# EXPERIMENTAL AND THEORETICAL STUDY OF THE PHENOMENA OF CORROSION BY CARBON DIOXIDE UNDER DEWING CONDITIONS AT THE TOP OF A HORIZONTAL PIPELINE IN THE PRESENCE OF A NON-CONDENSABLE GAS

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## EXPERIMENTAL AND THEORETICAL STUDY OF THE PHENOMENA OF CORROSION BY CARBON DIOXIDE UNDER DEWING CONDITIONS AT THE TOP OF A HORIZONTAL PIPELINE IN THE PRESENCE OF A NON-CONDENSABLE GAS

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Experimental and theoretical study of the phenomena of corrosion by carbon dioxide under dewing conditions at the top of a horizontal pipeline in the presence of noncondensable gas (219pp.)

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Under a stratified flow regime and under dewing conditions, internal corrosion can occur at the top of horizontal pipelines. Corrosive gases such as carbon dioxide dissolve in the freshly condensed water on the inner pipewall where continuous injection of inhibitors of corrosion is not possible. In absence of such inhibitors, a thorough understanding of the phenomena of corrosion under dewing conditions is needed to predict the corrosion risk.

The corrosion and condensation rates were studied experimentally in a full-scale flow-loop. The experimental data were compared with theoretical results obtained from a mechanistic model for the prediction of the corrosion rate during Top-of-the-Line Corrosion (TLC). This model solves the hydrodynamics of the condensed liquid and the heat and mass transfer in the gas phase to predict the condensation rate in a horizontal pipeline in the presence of a non-condensable gas. Further, the mass transfer in the condensed liquid is coupled to the thermodynamics of the vapor-liquid equilibrium and to an electrochemical model for the corrosion reaction at the wall. A Computational Fluid Dynamics (CFD) code was implemented to study the influence of mass transfer in the condensed water on the corrosion rate. Based on the chemistry of the condensed liquid the corrosion rate in the absence and in the presence of an iron carbonate scale is computed. The mechanistic model is tuned to a large set of experimental corrosion rates through the use of the superficial porosity accounting for the partial blockage of the corroding surface by the deposition of an iron carbonate scale.

Increasing the gas temperature led to larger condensation and corrosion rates. However, at a higher temperature the corrosion rate was found to decrease due to the formation of a corrosion products scale. The gas velocity was found to influence the condensation rate, which, in turn, influenced the corrosion rate. The total pressure and partial pressure of  $CO_2$  played a less significant role, particularly at low condensation rates. Temperature and condensation rate were found to be the two main parameters influencing the corrosion rate during TLC.

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#### CHAPTER I

#### **INTRODUCTION**

For economical reasons, multiphase effluents are now being sent unprocessed into pipelines rather than being separated and dried prior to transportation. Dry gas transportation shows some uncontested advantages: problems linked with the presence of water in the pipeline such as liquid holdup, slugging, hydrate formation and internal corrosion of the pipeline can be avoided. However, considering the high cost of offshore processing, wet gas transportation is now common practice. As a consequence, intensive research has been, and still is, carried out by the oil and gas industries to understand the problems related to the transport of unprocessed fluids produced from a well.

For the oil and gas companies, the economical implications of understanding internal corrosion of pipelines are considerable: in the oil industry, 25% of the failures are due to internal corrosion. In general, the capital cost of corrosion prevention is around 10% of the project cost and 5-15% of the operating costs. Altogether, the cost of corrosion in the developed countries during the last decade was around 2% of their Gross National Product. These numbers give an idea of the gigantic amount of money lost due the damages by corrosion or invested in corrosion prevention.

Top-of-the-Line Corrosion (TLC) is one of the forms of internal corrosion specific to wet gas transportation. It occurs mainly when significant heat transfer is possible between the warm, unprocessed well gases and a cold surrounding such as deepsea water or frozen land. Under large temperature gradients between the pipe and its surrounding, the water contained in the gas phase condenses on the whole circumference of the internal pipe wall (Figure I.1). Under the forces of gravity, the condensed water drains to the bottom where it accumulates leading to a stratified flow regime. Corrosion is first expected to occur at the bottom of the pipe where all the water collects. However, under sustained dewing conditions, a continuous thin film of condensed water forms around the internal pipe wall, allowing carbon dioxide or some other corrosive gases to dissolve. In this case, corrosion occurs at the top of the line as well.

Usually, corrosion prevention is achieved by the injection of inhibitors of corrosion. These chemicals are liquids that can dissolve either in the aqueous phase or organic phase. In the case of TLC, the injected inhibitors will accumulate at the bottom of the pipe but will not wet the top of the line where corrosion occurs in the condensing water. This explains why the top of the line represents the area of the pipe of main concern for further research on corrosion phenomena in wet gas.

