pressure, or at pressure higher than 5 atm. at ambient temperatures. The corrosion rate reached more than 100 mdd in the presence of salts.

- The corrosion rate decreases with increases partial pressure of **CO_2** and temperature.

2- CO_2 - H_2S Brine System

The corrosion rate is dependent on **PCO_2, PH_2S** and temperature in a complex manner primarily due to the formation of various iron sulfides.

- Hydrogen related degradation of steel is seemingly abated at temperature above 60 C °.
- The corrosion behavior and associated hydrogen entry into steels may not be reported in the gas transmission line because stable formation of dewdrop and the heterogeneous.

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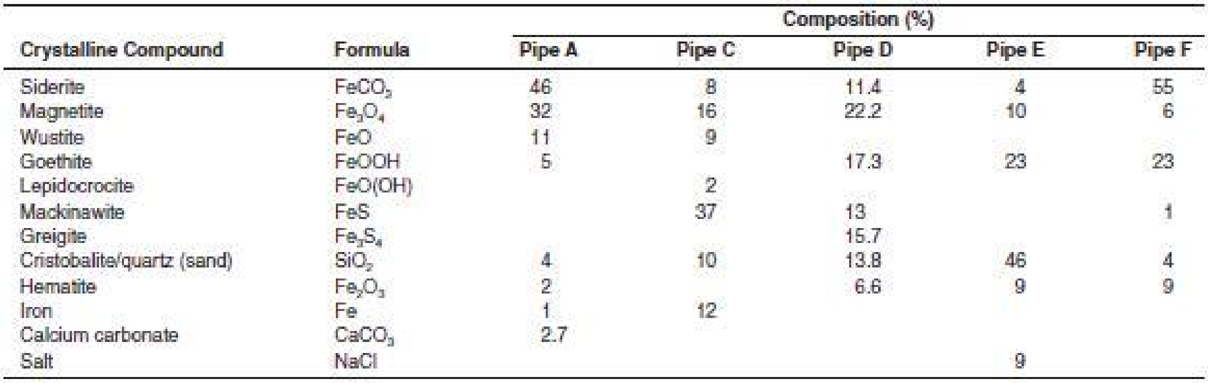
Table (1) The chemical Composition of X-60 pipeline steel

Element	C %	Si%	Mn%	P%	S%	Ti%	Cr%
Wt.%	0.03	0.22	0.94	0.08	0.008	0.063	0..63

Table (2) Composition of mixed gas of H_2S and CO_2 with different partial pressures.

Composition	1 atm	2 atm	3 atm	4 atm	5 atm	6 atm	7 atm
CO_2	1.0	0.9956	0.9914	0.9591	0.7740	0.535	0
H_2S	0	0.0044	0.0085	0.0409	0.226	0.465	1.0

Table (3) Compositions of surface layers as determined by X- Ray Diffraction.



Crystalline Compound	Formula	Composition (%)				
		Pipe A	Pipe C	Pipe D	Pipe E	Pipe F
Siderite	$FeCO_3$	46	8	11.4	4	55
Magnetite	Fe_3O_4	32	16	22.2	10	6
Wustite	FeO	11	9			
Goethite	FeOOH	5		17.3	23	23
Lepidocrocite	FeO(OH)		2			
Mackinawite	FeS		37	13		1
Greigite	Fe_3S_4			15.7		
Cristobalite/quartz (sand)	SiO_2	4	10	13.8	46	4
Hematite	Fe_2O_3	2		6.6	9	9
Iron	Fe	1	12			
Calcium carbonate	$CaCO_3$	2.7				
Salt	NaCl				9	

