



## Corrosion wastage model for ship crude oil tanks

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### ABSTRACT

This study investigates the effects of temperature, carbon dioxide and hydrogen sulphide concentrations on the corrosion behaviour of ship steels subjected to crude oil tank atmospheres. A new corrosion wastage model is proposed based on a standard non-linear time dependent corrosion model modified by the effect of the different environmental factors contained in the crude oil tank atmosphere. The new corrosion model assesses the corrosion degradation under stationary environmental conditions denoted as “short-term”. The long-term corrosion degradation is assessed by considering the succession of the various environmental conditions that can be present in the tank and adding the corrosion damage incurred during each of them. Corrosion records depending only on time are used to calibrate the standard model while the effect of environmental factors in increasing or decreasing the corrosion rate is based on formulations published by other authors. A numerical example of a representative application of the new corrosion model is presented, to demonstrate how to apply the model.

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### 1. Introduction

Crude oil is one of the most important raw materials for the production of energy and crude oil tankers play a strategic role in its transportation. The risk of oil tanker accidents is particularly high, which has been shown in the last decades by many accidents with enormous mass of oil spillage into the sea. These oil spillage disasters endangered the natural life and caused an economical loss due to crude oil loss, ship damage or ship out of service time and due to the expenses necessary to deal with oil pollution.

An example is the Prestige accident of November 2002, which spilled more than 35,000 tones, with a similar amount left inside the sunken tanker leading to the pollution of many kilometres of coast in Spain and France. The sinking of the Erika off the coast of France in December 1999 spilled 20,000 tones of oil and polluted 400 km of the French coast. The investigations into the Erika incident carried out by the French government and the Maltese maritime authority concluded that age, corrosion, insufficient maintenance and inadequate surveys were all strong contributing factors to the structural failure of the ship. Although some of these accidents were caused by human errors, another big part is related to material degradation caused or influenced by undetected corrosion [1].

Corrosion is considered the most important factor leading to such age-related structural degradation of ships and of other types of steel structures. Corrosion involves the interaction between me-

tal or alloy and its surrounding environment, and it is affected by the properties of both the material and the surrounding environment. Corrosion can take different forms of general attack, pitting corrosion, stress corrosion cracking, corrosion fatigue, fretting corrosion, filiform corrosion, weld corrosion, bimetallic corrosion and bacterial corrosion. General corrosion, which is a common form of corrosion, is spread over the whole surface of the metal. Corrosion can lead to thickness reduction, and may facilitate fatigue cracks, brittle fracture and unstable failure. The importance of the studies of the crude oil tank corrosion increased considerably in the last few decades, because of the need to predict better the corrosion in oil tankers that have been prone to some spectacular disasters.

Crude oil has a complex composition and it varies widely in their physical/chemical properties. The melting point, boiling point, vapour pressure, partition coefficient and water solubility characteristics of crude oils can differ in the oil producing regions as well as within a specific production field. Despite these wide ranging physical and chemical characteristics, some generalizations can be made regarding the characteristics and influence of crude oil on corrosion. While the corrosion rates may vary, the chemicals causing the largest problems are almost universal. CO<sub>2</sub> and H<sub>2</sub>S gases, in combination with water, create most of the corrosion problems in crude oil tanks. Other problems include microbiological activity and the solids accumulation.

The corrosion in the ballast tanks is much different from that in the cargo tanks and both of them are different from the corrosion behaviour in the void spaces of the double bottom and double hull, and machinery space. Even inside the same tank, the corrosion through the void space above the liquid level is different from

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the immersed part and both are different from the corrosion behaviour in the tank bottom.

In the ballast tanks, the void space above the water level is highly humid and rich in chlorides and affected by the sloshing of the ballast water, making the corrosion through that region much severe. The immersed side and bottom parts of the ballast tank are attacked by corrosion similar to the corrosion under sea water immersion conditions that happens at the external hull of the vessel. The ballast water remains almost in stagnant condition with respect to the tank boundaries, while the external hull of the vessel is subjected to a relative flow velocity between it and the sea water during navigation periods, which increases the corrosion attack. Significant corrosion of elements in ballast tanks adjacent to heated cargo tanks or tanks with consumables is also possible.

In the cargo tanks, the upper region suffers more from corrosive gases evaporated from the cargo, such as sulphur compounds gases, which dissolve in water vapour composing a diluted acid environment that has a very corrosive effect. The side shell of cargo tanks is usually immersed in crude oil during loading condition. The corrosion attack through this region is much dependent on the chemical and physical characteristics of the crude oil. For cargo tanks loaded with heavy crude oils, a protective waxy film is formed on the side boundary of the tank protecting it from the corrosive environment. The protection of this film decrease as the viscosity of the cargo oil decreases, until reaches to a minimum value in the products tanks. At the cargo tank bottom, where a lot of sediment, sand, water and other impurities accumulate, a very corrosive environment develops besides the wear effect resulting from the motion of these impurities against the tank bottom.

Time in ballast or cargo, tank washing and inerting (for tankers), corrosion protection systems effectiveness and component location and orientation have a great effect on the corrosion behaviour. An increased degree of local structural flexibility has been claimed to increase corrosion rates as time progresses because of continuous scale loss. This implies that the corrosion models developed on the basis of statistical analysis of operational data will usually be different according to the types of ships and cargoes or structural member locations and categories.

A number of studies related to corrosion evaluation in ship structures have been performed. Melchers [2] considered probabilistic corrosion modelling based on corrosion mechanics principles for steel immersed in salt-water, and noted the effect of environmental and other factors that should be included in model development, including temperature, dissolved oxygen, salinity, calcium carbonate and pH, water velocity and marine growth. Paik et al. [3] presented a mathematical model for predicting time variant corrosion wastage of the structures of single and double hull tankers, floating, storage, and off-loading units (FSOs), and floating, production, storage, and off-loading units (FPSOs).

Wang et al. [4] provided a database of thickness measurements in ships, from which the trends of corrosion wastage in oil tankers could be derived. They summarized the mean values, standard deviations and maximum values of corrosion wastage measurements of various structural members for 20 years of service. The wastage measurements were categorized according to location (structural member) and usage space. The locations are deck, side, bottom and longitudinal bulkheads. Both plates, and web and flanges of longitudinals were investigated. In line with classification rules for new constructions, two usage spaces were considered (cargo tanks and ballast tanks). From this database, it can be observed that corrosion wastage inside ship tanks exhibits a high level of variability. The maximum corrosion wastage is much higher than the average. For example, for 20 years old ships the maximum observed wastage in deck plate in cargo tanks is 8.70 mm, while the average wastage is 1.1 mm. Some structural members exhibited standard deviations higher than the averages. The maximum

corrosion wastage seems to be higher in cargo tanks than in ballast tanks and the average corrosion wastage does not seem to depend on the usage spaces (cargo or ballast tank). Wang et al. [5] have also assessed the risks of corrosion wastage to aging ships' structural integrity using the corrosion wastage database. Similar other statistics about corrosion rates corresponding to the different crude oil tanker locations are indicated by Yamamoto and Ikegami [6] and Paik et al. [3].

Zayed et al. [7] and Panayotova et al. [8] have identified the factors governing marine corrosion phenomena on structural steel components in open and closed spaces and for marine environment. Garbatov et al. [9] have analyzed measured data of corrosion wastage of deck hull structures of bulk carriers, which are predominantly subjected to corrosion in atmospheric conditions during the entire ship service life. It has been shown that the non-linear corrosion wastage model is well accepted in representing realistic situations for ship plates of different areas of the ship hull. Extensive studies have been performed by Garbatov et al. [10] for the corrosion wastage of deck plates of ballast and cargo tanks.

Guedes Soares et al. [11,12] studied the effect of the different marine immersion and atmospheric factors on the behaviour of marine corrosion wastage under immersion and atmospheric conditions respectively all over the ship's service life. The studies proposed a new corrosion wastage model based on the non-linear time dependent corrosion model accounting for various immersion and atmospheric environmental factors.

The present study addresses specifically the corrosion in ship tanks and it considers the internal tank environment divided into three zones. The first zone includes the void space above the crude oil level. The second one includes the immersed tank sides in crude oil. The third zone includes the tank bottom. The present study aims at identifying different chemical and physical factors affecting the corrosion behaviour within the crude oil tank atmosphere (first zone) through the ship's service life. The model proposed here is based on considering a standard corrosion model at certain reference tank conditions. Then this standard corrosion model is corrected to represent the corrosion behaviour at different tank conditions. The non-linear time variant corrosion model of Guedes Soares and Garbatov [13] is considered to be the reference corrosion model with parameters fitted to the appropriate corrosion data. Finally, an application example is included to demonstrate the application of the present model on the corrosion degradation of the deck plating of the crude oil tanker.

The present work is a continuation of the approach that has already been developed by Guedes Soares et al. [11] where the effects of different marine environmental factors on the corrosion behaviour of steel plates totally immersed in salt-water were studied.