The project of research presented here was initiated and sponsored by the French petroleum company TotalFinaElf in order to understand the mechanisms involved during TLC. Since it is not possible to prevent TLC with the existing inhibition technologies and without high expenses and interruption of the production, it is of prime importance to be able to predict the conditions under which TLC is going to occur. The ultimate goal for the company is to optimize the design of pipelines, for example by selecting corrosion resistant alloy, so that conditions leading to TLC can be avoided. For this purpose, the corrosion rate should be predicted in order to estimate the lifetime of the pipeline. The Institute for Corrosion and Multiphase Technology (Athens, OH) possesses facilities allowing close reproduction of the conditions in the field where TLC is encountered.



a. Water vapor and carbon dioxide diffusion-convection to the wall.



b. Water filmwise condensation on the cooled wall. Carbon dioxide dissolution in the condensed water



c. Water draining to the bottom, stratified flow regime



In a full-scale flow-loop, the condensing and corrosive conditions of TLC are reproduced over a large range of temperatures, pressures, gas velocities, and heat exchanges. Some unique facilities and an extensive experience in corrosion measurement make the Institute one of the very few places in the world able to experiment with corrosion in such conditions. The aim of this project of research is to first determine the parameters that influence the condensation and the corrosion rate in horizontal pipelines in the presence of non-condensable gas (carbon dioxide). This task requests the development and testing of a new kind of instrumentation for corrosion measurements under dewing conditions. Once identified, the influencing parameters are to be experimentally correlated to the condensation and the corrosion rate. The correlations obtained from these study offer a practical way to estimate the lifetime (with respect to corrosion) of a wet gas pipeline. Also, such correlations offer an estimation of the heat loss between the pipeline and the surroundings, depending on the internal parameters in the pipeline.

The research involved here is also theoretical since a deep insight into the phenomena involved during TLC is needed. For these purposes, a mechanistic model involving the thermodynamic, heat and mass transfer, hydrodynamic, chemistry, and electrochemistry of the fluids present in the pipeline is developed. This global approach of the phenomena involved in corrosion, their mechanisms, and how they are interrelated is quite innovative and agrees with some of the recent approaches published in the specialized literature.

Eventually, the mechanistic model developed and tuned against experimental data will be used by the industry to develop a software predicting the condensation rate and the corrosion rate upon the input of primary parameters. This software should help the oil and gas industry make decision about the TLC risks.

#### CHAPTER II

#### LITERATURE REVIEW

#### **II.1** Research specific to Top-Of-The Line corrosion

The TLC phenomenon is not a recent problem. In 1960, a case of TLC was reported in the sour gas field of Lacq in France (Estavoyer, 1981). Author reports that low gas velocities leading to a stratified, or stratified-wavy, flow regime are necessary for TLC to take place. Under such flow regimes, the inhibitors injected to minimize the corrosion occurring at the bottom of the line could not reach the corrosion-exposed area at the top. This observation is confirmed by the fact that no corrosion is detected at the top of a line where an annular inhibited flow is observed.

In the last decade, TLC has been subject to increasing research in view of the numerous field cases reported. Olsen and Dugstad (1991) conducted a systematic research on the parameters influencing TLC. Of first interest is the influence of temperature on the product of corrosion, namely iron carbonate. It appears that at high temperatures (70°C and above) and low condensation rate, a protective, hard to remove film of iron carbonate forms at the surface of the wall. This film still exists but is no longer protective when the temperature drops (50°C and below), and can be removed easily. One way the authors interpret the formation of a film is that the condensation rate in this case is not high enough to lower the iron ion concentration below the saturation point at which iron carbonate precipitates. One can assume that there exists a critical condensation rate above which no saturation of the condensed water by the products of

corrosion can be reached. In the case of TLC where the continuous injection of inhibitors does not minimize the corrosion rate, the formation of a natural protective layer is an inherent way of controlling corrosion. Thus, a perfect understanding on how and when this protective layer forms is a key point of TLC remediation. Olsen and Dugstad (1991) also studied the influence of the gas flow rate on the corrosion rate. They noticed that the higher the gas flow rate, the higher the observed corrosion rate. An increase in gas flow rate would also correspond to an increase in condensation rate. According to this, it is simple to conclude that the gas flow rate influences the condensation rate, which in turn influences the corrosion rate. They also noticed that the higher the bulk temperature in the gas phase, the higher the condensation rate would be. No further explanations were given on this specific point and the authors concluded that four cases are possible:

- At very high condensation rates, the steel is flushed with almost pure  $CO_2$  containing water (the concentration of products of corrosion is negligible and does not influence the corrosion rate), and the corrosion rate can reach several millimeters per year. No iron carbonate was observed on the steel surface.
- At high condensation rates, corrosion is reduced due to accumulation of iron ions that will increase the pH (even if saturation is not reached). The corrosion rate is governed by the rate of the corrosion reaction and the rate of condensation, which increases and decreases the iron concentration, respectively. The iron concentration at which these two counteracting reactions are balanced determines the corrosion rate.
- At low condensation rates (below the critical condensation rate) and low temperature, the solution is saturated with iron ions, but a non-protective scale

will form (due to the slow kinetics of precipitation at a low temperature). The iron ion concentration remains constant, as does the pH of the saturated solution. The condensation rate does not influence the corrosion rate anymore. A balance is achieved between the film build-up and the film removal and the maximum corrosion rate corresponds to that of saturated water.

• At low condensation rates (below the critical condensation rate) and high temperatures, a protective film forms. The solubility product of iron carbonate in water is lowered, thus reducing the saturation level in the water. As a consequence, the maximum corrosion rate is decreased.

Olsen and Dugstad (1991) did not suggest any mechanistic model or correlation to relate the corrosion rate with temperature, condensation rate, gas flow rate, or iron concentration. However, their study on the parameters influencing TLC is an important database on TLC. From their data one can deduce the complex influence of temperature: it will to some extent increase the corrosion rate by increasing the condensation rate and the kinetics of reaction, but also minimize it by aiding in protective film formation.

In 1993, de Waard (1993) developed an empirical model allowing the calculation of the corrosion rate in full pipe flow as a function of the temperature, partial pressure of CO<sub>2</sub>, and pH of the solution. This model predicts the corrosion rate but gives very conservative results if applied to the TLC case. In order to adapt this model to the dewing conditions, de Waard (1993) introduced a correcting factor, F=0.1, for a condensation rate below an experimentally determined critical condensation rate of 0.25 ml/m<sup>2</sup>/s.

