

Mechanistic Modelling of Hydrogen Sulphide and Carbon Dioxide Corrosion of Pipes Conveying Petroleum Crude-Oil and Gas

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Abstract

Although, corrosion of pipelines conveying petroleum crude-oil and gas is an electrochemical process, it however, involves several chemical reactions occurring in the bulk solution, prior to the surface of the metal. The occurrence of these chemical reactions can alter significantly the rate of the electrochemical processes at the metal's surface; especially when as a result of high local concentrations of reacting species, the solubility limit of the product formed (iron carbonate or/and iron sulphide) is exceeded and the precipitation of inhibiting surface films occurs on the metal's surface. Thus, this paper investigated the effects of the chemical reactions on the rate of corrosion of steel pipes conveying petroleum crude-oil and gas with the presence of hydrogen sulphide (H₂S) and carbon dioxide (CO₂). The results affirmed what were reported in the literature that corrosion of steel pipes is as a result of the formation of acidic solution due to the transportation of hydrogen sulphide (H₂S), carbon dioxide (CO₂) and water along with the crude oil and gas. In addition, it also ascertained that corrosion severity depends on the pH of the solution, and the higher the pH value, the less severe the corrosion. In other words, corrosion occurs at a faster rate in acidic pH, compared to neutral and alkaline pH. It further established that H₂S corrosion is more severe than that of CO₂, and also, pipeline corrosion could be catastrophic leading to failures of pipelines and environmental pollution, etc. due to open cracks formed.

Keywords: Corrosion; Hydrogen sulphide; Carbon dioxide; Pipeline; Oil and gas

Introduction

With most crude oil and natural gas from oil reservoirs/ gas wells containing some amount of carbon dioxide (CO₂) and hydrogen sulphide (H₂S), oil and gas pipelines are prone to experience stress induced cracking (SIC) due to the partial pressure of CO₂ and/or H₂S [1]. Steel pipes corrode in acidic solution [2-9], and acidic solution is formed in pipelines due to the transport of water along with carbon dioxide or/and hydrogen sulphide (CO₂ and/or H₂S) at certain conditions [10]. This causes several severe problems in pipes, including strength reduction, life-span reduction, loss of metallic properties, wastage of metal, production losses and loss of life [11-13]. The extent of corrosion of pipelines depends on several factors including operating parameters (such as temperature, pH, partial pressure, composition/ mole fraction), multiphase flow, water chemistry, flow velocity, oil or/and water wetting and composition, surface condition of the steel, and the types and properties of the corrosion products formed [14]. Although, corrosion is an electrochemical process, it however, involves several chemical reactions occurring in the bulk solution, prior to the surface of the metal [15]. The occurrence of these chemical reactions can alter significantly the rate of the electrochemical processes at the metal's surface; especially when as a result of high local concentrations of reacting species, the solubility limit of the product formed (iron carbonate or/and iron sulphide) is exceeded and the precipitation of inhibiting surface films occurs on the metal's surface. Thus, this paper investigates the effects of the chemical reactions on the rate of corrosion of steel pipes due to the flow of H₂S and a combined H₂S and CO₂.

Model Formulation of Hydrogen Sulphide (H₂S) Corrosion of Oil and Gas Pipelines

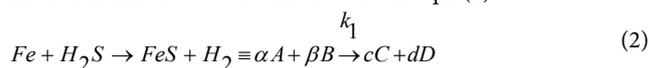
Model formulation

Eqn. (1) was obtained by performing a special balance on the steel with the following assumptions: mass conservation, open system, steady state i.e. no accumulation and constant reaction rate.

$$\frac{dC_A}{dt} = (-r_a) \quad (1)$$

Where a is Fe, $(-r_a)$ is the consumption rate of Fe, and $\frac{dC_A}{dt}$ is the rate of change of Fe.

The process of transporting Hydrogen sulphide and water in pipes conveying petroleum crude oil and gas is a continuous process and therefore, it was assumed that the iron (Fe) component of the pipe is the limiting specie as Hydrogen sulphide is continuously being supplied together with the transporting crude-oil and gas. Hence, a Pseudo order reaction kinetics was assumed to obtain eqn. (3).



$$(-r_A) = -K_1 C_A^\alpha \quad (3)$$

$$\text{Where } K_1 = k_1 C_B^\beta \quad (4)$$

Where A is the iron specie (Fe), B is the Hydrogen Sulphide (H₂S), C is the Iron Sulphide (FeS), D is the Hydrogen (H₂) specie, α is the number of moles of Iron reacted i.e. the order of reaction in respect to the iron specie, β is the number of moles of Hydrogen sulphide reacted, c is the number of moles of Iron sulphide produced, d is the number of moles of hydrogen gas produced, k_1 is the reaction kinetic specie, C_A is

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the concentration of Iron, and C_B is the concentration of H_2S .