## 2. Standard conditions

The mean value curve representing the time dependent standard corrosion deterioration in crude oil tanks is given by the non-linear time variant model proposed by Guedes Soares and Garbatov [13]:

$$\frac{\partial d_n(t)}{\partial t} = \begin{cases} \frac{d_\infty}{\tau_t} \exp[-(t - \tau_c)/\tau_t], & t > \tau_c \\ 0, & t \leq \tau_c \end{cases} \quad (1)$$

$$d_n(t) = \begin{cases} d_\infty[1 - \exp(-(t - \tau_c)/\tau_t)], & t > \tau_c \\ 0, & t \leq \tau_c \end{cases} \quad (2)$$

where  $\partial d_n(t)/\partial t$  and  $d_n(t)$  are the nominal corrosion rate and depth, and the model is governed by  $d_\infty$  that is the long-term thickness of the corrosion wastage,  $\tau_c$  is the coating life, which is equal to the time interval between the painting of the surface and the time

when its effectiveness is lost, and  $\tau_t$  is the transition time under average conditions.

This approach uses information from the physics of the basic corrosion process to determine the main trend of the time variation of corrosion wastage as determined by the governing corrosion mechanism, as reflected on the model of Guedes Soares and Garbatov [13]. This model does not intend to represent accurately the time variation of corrosion as determined by all the possible corrosion mechanisms. Instead, it takes the view to represent the main trend that can be originated by the dominant mechanism and then it relies on fitting the shape of the model to experimental data, for which it uses three free parameters. This approach circumvents the necessity of using experimental results that would reproduce in an accurate way the conditions under study, which have a too large variability for one to aim at representing it in detail.

The process of corrosion initiation on the coated surface is not discussed here, but can be found in Guedes Soares et al. [11] where the effects of different marine environmental factors on the corrosion behaviour of steel plates totally immersed in salt-water were studied.

The nominal corrosion under crude oil tank atmospheric conditions and its governing parameters are normally derived based on the measured data during a very long period of time and performing a regression analysis in order to fit the proposed model to this data using the least squares approach. Garbatov et al. [10] already analyzed and fitted this model based on two sets of corrosion data for deck plates of ballast and cargo tanks of tankers provided by Wang et al. [4,5], ABS [14]. The descriptor parameters of the model were as indicated in Table 1.

This corrosion data are collected from several tanker ships with different ages, geometric characteristics, navigating through various routes through the world and carrying different crude oil types. This means that these corrosion data sets represent marine or crude oil tank corrosion under long-term mixed environmental or tank conditions. These conditions change through the ship route, season and crude oil type. From this, one can assume that fitting the standard corrosion model to this data and its resulting parameters correspond to long-term mean values of the different environmental and tank conditions. Therefore, it is important to define the most important factors affecting the corrosion process in the crude oil tank and the mean value corresponding to each one. These values will be considered in this study as the nominal or standard tank conditions relating to the standard corrosion model and its parameters. This study will consider the most important factors affecting corrosion in crude oil tanks, such as hydrogen sulphide ( $H_2S$ ), carbon dioxide ( $CO_2$ ) and temperature [7].

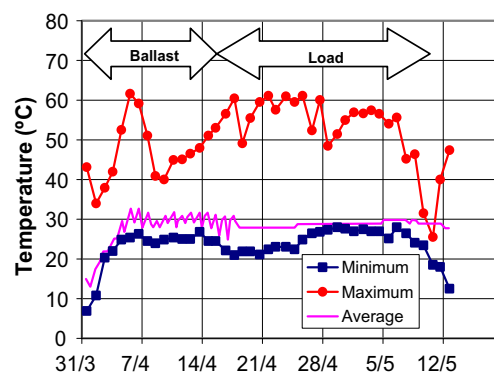
Katoh et al. [15] and Yasunaga et al. [16] have shown detailed analysis results of gaseous composition in crude oil tank (see Table 2).  $H_2S$  gas is detected in high concentration even in empty condition. The standard  $H_2S$  and  $CO_2$  concentrations are estimated for this study as the mean value of the different values indicated in Table 2 through the different crude oil tanks, types and cargo loading ratios.

Yasunaga et al. [16] investigated daily temperature changes of an upper deck plate by on board measurement (see Fig. 1). This measurement was carried out on several VLCCs including S/H and D/H tankers and confirmed that there was no distinctive difference

**Table 2**

Detailed analysis results of gas composition in crude oil tanks [15,16]

COT No.	3S	4C	4S	5C	5S
Crude oil type	A	B	C	D	E empty
Cargo loading ratio [%]	93	89	92	31	0
Gas [vol. %]					
$H_2S$ [vol. ppm]	2790	1330	498	817	550
$H_2O$ [vol. %]	4.9	3.9	5.3	2.5	3.2
$O_2$	1.7	2.5	1.8	3.9	4.5
$CO_2$	3.7	4.0	2.2	10.9	13.2
$SO_x$ [vol. ppm]	1.3	3.9	1.6	2.7	0.7
$N_2$	32.9	45.0	25.7	62.0	69.5
$C_xH_y$	54.9	42.4	62.2	15.0	4.4
CO	0.0	0.0	0.0	0.0	0.0



**Fig. 1.** Daily temperature change of upper deck [16].

**Table 3**

Mean values of the environmental parameters inside crude oil tanks

Factor	Value	Units	Refs.
Hydrogen sulphide ( $H_2S$ )	1197	ppm [vol.]	[16,15]
Carbon dioxide ( $CO_2$ )	6.8	% [vol.]	[16,15]
Temperature	28.8	°C	[16]

by the two ship structures. The standard temperature is estimated here as the mean value of all average measurements indicated in Fig. 1 (see Table 3).

Table 3 summarises the mean values of the environmental parameters that are considered to affect the corrosion rates in crude oil tanks. These are the values that will be associated with the reference conditions for which the corrosion model in Eqs. (1) and (2) is fitted to operational data.

### 3. Long-term corrosion model

The corrosion degradation given by Eqs. (1) and (2) gives the nominal atmospheric tank corrosion rate and corrosion depth at nominal conditions, which should be further corrected for the actual value of the environmental variables. The influence of atmospheric tank variables on corrosion rate is modelled by multiplicative factors that increase or decrease the corrosion rate predicted by the corrosion model with the average or nominal values of the environmental variables. This influence is derived from experimental data reported by various authors.

The corrosion correction factors for each environmental variable can be estimated from the models described in the following section where the effect of hydrogen sulphide ( $H_2S$ ), carbon dioxide ( $CO_2$ ) and temperature are the only considered variables for this study. Therefore, the corrosion at any environmental conditions can be estimated as

**Table 1**

Corrosion model parameters after fitting to data [10]

	$\tau_c$	$\tau_t$	$d_\infty$
Ballast	10.54	17.54	1.85
Cargo	11.494	11.23	1.91

$$\frac{\partial d_{c,k}(t)}{\partial t} = f(H_2S_r)f(CO_{2,r})f(T_r)\frac{\partial d_n(t)}{\partial t} = \prod_{j=1}^3 f(x_j)\frac{\partial d_n(t)}{\partial t} \quad (3)$$

$$d_{c,k}(t) = f(H_2S_r)f(CO_{2,r})f(T_r)d_n(t) = \prod_{j=1}^3 f(x_j)d_n(t)$$

where  $\frac{\partial d_{c,k}(t)}{\partial t}$  and  $d_{c,k}(t)$  represent the corrected corrosion rates and corrosion thickness, respectively, through the  $k$ th interval of the vessel route,  $\frac{\partial d_n(t)}{\partial t}$  and  $d_n(t)$  are the nominal corrosion rate and corrosion thickness, respectively, and  $f(x_j)$  are the correction factor corresponding to the effect of the tank parameter  $x_j$ .

This model assumes that there is not correlation among the effects implying that the changes in each of them have additive effects. There is no data to support this assumption but it is expected that even if this assumption is not fully correct, the effect of the interactions will be small as compared with the effect of the changes due to each factor individually.

During the service lifetime of a ship, different tank environmental conditions will be encountered. The total time span may be regarded as a sequence of short intervals, during which the tank environmental conditions remain constant. The corrosion correction factors corresponding to the different tank environmental conditions for each of such interval throughout the lifetime of a ship can be estimated. Likewise, the total lifetime tank corrosion may be determined by adding the corrosion wastage experienced during each of the intervals. Typically the duration of each condition will coincide with the voyage duration and Guedes Soares [17] has already provided some data on the different voyage durations of different ship types.