The correlation obtained by de Waard is:

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$$log(CR) = log(F) \times 5.8 - \frac{1710}{273 + t} + 0.67 \times log(P_{CO_2})$$
(II.1)

*CR* is the corrosion rate (mm/yr), *t* is the temperature (°C), and  $P_{CO2}$  is the partial pressure of CO<sub>2</sub> (bar).

It was not before 1999 and the case history presented by Gunaltun (Gunaltun, 1999) that a complete description of a TLC case was made. Gunaltun reported the visual inspection of a wet gas pipeline from the field that suffered severe TLC damage. This description provides a better understanding of the TLC process. First, it comes out of the visual observation that three areas of the pipe wall must be considered independently because they are subject to different types of corrosion:

- The bottom of the line is subject to uniform corrosion at a low rate due to injected inhibitors.
- The top of the line (from 10 o'clock to 2 o'clock) is covered with a carbonate scale and with several deep pits.
- The sidewall is uniformly corroded at a much higher rate than the bottom. No carbonate scale formed on this surface. This was explained by the author to be the consequence of a "washing effect": as the water condenses, it drains to the bottom of the pipe under its gravity. Whereas at the top of the line, the surface tension of water allows the formation of droplets that get saturated by corrosion products, thus allowing the partial formation of a carbonate scale.

The author also reports a gas velocity of 7-8 m/s and a stratified flow regime. The shear stress applied to the condensed liquid at the wall was estimated to be 40 Pa and thus negligible compared to gravity forces. The gas temperature was around 80°C and the

surrounding temperature around 25°C, thus causing significant condensation rates. The pH estimated in the freshly condensed water droplet is 4.1 and the pH at saturation is 5.2. It appears that the pH of the condensed liquid gives a good idea of the solubility level of iron ion in the water phase. The corrosion rates measured were of an order of magnitude larger than the one obtained experimentally by Olsen and Dugstad (as high as 2 mm/y) for a condensation rate around 1.5 ml/m<sup>2</sup>/s. Gunaltun concluded by emphasizing the importance of studying the influence of the condensation rate, and particularly the value of the critical condensation rate.

In 2000, Pots published a paper focusing on TLC under scaling conditions (Pots, 2000). He presented the so-called iron supersaturation model to describe the evolution of the corrosion rate as a function of the iron discharge via the condensation rate and as a function of the precipitation rate for the carbonate scale. The iron discharge is expressed as:

$$CR = 2.26 \times 10^8 \times [Fe^{2+}]_{supersat} \times \frac{G_w}{?_w}$$
(II.2)

 $[Fe^{2+}]_{supersat}$  is the iron concentration in the condensed liquid,  $G_w$  is the condensation rate, and  $?_w$  is the density of water. In order to determine the precipitation rate (*PR*) of the carbonate scale, the model uses the expression derived by Van Hunnik (1996):

$$PR = \frac{A}{V} \times A_p \times e \frac{-E_a}{RT} \times K_{sp} \times (s-1)(1-\frac{1}{s})$$
(II.3)

*s* is the supersaturation level:

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$$s = \frac{[Fe^{2+}][CO_3^{2-}]}{K_{sp}}$$
(II.4)

 $A_p$  and  $E_a$  are constants,  $K_{sp}$  is the solubility product, R is the ideal gas constant, A/V is the surface to volume ratio, and T is the absolute temperature. According to Pots' model, the iron concentration is obtained by equating the corrosion rate and the precipitation rate. In turn, the value obtained for the iron concentration allows the calculation of the corrosion rate. Pots compared his model with the experimental data from Olsen and Dugstad (1991), and also with the field data from Gunaltun (1999). The calculated values were in good agreement in both cases. Also, in a comparison with other models, Pots confirmed that de Waard's model is too conservative and the saturation model introduced by Oddo and Tomson (1982) is too optimistic. Thus, this supersaturation model can be considered to be the most accurate model available for TLC under scaling conditions. This model shows the importance of the role played by the condensation rate. In his analysis, Pots insists on the importance of an accurate calculation of the heat transfer coefficient between the gas phase and the surrounding. However, his paper remains unclear as to how he actually calculated this heat transfer coefficient and thus the condensation rate that can be expected. He suggests basing the condensation rate calculation on the temperature drop between the gas bulk and the pipe wall and calculating the maximum mass transfer of water through the gas diffusion boundary layer at the wall. The calculation of the condensation rate of water is a complex task in the case of a gas mixture with non-condensable gas, and requires a much deeper analysis than Pots considered. The experimental validation of the condensation rates

predicted by Pots' model seems questionable, given the fact that the experimental condensation rate were obtained by the condensation of water vapor on the external surface of a cooled carbon steel tube. In the case history reported by Gunaltun and the experimental case reported by Olsen and Dugstad, the condensation would take place on the inner wall of a cooled pipe. This, obviously, is not equivalent to the experimental conditions run by Pots. Moreover, nowhere in his paper does Pots mention the molar or mass composition of his gas mixture, which makes it impossible to compare the condensation rate obtained with some other works done in this area.