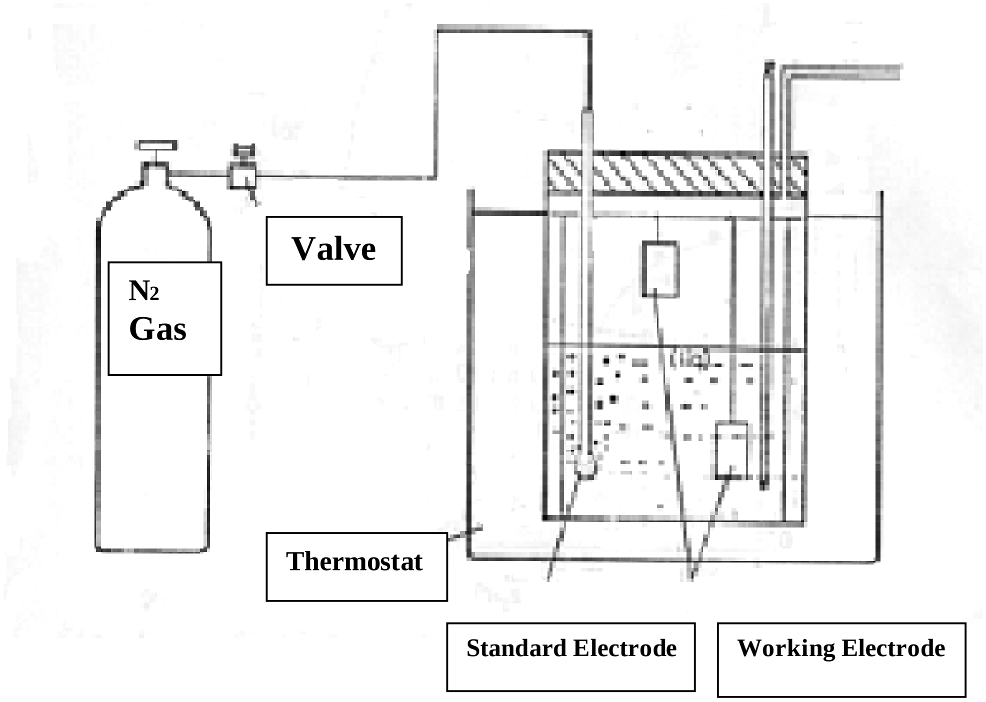


Figure (1) Schematic illustration of the experimental Apparatus for corrosion tests

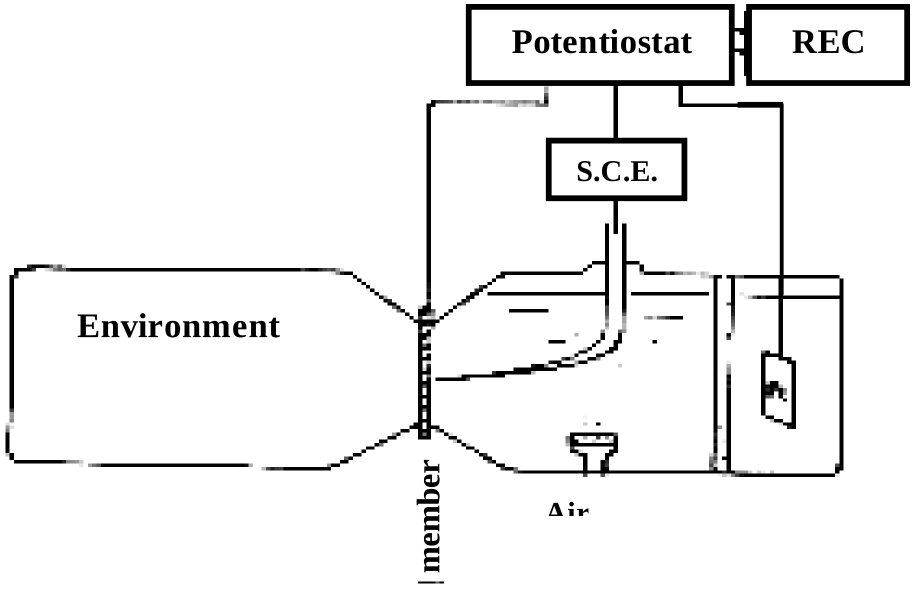


Figure (2) Schematic illustration of the experimental apparatus for hydrogen permeation measurements

