

STUDY OF THE INFLUENCE OF THE WATER pH ON THE DETERMINATION OF CORROSIVENESS OF PETROLEUM DERIVATIVE ON CARBON STEEL

V. Y. Nagayassu^{*1}, Z. Panossian² and M. M. Seckler³**Abstract**

Light petroleum derivatives consist of nonpolar hydrocarbons, which are aggressive to carbon steel due to the presence of water. In this study, we show both experimentally and theoretically that the water-phase pH during corrosion is controlled by the interaction of the aqueous phase with the atmospheric CO₂ and with iron corrosion products in both solution and precipitates. During the corrosion process, the pH of the solution changes, regardless of its initial value, towards a neutral value. This behaviour explains why the corrosiveness of a petroleum derivative emulsion is not influenced by the initial water-phase pH.

Keywords: Carbon Steel, Fuel Corrosiveness, Petroleum Derivate, Naphtha

ESTUDO DA INFLUÊNCIA DO pH DA ÁGUA NA DETERMINAÇÃO DA CORROSIVIDADE DE DERIVADOS DE PETRÓLEO AO AÇO-CARBONO

Resumo

Derivados claros de petróleo consistem de hidrocarbonetos não polares os quais são agressivos ao aço-carbono devido à presença de água. Neste trabalho, será mostrado experimentalmente e teoricamente que o pH da fase aquosa durante a corrosão é controlado pela interação da fase aquosa com o CO₂ atmosférico e com os produtos de corrosão de ferro tanto em solução, quanto no precipitado. Durante o processo de corrosão, o pH da solução varia, independentemente do seu valor inicial, no sentido de um valor neutro. Este comportamento explica a razão da corrosividade de uma emulsão de derivado de petróleo não ser influenciada pelo pH inicial da fase aquosa.

Palavras-chave: Aço-carbono, Corrosividade, Derivado de Petróleo, Nafta

1. INTRODUCTION

Light petroleum derivatives such as gasoline and naphtha consist mainly of nonpolar hydrocarbons, which are not aggressive to carbon steel in the absence of water [1,2]. However, these derivatives are often mixed with water, which is originated during the refining processing and during storage in nonhermetic tanks [1]. Water is slightly soluble in

light petroleum derivatives, and thus it partly emulsifies. The amount of emulsified water depends, among other factors, on the degree of stirring. A large amount of water may be kept emulsified as long as a high degree of stirring is maintained. When stirring ceases, the water droplets coalesce and form an aqueous phase beneath an organic phase. In such conditions, light petroleum derivatives become very corrosive to carbon steel. Knowledge of the corrosiveness of such petroleum derivative water emulsions is important in relation to the physical integrity of carbon-steel tanks and pipelines used for their storage and transportation, respectively. Therefore, before petroleum derivatives (gasoline and distillate fuels) are transported through pipelines, their corrosiveness is determined by means of the NACE standard TM-0172 [3]. This test consists of visual evaluation of the corroded area of carbon steel specimens (coupons) after their immersion for 4 h, under stirring, in the tested petroleum derivatives previously mixed with 10 % distilled water of pH 7.0. The degree of corrosiveness of the derivatives is given as the percentage of the specimen surface area that is corroded, as opposed to other methods that are based on the weight loss.

Today, the role of water in the corrosiveness of light petroleum derivatives is widely accepted. In view of the difficulty of preventing water intake, the corrosion is usually controlled in the petrochemical industry by adding corrosion inhibitors to the white petroleum derivatives. Thus, much research in this area focuses on the efficiency of corrosion inhibitors (a review on the subject is given in [4]).

An extensive literature search revealed that there are many fundamental studies related to crude petroleum-water mixtures, but studies related to petroleum derivative-water emulsions are rare. The interest in petroleum-water mixtures is probably due to the complexity of the formation water present in crude petroleum, which exhibits high concentrations of a great variety of dissolved salts and gases, such as chloride, CO₂ and H₂S [1, 5 - 8], while the water in light petroleum derivatives presents a lower concentration of corrosive impurities [1,9].

Kirkov [9] has mentioned that the solubility of oxygen and ionic species is very low in petroleum derivatives, and thus the expected corrosion rates

³ Universidade de São Paulo, Escola Politécnica, Departamento de Engenharia Química, 05508-010, São Paulo, Brasil, e-mail: mseckler@abeq.org.br
* A quem a correspondência deve ser dirigida, e-mail: vann@ipt.br

of carbon steel are very low. He pointed out that the presence of moisture in petroleum derivatives increases the rate of carbon steel corrosion to a higher degree than that in which HCl affects the dissolution of metals in an aqueous solution. According to Kirkov, this fact indicates that the mechanism of metal corrosion in a light petroleum derivative is a more complex phenomenon than the electrochemical processes of metal dissolution in aqueous solutions.

The deleterious effect of moisture on the corrosiveness of petroleum derivatives was argued by Foroulis [1] as well as by Groysman and Erdman [2], however, the role of oxygen was not. According to these authors, the solubility of oxygen in crude oil is very low, but it becomes considerably high in light refined products such as gasoline and naphtha, reaching values between 60 ppm and 70 ppm. These values are much higher than the solubility of oxygen in water which is almost 8 ppm. The oxygen solubility in different nonaqueous fluids was investigated by Hale [10], who confirmed the high solubility of oxygen in light hydrocarbons.

Groysman and Erdman [2] concluded that the main cause of the corrosiveness of light petroleum products (naphtha and gasoline) is the presence of water and dissolved oxygen. They found that the corrosion mechanism in the naphtha-water or gasoline-water mixtures was similar to the mechanism of atmospheric corrosion under a wet film of electrolyte. In this case, naphtha and gasoline provided a reservoir of oxygen (instead of the atmosphere) and corrosive species such as chlorides, sulphates, nitrates and organic acids. In some instances, naphtha can also be considered as a reservoir of corrosive organic compounds, which are produced by its bacterial degradation [11,12].

From the above discussion, it appears that the corrosiveness of petroleum derivative emulsions has been generally associated with the presence, in the aqueous phase, of dissolved oxygen, of compounds transported from the organic phase and of organic compounds produced

by bacterial activity. Given the low concentrations of such corrosive impurities [1,9], it is likely that the composition of the aqueous solution is also influenced by its interaction with external systems other than the petroleum derivatives, such as the air and the metal surface with, for example, the atmospheric carbon dioxide and corrosion products such as iron hydroxides, respectively. These compounds participate in chemical reactions in the aqueous phase that may consume or produce hydroxyl ions, thereby affecting the water pH.

In Brazil, the residual water found in pipelines is often of an acidic nature (pH of about 4). Therefore, the NACE method has been modified by the local oil industry to better simulate this condition: the distilled water added to the derivatives is previously acidified to a pH of 4.5 with HCl.

Surprisingly, Ferreira *et al.* [13] found experimentally that the pH does not affect the corrosiveness of such emulsions. We also came to the same results in a comprehensive study that took into account, in addition to the water pH, the water amount, temperature, stirring intensity and corrosion time [14]. In the present work, we further investigate the effect of the water pH on the corrosion of carbon steel in the presence of petroleum derivative emulsions. We explain, both experimentally and theoretically, how the interactions of the water-phase with atmospheric carbon dioxide and with the corrosion products determine the solution pH in the course of the corrosion process.

2. EXPERIMENTAL

All the experiments were conducted using commercial grade naphtha and distilled water following the NACE TM-0172 [3] test method. Therefore, all the materials and equipment described in the test method were used, which included a cylindrical AISI 1020 carbon steel specimen with a conical base (81.0 mm x 12.7 mm), a grinding and polishing apparatus, a modified 400 mL Berzelius-type glass beaker (Fig. 1a), an appropriate beaker cover, a rust-preventing oil bath and a thermometer.