Eqns. (5) and (6) were obtained by solving eqn. (1).

$$\text{For } \alpha = 1, t = \frac{1}{K_1} \left[\ln(C_A) \right]_{C_A}^{C_{Ao}} \equiv \frac{1}{K_1} \ln \left(\frac{C_{Ao}}{C_A} \right) \quad (5)$$

$$\text{For } \alpha \neq 1, t = \frac{1}{K_1} \left[\frac{C_A^{(\lambda+1)}}{(\lambda+1)} \right]_{C_A}^{C_{Ao}} \quad (6)$$

Where λ is $-\alpha$ and t is the corrosion reaction time.

Knowing the kinetics parameters i.e. Pseudo order reaction constant (K_1) and concentration of the steel pipe (C_A), eqns. (5) and (6) could be used to describe and predict the corrosion rate and time required for the complete depletion of the steel pipe. However, due to the complexity of deducing the concentration of the iron component of the steel with time, eqns. (5) and (6) were converted into dimensionless equations (eqns. (8) and (9)) via defining a dimensionless term, known as conversion (X), as the ratio of the amount of iron reacted to the amount of iron initially present.

$$X = \frac{(C_{Ao} - C_A)}{C_{Ao}} \quad (7)$$

$$\text{For } \alpha = 1; t = \frac{1}{K_1} \ln \left(\frac{1}{1-X} \right) \quad (8)$$

$$\text{For } \alpha \neq 1; t = - \frac{1}{\left(K_1 \frac{C_{Ao}^\alpha}{C_{Ao}} \right)} \left[\frac{(1-X)^{(\lambda+1)}}{\lambda+1} \right]_0^X \quad (9)$$

Derivation of the kinetics parameters i.e. K_1 and α

Eqn. (1) was linearized (i.e. eqn. (10)) and used to extract H_2S corrosion kinetic parameters from the experimental work done by Koteswaran [16] at pH levels of 3, 7 and 10 (Figures 1-3).

$$\ln(-r_a) = \alpha \ln(C_A) + \ln(K_1) \quad (10)$$

Solution of formulated model of H_2S corrosion of oil and gas stainless steel pipes

The kinetic parameters shown in Table 1 were substituted in eqn. (9) to estimate the corrosion time for a given conversion of iron. This is shown in Figure 4.

From Figures 4 and 5, the following conclusions could be drawn:

- Corrosion of steel pipes is as a result of the formation of acidic solution.
- Acidic solution in petroleum crude oil and gas pipe is formed due to the transportation of hydrogen sulphide and water along with the crude oil and gas.

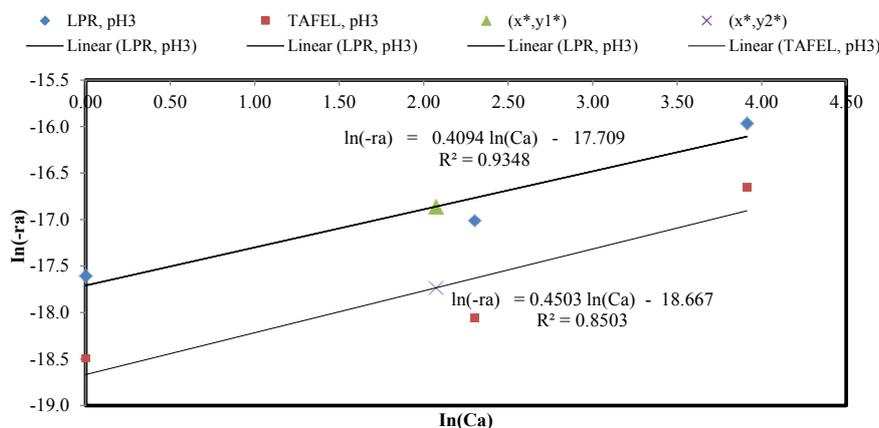


Figure 1: Extraction of H_2S Corrosion Reaction Kinetics at pH 3.

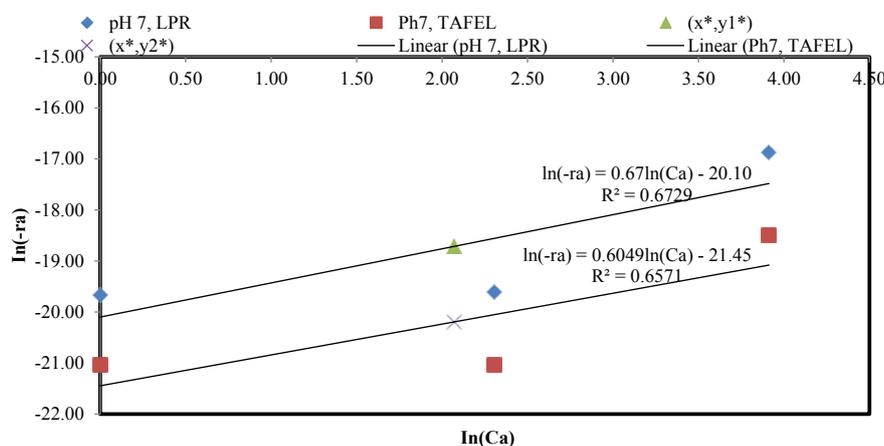


Figure 2: Extraction of H_2S Corrosion Reaction Kinetics Data pH 7.