The long-term estimate requires the summing of the effect of the complete set of corrosion correction factors for each specified tank condition, that is, each combination of tank environmental factors. The long-term prediction of tank corrosion wastage for the ship tank lifetime  $[d_L(t)]$  is a weighted sum of the various short-term predictions of tank corrosion wastage, each of which is for a particular combination of the different tank environmental conditions through a certain interval of time:

$$d_L(t) = \sum_{k=1}^n p_k d_{c,k}(t) = \sum_{k=1}^n p_k \prod_{j=1}^m f_k(x_j) d_n(t) \quad (4)$$

where  $p_k$  is a weighting factor representing the relative duration of the  $k$ th short-term interval,  $f_k(x_j)$  is the corrosion correction factor for the  $k$ th interval and  $x_j$  environmental factor,  $n$  is the total number of the short-term corrosion intervals and  $m$  is the total number of tank environmental parameters affecting corrosion wastage.

The sensitivity of the long-term corrosion wastage,  $d_L(t)$ , given by Eq. (4), with respect to any tank environmental factor,  $x_i$ , is given as the partial derivative of  $d_L(t)$  with respect to the particular factor,  $x_i$ . Assuming that all tank environmental factors are independent from each other, the sensitivity of the long-term corrosion wastage,  $d_L(t)$ , can be calculated as

$$\frac{\partial d_L(t)}{\partial x_i} = \sum_{k=1}^n p_k \left[ \frac{d}{dx_i} f_k(x_i) \prod_{j=1}^{m-1} f_k(x_j) \right] d_n(t) \quad (5)$$

The common and systematic way of verification the proposed corrosion models by using an actual corrosion measurement results is usually possible to obtain for the case of short-term models dealing with the effect of one parameter as this can be monitored in laboratory conditions.

However, in case of the models that predict the corrosion degradation on the long-term, it is not possible to validate them due to unavailability of such kind of measurements. In order to validate the long-term time dependent model that predicts the corrosion degradation of structural elements along the ship life, as proposed

in this study, it is necessary to have records both of the corrosion wastage as well as of the relevant environmental parameters. Unfortunately, this does not happen in practice and only structural elements thicknesses are measured during the ship inspection periods.

Unavailability of the proper corrosion measurements necessary for the validation of the long-term time dependent corrosion model should not detract from developing new models of such kind, as they can serve as guides about the data that is necessary to start collecting systematically in ships. In fact, there is a strong need to have mathematical models capable of predicting the corrosion degradation under different combination of service conditions so that one is able to predict the expected differences between ships.

The reference corrosion model used in this study is based on fitting the mathematical function of Eqs. (1) and (2) to measured corrosion data sets gathered during thickness measurements of tankers deck plates. The correction factors are based on corrosion data or formulations developed by authors that studied the effect of each parameter. The effect of the sequential application of the effects should then add to the corrosion damage.

#### 4. Crude oil chemistry

Crude oils can vary greatly in composition, viscosity, density, and flammability. They can be found in a continuum ranging from highly flammable, light liquids (similar to gas condensate), to highly viscous and heavy tar-like materials. There is not two batches of crude oil are chemically identical. Crude oil is categorized based on the molecular weight distribution of their constituents, and distinctions are made between them as light, medium, and heavy crude oil.

Light-weight components are characterized by the hydrocarbon compounds containing up to 10 carbon atoms, a boiling range up to 150 °C, rapid and complete evaporation (usually within one day), high water solubility, high acute toxicity and no potential for bioaccumulation (they evaporate instead).

Medium-weight components are characterized by hydrocarbon compounds containing between 10 and 22 carbon atoms, a boiling range from about 150 to 400 °C, evaporation rates of up to several days (although there will be some residue which does not evaporate at ambient temperatures), low water-soluble fraction (at most a few mg/L), moderate acute toxicity and moderate potential for bioaccumulation.

The heavy-weight components are characterized by hydrocarbon compounds containing more than 20 carbon atoms, almost no loss by evaporation, almost no water-soluble fraction, potential for bioaccumulation (via sorption on to sediments otherwise not highly bio-available), potential for chronic toxicity, most of the components are waxes and long-term persistence in sediments as tar balls or asphalt pavements.

Representative crude contains 84% carbon, 14% hydrogen, 1–3% sulphur, and approximately 1.0% nitrogen, 1.0% oxygen and 0.1% minerals and salts. Crude oils are composed of paraffinic, naphthenic (cycloparaffinic) and aromatic compounds, and are identified based on the predominant proportion of similar hydrocarbon molecules. Paraffinic crude oils are rich in straight chain and branched paraffins; naphthenic crude oils contain mainly naphthenic and aromatic hydrocarbons. Mixed base crude oils have varying amounts of each type of hydrocarbon [18].

Crude oils are further classified by viscosity, specific gravity (density) and by API gravity. The higher the API gravity (the lower the specific gravity), the more valuable is the crude. A crude with a high API gravity ( $>33^\circ\text{API}$ ), and high percentage hydrogen usually contains a higher concentration of naphtha, which can be processed readily to make gasoline and is considered a light crude.



Heavy crudes, i.e. those with *API* gravity  $<28^\circ\text{API}$ , contain high percentage carbon and low percentage hydrogen are usually rich in aromatics and tend to contain more residual material (e.g. asphalts) and heteroatoms (e.g. sulphur, nitrogen, oxygen-containing hydrocarbon analogs). The “heavy crude oils” require more steps in processing, and are more costly to refine.

Crude oils also contain varying amounts of non-hydrocarbon sulphur, nitrogen, oxygen and trace metals. Sulphur is present as hydrogen sulphide ( $\text{H}_2\text{S}$ ), as thiols, mercaptans, sulphides, benzo-thiophenes, polysulphides, or as elemental sulphur.

As a rule, the proportion, stability and complexity of sulphur compounds are greater in heavier crude oil fractions.  $\text{H}_2\text{S}$  is a primary contributor to corrosion in storage and refinery process units.  $\text{H}_2\text{S}$  is very soluble in water and forms weak acids which can lead to pitting of steel and other alloys, partly because of the acidity formed and partly because a sulphide film is formed from sulphide ions ( $\text{HS}^-$  and  $\text{S}^{2-}$ ) which is cathodic to most alloys. Combustion of sulphur-containing petroleum products can produce undesirable by-products such as sulphuric acid and sulphur dioxide. Total sulphur contents of crude oils spans a range of  $<0.1$ – $5.0\%$  by elemental analysis. In general, as *API* gravity decreases, sulphur content increases. For example, a light US crude (Rodessa, Louisiana) has an *API* gravity of 42.8 and a sulphur content of  $0.28\%$ , while an extremely heavy crude from Venezuela has an *API* gravity of 9.5 and contains  $5.25\%$  sulphur. Sulphur is removed during refining by catalytic hydro treating or by caustic wash (sweetening) processes. Corrosion resulting from the presence of hydrogen sulphide ( $\text{H}_2\text{S}$ ) is commonly denoted as sour corrosion, while corrosion arising from the presence of water containing dissolved carbon dioxide is commonly denoted as sweet corrosion.

Nitrogen types include anilines, pyridines, quinolines, pyrrols, carbazoles, benzonitrils and amides. Nitrogen is found in lighter fractions as basic compounds and in heavier fractions as non-basic compounds. Total nitrogen varies from  $<0.01\%$  to  $1.0\%$  by elemental analysis.

Oxygen compounds are generally phenols, ketones and carboxylic acids. Metals found in crude oil include nickel, iron, vanadium, and arsenic in small quantities. These are removed during refining to avoid poisoning of catalysts, and when burning heavy fuel oils, to minimize deposits of vanadium oxide, and nickel oxide in furnace boxes, ducts and tubes.

In most crude oils, chloride salts are found either dissolved in water that is emulsified in crude oil or as suspended solids. Salts also originate from brines injected for secondary recovery or from seawater ballast in marine tankers. Typically, the salts in crude oils consist of  $75\%$  sodium chloride,  $15\%$  magnesium chloride, and  $10\%$  calcium chloride [19].

## 5. Factors affecting crude oil tank corrosion

Crude oil tanks can be fully loaded or empty during the ballast condition. In the case of full load condition, a void space is usually left above the crude oil level. In the case of ballast condition, all the tank space is almost void except the tank bottom, where a shallow layer of crude oil and washing water usually settle on it. Tank heads are subjected to aggressive corrosion because of the condensation. As water condenses on the tank top, it will absorb acid gases from the tank fluids. Tank bottom corrosion occurs mostly with crude oil tanks and is caused by water and salt entrained in the crude oil. A layer of water usually settles out and can become highly corrosive. Under deposit corrosion can be severe under accumulated sludge and debris in tank bottoms. These deposits are also prime areas for the growth of sulphate reducing bacteria.

Cargoes of crude oil and some refined products leave an oily or waxy film on tank surfaces. This film can actually prevent corro-

sion of the steel. However, when the tank is washed, this film is washed away in areas that are hit by the water stream directly. Other areas shaded by structural members or perhaps hit with less forceful spray due to their distance from the nozzle, retain their film. This incomplete washing may cause corrosion to occur at areas of bare steel later exposed to salt-water ballast or a moist salt atmosphere.