Following the case history published in 1999, Gunaltun and Larrey (2000) correlated the corrosion rate with the calculated condensation rates for the specific pipeline of the Tunu field, Borneo. The computation was done including thermodynamics, hydrodynamics, and thermal exchanges packages. This complete approach shows the complexity of determining the actual condensation rate inside a pipeline. The first step is to determine the composition of each phase by assuming that the different phases are at equilibrium. The equation of state chosen in this case is the Soave-Redlich-Kwong equation. Secondly, a hydrodynamic package is needed to determine the actual flow regime and confirm that the TLC can occur at a specific location in the pipeline. The two-phase hydrodynamic model Tacite (Gunaltun, 2000) is a one dimensional (axial) CFD package solving the equation of mass, momentum, and energy for each computational point of the line. By coupling this hydrodynamic package to a thermal exchange package, it is possible to calculate the local temperature and axial velocity of each phase at a given point of the line. The thermal exchange package

determines the radial heat transfer in the pipeline for a steady state flow according to the equation:

$$dQ = U_0 \times 2pR_0 \times (T_F - T_A) \times dL \tag{II.5}$$

dQ is the differential heat loss (W), dL is the elementary length pipe,  $U_0$  is the overall heat transfer coefficient (W/m<sup>2</sup>/K),  $T_F$  is the fluid temperature (K) at the center line,  $T_A$  is the ambient external temperature, and  $R_0$  is the reference radius (m). The overall heat transfer coefficient is equal to:

$$U_0 = \frac{1}{\frac{1}{H_{i0}} + \frac{1}{H_{e0}} + \frac{1}{H_{th0}}}$$
(II.6)

 $H_{i0}$  is the internal (inner wall to effluents) convection coefficient (W/m<sup>2</sup>/K),  $H_{e0}$  is the external (external wall to surrounding fluid) convection coefficient (W/m<sup>2</sup>/K), and  $H_{th0}$  is the effective heat transfer coefficient of the pipe wall, the coating layers, and the insulation layers of the pipe (W/m<sup>2</sup>/K).  $H_{th0}$  is usually well known or made available by the insulating material vendors.  $H_{e0}$  is dependent on the external flow conditions.  $H_{i0}$  is the fluid flow characteristics. In Gunaltun's paper, the thermal resistance associated with  $H_{i0}$ , namely  $R_{i0} = \frac{1}{H_{i0}}$ , is considered to be negligible compared to the thermal resistance associated with the heat transfer coefficient  $H_{th0}$ . This assumption is

completely justified as long as a substantial amount of concrete and heat insulation coating is present of the pipe. However, as was already mentioned, the TLC takes place

when the pipe is in direct contact with the surrounding (no concrete and insulation layer coating). Thus, the assumption of a negligible internal thermal resistance is not acceptable in the specific case of TLC. There is a real need to determine a procedure to calculate accurately the heat transfer coefficient,  $H_{i0}$ , in order to obtain an accurate value of the heat transferred during TLC and thus an accurate condensation rate. Since the model was tuned to match the actual pressure and temperature profiles in the line by modifying the viscosity and the external convection coefficient  $H_{e0}$  respectively, it is probable that the amount of heat removed between two computational points of the pipeline corresponds quite well with the heat lost by the pipeline in reality over the same length of pipe. In that sense, over the length of pipe that represents a step in computation, the average condensation rate is accurately calculated. This does not mean, however, that locally, the condensation rate is properly estimated. The computation step used for the modeling is 5 meters at a location of the pipeline where TLC is expected to take place and 50 meters otherwise. Over such a length of pipe, the temperature profile of the effluents is not known, leaving doubt as to the actual local condensation rate. According to the visual inspection and the calculated condensation rates, Gunaltun and Larrey concluded from this study that the critical condensation rate lies between 0.15 ml/m<sup>2</sup>/s and  $0.25 \text{ ml/m}^2/\text{s}$ . They also confirmed that the influence of the gas flow rate is significant, as is the influence of the inlet temperature of the effluents. One more time, Gunaltun emphasizes the importance of studying the critical condensation rate to properly determine the TLC rate. He also introduces the idea that the critical condensation rate is not unique, but rather a function of temperature.

In 2000, Edwards (2000) focused on the influence of different parameters on TLC during flow in pipelines. The author researched how temperature, pressure, liquid holdup, and flow regime would modify the corrosion rate. Also, the pH was calculated using the Oddo and Tomson (1982) saturation method. He related the water condensation rate with the rate at which the temperature changes beginning with the temperature at the inlet conditions. He confirmed that in the sections of the pipe where the saturated gas would reach equilibrium with the surrounding, no TLC was reported. In agreement with Gunaltun (1999), Edwards confirmed that no inhibition of the top of the line was possible under stratified flow regime. When corrosion would take place, he also observed that the products of corrosion would buffer the pH of the solution thus diminishing the corrosion rate from its value under pure water condensation. More interesting, Edwards actually suggests a way to calculate the corrosion rate when no saturation of the condensed water is possible. At a high condensation rate, a continuous sheet of water should form, and Edwards suggests using the de Waard model (1993) for the computation of the corrosion rate. Since the water is renewed very fast, the author also suggests taking the pH of condensed water at a low level, namely 3.6. In the case of a gradual cooling of the gas, Edwards mentioned that the occurrence of corrosion should follow a statistical function according to where a water droplet would happen to form. He concluded that if a sufficient understanding of the conditions present in the pipeline is achieved, the prediction of the location and the severity of water drop are possible. Hence, an estimation of TLC could be achieved. However, the author mentions the difficult task of achieving such a prediction of TLC according to the fact that multiple forms of corrosion occur during TLC.

Recently, more papers have been published by Schmidt (2001) and Gunaltun (2001) on how to monitor TLC by the use of spreading agents for inhibitors and inhibitor batch treatment, respectively. These two papers show that, currently, the answer for TLC remediation is not known, or that it cannot be achieved without incurring a high expense of batch-treating.