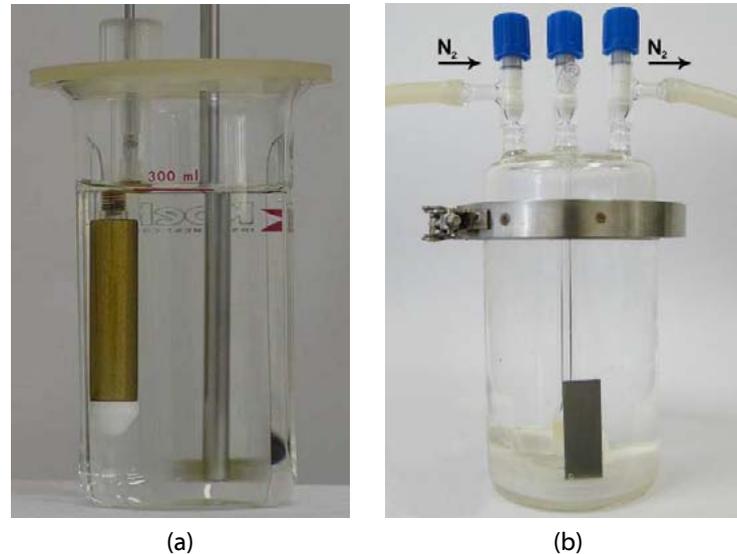


Fig. 1 – Immersion experiments in naturally aerated distilled water using a modified 400 mL Berzelius type glass beaker (a) and in nonaerated distilled water using an hermetic cell with a cover provided with valves which were used to introduce ultrapure nitrogen gas (b)

The NACE test method [3] presents a step-by-step test procedure. A brief description of this procedure is as follows:

- a. Specimen preparation:** the specimens were cleaned with acetone, mounted in the chuck of the grinding and polishing apparatus and rotated at speeds ranging from 1,700 rpm to 1,800 rpm while a 100 grit J-weight silicon carbide abrasive cloth was applied. The polishing was done until a uniform, finely scratched surface free from longitudinal scratches was obtained.
- b. Testing procedure:** 300 mL of the petroleum derivative to be tested was added into the beaker, and the beaker was placed in the oil bath, which was maintained at a temperature that kept the petroleum derivative at (38 ± 1) °C. The cover, the specimen, the thermometer and the stirrer were adequately installed, and the petroleum derivative was submitted to stirring at $(1,000 \pm 50)$ rpm for 30 min to ensure complete wetting of the steel specimen. After 30

min, distilled water (30 mL) was added. The stirring was maintained for a 3.5-hour period. After the completion of the test, the stirring was stopped and the specimen was removed. The specimen was washed with xylene followed by acetone.

- c. Classification of the tested petroleum derivative corrosiveness:** each specimen was inspected with a lighted glass of 2x magnification, and its corroded area was visually estimated.

Initially, the effects of the following variables on the corrosiveness of naphtha-water emulsions were studied: water-phase pH, water amount, temperature, stirring intensity, test period and carbon steel specimen geometry.

Simple immersion experiments in naturally aerated distilled water with different pH values were also conducted using the above-mentioned beaker (Fig. 1a). Additionally, an immersion experiment in nonaerated distilled water was conducted using an hermetic cell with a cover, which was provided with valves made of glass and polytetrafluoroethylene (PTFE), which were used to introduce ultrapure nitrogen gas to the tested water (Fig. 1b). In the interior of the cell, a test specimen holder made of polytetrafluoroethylene (PTFE) was inserted. The latter experiment was conducted using an AISI 1020 carbon steel plate (60 mm x 20 mm). In these experiments, the above-mentioned specimen preparation procedures were adopted.

Diluted hydrochloric acid and sodium hydroxide solutions were used to vary the water pH. All the reagents used were analytical grade.

The corrosion product composition was determined by X-ray diffraction using a Rigaku, model RINT 2000.

3. RESULTS

An experimental design with all considered variables was executed. Table 1 shows the selected variables and their levels. It was found that 216 experiments would be needed. To reduce the number of experiments, an asymmetric fractional factorial design of $3^3 \cdot 2^3 / 36$ was implemented. Thus, it was possible to evaluate the main effects and the interactions between two factors (independent variables) in an answer expressed as the percentage of a corroded area of carbon steel specimens (dependent variable). Table 2 shows the established design of the experiments. Each independent variable assumed all the levels considered, taking into account, as mentioned previously, combinations of each of the two selected factors.

Table 1 - Studied variables and their values.

Variable name	Level 1	Level 2	Level 3	Number of levels
Stirring intensity	Intermittent stirring	Continuous stirring 1050 rpm	-	2
Geometry of solid specimen	Cylinder with flat base	Cylinder with conic base	-	2
Temperature	25 °C	38 °C	-	2
Water content	5 %	10 %	20 %	3
Time	4 h	8 h	16 h	3
Water pH	4.5	7.0	10.0	3
Number of experiments = product of levels = 2×2 ×2 ×3 ×3 ×3 = 23×33 =				216

Table 2 - Established experimental designs.

Random run	Standard run	Stirring	Geometry	T (°C)	Water (%)	t (h)	Initial pH	Corroded area (%)
05	01	Intermittent	Cylindrical	25	5	4	4.5	82
03	02	Intermittent	Cylindrical	25	10	8	7.0	90
21	03	Intermittent	Cylindrical	25	20	16	10	65
32	04	Intermittent	Cylindrical	25	5	4	4.5	90
36	05	Intermittent	Cylindrical	25	10	8	7.0	83
24	06	Intermittent	Cylindrical	25	20	16	10	68
14	07	Intermittent	Cylindrical	38	5	4	7.0	90
30	08	Intermittent	Cylindrical	38	10	8	10	95
15	09	Intermittent	Cylindrical	38	20	16	4.5	65
25	10	Intermittent	Conic	25	5	4	10	100
17	11	Intermittent	Conic	25	10	8	4.5	88
19	12	Intermittent	Conic	25	20	16	7.0	75
01	13	Intermittent	Conic	38	5	8	10.0	88
13	14	Intermittent	Conic	38	10	16	4.5	92
11	15	Intermittent	Conic	38	20	4	7.0	55
09	16	Intermittent	Conic	38	5	8	10	95
10	17	Intermittent	Conic	38	10	16	4.5	95
16	18	Intermittent	Conic	38	20	4	7.0	65
33	19	Continuous	Cylindrical	38	5	8	4.5	95 (cont.)

Table 2 (cont.) - Established experimental designs.

Random run	Standard run	Stirring	Geometry	T (°C)	Water (%)	t (h)	Initial pH	Corroded area (%)
34	20	Continuous	Cylindrical	38	10	16	7.0	85
27	21	Continuous	Cylindrical	38	20	4	10.0	73
04	22	Continuous	Cylindrical	38	5	8	7.0	88
02	23	Continuous	Cylindrical	38	10	16	10.0	88
08	24	Continuous	Cylindrical	38	20	4	4.5	60
22	25	Continuous	Cylindrical	25	5	16	7.0	94
12	26	Continuous	Cylindrical	25	10	4	10.0	77
28	27	Continuous	Cylindrical	25	20	8	4.5	77
18	28	Continuous	Conic	38	5	16	7.0	96
23	29	Continuous	Conic	38	10	4	10.0	68
20	30	Continuous	Conic	38	20	8	4.5	73
31	31	Continuous	Conic	25	5	16	10	95
35	32	Continuous	Conic	25	10	4	4.5	85
29	33	Continuous	Conic	25	20	8	7.0	77
07	34	Continuous	Conic	25	5	16	4.5	96
26	35	Continuous	Conic	25	10	4	7.0	85
06	36	Continuous	Conic	25	20	8	10	63

The results obtained for the experiments shown in Table 2 were analysed, and, among other conclusions described elsewhere [4, 14], no influence of the water-phase pH on the corroded area was found. Similar results were found by Ferreira *et al.* [13]. These results were unexpected because it is widely known that acidic media are more aggressive to carbon steel than neutral and alkaline solutions. To clarify this unexpected behaviour, the results related to water pH influence were carefully analysed. Thus, the water pH values after completion of the experiments conducted under the 36 described conditions were compared to the pH values before the experiments, as shown in Table 3.

Observation of Table 3 reveals that:

- Regardless of the initial pH, the aqueous phase tended to assume a value close to neutral.
- In general, the final pH values for experiments initiated with acidified water were slightly lower than those initiated with neutral or alkaline water.