The warm, moist, salt-laden atmosphere, which remains after hot salt-water washing, is ideal for corrosion to occur. Cold water washing is reported to result in less corrosion than hot water washing. Corrosion of refined product tankers is greatest in tanks that are washed the most. After salt-water washing, a certain amount of water, often several inches deep, usually remains in the bottom of tanks. This water is left because the tank stripping system is unable to empty the entire bottom area of water. This remaining water is left to contribute bottom pitting corrosion.

Oxygen is responsible for a great deal of the corrosion encountered in oil and gas transportation and production, where much of the processing and handling occurs at near-ambient pressure. This makes oxygen contamination through leaking pump seals, casting and process vents, open hatches and open handling highly likely.

Inert gas systems remove an unsafe atmosphere initially in the tank and replace it with a safe atmosphere with oxygen content of no greater than  $11\%$ , which makes it impossible for combustion to occur. These systems are required to prevent explosions, but experience indicates that they also have an effect on tank corrosion. An inert gas system can, depending on its type, application, and gas quality, either aggravate corrosion conditions or minimize them. By reducing the oxygen content of a tank, corrosion can be reduced. However, while reducing oxygen content to below  $5\%$ , inert gas may also introduce corrosive elements into a tank. Sulphur dioxide ( $\text{SO}_2$ ) and sulphur trioxide ( $\text{SO}_3$ ) contained in inert gas can combine with the warm moist atmosphere in a tank to form sulphuric acid which can cause accelerated corrosion of either bare or coated tank surfaces [20].

Organic nitrogen compounds, such as indole, carbazole, pyridine, or quinoline, are present in many crude oils, but do not contribute to corrosion problems unless converted to ammonia or hydrogen cyanide [21]. This occurs primarily in catalytic cracking, hydrotreatment, and hydrocracking operations where ammonia and hydrogen cyanide, in combination with hydrogen sulphide and other constituents, become the major constituents of sour water that can be highly corrosive to carbon steel [22].

In situ corrosives are limited to carbon dioxide, hydrogen sulphide, polysulphide, organic acids, and elemental sulphur. Additional unique aspects are extremes of temperature and particularly, pressure encountered.

This study will concentrate on tank corrosion through the atmospheric void space above the crude oil cargo level and mainly the corrosion of deck plating. Hydrogen sulphide ( $\text{H}_2\text{S}$ ), carbon dioxide ( $\text{CO}_2$ ) and temperature are the only considered factors affecting corrosion through this study.

## 6. Hydrogen sulphide ( $\text{H}_2\text{S}$ )

Hydrogen sulphide, when dissolved in water, is a weak acid and is therefore corrosive because it is a source of hydrogen ions. Hydrogen sulphide may also play other roles in corrosion. It acts as a catalyst to promote absorption by steel of atomic hydrogen formed by the cathodic reduction of hydrogen ions. This accounts for its role in promoting sulphide stress cracking of high strength steels.

In dilute sulphuric acid the corrosion rate increases with acid concentration, reaching a maximum at about  $47\text{ wt. percentage}$  concentration, after which it decreases to  $0.005$ – $0.05\text{ ipy}$  for

65–100% acid. The corrosion rate increases again with sulphuric acid concentrations above 100% (fuming sulphuric acid) [23,24].

From the different sulphur compounds, diluted sulphuric acid is considered the most aggressive and corrosive sulphuric compound, which is formed in the crude oil tank, holds due to hydration of sulphur compound by water or water vapour already existing in tanks due to seawater tank washing or the seawater already exists in the crude oil.

Brondel et al. [25] has illustrated the effects of the different gases encountered with the crude oil on the overall corrosion rate of carbon steel. The relationship between the corrosion rate and hydrogen sulphide concentration is fitted well to a power function of the following form (see Fig. 2):

$$\frac{\partial d(t)}{\partial t} = 0.5363 \text{H}_2\text{S}^{0.3973} - 1.439, \quad R^2 = 0.987 \quad (6)$$

where  $\partial d(t)/\partial t$  is the corrosion rate in (mil/year),  $\text{H}_2\text{S}$  represents hydrogen sulphide concentration in (ppm) and  $R^2$  measures how successful the fit is in explaining the variation of the data. Described in another way,  $R^2$  is the square of the correlation between the response values and the predicted response values, and thus can take any value between zero and one, with a value closer to one indicating a better fit.

It should be noted that the previous fitting is based on some points taken along the curve indicated by Brondel et al. [25], where neither the equation nor the data of that curve are given.

The relationship between corrosion rate and hydrogen sulphide concentration is illustrated by Brondel et al. [25] up to hydrogen sulphide concentration of 800 ppm as indicated in Fig. 2. Using hydrogen sulphide concentration higher than this value will be an extrapolation of Brondel et al. [25] relationship.

Hydrogen sulphide concentration ratio  $\text{H}_2\text{S}_r$  is defined as the ratio between the actual hydrogen sulphide concentration  $\text{H}_2\text{S}$  and the nominal one,  $\text{H}_2\text{S}_n$  which is indicated in Table 3,

$$\text{H}_2\text{S}_r = \frac{\text{H}_2\text{S}}{\text{H}_2\text{S}_n} = \frac{\text{H}_2\text{S}}{1197} \quad (7)$$

At the nominal hydrogen sulphide concentration  $\text{H}_2\text{S}_n$ , the nominal corrosion rate  $\partial d_n(t)/\partial t$  is estimated from Eq. (6), and equal to 7.5216 mil/year.

By substitution of  $\text{H}_2\text{S}$  equal to  $1197(\text{H}_2\text{S}_r)$  from Eq. (7) into Eq. (6) and dividing the equation by the nominal corrosion rate  $\partial d_n(t)/\partial t$ , one gets the following relation (see Fig. 3):

$$f(\text{H}_2\text{S}_r) = 1.1913[(\text{H}_2\text{S}_r)^{0.3973} - 1] + 1 \quad (8)$$

where  $f(\text{H}_2\text{S}_r)$  is the corrosion rate correction factor for hydrogen sulphide (corrosion rate at actual hydrogen sulphide concentration/corrosion rate at nominal conditions). The sensitivity of the corro-

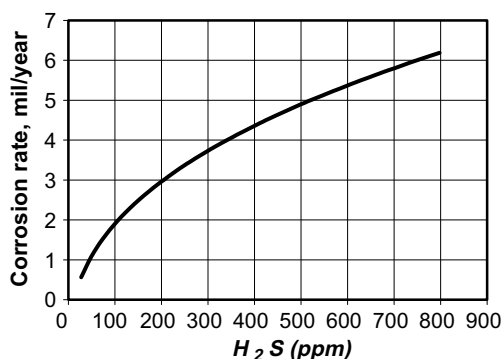


Fig. 2. Relationship between corrosion rate and hydrogen sulphide concentration.

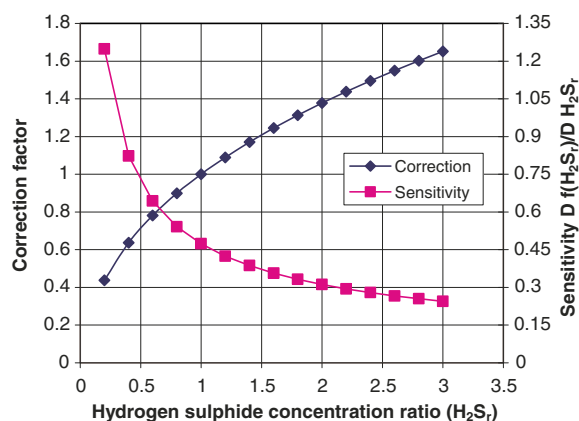


Fig. 3. Hydrogen sulphide correction and sensitivity at different concentration.

sion rate correction factor  $f(\text{H}_2\text{S}_r)$  to hydrogen sulphide is given here as the first derivative of  $f(\text{H}_2\text{S}_r)$  with respect to the hydrogen sulphide concentration ratio  $\text{H}_2\text{S}_r$  (see Fig. 3):

$$\frac{\partial f(\text{H}_2\text{S}_r)}{\partial \text{H}_2\text{S}_r} = 0.4733 \text{H}_2\text{S}_r^{-0.6027} \quad (9)$$

It should be noted that in Fig. 3 the symbols on the lines are simply intended to identify the line and should not be considered as data points.