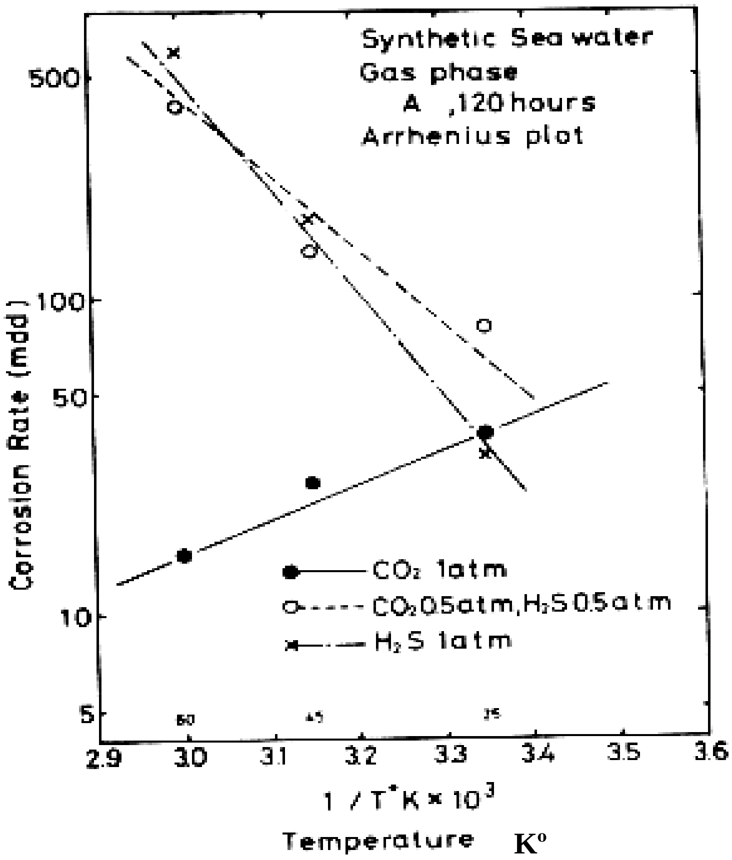


Figure (3) Temperature and gas composition dependence on the corrosion rate.

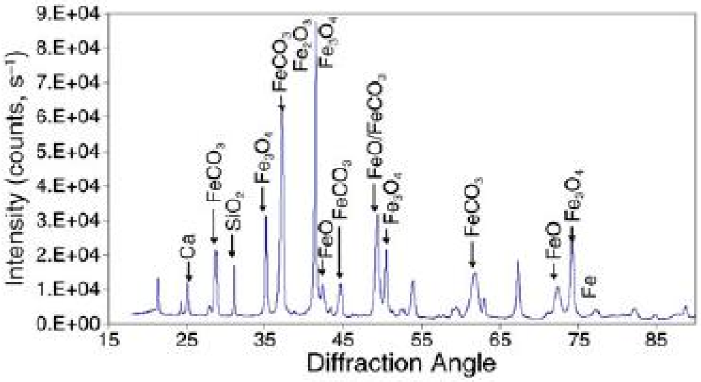


Figure (4) X-Ray Diffraction 0f surface layer.