Three additional experiments were conducted, each of which utilised initial water pH values of 4.5, 7.0 and 10.0, for which the pH of the aqueous phase was measured every 10 minutes. The results are shown in Fig. 2.

Table 3 - pH values before and after the naphtha-water emulsion corrosiveness experiments conducted under the 36 conditions presented in Table 2.

Run	pH before	pH after	Run	pH before	pH after	Run	pH before	pH after
01	4.5	6.60	02	7.0	7.47	03	10.0	7.91
04	4.5	6.87	05	7.0	7.19	06	10.0	7.87
09	4.5	7.08	07	7.0	7.27	08	10.0	7.54
11	4.5	6.81	12	7.0	8.02	10	10.0	7.68
14	4.5	7.35	15	7.0	7.39	13	10.0	7.73
17	4.5	6.86	18	7.0	7.51	16	10.0	7.95
19	4.5	6.77	20	7.0	7.49	21	10.0	7.44
24	4.5	6.70	22	7.0	7.49	23	10.0	7.85
27	4.5	5.94	25	7.0	7.58	26	10.0	8.10
30	4.5	6.62	28	7.0	7.82	29	10.0	8.31
32	4.5	6.42	33	7.0	7.28	31	10.0	7.59
34	4.5	7.50	35	7.0	7.19	36	10.0	8.02

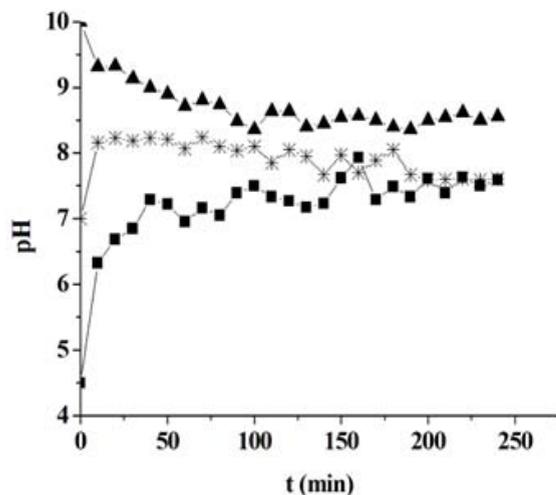


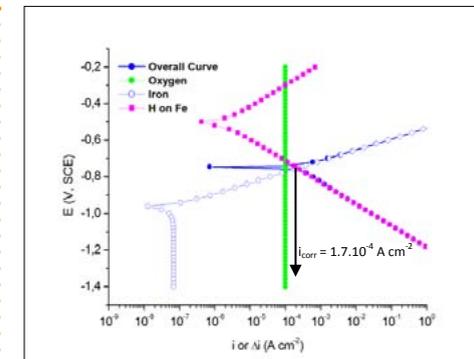
Fig. 2 - Variation of the water pH during the naphtha-water emulsion corrosiveness experiments with initial water pH values of 4.5, 7.0 and 10.0.

Observation of Fig. 2 shows that:

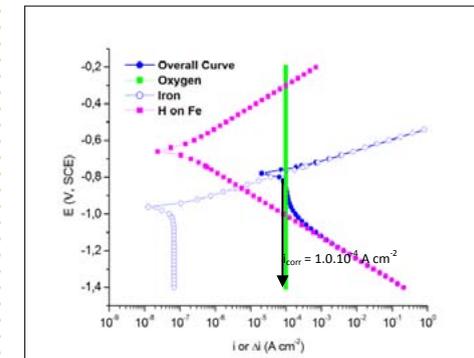
- For the three cases, the water pH varied towards a value close to neutral.
- For an initial water pH of 4.5, a rapid increase in water pH took place initially until a value close to neutral was reached. Subsequently, the pH stabilised close to neutral.
- For an initial water pH of 7.0, a fast initial increase in water pH took place. In this case, it occurred until a pH value of about 8.0 was reached. Subsequently, the pH decreased slowly towards values close to neutral.
- For an initial water pH of 10.0, the pH dropped rapidly at first, and thereafter it decreased slowly towards values slightly higher than neutral.

Firstly, the issue was raised about the nature of the cathodic reaction: in the experiments, an intense stirring was applied, and thus the water added to the derivative became saturated in oxygen, leading to the supposition that oxygen reduction would be the predominant cathodic reaction. The only exception may be the experiment with initial water pH of 4.5. At this pH, hydrogen reduction also may occur. However, as can be seen in Fig. 2, in the beginning of this experiment, a deep increase of the pH occurred reaching values higher than 6.0. At this pH, the main cathodic reaction is also the oxygen reduction.

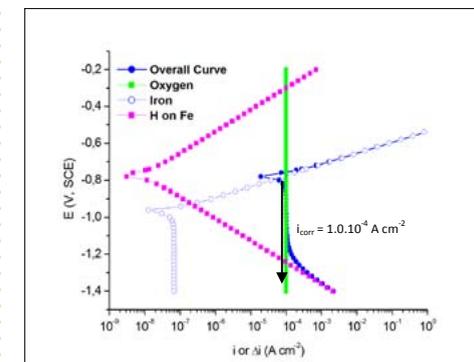
In order to verify this hypothesis, polarisation curves were experimentally determined for carbon steel immersed in water in stirring conditions similar to the experiments. The limiting current found for oxygen reduction was of the order of $1.10 \cdot 10^{-4} \text{ A} \cdot \text{cm}^{-2}$. Using this information and the electrochemical parameters (shown in Fig. 3) of the corrosion reactions of carbon steel, theoretical polarisation curves were built for the three pH values considered. These curves are shown in Fig. 3.



a) pH=4.5



b) pH=7.0



c) pH=10.0

Fig. 3 - Theoretical polarization curves for carbon steel in distilled water, for a limiting current density of oxygen of $1.10 \cdot 10^{-4} \text{ A} \cdot \text{cm}^{-2}$ and pH values of 4.5, 7.0 and 10.0.

The electrochemical parameters used in Fig.3 were [15]:

$$E_{H^+/H_2} = (-0.059\text{pH} - 0.241) \text{ V, SCE}$$

$$i_{o(H^+/H_2 \text{ on Fe})} = 10^{-6} \text{ A cm}^{-2}$$

$$b_{a(H^+/H_2)} = \left| b_{c(H^+/H_2)} \right| = 0.118 \text{ V / decade}$$

$$E_{Fe^{2+}/Fe} = -0.865 \text{ V, SCE for } a_{Fe^{2+}} = 10^{-6} \text{ mol L}^{-1}$$

$$i_{o(Fe^{2+}/Fe)} = 3.6 \times 10^{-6} \text{ A cm}^{-2} \text{ for } a_{Fe^{2+}} = 10^{-6} \text{ mol L}^{-1}$$

$$b_{a(Fe^{2+}/Fe)} = \left| b_{c(Fe^{2+}/Fe)} \right| = 0.059 \text{ V / decade}$$

Fig. 3 shows that, for water pH values of 7.0 and 10.0, the reaction of oxygen reduction determines the rate of carbon steel corrosion, whereas the influence of the hydrogen cation reduction is expected for the pH of 4.5. However, as the water pH rapidly approaches neutrality, the action of hydrogen reduction becomes negligible.

Based on the above results, it was concluded that the reaction of oxygen reduction is indeed the predominant cathodic reaction for water pH values of 4.5 to 10.

The following questions still remain:

- Why does the water pH tend to reach a value close to neutral, regardless of the initial pH?
- Is this variation of water pH related to some action of the petroleum derivatives?

To investigate these questions, three additional experiments were performed with distilled water, without a petroleum derivative addition, with water pH values of 4.5, 7.0 and 9.5, adopting a stirring speed of 1,050 rpm and a temperature of 25 °C. For each experiment, the water pH was measured every 10 minutes. Additionally, the pH was measured at the end of the experiments before and after boiling the aqueous solution.

The results are shown in Fig. 4. The pH variation with time was almost the same as in the case of the petroleum derivative-water emulsion presented previously (Fig. 2). Therefore, the variations in water pH are not related to the presence of the derivatives. Fig. 4 also shows that, in all cases, the water pH changed after boiling. The water pH being affected by the absorption of carbon dioxide from the atmosphere is a well-known fact.