## 7. Carbon dioxide ( $\text{CO}_2$ ) and temperature

Carbon dioxide, like hydrogen sulphide, is a weakly acidic gas and becomes corrosive when dissolved in water. However,  $\text{CO}_2$  must first hydrate to carbonic acid  $\text{H}_2\text{CO}_3$  (a relatively slow reaction) before it is acidic. As a starting point for the prediction of corrosion rates of carbon steel in  $\text{CO}_2$ -containing environments, the equation of De Waard and Milliams [26] has gained wide acceptance. Based on their experimental data from electrochemical studies, they presented a regression between the corrosion rate and temperature and  $\text{CO}_2$  partial pressure. This equation contained two temperature-dependent terms:

$$\log \frac{\partial d_B(t)}{\partial t} = 7.96 - \frac{2320}{T + 273} - 0.00555T + 0.67 \log(P_{\text{CO}_2}) \quad (10)$$

where  $\partial d_B(t)/\partial t$  is the corrosion rate in mm/year,  $T$  is the temperature in  $^\circ\text{C}$ , and  $P_{\text{CO}_2}$  ( $= \text{mol}\% \text{CO}_2 \cdot \text{total pressure } P$ ) is the partial pressure of  $\text{CO}_2$  in bar ( $10^5 \text{ Pa}$ ).

A re-evaluation of the data used has shown that it is possible to simplify the equation as [27]

$$\log \frac{\partial d_B(t)}{\partial t} = 5.8 - \frac{1710}{T + 273} + 0.67 \log(P_{\text{CO}_2}) \quad (11)$$

The resulting corrosion rates obtained with Eq. (11), which do not differ significantly from those obtained with Eq. (10), represent a “worst case” prediction.

The De Waard et al. [27] proposed model systematically modifies this prediction, Eq. (11), by multiplying  $\partial d_B(t)/\partial t$  with factors, each of which is associated with the effect of one physical or chemical effect that can cause deviations from Eq. (11).

These factors are in almost all cases smaller than one and tend to reduce the corrosion rates predicted with this equation, which in many cases, would otherwise give over-conservative results. Only for the case of correction for pH of a medium that is undersaturated with corrosion product,  $\text{FeCO}_3$  or  $\text{Fe}_3\text{O}_4$  a correction factor bigger than one may be obtained.

The first correction considered by De Waard et al. [27] for the basic corrosion rate estimated by Eq. (11) is for the effect of the higher total pressure. An increase in the total pressure  $P$  of the gas will lead to an increase in corrosion rate. However, with increasing pressure, the non-ideality of the natural gas will play an increasing role, and instead of the  $\text{CO}_2$  partial pressure, the  $\text{CO}_2$  fugacity  $f_{\text{CO}_2}$  should be used as

$$\log \frac{\partial d_B(t)}{\partial t} = 5.8 - \frac{1710}{T + 273} + 0.67 \log(f_{\text{CO}_2}) \quad (12)$$

$$f_{\text{CO}_2} = aP_{\text{CO}_2} \quad (13)$$

where  $a$  is the fugacity coefficient, analogous to activity coefficients in solutions. For the binary system  $\text{CO}_2$ – $\text{CH}_4$  calculations were done and the results can be used as a conservative estimate for  $a$ . The presence of other gases will generally further reduce the fugacity coefficient. As a first estimate, the multiplier  $F_{\text{system}}$  to be applied to the corrosion rate given by Eq. (11) can describe the effect on corrosion rate.

$$\log F_{\text{system}} = 0.67 \left( 0.0031 - \frac{1.4}{T} \right) P \quad (14)$$

where  $T$  is the temperature in K. It has been noted by Moiseeva [28] that Eq. (11) is valid for  $P_{\text{CO}_2} < 1.0$  MPa (10.0 bar). It is also clear from the figures indicated by De Waard et al. [27] that low values of total system pressure have no effect on corrosion rate. At very low total system pressure (atmospheric pressure as an example), the fugacity coefficient is almost equal to one, so, the  $\text{CO}_2$  fugacity is almost equal to its partial pressure and Eq. (12) is almost equal to Eq. (11). Since crude oil is carried by the ship tanks under atmospheric pressure (1.01325 bar), so, Eq. (11) is valid, in this case, and could be used without any correction for total pressure.

De Waard et al. [27] corrected the basic corrosion rate estimated by Eq. (11) for the high temperature protective films. They indicated that at lower temperatures (e.g., less than 60 °C) the corrosion product film has a smudge-like appearance and is easily removed. At higher temperatures, the film is different in texture, is more protective, and is less easily washed away. Further increase in temperature results in lower corrosion rates. This temperature is referred to here as the scaling temperature.

The formula for the scale factor used in the model is

$$\log F_{\text{scale}} = \frac{2400}{T} - 0.6 \log(f_{\text{CO}_2}) - 6.7 \quad (15)$$

With a maximum value for  $F_{\text{scale}}$  of 1, when Eq. (15) gives a higher value. This factor is used to correct the corrosion rate given by Eq. (12) by multiplying  $\partial d_B / \partial t$  with  $F_{\text{scale}}$ . The temperature at which  $\log(F_{\text{scale}}) = 0$  is the scaling temperature

$$T_{\text{scale}} \text{ (K)} = \frac{2400}{6.7 + 0.6 \log(f_{\text{CO}_2})} \quad (16)$$

This is the temperature where the corrosion rate goes through a maximum (peak value). The scaling temperature decreases with increasing  $\text{CO}_2$  pressure.

For temperature and pressure combinations below the scaling temperature, the corrosion rate estimated by Eq. (11) does not need to be corrected for this effect. Eqs. (15) and (16) can be combined as

$$\log(F_{\text{scale}}) = 2400 \left( \frac{1}{T} - \frac{1}{T_{\text{scale}}} \right) \quad (17)$$

where  $T > T_{\text{scale}}$ , otherwise,  $F_{\text{scale}} = 1$ .

Based on the guidelines provided by Energy Institute [29], crude oil is carried by the ship tanks under temperature which is usually less than 60 °C depending on crude oil type. The crude oil is carried in the ship tanks under atmospheric total system pressure, and so,

$\text{CO}_2$  partial pressure will be much less depending on  $\text{CO}_2$  concentration. It can be noted from the figures indicated by De Waard et al. [27] that all crude oils are carried under temperatures below the scaling ones. It is stated; also, by Moiseeva [28] that Eq. (11) is valid for  $t < 140$  °C. Therefore, Eq. (11) is valid, and could be adapted to crude oil tank atmosphere, without any correction for high temperature.

De Waard et al. [27] corrected the basic corrosion rate estimated by Eq. (11) for the effect of  $\text{Fe}^{++}$  and pH. They indicated that the contamination of the  $\text{CO}_2$  solution with corrosion product reduces the corrosion rate. Without the presence of corrosion products, much higher corrosion rates are possible, as is demonstrated by comparison of data from “once-through” and from constant volume tests. In order to describe this effect, the pH shift caused by the presence of dissolved  $\text{Fe}^{++}$ , as predicted from Eqs. (18) and (19), was chosen as a parameter.

Initially, the pH is that of water and  $\text{CO}_2$  only [26],

$$\text{pH}(\text{water} + \text{CO}_2 \text{ only}) = 3.71 + 0.00417T - 0.5 \log(f_{\text{CO}_2}) \quad (18)$$

From the results (for 10% NaCl), the pH at the onset of  $\text{FeCO}_3$  or  $\text{Fe}_3\text{O}_4$  saturation can be approximated by

$$\text{pH}_{\text{sat}} = \min \left\{ \begin{array}{l} 1.36 + \frac{1307}{T+273} - 0.17 \log(f_{\text{CO}_2}) \\ 5.4 - 0.66 \log(f_{\text{CO}_2}) \end{array} \right. \quad (19)$$

The smallest  $\text{pH}_{\text{sat}}$  refers to corrosion product that is more stable and more likely to form first. These results confirm the earlier study published by Dunlop et al. [30].

The following regression was found:

$$\log F_{\text{pH}} = 0.32(\text{pH}_{\text{sat}} - \text{pH}_{\text{act}}), \quad \text{pH}_{\text{sat}} > \text{pH}_{\text{act}} \quad (20)$$

where  $F_{\text{pH}}$  is a correction factor for the corrosion rate of Eq. (11), and  $\text{pH}_{\text{act}}$  is the actual pH. When  $\text{pH}_{\text{act}} = \text{pH}_{\text{sat}}$ , no correction is needed, that is,  $F_{\text{pH}} = 1$ . When  $\text{pH}_{\text{act}}$  is the initial pH, the corrosion rates in “once-through” tests were a factor 2.2–3.3 higher for a temperature range of 80–20 °C. When  $\text{pH}_{\text{act}} > \text{pH}_{\text{sat}}$  because of the presence of alkaline substances,  $\text{NaHCO}_3$ , for example, the validity of Eq. (20) is doubtful since it could relate to over-saturation w.r.t.  $\text{Fe}^{++}$ . In this case the formula proposed by Dugstad and Videm [31] can be used for the solutions that are  $\text{Fe}^{++}$  saturated:

$$\log F_{\text{pH}} = -0.13(\text{pH}_{\text{act}} - \text{pH}_{\text{sat}})^{1.6}, \quad \text{pH}_{\text{sat}} < \text{pH}_{\text{act}} \quad (21)$$

The effect of hydrocarbon liquid is also considered by De Waard et al. [27] in order to correct the basic corrosion rate estimated by Eq. (11). They indicated that the presence of crude oil, for example, in a line with “live” oil and gas, could have a beneficial effect on corrosion by  $\text{CO}_2$ . In the model, this is taken into account with the oil factor  $F_{\text{oil}}$  as

$$F_{\text{oil}} = 0 \text{ if water cut} < 30\% \text{ and } V_{\text{crude}} > 1 \text{ m/s} \quad (22)$$

This expresses the view that the steel can be expected to be oil-wetted if all water is entrained in the crude. Otherwise  $F_{\text{oil}} = 1$ . If the flow rate,  $V_{\text{crude}}$ , of the oil is too low, water can separate and cause corrosion on the bottom of the line. This critical flow rate can be calculated and is less than 1 m/s for normal crudes [32]. At higher flow rates, the water will be dispersed in the oil. Work done by Lotz et al. [33] indicates that in that case at least 30% water can be accommodated before the steel is water-wetted. It should be emphasized that light hydrocarbon condensates, for example, natural gas liquids, do not offer any protection in the absence of an inhibitor, regardless of the water content.