## II.2 Previous research specific to heat and mass transfer under dewing conditions in a horizontal pipe

An important amount of research has been conducted in the last decade to understand and predict top-of-the-line corrosion. Most of the works published conclude with the importance of an accurate prediction of the condensation rate for a better modeling of TLC. However, none of these previous works have shown the means of calculating accurately the value of the condensation rate.

Heterogeneous condensation occurs where the condensing gas is placed in contact with a wall, the temperature of which is lower than the saturation temperature of the gas. At the wall, a condensate forms as a consequence of its contact with the subcooled wall. Further vapor can condense upon the previously formed condensate. Condensation of vapor is, therefore, always associated with mass transfer from the vapor phase to the condensate. During condensation the overall heat transfer process can be subdivided into several steps in which several thermal resistances connected in series, must be overcome. These thermal resistances are associated with vapor phase, the condensed liquid film, the pipe wall, the coating, and the external environment as shown in Figure II.1.



Figure II.1: Equivalent circuit of heat transfer resistances for a pipeline and its surrounding

The relative importance of these resistances compared to the total thermal resistance can be very different. During the first step, vapor arrives at the phase interface under the influence of flow (convective transport) and diffusion (diffusive transport). The second step consists of the condensation of the vapor at the interface. Then, the enthalpy released at the interface is transported through by convection and diffusion to the cool wall. Further on, the heat exchanged at the wall is transported through the pipe wall. The last step is the convection and diffusion of the heat within the surrounding medium. A thermal resistance can be associated with each of these steps.

The thermal resistance in the vapor phase is often small because of good mixing under turbulent conditions. However, it becomes substantial during the condensation of a mixture of vapors and inert gases because of the impeding effect of diffusion. This is the case studied in the present work.

For the conversion of the vapor into liquid, it is necessary that a temperature drop at the interface between the liquid and the vapor exists. Most of the time, this temperature drop is a few hundredths of a degree (Tanasawa, 1991). Correspondingly, the heat transfer resistance at the interface is also negligible and will be considered as such in the rest of this work.

The thermal resistance in the condensed liquid film is the controlling parameter most of the time. However, at very low condensation rates, which is the case when the vapor phase represents a small fraction of the gas phase, the condensate film formed on the wall surface may be very thin (or even discontinuous). The thermal resistance in the liquid film may then be neglected.

Metals are known to be very good conductors. Thus, the thermal resistance in the pipe wall may be neglected (except for thick pipes). However, if some coating or insulation layers are added to the pipe, the resistance to thermal conduction can become the dominant phenomenon. Usually the materials that compose the pipe wall and the coating or the insulation are well known as well as the corresponding conductivities.

The final thermal resistance is due to the external surrounding of the pipe. Depending on the flow and the nature of the fluid (or even the solid) surrounding the pipe, this resistance can change drastically. It would be difficult to give an exhaustive list of the surrounding conditions that may exist. For the time being, it will be assumed that the temperature of the external wall of the pipe (or the coating layer) is known so that the computation of the external thermal resistance is not needed. According to the assumptions previously made, the three resistances to be computed and compared are the vapor phase, the liquid phase, and the wall thermal resistances. The complexity of the task comes from the fact that during the condensation of a vapor from a mixture of vapor and inert gas, none of these resistances is much larger than the others, a priori. Thus, each of them needs to be calculated. The resistance in the metal and insulation is considered to be known and must be compared with the two others thermal resistances. Thus, this work focuses on the estimation of the liquid and vapor thermal resistances. Reading the following paragraphs in which many details are furnished, it must not be forgotten that the ultimate objective of this work is the computation of the condensation rate.

#### II.2.1 The thermal resistance in the liquid

Condensation on a solid surface can happen in two different ways. The first one and the most common form is filmwise condensation. In this case, the condensate forms a continuous film, which covers the surface. This takes place when the liquid wets the surface. The film flows over the surface under the action of gravity or other forces, such as shear stresses due to vapor flow. The second form of condensation is called dropwise condensation. At the contact of the cool wall, the vapor liquefies and forms drops, which grow by direct condensation of water on the drop and by coalescence with other droplets in their path. This process continues until the drops are swept off the surface by the action of gravity or other forces. The details of dropwise condensation are not completely understood but are known to consist of a combination of several random processes and to take place when the liquid does not wet the surface (Tanasawa, 1991). It has been experimentally observed that water vapor will condense dropwise on metal surfaces only with the use of promoters (Merte, 1973). Thus, for the case of common carbon steel pipe it is impossible to maintain dropwise condensation. This is not to be confused with the fact that water condensing as a film can further accumulate to form a droplet if the surface tension forces prevent it from flowing downward on the surface of the pipe.



Figure II.2: Different types of condensation

Since the condensation of interest is filmwise, the flow characteristics of the condensed film need to be studied. Stephan (1992) defines three categories of flow: laminar film with stagnant vapor, laminar film with flowing vapor, or turbulent film with flowing vapor. Laminar films are obtained when the gravity forces are dominant and when the Reynolds number in the liquid film remains low. An empirical equation was suggested by Grober (1961) to determine the critical Reynolds number (see Figure II.3):



Figure II.3: Transition from laminar to turbulent film condensation for a vertical plate. From Grober et al. (1961)

The corresponding correlation is:

$$Re' = 0.3 \times 10^{-2} \times \left[ \frac{?_l ?_l g^{1/3} (T_b - T_w) L}{\mu_l^{5/3} ? h_v} \right]^{3/2}$$
(II.7)

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$$Re' = \frac{\dot{m}_l}{\mu_l} = \frac{h(T_b - T_w)L}{\mu_l ? h_v}$$
(II.8)