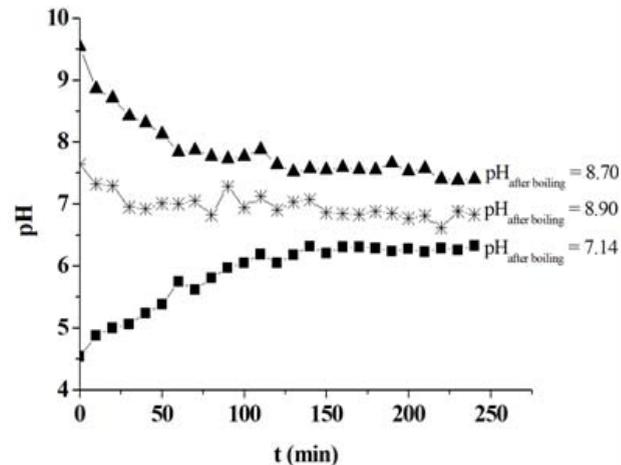


Fig. 4 – Variation of the water pH with time for experiments without addition of petroleum derivatives and with immersion of carbon steel specimen in distilled water with different initial water pH values.

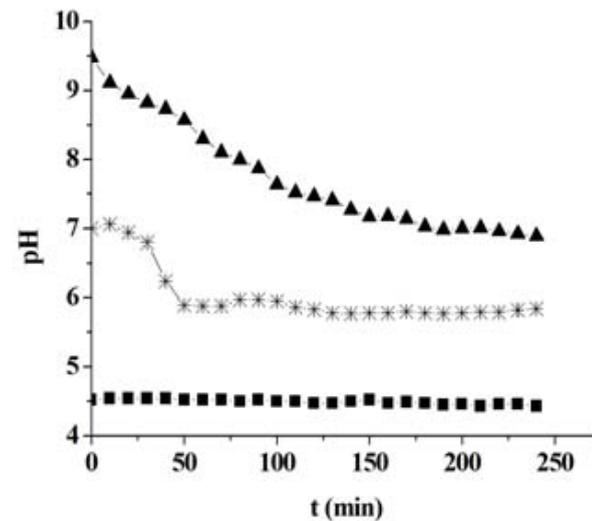


Fig. 5 – Variation of water pH with time for experiments without a petroleum derivative and without a carbon steel specimen.

The following question still needs an explanation: is the water pH variation towards neutral values somehow related to carbon steel? To answer this question, three additional experiments were performed, similar to the previous ones, but in the absence of the carbon steel specimen. The water pH was measured every 10 minutes. The results are shown in Fig. 5.

Fig. 5 shows that, for the initial water pH value of 9.5, the pH decreased with and without the carbon steel specimen, showing that this behaviour does not depend on the presence of carbon steel (compare with Fig. 2), unlike the experiment at a water pH of 4.5 and 7.0. For the latter, an initial increase followed by a slow decrease was observed in the presence of the carbon steel specimen (Fig. 2) and only a decrease of the pH was observed without the carbon steel specimen. The initial increase in the presence of carbon steel is a consequence of the alkalization resulted from the reduction of dissolved oxygen due to the corrosion process and the decrease for both experiments is due to carbon dioxide absorption.

In the case of pH 9.5, an initial alkalization in the presence of the carbon steel specimen is not observed because the ferrous ions generated by the corrosion reaction reacted with the hydroxyl ions generated by the oxygen reduction because the pH is higher than 9.2.

For a water pH of 4.5, no change in the pH was observed without the carbon steel specimen (Fig. 5) and an increase of the pH is observed in the presence of carbon steel specimen (Fig. 2).

It is convenient to mention that in all experiments described up to this point, the corrosion products adhering to the surface of the specimens as well as those in solution assumed a reddish colour, indicating the presence of ferric ions, which was actually expected, as all experiments were performed in open cells under intense stirring and therefore in aerated media. For confirmation, the corrosion products formed at the surface of one specimen, as well as those present in the aqueous solution, were analysed by X-ray diffractometry. The corrosion products were found to be composed of ferric oxides containing ferrous oxides, namely:

- surface products: lepidocrocite (basic iron III oxide), magnetite (oxide of iron II and III) and maghemite (oxide of iron III);
- aqueous phase product: lepidocrocite.

4. THEORY AND DISCUSSION

The theoretical analysis to elucidate the results obtained in all experiments was done by considering the following systems: pure water in contact with the atmosphere (aerated condition), pure water in contact with iron and with (aerated condition) and without (nonaerated condition) contact with the atmosphere and pure water in contact with iron and with a CO₂-free atmosphere (aerated).

Variation of the pH of pure water in contact with the atmosphere (Aerated Condition)

The experiments shown in Fig. 5 were conducted using distilled water with three different pH values in contact with atmospheric air, i.e., in a natural aerated condition. In these cases, the observed pH variation can only be attributed to the absorption of atmospheric CO₂.

Carbon dioxide is present in the atmosphere in concentrations of about 0.03 % [16]. This gas dissolves in water and reacts with it, forming carbonic acid (H₂CO₃), which in turn dissociates to form the bicarbonate ion HCO₃⁻ and the carbonate ion CO₃²⁻. Table 4 presents the main reactions occurring among the species present in the H₂O-CO₂ system as well as the equilibrium constants and concentrations (partial pressures).

Table 4 - Possible reactions in the H₂O - CO₂ system [16,17].

Species/or reaction	Data
CO _{2(g)} ^α	In the atmosphere at sea level ≈ 0.03 % P _{CO₂} = 3.10 ⁻⁴ atm ^α
CO _{2(g)} + H ₂ O ⇌ H ₂ CO ₃ ^α	K = $\frac{[H_2CO_3]}{P_{CO_2}}$ = 26.9
CO _{2(g)} + H ₂ O ⇌ CO ₃ ²⁻ + 2H ⁺ ^α	K = $\frac{[HCO_3^-].[H^+]}{P_{CO_2}}$ = 0.15.10 ⁻⁷
CO _{2(g)} + H ₂ O ⇌ HCO ₃ ⁻ + H ⁺ ^α	K = $\frac{[CO_3^{2-}].[H^+]^2}{P_{CO_2}}$ = 0.72.10 ⁻¹⁸
H ₂ O ⇌ H ⁺ + OH ⁻ ^α	[H ⁺].[OH ⁻] = 10 ⁻¹⁴ α

Table 4 shows that the determination of the equilibrium pH requires the solution of a system of nonlinear equations. To this end, the method of intuitive approximation can be applied [18] in combination with simplifying hypotheses. The consistency of the solution is verified against the original equations. If the solution is unacceptable (because the hypotheses are not suitable), successive approximations are performed until an acceptable solution is found. The solution in each attempt is used as a guess for the next attempt. A more complete and accurate solution is obtained numerically. As an example, the equilibrium pH value of distilled water with a pH of 7 in contact with atmospheric air was calculated using the method of intuitive approximation. This calculation is shown in Appendix A.

The software MINTQA2/PRODEFA2 [19] was used to calculate the equilibrium pH of the water in contact with atmospheric air for various initial water pH values (including pH of 7) to simulate the conditions found in the experiments of Fig. 5. The results are shown in Table 5.

Table 5 - Initial and final pH values of water in contact with atmospheric air. Experimental values along with values calculated with the software. MINTQA2/PRODEFA2 [19].

System	Input data	pH	
		Experimental	Calculated
Distilled water at pH 4.5 (with HCl) saturated with atmospheric CO ₂	P _{CO₂} = 3.10 ⁻⁴ atm [Cl ⁻] = 3.177.10 ⁻⁵ mol/L	4.43	4.50
Distilled water at pH 7.0 saturated with atmospheric CO ₂	P _{CO₂} = 3.10 ⁻⁴ atm	5.84	5.68
Distilled water at pH 9.48 (with NaOH) saturated with atmospheric CO ₂	P _{CO₂} = 3.10 ⁻⁴ atm [Na ⁺] = 3.054.10 ⁻⁵ mol/L	6.89	6.84

It can be seen that the estimated values when considering CO₂ absorption are very close to the experimental values. Therefore, one can conclude that the variations in water pH observed when distilled water is brought into contact with atmospheric air are due to CO₂ absorption. The absorption is more important for higher water pH and is negligible for acidic water.