However, in the case of crude oil tank, any water entrained in the crude oil will settle on the tank bottom or evaporate and condensate on the tank head. At the same time, the crude oil is stagnant inside the tank and there is not any flow effect. Under these conditions one can consider that the corrosion of the side shell

from the upper level of the crude oil to the tank bottom is neglected ( $F_{oil} = 0$ ) since all of that area is completely crude oil-wetted and protected from any water-wetted corrosion. At the same time both of the tank bottom and tank head will be subjected to water-wetted corrosion ( $F_{oil} = 1$ ).

De Waard et al. [27] studied the effect of condensation in the correction of the basic corrosion model. Van Gelder et al. [34] have shown that corrosion rates of steel exposed to condensing water phase in a  $CO_2$  atmosphere quickly decrease with time. For wet water-saturated gas, some very conclusive tests were carried out using pipe with a radioactive segment in the top. The results are indicated, as the ratio observed/nomogram rates as a function of water condensation rate in  $g/(m^2 s)$ . This ratio has been named the condensation factor  $F_{cond}$ . The data can be conservatively described by

$$F_{cond} = \begin{cases} 0.4 \cdot (\text{condensation rate}), & \text{condensation rate} < 2.5 \\ 1, & \text{condensation rate} \geq 2.5 \end{cases} \quad (23)$$

For the wet gas transport, cooling rates and flow rates in pipelines are normally such that condensation rates are far below  $0.25 g/(m^2 s)$ . For such systems, taking  $F_{cond} = 0.1$  will cover all conditions in a conservative manner without having to actually calculate the condensation rates.

For the case of crude oil tank of tanker ships, condensation will be limited to the atmospheric zone above the crude oil level up to the tank head. This zone is very humid and has intensive concentration of gases evaporated from the crude oil. Due to lack of data regarding evaporation and condensation through that zone, the condensation factor  $F_{cond}$  will be conservatively assumed equal to one.

De Waard et al. [27] considered also the effect of glycol (and also other inhibitors) which often added to wet gas pipelines to prevent the formation of hydrates. For analytical grades of glycol, the effect on corrosion rate could be expressed as a multiplier  $F_{glyc}$ :

$$\log F_{glyc} = A \log(W\%) - 2A \quad (24)$$

where  $W\%$  is the water content of water/glycol mixture, in  $\%W$ .  $A$  is a constant.

For the case of corrosion inside crude oil tanks considered here, no glycol or inhibitors corrections will be considered.

The model proposed by De Waard et al. [27] will be used in this study to assess the corrosion inside crude oil tanks due to carbon dioxide and temperature. Since this model will be adapted to the corrosion inside crude oil tank, not all the correction factors indicated by De Waard et al. [27] will be used. Based on the discussion above, the basic corrosion rate estimated by Eq. (11) will be corrected only for the effect of  $Fe^{++}$  and pH.

The standard concentration of  $CO_2$ , indicated in Table 3, through the crude oil tank atmosphere, is expressed as a volumetric percentage. It is important to convert this volumetric percentage to partial pressure in order to substitute in Eq. (11). The partial pressure of an individual gas component in an ideal gas can be obtained using this expression:

$$P_i = x_i P \quad (25)$$

where  $x_i$  is the mole fraction of any individual gas component in a gas mixture,  $P_i$  is the partial pressure of any individual gas component in a gas mixture and  $P$  is the pressure of the gas mixture. The mole fraction of a gas component in a gas mixture is equal to the volumetric fraction of that component in a gas mixture.

The total pressure of the gas mixture thought the crude oil tank atmosphere is assumed equal to the atmospheric pressure (1.01325 bars). Considering the standard volumetric fraction of  $CO_2$  indicated in Table 3, the nominal or standard  $CO_2$  partial pressure  $P_{CO_2,n}$  will be equal to 0.0689 bars.

The  $CO_2$  partial pressure ratio  $P_{CO_2,r}$  is defined as the ratio between the actual  $CO_2$  partial pressure  $P_{CO_2}$  and the nominal one  $P_{CO_2,n}$ , which is indicated in Table 3,

$$P_{CO_2,r} = \frac{P_{CO_2}}{P_{CO_2,n}} = \frac{P_{CO_2}}{0.0689} \quad (26)$$

The temperature ratio  $T_r$  is defined as the ratio between the actual temperature  $t$  and the nominal one  $T_n$ ,

$$T_r = \frac{T}{T_n} = \frac{T}{28.8} \quad (27)$$

At the nominal condition of temperature,  $t_n$  and  $CO_2$  partial pressure  $P_{CO_2,n}$ , the nominal basic corrosion rate  $\partial d_{B,n}(t)/\partial t$  is estimated from Eq. (11), and equal to 0.2268 mm/year.

This value should be corrected for the effect of  $Fe^{++}$  and pH. The actual pH ( $pH_{act}$ ) is calculated from Eq. (18), and equal to 4.411.

The pH at the onset of  $FeCO_3$  or  $Fe_3O_4$  saturation  $pH_{sat}$  can be approximated by the smallest value of Eq. (19):

$$pH_{sat} = \min \left\{ \begin{aligned} &1.36 + \frac{1307}{28.8 + 273} - 0.17 \log(0.0689) = 5.8882 \\ &5.4 - 0.66 \log(0.0689) = 6.1668 \end{aligned} \right\} \quad (28)$$

Since  $pH_{sat} > pH_{act}$ , the correction factor for the effect of  $Fe^{++}$  and pH,  $F_{pH}$ , is calculated from Eq. (20), and equal to 2.9696.

Therefore, the nominal corrosion rate  $\partial d_n/\partial t$  is estimated by multiplying the nominal basic corrosion rate  $\partial d_{B,n}/\partial t$ , estimated from Eq. (11), by  $F_{pH}$ , and equal to 0.6735 mm/year.

By substitution of  $P_{CO_2}$  equal to 0.0689 ( $P_{CO_2,r}$ ) from Eq. (26) and  $t$  equal to 28.8 ( $T_r$ ) from Eq. (27) into Eq. (11) and multiplying  $\partial d_B(t)/\partial t$  by the correction  $F_{pH}$ , and dividing it by  $\partial d_n(t)/\partial t$ , one obtains the following relation:

$$\log[f(T_r, CO_{2,r})] = \log \left( \frac{\partial d(t)}{\partial t} \right) = \log(F_{pH}(T_r, P_{CO_2,r})) - \frac{1710}{28.8 T_r + 273} + 0.67 \log(P_{CO_2,r}) + 5.1933 \quad (29)$$

Fig. 4 shows the correction surface calculated from Eq. (29) at different values of carbon dioxide and temperature ratios.

The sensitivity of  $f(T_r, CO_{2,r})$ , as given by Eq. (29), to temperature or  $CO_2$  ratio is estimated as the first derivative of it with respect to  $T_r$  or  $CO_{2,r}$ , respectively. These derivatives are estimated numerically since it is difficult to be calculated analytically.  $pH_{sat}$  is calculated as the minimum of two formulations and  $F_{pH}$  formulation is

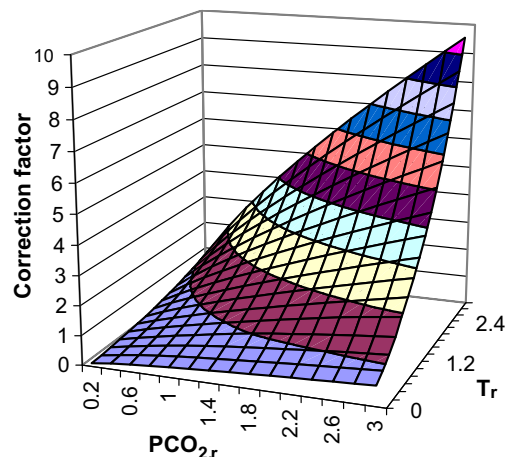


Fig. 4. Correction with respect to  $CO_2$  and temperature.