 $?_l$  is the liquid viscosity,  $?_l$  is the liquid density,  $T_b$  is the bulk temperature,  $T_w$  is the wall temperature, L is the length of the vertical plate,  $\mu_l$  is the liquid viscosity,  $?h_v$  is the energy of vaporization, and  $\overline{h}$  is the heat transfer coefficient through the condensed liquid. The transition from laminar film to turbulent film occurs for a Reynolds number equal to 350. The assumption made from this point forward is that the flow in the condensed film is laminar. It is also assumed that the shear stress forces due to the gas phase are negligible compared to the gravity forces applied on the condensate. Nusselt also made such assumptions when he developed his theory of film condensation (Nusselt, 1916). Moreover, he assumed a linear temperature profile within the film and a temperature at the gas-liquid interface equal to the saturation temperature of pure steam at the chosen pressure. The equation he obtained for heat transfer coefficient and for a vertical plate is:

$$h = \left(\frac{?_l \times (?_l - ?_g) \times g \times ?h_v \times ?_l^3}{4 \times \mu_l \times (T_b - T_w) \times z}\right)^{l/4}$$
(II.9)

The corresponding film thickness is given by the equation:

$$d = \left[\frac{4 \times ?_l \times \mu_l \times (T_b - T_w) \times z}{?_l \times (?_l - ?_g) \times g \times ?h_v}\right]^{1/4}$$
(II.10)

In the case of TLC, this equation needs to be adapted to the cylindrical geometry of the pipe, which affects the velocity profile in the film and consequently the film thickness.

The derivation of the heat transfer coefficient and the film thickness for a cylindrical geometry will be done later in this project.

Nusselt's theory was further modified to make it more general. Rohsenow (1956) introduced the influence of the subcooling of the liquid and superheating of the vapor in the previous equation. Further modifications also include the fact that the temperature profile is slightly curved. All these modifications can be easily included in Equations II.2 and II.3 by replacing the enthalpy of vaporization by:

$$?h_v^* = ?h_v + C_{Pg} \times (T_b - T_{sat}) + 0.68 \times C_{Pl} \times (T_{sat} - T_w)$$
(II.11)

Chato (1962) actually solved the momentum and energy equation in the liquid film condensing on the inner wall of a pipe (for pure steam). The equation he proposes for the global heat transfer coefficient is:

$$\overline{h} = 0.555 \times \left( \frac{?_l \times (?_l - ?_g) \times g \times \mathbf{D}h_v \times ?_l^3}{\mu_l \times (T_b - T_w) \times D} \right)^{1/4}$$
(II.12)

Equation II.12 is valid in the gas phase for Reynolds numbers lower than 35,000. Depending on what velocity is set for the gas flow, this critical Reynolds number might be surpassed. Therefore Equation II.12 is not suitable for a large range of gas velocities. Moreover, even if the work done by Chato offers a good source of comparison for further research, it is important to include the influence of non-condensable gas that may change the temperature difference used in Equation II.12.

Up to this point it was supposed that the vapor condenses on the wall and drains continuously to the bottom of the pipe. Therefore, the water will tend to accumulate at the bottom and form a pool as described in Figure II.4. The assumption made here is that the
flow regime remains stratified along the entire length of the condensing area. Under stratified flow, the pool at the bottom is the only aspect of the flow that is not covered by filmwise condensation described previously. According to Chato (1962) the heat transfer coefficient through the pool at the bottom is negligible so that the modified Nusselt theory of filmwise condensation only applies on the upper area of the pipe (above the pool).



Figure II.4: Cross section of a pipe during condensation under stratified flow. From deWaard (1993).

In summary, Nusselt's filmwise condensation theory for a vertical plate offers a "base-model" that must be adapted to: the cylindrical geometry of a pipe and the fact that a mixture of vapor and gases flows in the pipe rather than a pure vapor. The velocity profile in the condensed liquid must be computed and related to the local condensation rate according to Nusselt's theory. Also, the temperature difference across the liquid film must be adapted to the present case, and this requires solving the heat, momentum, and mass transfer in the gas phase.

At this point, it can be determined how to compute the thermal resistance in the liquid film, according to the fact that the interface temperature is known. The following paragraph presents an approach on how to determine this interfacial temperature and on how to determine the vapor mass transfer within the gas phase, which is going to influence the condensation rate.

# II.2.2 The thermal and mass transfer resistance in the gas phase



Figure II.5: Schematic of the gas-liquid interface

In the case of condensation of a pure saturated vapor, the vapor pressure  $P_{v}$ , which is also equal to the saturation pressure  $P_{s}$ , is equal to the total pressure of the gas phase P. The temperature is the saturation temperature  $T_{s}$ , corresponding to the vapor

pressure. If vapor condenses in the presence of non-condensable gas, it must diffuse through the gas to the phase interface. For this to happen, a partial pressure gradient of the vapor toward the phase interface is necessary (Tanasawa, 1991). This gradient is due to the condensation of vapor at the interface, which lowers the vapor mass fraction and thus decreases the partial pressure at this same location (see Figure II.5).