Variation of the pH for pure water in contact with Iron and with (Aerated Condition) and without (Nonaerated Condition) contact with a CO₂-Free atmosphere
When an iron specimen is immersed in distilled water, even at pH 7.0, in contact with CO₂-free atmospheric air (aerated condition), several reactions take place; therefore, the calculation of the final pH is more complex than in the previous discussion where iron was absent. Table 6 shows some of the possible reactions in this system, after iron corrosion, as well as their equilibrium constants. The dissolved species considered were Fe²⁺, Fe³⁺, H⁺ and OH⁻, and the precipitated solids taken into account were Fe(OH)₂ and Fe(OH)₃. Actually, many other compounds can be formed, such as soluble complexes (e.g., FeOH⁺) or solids such as magnetite (Fe₃O₄), hematite (Fe₂O₃), goethite (α-FeOOH), lepidocrocite (γ-FeOOH) and ferrous oxide FeO. The simplification of adopting only Fe(OH)₂ or Fe(OH)₃ is justified based on the fact that the free energy of formation of the Fe³⁺ compounds (main constituents of the corrosion products) are of the same order of magnitude among each other, and similarly for the Fe²⁺ compounds [17, 20].

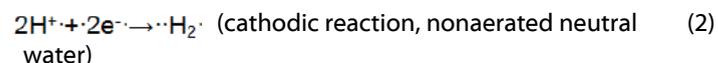
Table 6 - Possible reactions in the system Fe²⁺, Fe³⁺, OH⁻, H⁺, H₂O and their equilibrium constants [17, 21].

Species/Reaction	Equilibrium constants
H ₂ O ⇌ H ⁺ + OH ⁻	K = [H ⁺].[OH ⁻] = 10 ⁻¹⁴
Fe(OH) ₂ ⇌ Fe ²⁺ + 2OH ⁻	K _{ps} = [Fe ²⁺].[OH ⁻] ² = 2.10 ⁻¹⁶
Fe(OH) ₃ ⇌ Fe ³⁺ + 3OH ⁻	K _{ps} = [Fe ³⁺].[OH ⁻] ³ = 6.10 ⁻³⁸

To better understand the variations in water pH observed in the experiments of Fig. 4, two simplified conditions were considered: the Fe/H₂O system isolated from atmospheric air with a predominance of Fe²⁺ species and the same system in contact with CO₂-free atmospheric air with a predominance of Fe³⁺ species. Thereafter, the observed pH variations will be explained.

Fe/H₂O system isolated from atmospheric air (water with pH 7.0)

The reactions responsible for the iron corrosion are the following:



From the equations above, one can conclude that corrosion promotes the alkalisation of water, a well-established fact.

These reactions proceed until the solubility limit of Fe(OH)₂ is reached. At this point, precipitation of Fe(OH)₂ takes place, i.e.,

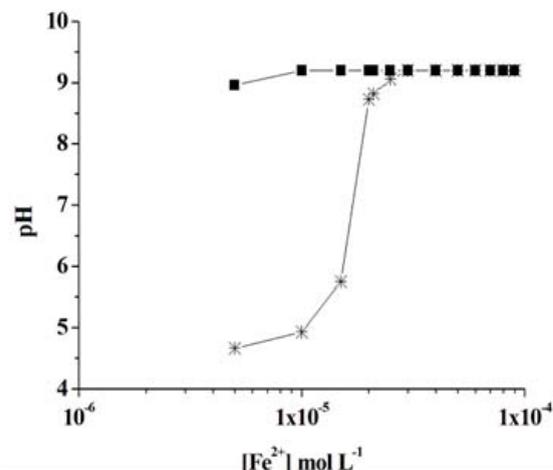


Once formed, solid Fe(OH)₂ remains in equilibrium with the soluble species that it originated from.

Using the method of successive approximations, it is possible to calculate the saturation pH for Fe(OH)₂, i.e., the pH at which Fe(OH)₂ precipitation starts (see Appendix B). A pH value of 9.2 was derived, which is the same as the literature value for the pH of a saturated Fe(OH)₂ solution [20].

During the corrosion of iron in water with pH 7.0, an increase of pH values is observed until the saturation point of Fe(OH)₂, which occurs at pH 9.2.

After this point, the water pH remains constant. Fig. 6 illustrates this



fact by means of calculations with the software MINTQA2/PRODEFA2 [19].

Fig. 6 – Dependency of pH of water in contact with iron. When Fe(OH)₂ precipitation starts the pH assumes a constant value of 9.2.

If the initial water pH were lower than 7.0, the same behaviour would be observed, i.e., the corrosion of iron would cause an increase in the pH and in the concentration of Fe²⁺ up to the solubility limit of Fe(OH)₂. The amount of Fe²⁺ ions necessary to reach saturation would be greater for smaller initial pH values.

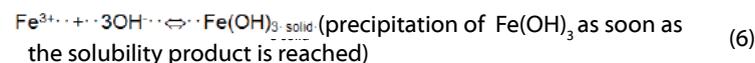
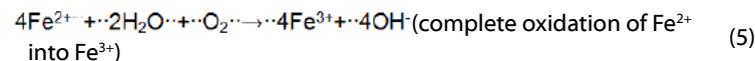
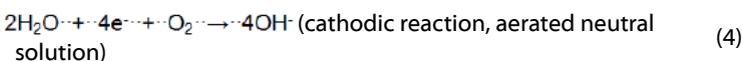
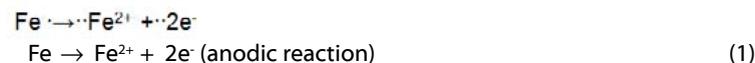
If the initial pH is higher than 9.2, the solution rapidly becomes supersaturated with respect to solid Fe(OH)₂ as soon as the corrosion starts. The pH might remain above 9.2 in a super saturation condition. However, after some time, Fe(OH)₂ precipitation takes place, with a consequent pH decrease to the equilibrium value of 9.2.

As an example, the amount of Fe²⁺ necessary for the formation of the first Fe(OH)₂ crystal in water, which has an initial pH of 9.5, is calculated below:

$$\begin{aligned} \text{pH} &= 9.5 \\ \text{pOH} &= 14 - 9.5 = 4.5 \\ [\text{OH}^-] &= 10^{-4.5} \\ [\text{Fe}^{2+}] \cdot [\text{OH}^-]^2 &= 2.10^{-15} \\ [\text{Fe}^{2+}] &= \frac{2.10^{-15}}{(10^{-4.5})^2} = 2.10^{-6} \text{ mol L}^{-1} \end{aligned}$$

Fe/H₂O system in contact with CO₂-Free atmospheric air (water with pH 7.0)

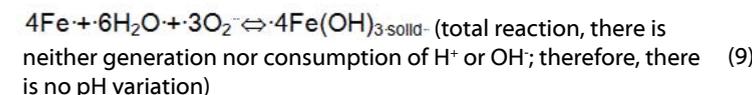
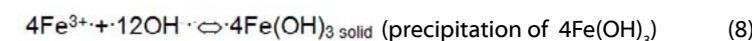
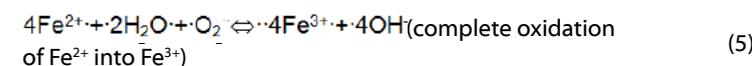
Under these conditions, the reactions responsible for iron corrosion are



It is possible to calculate, by the method of intuitive approximation, the equilibrium pH of this system by assuming that after oxidation of both metallic iron and the total amount of generated Fe²⁺ ions, precipitation of Fe(OH)₃ takes place immediately upon saturation of the solution (see

Appendix C). Once formed, solid Fe(OH)₃ remains in equilibrium with the soluble species that it originated from.

Because the solubility of Fe(OH)₃ is very low (see Table 6), all Fe³⁺ and OH⁻ ions produced by iron corrosion react with each other to form Fe(OH)₃, leaving the solution almost free of these ions. Therefore, iron corrosion in these circumstances would not cause the pH to change. This assertion can be better understood from the partial and total equations given below:



A very important fact to note is the oxidation of Fe²⁺ into Fe³⁺ ions. In practice, this reaction is never complete, so a residual amount of Fe²⁺ ions remains in solution. However, this reaction is favoured in acidic media because it produces OH⁻ ions. Therefore, during iron corrosion, the more acidic the solution, the more pronounced the oxidation of Fe²⁺ into Fe³⁺.