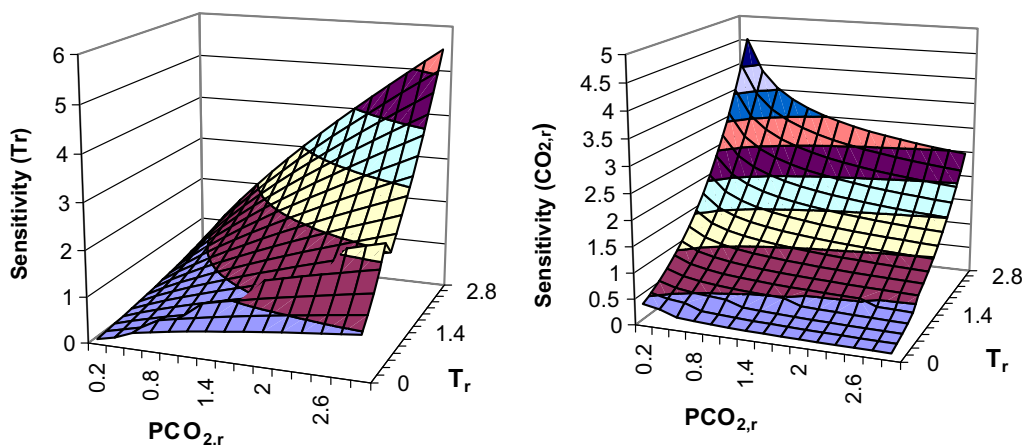


Fig. 5. Sensitivity with respect to  $\text{CO}_2$  and temperature.

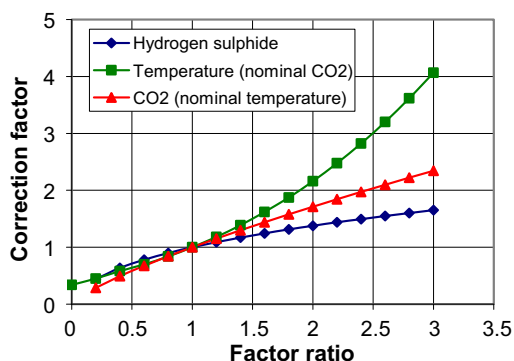


Fig. 6. Correction factors of the various tank environmental parameters.

defined based on  $\text{pH}_{\text{sat}}$  and  $\text{pH}_{\text{act}}$  values. From Fig. 5 (left) it can be observed that the sensitivity of  $f(T_r, \text{CO}_{2,r})$  to temperature ratio is directly proportional to both carbon dioxide and temperature ratios. From Fig. 5 (right) it can be observed that the sensitivity of  $f(T_r, \text{CO}_{2,r})$  to  $\text{CO}_2$  ratio is directly proportional to temperature ratio and inversely proportional to carbon dioxide ratio. The sudden changes in the shape of  $f(T_r, \text{CO}_{2,r})$  surface, as shown in Fig. 5, are corresponding to  $T_r$  and  $\text{CO}_{2,r}$ -values where  $\text{pH}_{\text{sat}}$  or  $F_{\text{pH}}$  is calculated from different formulations.

Fig. 6 shows the different correction factor models considered for the crude oil tank atmosphere after calibration to real data. It is important to notice that the temperature correction curve corresponds to the nominal  $\text{CO}_2$  for all temperature ratios and the  $\text{CO}_2$  correction curve corresponds to the nominal temperature value for all  $\text{CO}_2$  ratios.

## 8. Numerical example

This numerical example represents a simple application of the proposed model on the assessment of the corrosion degradation through the atmospheric space inside the crude oil tanks. As stated earlier the corrosion model proposed by Guedes Soares and Garbatov [13] will be considered here as the standard model and its parameters which are used here are obtained from the regression analysis of Garbatov et al. [10], as indicated in Table 1. The data used to fit that model is collected based on corrosion measurement of deck plating through the crude oil tanks from many tanker ships navigating through different environments, under different operational conditions and carrying different crude oil types, it could be

assumed that the fitted model is corresponding to mean physical and chemical conditions. These mean conditions are considered here as the standard conditions. The corrosion measurements are usually performed without any assessment of the physical or chemical conditions of the ship tanks as happened with the data used by Garbatov et al. [10]. Therefore, the standard average conditions considered here (see Table 3), are estimated by averaging the data given by Katoh et al. [15] (see Table 2 and Fig. 1).

The results of gas composition inside crude oil tanks, indicated in Table 2, are considered through this example as five different crude oil tank cases. The corrosion degradation of the deck plating for each tank case will be assessed by the proposed model as a short-term assessment. Then all of the cases will be combined together to estimate the long-term assessment of the corrosion degradation in the deck plating of oil tankers. Both of the concentrations of hydrogen sulphide  $\text{H}_2\text{S}$  and carbon dioxide  $\text{CO}_2$  are available for each case while the temperature corresponding to each one is not defined. For this reason, the temperature corresponding to each case is assumed to be the same and equal to the standard value indicated in Table 3.

The actual ratios of hydrogen sulphide, carbon dioxide and temperature corresponding to each tank case are calculated by dividing their values by the nominal ones indicated in Table 3. Then, the corresponding corrections are assessed from Eqs. (8) and (29). Eq. (29) combines the corrections for both carbon dioxide and temperature together.

The short-term corrosion degradation assessment corresponding to each tank case is estimated by correcting the standard corrosion model given by Eq. (2) to the actual conditions of each tank case using Eq. (3). Then the long-term corrosion degradation is assessed, using Eq. (4), assuming the ship tanks subjected to all the tank cases indicated in Table 2 through the ship's life. It is assumed here that the ship tanks will be subjected to each individual tank case for equal periods through the vessel life. Since there are five tank cases, this implies that the weighting factors indicated by Eq. (4) will be of the same value and equal to 0.2 (see Fig. 7).

It is assumed for the analysis that the coating life has the same performance through any tank case and for short-term and long-term analysis conditions.

It can be noted from Fig. 7 that the tank case 5C shows the most short-term aggressive corrosion degradation while the tank case 4S shows the lowest one. This observation can be explained by comparing it with the concentrations of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  through the different tank cases indicated in Table 2. From this comparison one observes that the tank case 5C can indicate the highest concentrations of  $\text{H}_2\text{S}$  and  $\text{CO}_2$  compared with the others, while the tank case

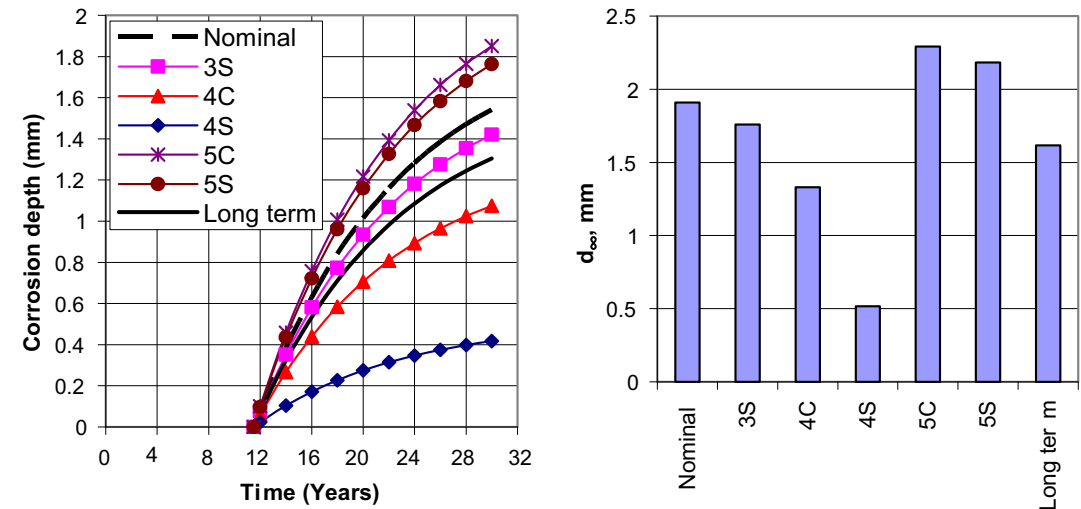


Fig. 7. Short-terms corrosion depth through the ship life (left) and characteristic parameter of long-term corrosion depth,  $d_{\infty}$  (right).