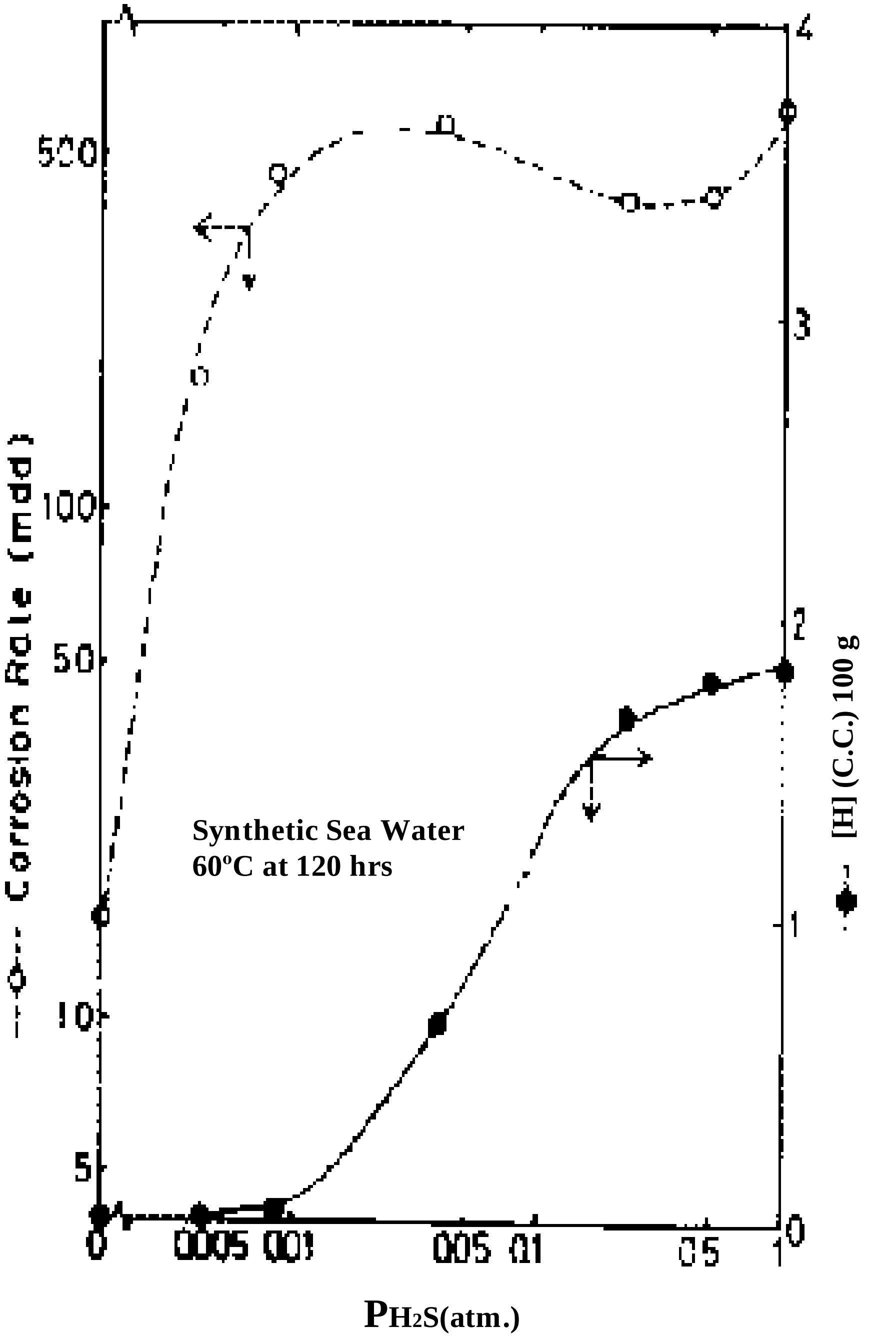


Figure (5) Effect of partial pressure of H_2S on the corrosion rate and hydrogen content at 60 °C.