Fe/H₂O System in contact with CO₂-Free atmospheric air, with partial oxidation of Fe²⁺ into Fe³⁺ (water with pH 7.0)

The problem now proposed is very similar to the experiment shown in Fig. 4 after boiling. By application of the previously presented results to the Fe/H₂O system in contact with CO₂-free atmospheric air, the following reactions would take place:

a) **Step 1:** iron corrosion with generation of Fe²⁺ ions and consumption of H⁺ ions (or generation of OH⁻ ions). This process leads to a gradual increase of the solution pH.

b) **Step 2:** oxidation of some of the Fe²⁺ ions formed in Step 1 into Fe³⁺ ions, followed by precipitation of Fe(OH)₃. The formation of Fe³⁺ and the precipitation of Fe(OH)₃ do not by themselves alter the solution pH.

c) **Step 3:** saturation of the solution with Fe²⁺ ions and precipitation of Fe(OH)₂. From this point on, the solution pH remains at a value of 9.2.

Therefore, the final pH of the solution is governed by the amount of dissolved Fe^{2+} ions that have not yet been transformed into Fe^{3+} .

In short, when an iron specimen is immersed in water in contact with CO_2 -free atmospheric air, the water pH might, for a finite period of time, reach a value between the initial value and the saturation pH 9.2 for $\text{Fe}(\text{OH})_2$. The more alkaline the solution, the closer the pH approaches the $\text{Fe}(\text{OH})_2$ saturation value; the more acidic the solution, the closer the pH remains at the initial value.

Variation of the pH for pure water in contact with iron and with CO_2 -containing atmospheric air

Finally, it is necessary to consider the presence of CO_2 in the atmosphere. The system in question consists of an iron specimen immersed in pure water (pH 7.0) in contact with air, i.e., in contact with both O_2 and CO_2 .

The first question that arises is whether the CO_2 absorbed in the aqueous solution remains in dissolved form (HCO_3^- or CO_3^{2-}) or precipitates as Fe^{2+} or Fe^{3+} iron compounds, such as FeCO_3 ($K_{ps} = 3.13 \times 10^{-11}$) [22].

For pure water (pH 7.0), the amount of CO_3^{2-} present following atmospheric CO_2 absorption is very small, of the order of $3.75 \times 10^{-11} \text{ mol L}^{-1}$ (see Appendix A). The corresponding amount of Fe^{2+} ions necessary for FeCO_3 precipitation is very high, so it can be assumed that no precipitation occurs. Pourbaix[20] described an experiment in which an iron specimen was immersed in an aerated solution saturated with sodium bicarbonate (pH 8.4). Under these conditions, iron remains passive due to the formation of iron oxides/hydroxides upon its surface, without the formation of carbonate-containing compounds. In addition, simulations performed for the conditions of the experiment shown in Fig. 4 with the software MINTEQA2/PRODEFA2 [19] revealed that iron carbonate does not form.

Therefore, one can assume that under the experimental conditions investigated here, all carbonate absorbed from the air remains in dissolved form as HCO_3^- and CO_3^{2-} ions, the amount of the latter being negligible. Therefore, pH variations are consequences of CO_2 absorption, iron corrosion and the precipitation of iron oxides/hydroxides.

Discussion of the experimental results

The experimental results previously presented in Fig. 4 and Fig. 5 are summarised in Table 7. This table shows that water with a pH of 4.5 in contact with air does not undergo a change in pH. This finding is expected

because the only possible cause for pH variation is CO_2 absorption from air, which is negligible under these acidic conditions.

Table 7 - Summary of experimental results of figures 4 and 5.

Initial pH	pH after 4 h in contact with air	pH of solution in contact with air and a steel specimen	
		After 4 h	After 4 h, after boiling
4.5	4.4	6.3	7.14
7.6	---	6.8	8.9
7.0	5.84	---	---
9.5	6.89	7.4	8.7

However, when a steel specimen is immersed in this same water, the pH immediately starts to increase (Fig. 2) due to steel corrosion, as expected. However, the pH stabilises close to the neutral value because there are reactions that either produce or consume OH. The former consists of the cathodic reactions (reactions 2 and/or 4) and of the oxidation of Fe^{2+} into Fe^{3+} (reaction 5). The latter includes the precipitation of iron oxides/hydroxides (reactions 3 and 6), which is favoured due to alkanisation.

With neutral (pH 7.0) and alkaline (pH 9.5) water, the contact with air is sufficient to promote a decrease in pH, which is more pronounced for the most alkaline water of both. This pH decrease is a consequence of the absorption of atmospheric CO_2 , where the most alkaline water absorbs more CO_2 . The pH decrease persists in the presence of an iron specimen, even though the iron corrosion contributes to an increase of the pH. The role of CO_2 is confirmed by the observed increase of water pH when CO_2 is removed by boiling (Fig. 4).

For solutions (pH 4.5, 7.0 or 9.5) kept in an inert atmosphere, the final equilibrium pH is determined by the solubility product of ferrous oxide/hydroxide, which is 9.2.

The factors that control the water-phase pH variation during corrosion of carbon steel in petroleum derivative emulsions are now understood: the oxidation of Fe into Fe^{2+} and of Fe^{2+} to Fe^{3+} , the precipitation of iron oxides/hydroxides and the absorption of atmospheric CO_2 .

Therefore, the interactions of the aqueous phase of the petroleum derivative emulsions with the atmospheric carbon dioxide and with the corrosion products determine the changes in pH during the corrosion processes. Understanding such pH variations may largely contribute to the

establishment of corrosion mechanisms and kinetics.

5. CONCLUSIONS

The pH of the aqueous phase in petroleum derivative emulsions is controlled during corrosion by the interactions of water with the atmosphere and with corrosion products. In aerated conditions, such interactions are represented by the absorption of CO_2 from the air and by the oxidation of iron, respectively. The latter involves the transportation of Fe^{2+} ions into the aqueous solution, their partial oxidation to Fe^{3+} and the subsequent precipitation of some of the Fe^{2+} and Fe^{3+} ions as iron oxides/hydroxides. The chemical reactions and phase equilibria are such that, during the corrosion process, the pH of the solution changes, regardless of its initial value, towards a value close to neutral. The timescale for such pH changes is of the order of minutes. Therefore, the interactions of the aqueous phase with the air and corrosion products explain why the corrosiveness of a petroleum derivative emulsion is not influenced by the initial water-phase pH.

ACKNOWLEDGEMENTS

The financial support from CNPq - National Council for Scientific and Technological Development (Brazil) is gratefully appreciated. The authors also thank Renata Angelon Brunelli, Gislaire Maria Bragagnolo Nunes and Johny Hernandes de Oliveira for their assistance with experiments.

APPENDIX A

pH of Distilled Water in Contact With Atmospheric Air

In the conditions considered¹, there are two sources of H⁺:

a) the auto ionisation of water:



where:

$$[\text{H}^+]_{\text{H}_2\text{O}} = [\text{OH}^-]_{\text{H}_2\text{O}}$$

$[\text{H}^+]_{\text{H}_2\text{O}}$ the H⁺ originating from the auto-ionisation of water

$[\text{OH}^-]_{\text{H}_2\text{O}}$ the OH⁻ originating from the auto-ionisation of water

b) the absorption of CO₂, the formation of H₂CO₃ and the dissociation of this acid²:



or the total reaction:



In the total CO₂ reaction, it can be observed clearly that if **n moles** of CO₂ react with water, the formation of **n moles** of HCO₃⁻ and **n moles** of H⁺ will result:

$$[\text{CO}_2]_{\text{used to form HCO}_3^-} = [\text{HCO}_3^-]_{\text{formed by CO}_2} = [\text{H}^+]_{\text{formed by CO}_2}$$

For simplification $[\text{HCO}_3^-]$ will be used to designate the HCO₃⁻ formed by CO₂, and $[\text{H}^+]_{\text{CO}_2}$ will be used to designate the quantity of H⁺ formed by CO₂ (reaction A.4).