The vapor condenses at the saturation temperature corresponding to the partial vapor pressure at the interface. This temperature, denoted  $T_i$ , is lower than  $T_s$ . The driving force for heat transfer across the condensate film decreases from  $T_s - T_w$  to  $T_i - T_w$ . It results in a reduction of the condensing rate. Depending upon the gas content, the saturation temperature  $T_i$  at the interface can be considerably lower than the saturation temperature corresponding to the bulk conditions  $T_b$  (Minkowycz, 1966). The influence of non-condensable gas on the condensation rate is twofold. First, it reduces the temperature difference across the film as previously shown. Second, the mass diffusion through the boundary layer limits the amount of vapor available at the interface for condensation. In order to determine the global effect of non-condensable gas, the ratio of the heat transfer coefficient with non-condensable gas and the heat transfer coefficient with pure vapor (Nusselt's theory) is used (Stephan, 1980). To obtain this ratio, the mass transfer resistance in the concentration boundary layer (where the partial pressure of vapor decreases) and the temperature at the interface  $T_i$ , must be known. Transport of momentum, heat, and mass are coupled (Tanasawa, 1991) and need to be solved simultaneously. The energy balance applied at the condensate surface gives:

$$q_l = q_g + \dot{m} \times ?h_v \tag{II.13}$$

 $q_l$  is the heat flux removed by conduction in the condensate,  $q_g$  is the heat flux supplied by convection of the vapor to the condensate surface, and  $\dot{m}$  is the condensation rate.  $q_l$  and  $q_g$  can be written as:

$$q_{l} = h_{l}(T_{i} - T_{w}) = h_{w}(T_{w} - T_{ext})$$
(II.14)

$$q_g = h_g \left( T_b - T_i \right) \tag{II.15}$$

 $h_l$ ,  $h_g$ , and  $h_w$  are the heat transfer coefficient in the liquid, gas, and pipewall respectively,  $T_w$  is the temperature of the wall, and  $T_{ext}$  is the temperature of the surrounding of the pipe, which is assumed to be constant. It is further assumed that the thermodynamic equilibrium between the gas phase and the liquid phase is obtained and that the mixture mass flow rate  $\dot{M}_g$  flows to the condensing surface. Figure II.6 describes the different fluxes of water vapor moving toward the interface. According to the mass balance applied to the condensing vapor at the surface of the condensate film:

$$M_l = M_g \times y_i + j \times A \tag{II.16}$$

 $\dot{M}_{i}$  is the condensate mass flow rate,  $y_{i}$  is the mass fraction of vapor at the interface, A is the surface of condensation, and j is the diffusion flux of vapor given by:

$$j = -D \times \mathbf{r}_{g} \left(\frac{\partial y}{\partial x}\right)_{i} \tag{II.17}$$

*D* is the diffusivity of the vapor in the gas mixture,  $r_g$  is the density of the gas mixture, and y is the mass fraction of the vapor in the gas mixture.



Figure II.6: Mass balance and concentration profile at the gas-liquid interface

The first term on the right hand side of Equation II.16 is the convective term due to the global movement of the gaseous phase toward the wall. The second term is the diffusion term of the vapor to the wall. By introducing the mass transfer coefficient  $\beta_g$ , the diffusion flux can also be written as:

$$j = \boldsymbol{r}_{g} \times \boldsymbol{b}_{g} \times (y_{i} - y_{b})$$
(II.18)

 $y_b$  is the mass fraction of vapor in the bulk and  $\beta_g$  is the mass transfer coefficient in the gas phase. At steady state, there is no accumulation of mass at the interface. Thus the global mass balance at the interface gives:

$$\dot{M}_{l} = \dot{M}_{g} = \dot{M} \tag{II.19}$$

Substituting Equations II.19 and II.18 into Equation II.16, one obtains:

$$\frac{M}{A} = -?_g \times \beta_g \times \frac{y_i - y_b}{y_i - 1} \tag{II.20}$$

Substituting Equations II.20, II.14, and II.15 into Equation II.13, the following expression is obtained:

$$\frac{h_l}{\frac{h_l}{h_w} + 1} (T_i - T_{ext}) = h_g (T_b - T_i) - \mathbf{r}_g \times \mathbf{b}_g \times \frac{y_i - y_b}{y_i - 1} \times \mathbf{D}h_v$$
(II.21)

To obtain this last equation, one needs to write:

$$\dot{m} = \frac{\dot{M}}{A} \tag{II.22}$$

$$q_{l} = \frac{h_{l}(T_{i} - T_{ext})}{\frac{h_{l}}{h_{w}} + 1}$$
(II.23)

Equation II.23 is obtained from the double equality in Equation II.14. The derivation of this last equation is necessary to explain the strong coupling of the mass, momentum, and energy transfers. Equation II.21 needs to be solved for the temperature  $T_i$  at the interface. Once  $T_i$  is known, the heat flux at the interface is known and so is the condensation rate according to Equations II.14, II.15, and II.13. In Equation II.21, the mass fraction  $y_i$  is the one obtained at saturation conditions (supposed to be known) at the gas-liquid interface. Thus, it is dependent on the temperature,  $T_i$ , which is also the saturation temperature at the interface. In addition, the heat transfer coefficient,  $h_l$  is also dependent upon the temperature,  $T_i$ , as was mentioned at the beginning of the literature review on condensation rate. As will be shown in more detail later on in this work,  $h_l$  is also

dependent on the velocity profile in the liquid phase. Eventually, the computation of  $h_g$ and  $\boldsymbol{b}_g$  is highly dependent on the mass and momentum transfer in the gas phase.