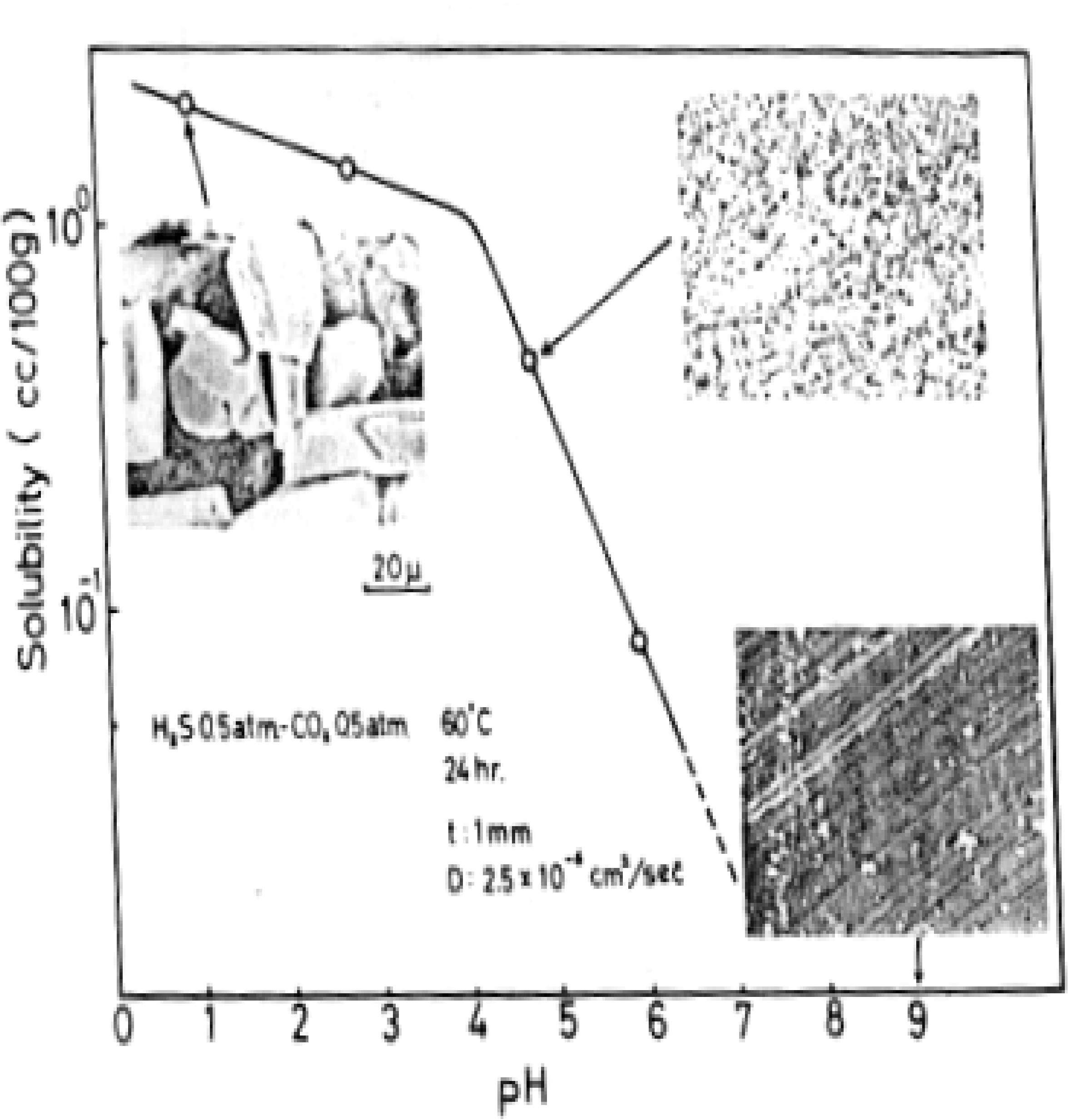
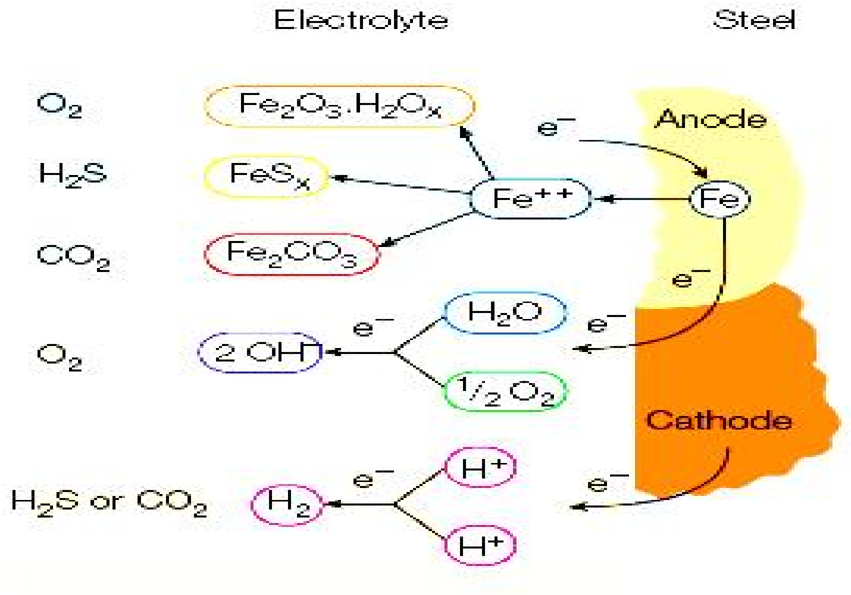