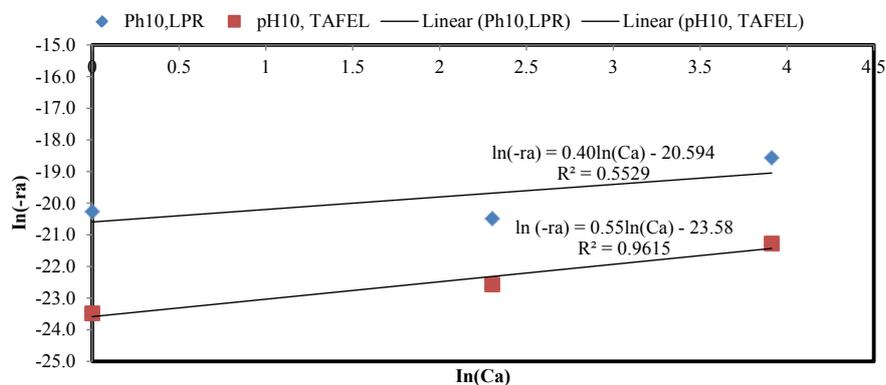


Figure 3: Extraction of H₂S Corrosion Reaction Kinetics Data pH 10.

pH	Average K ₁	Average α
3	1.410 × 10 ⁻⁸	0.430
7	1.178 × 10 ⁻⁹	0.637
10	5.976 × 10 ⁻¹⁰	0.437

Table 1: H₂S corrosion Kinetic Parameters from the Work done by Koteeswaran (2010) at pH Levels of 3, 7 and 10.

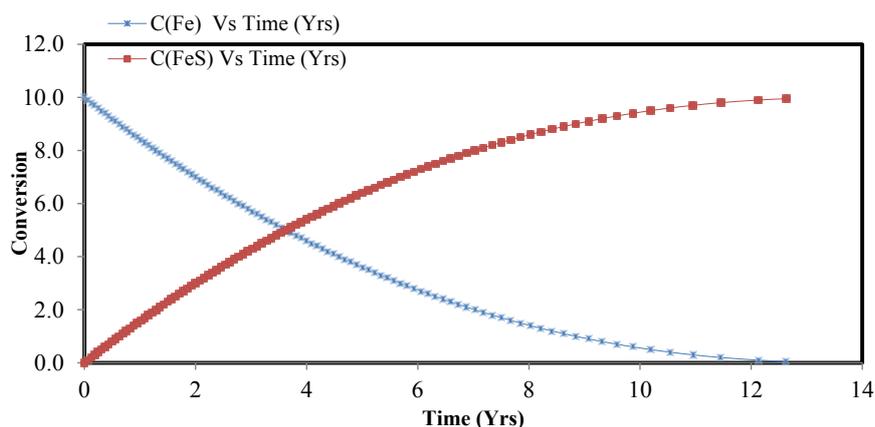


Figure 4: Conversion vs Time Graph for H₂S Corrosion, pH 3, Order = 0.372.

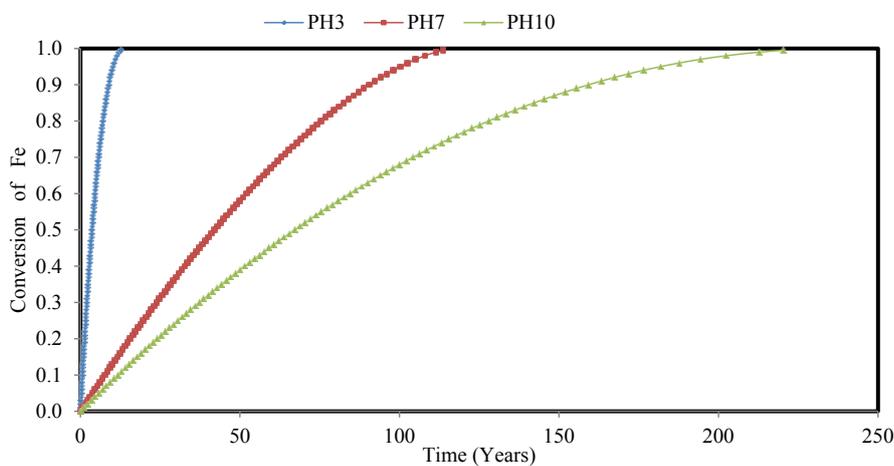


Figure 5: Conversion of Fe against Time at pH of 3, 7 and 10.