Based on the above, it is possible to say that when water is in contact with a CO₂ containing atmosphere, the CO₂ absorption will displace the

¹For simplification, H⁺ will be used instead of H₃O⁺

²For simplification, only the formation of HCO₃⁻ will be considered, as the dissociation of the H₂CO₃ for the formation of CO₃²⁻ is negligible.

auto-ionisation of water, according to the Le Chatelier principle, in order to decrease it, i.e., $[\text{H}^+]_{\text{H}_2\text{O}}$ will be less than 10⁻⁷ mol L⁻¹.

Considering all possible reactions, the following equations can be written:

$$[\text{H}^+]_{\text{equilibrium}} = [\text{H}^+]_{\text{H}_2\text{O}} + [\text{H}^+]_{\text{CO}_2}$$

$$[\text{H}^+]_{\text{CO}_2} = [\text{HCO}_3^-]$$

$$[\text{H}^+]_{\text{H}_2\text{O}} = [\text{OH}^-]_{\text{H}_2\text{O}}$$

$$[\text{H}^+]_{\text{CO}_2} + [\text{H}^+]_{\text{H}_2\text{O}} = [\text{HCO}_3^-] + [\text{OH}^-]_{\text{H}_2\text{O}}$$

$$\frac{[\text{HCO}_3^-] \cdot [\text{H}^+]_{\text{equilibrium}}}{p_{\text{CO}_2}} = 0.15 \cdot 10^{-7} \quad (\text{from Table 4})$$

$$[\text{H}^+]_{\text{equilibrium}} \cdot [\text{OH}^-]_{\text{H}_2\text{O}} = 10^{-14}$$

$$\text{pH} = -\log [\text{H}^+]_{\text{equilibrium}}$$

For the resolution of the above problem, it was assumed that:

a) contour condition: the amount of CO₂ absorption by water is negligible when compared with the amount of CO₂ present in the atmosphere, which means that this absorption does not affect the partial pressure of CO₂ (infinite source of CO₂), i.e.,

$$p_{\text{CO}_2} = p_{\text{CO}_2 \text{ before the absorption}} = p_{\text{CO}_2 \text{ after the absorption}}$$

hypothesis 1: the amount of H⁺ produced by the auto-ionisation of water is not affected by the absorption of CO₂ and it is equal to 10⁻⁷ mol L⁻¹, i.e.,

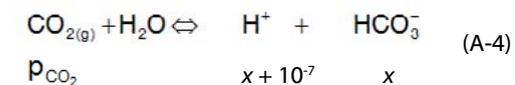
$$[\text{H}^+]_{\text{equilibrium}} = [\text{H}^+]_{\text{CO}_2} + 10^{-7}$$

Hypothesis 2: the formation of CO₃²⁻, according to the reaction



is negligible at pH=7.

Consideration of all the above hypotheses results in:



$$\frac{[\text{HCO}_3^-] \cdot [\text{H}^+]_{\text{equilibrium}}}{p_{\text{CO}_2}} = 0.15 \cdot 10^{-7} \quad (\text{from Table 4})$$

$$\frac{x(x + 10^{-7})}{3 \cdot 10^{-4}} = 0.15 \cdot 10^{-7} \quad (p_{\text{CO}_2} = 3 \cdot 10^{-4} \text{ atm from Table 4})$$

Then, the solution of the second-level equation is:

$$x = 23 \cdot 10^{-7} \text{ mol L}^{-1}$$

$$[\text{H}^+]_{\text{equilibrium}} = x + 10^{-7} = 24 \cdot 10^{-7} \text{ mol L}^{-1}$$

$$\text{pH} = -\log [\text{H}^+]_{\text{equilibrium}} = 5.62$$

Once the solution of the problem is found, its consistency should be verified:

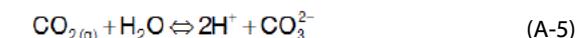
$$\text{Hypothesis 1} \Rightarrow [\text{H}^+]_{\text{H}_2\text{O}} = 10^{-7} \text{ mol L}^{-1}$$

$$[\text{H}^+]_{\text{H}_2\text{O}} = [\text{OH}^-]_{\text{H}_2\text{O}} = \frac{10^{-14}}{[\text{H}^+]_{\text{equilibrium}}} = \frac{10^{-14}}{24 \cdot 10^{-7}} = 4.2 \cdot 10^{-9} \text{ mol L}^{-1}$$

It was verified that the absorption of CO₂ does decrease the auto-ionisation of water, which is in disagreement with hypothesis 1. In this case, the amount of H⁺ after the CO₂ absorption is given by:

$$[\text{H}^+]_{\text{equilibrium}} = [\text{H}^+]_{\text{CO}_2}$$

Hypothesis 2



where

$$p_{\text{CO}_2(\text{g})} = 3.10^{-4} \text{ atm (from Table 4)}$$

$$[\text{H}^+]_{\text{equilibrium}} = 24.10^{-7} \text{ mol L}^{-1}$$

$$K = \frac{[\text{H}^+]_{\text{equilibrium}}^2 \cdot [\text{CO}_3^{2-}]}{p_{\text{CO}_2}} = 0.72.10^{-18}$$

Resolving the above equilibrium equation, one obtains:

$$[\text{CO}_3^{2-}] = 3,75.10^{-11} \text{ mol L}^{-1}$$

It can be verified that the amount of $[\text{CO}_3^{2-}]$ formed is indeed negligible, which is in accordance with hypothesis 2, which is then accepted.

In order to improve the solution of the proposed problem, another calculation was performed with the following data:

$$[\text{HCO}_3^-] = x$$

$$[\text{H}^+]_{\text{equilibrium}} = x + 4.2.10^{-9} \text{ (hypothesis 1 corrected)}$$

$$p_{\text{CO}_2} = 3.10^{-4} \text{ atm (contour condition from Table 4)}$$

$$K = \frac{[\text{HCO}_3^-] \cdot [\text{H}^+]_{\text{equilibrium}}}{p_{\text{CO}_2}} = 0.15.10^{-7} \text{ (from Table 4)}$$

$$\frac{x(x + 4,2.10^{-9})}{3.10^{-4}} = 0.15.10^{-7}$$

$$x = 2,1.10^{-6} \text{ mol L}^{-1}$$

$$[\text{H}^+]_{\text{equilibrium}} = x + 4.2.10^{-9} = 2.1.10^{-6} + 4.2.10^{-9} \cong 2.1.10^{-6}$$

$$\text{pH} = 5.678$$

Once the new solution is obtained, it is necessary to test hypothesis 1 again:

$$\text{Hypothesis 1} \Rightarrow [\text{H}^+]_{\text{H}_2\text{O}} = 4.2.10^{-9} \text{ mol L}^{-1}$$

$$[\text{H}^+]_{\text{H}_2\text{O}} = [\text{OH}^-]_{\text{H}_2\text{O}} = \frac{10^{-14}}{[\text{H}^+]_{\text{equilibrium}}} = \frac{10^{-14}}{2.1.10^{-6}} = 4.76.10^{-9} \text{ mol L}^{-1}$$

The obtained value is very close to the previously established value, which means that it can be considered as very close to the exact value. Therefore, the pH value of 5.678 should be accepted as very close to the real one.