Figure (6) Relationship between pH containing environments and hydrogen entry for pipeline steel and the related surface observation.

{A}



{ B }

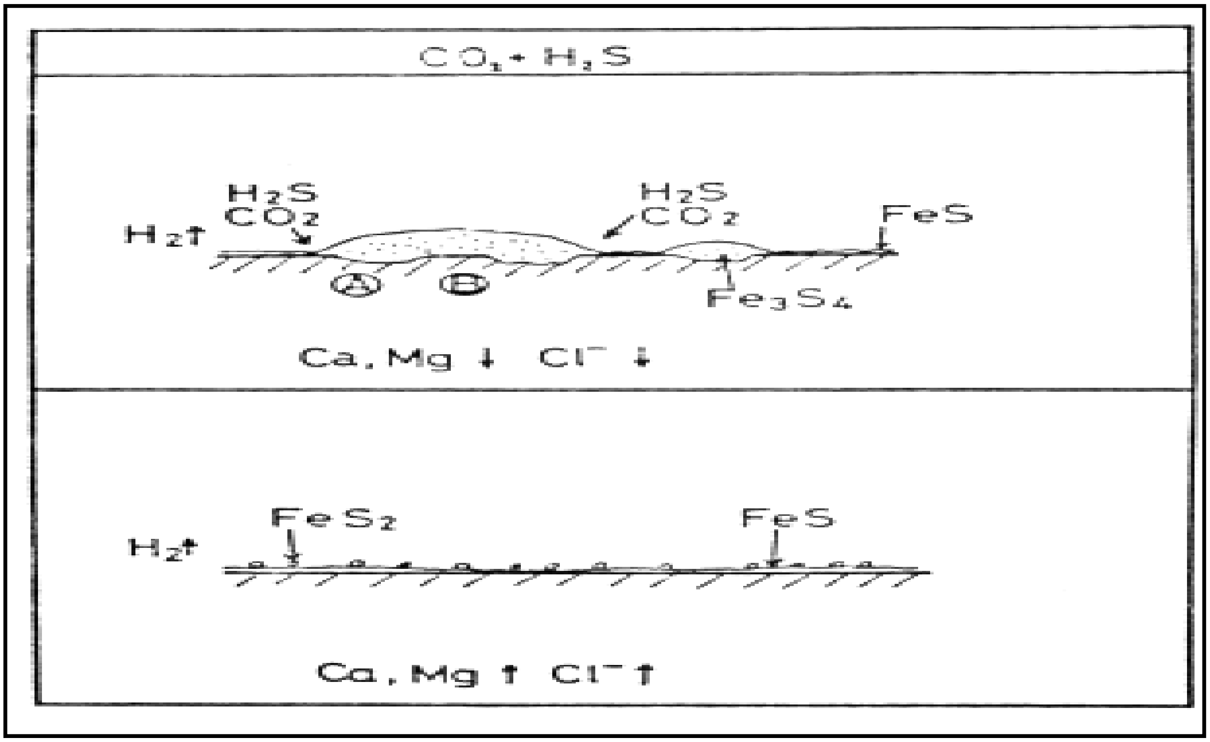


Figure (7) Schematic illustration of the Corrosion reaction in CO_2 H_2S brine system