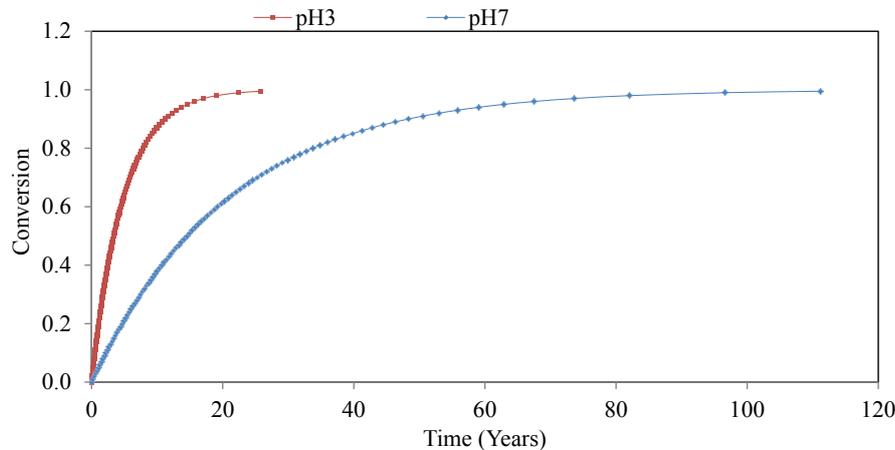


Figure 6: Conversion vs Time Graph for H₂S and CO₂ Corrosion, pH 3 and pH 7.

pH	K'
3	6.499 × 10 ⁻⁹
7	1.510 × 10 ⁻⁹

Table 2: Combine H₂S and CO₂ Corrosion Kinetics Parameters.

- Corrosion occurs at a faster rate in acidic pH, compared to neutral and alkaline pH; thus, the severity of corrosion depends on the solution's pH.
- Corrosion causes degradation and catastrophic failures of pipes as it can lead to open cracks; hence spillage of the pipe content i.e. crude oil, which would lead to environmental pollution.

Model Formulation of Hydrogen Sulphide (H₂S) and Carbon Dioxide (CO₂) Corrosion of Oil and Gas Pipelines

Model formulation

Using the same methodology as that of H₂S corrosion and assuming constant reaction rate constant and Pseudo First Order reaction kinetics, eqn. (11) was deduced.

$$\frac{d(C_A)}{dt} = (-r_a)_T = -K'C_{Fe} \quad (11)$$

$$\text{Where: } K' = (C_{CO_2}C_{H_2O} + KC_{H_2S}) = \left(C_{CO_2}C_{H_2O} + \frac{k_2}{k_1}C_{H_2S} \right) \quad (12)$$

Eqn. (11) was converted into dimensionless using the dimensionless parameter, conversion (X), and was solved to obtain eqn. (13)

$$t = \frac{1}{K'} \ln \left(\frac{1}{1-X} \right) \quad (13)$$

Derivation of the kinetics parameters i.e. K₁ and α

Corrosion rate experimental results data reported by Koteeswaran [16] and order of reaction 1 were substituted into eqn. (11) to deduce the K' values for pH 3 and 7. These values are tabulated in Table 2

Solution of formulated model of combined CO₂ and H₂S corrosion of oil and gas stainless steel pipes

The Kinetic parameters shown in Table 2 were substituted into eqn. (13) to deduce the conversion – time graph for the combined H₂S and CO₂ corrosion graph.

From Figure 6, the following conclusions could be drawn:

- Acidic solution that results in corrosion of petroleum crude oil and gas pipe could also be formed due to the transportation of carbon dioxide and water along with the crude oil and gas.
- Corrosion severity of carbon dioxide is greater than that of hydrogen sulphide.
- Corrosion occurs at a faster rate in acidic pH, compared to neutral and alkaline pH; thus, the severity of corrosion depends on the solution's pH.

Comparing Figures 5 and 6, it can be deduced that H₂S corrosion is more severe than that of CO₂ [17-20].

Conclusion

The results affirmed what was reported in the literature that corrosion of steel pipes occur as a result of the formation of acidic solution due to the presence of carbon dioxide, water and/or hydrogen sulphide in pipes. In addition, it also ascertained that corrosion severity depends on the pH of the solution, and the higher the pH value, the less severe the corrosion severity. Furthermore, it established that H₂S corrosion is more severe than that of CO₂. This is what was reported in the literature.

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