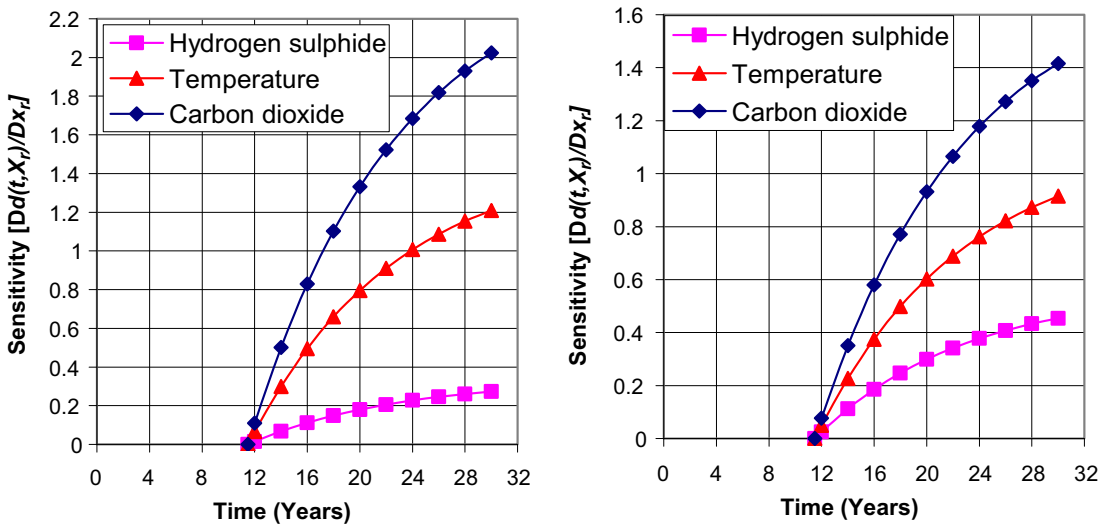


Fig. 8. Time variant sensitivity for the crude oil tank number 3S (left) and 4C (right) with respect to  $H_2S$ , T and  $CO_2$ .

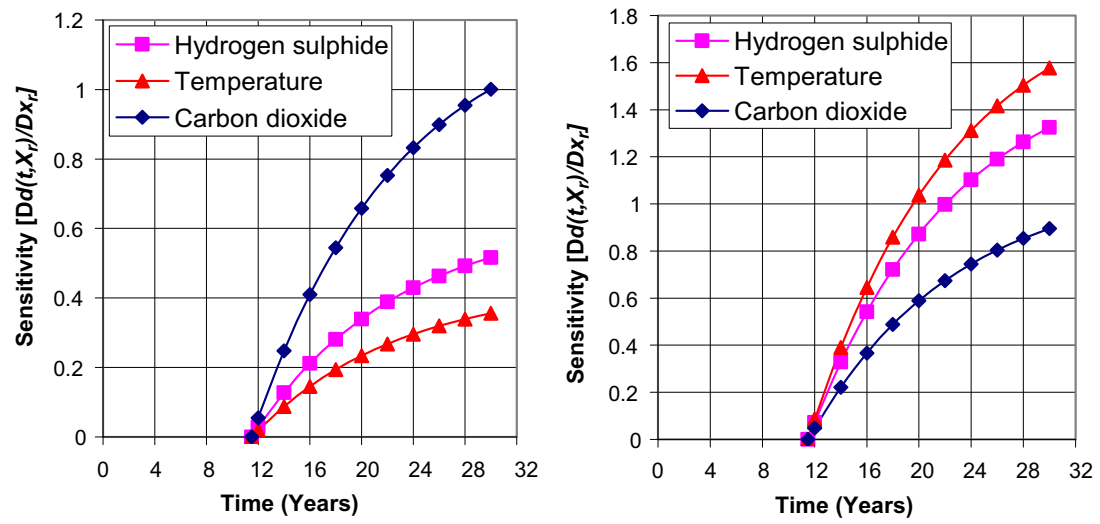


Fig. 9. Time variant sensitivity for the crude oil tank number 4S (left) and 5C (right) with respect to  $H_2S$ , T and  $CO_2$ .

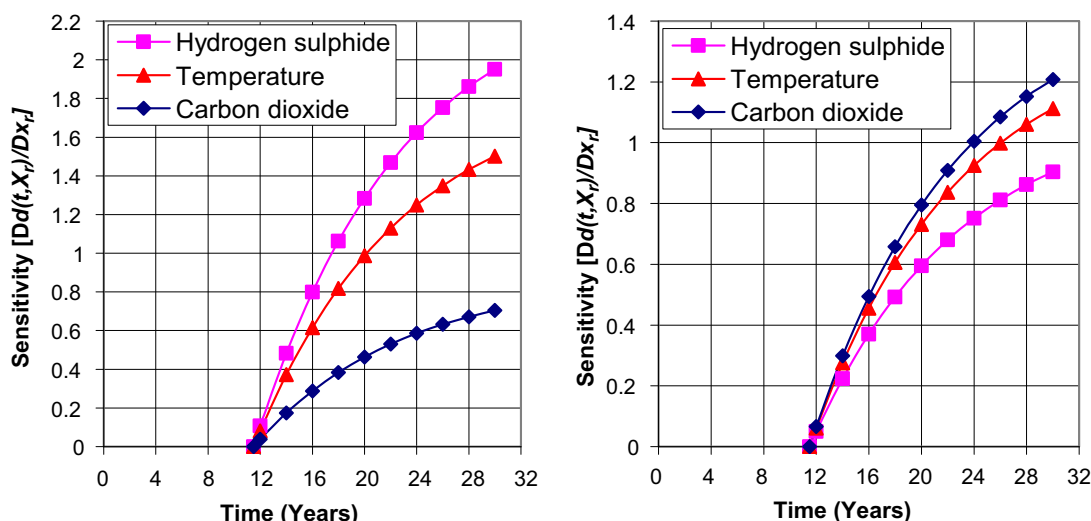


Fig. 10. Time variant sensitivity for the crude oil tank number 5S (left) and long-term corrosion depth (right) with respect to  $H_2S$ ,  $T$  and  $CO_2$ .

4S indicated the lowest concentrations of  $H_2S$  and  $CO_2$  compared with the other tank cases. These differences in concentrations increased the corrections for the tank case 5C and decreased it for the tank case 4S for both of the  $H_2S$  and  $CO_2$  as compared with the other tank spaces. It is observed also from Fig. 7 that the long-term corrosion trend is lower than the nominal one. Fig. 7 (right) shows the characteristic parameter  $d_\infty$  of long-term corrosion depths for the nominal, short-term and long-term analysis that agree with the trend of corrosion curves indicated in Fig. 7 (left). The transient time  $\tau_t$  and the coating life  $\tau_c$  are the same for all cases.

The sensitivity of corrosion degradation to hydrogen sulphide  $H_2S$  ratio for each tank case is estimated using Eq. (9) with  $CO_2$  and temperature corrections to the standard corrosion model. The sensitivity of corrosion degradation to  $CO_2$  or temperature ratios for each tank cases is assessed numerically with the first derivative of Eq. (29) with respect to  $CO_2$  or temperature ratio and hydrogen sulphide  $H_2S$  correction to the standard corrosion model. Then, the long-term sensitivity is estimated by weighting and summing the sensitivities corresponding to the different tank cases (see Figs. 8–10).

It can be observed from Figs. 8–10 that the sensitivity to the different factors for the case 3S and 4C is similar, while the sensitivities to the different factors for the case 3S shows more divergence between each factor than for the case 4C. For both cases the sensitivity to carbon dioxide is the highest while the sensitivity to hydrogen sulphide is the lowest. For the case 4S, the sensitivity to carbon dioxide is the highest while the sensitivity to temperature is the lowest. For the case 5C the sensitivity to temperature is the highest while the sensitivity to carbon dioxide is the lowest. For the case 5S, the sensitivity to hydrogen sulphide is the highest while the sensitivity to carbon dioxide is the lowest. For the long-term case, the sensitivity to carbon dioxide is the highest while the sensitivity to hydrogen sulphide is the lowest. It is observed also, that the differences between the long-term sensitivities to the different factors are smaller than those differences for the different tank cases.

## 9. Conclusions

The existing corrosion models applicable to ship structures depend only on time and thus cannot distinguish between ships that are subjected to harder or to more benign corrosion environments.

The model proposed in this paper extends one of the existing models by adding three variables that reflect the relative level of temperature, carbon dioxide and hydrogen sulphide concentrations, which is relevant to the rates of corrosion to be expected in ship tanks. The inclusion of these variables in the model will allow more accurate predictions of the expected corrosion levels and therefore a better planning of the corrosion inspections along the life of the ships with the consequent significant savings. The case study included in the paper demonstrates the type of results the model can provide.

The proposed equation serves also as a guide to ship-owners and Classification Societies about which variables need to be monitored to allow more accurate predictions of corrosion wastage in ship tanks. It is necessary that monitoring programs are put in place so as to produce the required data for validation of the proposed model in the long-term. In fact the availability of such data may allow some adjustment of the proposed equations for the effect of each of the parameters.

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