APPENDIX B

The Fe/H₂O System Isolated From Atmospheric Air (Water With pH 7.0)

In the considered system, Fe is corroded, Fe²⁺ is produced and alkalisation is promoted, according to the reactions:



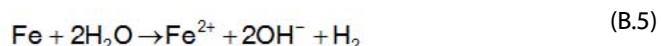
When the amount of Fe²⁺ reaches a critical value, precipitation of Fe(OH)₂ occurs as follows:



In this system, the auto-ionisation of water also occurs:



Combining reaction B.1, B.2 with B.4, one obtains:



From the reaction B.5, it can be seen that when Fe is oxidised, OH⁻ and Fe²⁺ are fo

$$[\text{OH}^-]_{\text{Fe}} = 2[\text{Fe}^{2+}]_{\text{Fe}}$$

where

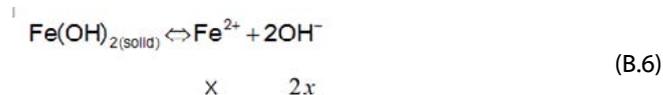
$[\text{OH}^-]_{\text{Fe}}$ = is the amount of OH⁻ formed through Fe oxidation

$[\text{Fe}^{2+}]_{\text{Fe}}$ = is the amount of Fe²⁺ formed through Fe oxidation

The production of OH⁻ displaces the auto-ionisation of water, according to the Le Chatelier principle, in order to decrease it. Therefore, for the resolution of this problem, the following hypothesis can be considered: the auto-ionisation of water does not affect the amount of OH⁻ at the equilibrium. Therefore, the amount of OH⁻ at the equilibrium is given by

$$[\text{OH}^-]_{\text{equilibrium}} = [\text{OH}^-]_{\text{Fe}} + [\text{OH}^-]_{\text{H}_2\text{O}} = [\text{OH}^-]_{\text{Fe}} + 10^{-7} \cong [\text{OH}^-]_{\text{Fe}}$$

Considering the above hypothesis, one can obtain:



$$K_{\text{ps}} = [\text{Fe}^{2+}] \cdot [\text{OH}^-]^2 = 2.10^{-15} \quad (\text{from Table 6})$$

$$x \cdot (2x)^2 = 2.10^{-15}$$

$$x = 0.79.10^{-5} \text{ mol L}^{-1}$$

Once the solution of the problem is obtained, its consistency should be verified:

$$[\text{OH}^-]_{\text{equilibrium}} = 2x + 10^{-7} \cong 2x \text{ (hypothesis)}$$

$$2x = 2 \cdot 0.79.10^{-5} = 1.58.10^{-5} = 158.10^{-7} \text{ mol L}^{-1}$$

The amount of OH⁻ formed due to the oxidation of Fe is 158-fold greater than that formed by the auto-ionisation of water, if it were assumed to be 10⁻⁷ mol L⁻¹. Because $[\text{OH}^-]_{\text{H}_2\text{O}}$ is less than 10⁻⁷ mol L⁻¹ (because the Fe oxidation decreases the auto-ionisation of water), it can be concluded that the amount of OH⁻ formed by the dissociation of Fe(OH)₂ is almost equal to the amount of OH⁻ present at the equilibrium state. Now, it is easy to estimate the pH value at the equilibrium state:

$$\text{pOH} = -\log [\text{OH}^-]_{\text{total}} = -\log(158.10^{-7}) = 4.80$$

$$= -\log [\text{OH}^-]_{\text{total}}$$

$$\text{pH} = 14 - \text{pOH} = 14 - 4.8 = 9.2$$

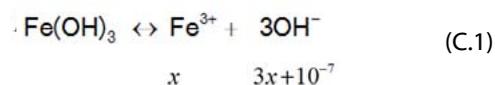
APPENDIX C

The Fe/H₂O System in Contact With CO₂-Free Atmospheric Air (Water With pH 7.0)

For the calculation of the equilibrium pH value of this system, it is necessary to consider the two sources of OH⁻: the auto-ionisation of water and the oxidation of Fe and of the Fe²⁺. Because the solubility product of Fe(OH)₃ is extremely low (6.10⁻³⁸, Table 6), the following hypothesis is considered: the amount of OH⁻ formed through the oxidation of Fe, followed by the oxidation of Fe²⁺ to Fe³⁺, does not affect the auto-ionisation of water, being much smaller than 10⁻⁷ mol L⁻¹.

$$[\text{OH}^-]_{\text{equilibrium}} = [\text{OH}^-]_{\text{H}_2\text{O}} + [\text{OH}^-]_{\text{Fe(OH)}_3} \cong [\text{OH}^-]_{\text{H}_2\text{O}} = 10^{-7}$$

Considering the above hypothesis:



where:

x = the amount of Fe³⁺

$3x+10^{-7} \cong 10^{-7}$ = the amount of the total OH⁻ ions present in the solution at the equilibrium (hypothesis)

$$[\text{Fe}^{3+}] \cdot [\text{OH}^-]^3 \text{ (from Table 6)}$$

$$x \cdot (10^{-7})^3 = 6.10^{-38}$$

$$x \cdot 10^{-24} = 6.10^{-38}$$

$$x = 6.10^{-17} \text{ mol L}^{-1}$$

Once the solution of the problem is obtained, its consistency should be verified:

$$[\text{OH}^-]_{\text{equilibrium}} = 3x+10^{-7} = 18.10^{-17} + 10^{-7} \cong 10^{-7} \text{ mol L}^{-1}$$

The amount of OH⁻ from the auto-ionisation of water is much higher than that formed by the dissociation of Fe(OH)₃. Now, it is easy to estimate the pH value at the equilibrium point:

$$\text{pOH} = -\log[\text{OH}^-] = -\log(10^{-7}) = 7$$

$$\text{pH} = 14 - 7 = 7$$

REFERENCES

- [1] Z. A. Foroulis, *Werkst. Korros.*, 33, 121-131 (1982).
- [2] A. Groysman, N. Erdman, *Corrosion*, 56, 1266-1271 (2000).
- [3] NACE Standard TM-017-2001. (Determining Corrosive Properties of Cargoes in Petroleum Product Pipelines), NACE International, Houston (2001).
- [4] V. Y. Nagayassu, Master Degree Thesis, University of São Paulo, Brazil (2006).
- [5] G. A. Lee, G. A. Haines, (Corrosion Problems of the Petroleum Industry), 1st Ed., Staples Printers Limited, Rochester, England (1960).
- [6] J. I. Bregman, (Corrosion Inhibitors), 1st Ed., Macmillan Company, N.Y., USA (1963)
- [7] P. Altoé, C. F. Moulin, S. L. Díaz and O. R. Mattos, *Electrochim. Acta*, 41, 1165-1172 (1996).
- [8] J. L. Benitez, C. Martínez and R. Roldan, *Oil Gas J.*, 100, 66-70 (2002).
- [9] P. Kirkov, *Electrochim. Acta*, 32, 921-926 (1987).
- [10] J. M. Hale, Orbisphere Document, Technical Bulletin No. 6 (2002).
- [11] A. Rajasekar, S. Maruthamuthu, N. Muthukumar, S. Mohanan, P. Subramanian and N. Palaniswamy, *Corros. Sci.*, 47, 257-271 (2005).
- [12] A. Rajasekar, S. Ponmariappan and S. Maruthamuthu, *Curr. Microbiol.*, 53, 374-381 (2007).
- [13] P. A. Ferreira, G. S. Pimenta, E. M. O. Paiva, R. F. Brito e E. O. Pinto, (Pré-seleção de Inibidores para Dutos de Produção com Aplicação de Técnica Eletroquímica e Gravimétrica), COTEQ 2002, Salvador, Brasil (2002),
- [14] Z. Panossian, V. Y. Nagayassu, A. A. G. Bernal and G. S. Pimenta, (Improvement of the NACE Test for Determination of the Corrosive Properties of Gasoline and Distillate Fuels), in *Proceedings of Corrosion 2009*, Paper No 09578, March, Atlanta, USA (2009).
- [15] M. Ohba, PhD Thesis, University of São Paulo, Brazil (2003).
- [16] Science is fun. Carbon dioxide. Available in: <http://scifun.chem.wisc.edu/chemweek/CO2/CO2.html>. Accessed on June 28 (2010).
- [17] M. Pourbaix, (Atlas of electrochemical equilibrium in aqueous solutions), 2nd Ed., NACE, Houston (1974).
- [18] B. H. Mahan, (University Chemistry), 1st Ed., Addison-Wesley (1970).
- [19] MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems, Computer Sciences Corporation, Assessment Branch, Ascl Corporation (1990).
- [20] M. Pourbaix, (Lectures on Electrochemical Corrosion), 1st Ed., CEBELCOR (1973).
- [21] J. B. Russel, (General Chemistry), Vol. 1, CIP-Brasil, McGraw-Hill (1992).
- [22] Faculté technologique de chimie. Available in: <http://www.ktf-split.hr/periodni/fr/abc/kpt.html>. Accessed on June 28 (2010).