Stephan and Laesecke (1980) derived some correlations for the determination of the heat transfer coefficient during forced convection on a vertical plate with parallel flow in the gas phase based on a typical dimensional analysis:

$$Nu = f(Re^{a}, Pr^{\beta})$$
(II.24)

$$Sh = f(Re^{?}, Sc^{d})$$
(II.25)

$$Nu = \frac{h_g \times x}{\frac{?_g}{}} \tag{II.26}$$

$$Sh = \frac{\beta_g \times x}{D} \tag{II.27}$$

$$Pr = \frac{\mu_g \times C_{pg}}{\frac{?_g}{?_g}} \tag{II.28}$$

$$Sc = \frac{\frac{2}{g}}{D}$$
(II.29)

*x* represents the distance to the top of the vertical plate. The value of the parameters *a*,  $\beta$ , *?*, and *d*, as well as the value of the function *f*, can be found in their work. These correlations allow for the calculation of the mass transfer coefficient  $\boldsymbol{b}_g$ . However, no such correlation is available for the case of flow in pipe.

Minkowycz and Sparrow (1966) solved the heat transfer on an isothermal vertical plate during condensation of steam and in the presence of air as non-condensable gas. The authors modeled the gas-liquid interface as a double boundary layer.



Figure II.7: Influence of the mass fraction and temperature gradient on the heat transfer. From Minkowycz and Sparrow (1966).

The thin liquid film can be naturally considered as a boundary layer. On the other side of the interface, the condensation process activates the transport of mass, momentum, and energy in the vapor-gas mixture. The region in which these transports occur may also be considered as a boundary layer. Thus, there is a pair of co-existing, interacting boundary layers. The authors formulated the governing equations for each boundary layer separately and then coupled them with the corresponding conditions of compatibility at the interface. It is beyond the scope of this review to explain in detail the analytical work achieved by Minkowycz and Sparrow. The results of the simulation show that reductions of more than 50% in the heat transfer rate are observed for bulk mass fraction of air as low as 0.005. The results are reported in Figure II.7 where it can be seen how important the role played by non-condensable gases is. At a fixed mass fraction of non-condensable gas, the reduction in heat transfer is larger as the bulk-to-wall temperature difference

increases. The influence of non-condensable gas is also strongly accentuated by the decrease of the bulk saturation temperature. The major temperature drop occurs in the mixture and therefore determines the amount of vapor that will condense on the wall.

Another experimental study of the influence of non-condensable gas on condensation is offered by Slegers and Seban (1970). The authors measured the heat transfer rate on a vertical plate during the condensation of steam with and without the presence of air as a non-condensable gas. In the presence of non-condensable gases, they also reported a significant change in temperature between the bulk of the gas mixture and the interface (see Figure II.8). They observed that the heat transfer obtained by Nusselt's theory would underpredict the experimental results. A correcting factor of 1.15 was suggested to fit the experimental and theoretical data. The difference may be due to the presence of waves at the gas-liquid interface. These waves produce some mixing that causes better heat transfer. The authors did not correlate the experimental condensation rates they obtained with the other parameters they studied (temperature, mass fraction, etc.). To the knowledge of the author, there is no correlation available for the computation of the heat transfer coefficient during the condensation of a vapor inside a horizontal pipe in the presence of a non-condensable gas. In the present project, it is proposed to derive a complete theory for the computation of the condensation rate based on the assumptions presented earlier. The complexity of understanding TLC comes from the fact that many phenomena are involved and coupled during corrosion under dewing conditions in the presence of a non-condensable gas. Thus, the mechanistic approach for the modeling of such phenomena requires the use of some well-known theories of hydrodynamics, thermodynamics, heat and mass transfer, chemistry, and electrochemistry.

These theories must be adapted to the special case of condensation and corrosion in pipelines and then coupled to solve their governing equations.



Figure II. 8: Temperature profile in the double boundary layer. From Slegers and Seban (1970).

## **CHAPTER III**

## EXPERIMENTAL SETUP AND PROCEDURE

## **III.1** Description of the flow loop

The design of the flow-loop is as presented in Figure III.1. The flow-loop is operated as follows: the tank is first filled with deionized water. The water is then de-oxygenated by bubbling  $CO_2$  gas through it and the system is pressurized. Meanwhile, heat is added to the system using electrical resistance-heaters, which are immersed directly into the water contained in the tank. When the tank temperature approaches the desired test temperature the gas pump is started to begin warming the system. A positive displacement gas pump provides the gas flow rate. The flow loop is a closed loop system, so the  $CO_2$  is re-circulated using the same gas pump. The gas flows out of the pump and into the mixing tank where the gas is combined with water vapor and then flows through four double pipe heat exchangers where the water vapor partially condenses. The gas mixture then travels into a separator where the liquid falls to the bottom to flow back into the tank and the gas is sent back to the pump for re-circulation. A ball valve allows the isolation at the separator from the tank. In this case, the condensed water is re-rerouted to a pressure vessel where it can be collected over time.

## III.1.1 The tank

The tank used for the storage of the water and its warming is a  $1m^3$  stainless steel tank with 3 insertion ports to insert the electrical resistances. It is rated for pressure below

20 bar. Both water and carbon dioxide can be fed into the tank from the bottom, allowing the bubbling of the gas into the liquid. The gas mixture coming from the pump enters the tank through a 4-inch port located above the level of the water, thus limiting the entrainment of liquid. The mixture of water vapor and carbon dioxide occurs in the upper part of the tank and exits the tank through another 4-inch port. The level of water in the tank is continuously monitored to make sure that, at any time, the electrical resistances are properly immersed.

#### III.1.2 The heaters

Immersed electrical resistances are used for heating the system. The reason for this is that a large quantity of heat is required to evaporate a significant amount of water that will subsequently condense in the loop. Since the space available for the heating device is limited (the access to the tank is limited to three 4 inch ports), this solution was chosen. However, some engineering challenges that come with the direct immersion of the resistances into the water need to be overcome. The environment created in the tank is corrosive and the temperature reached at the surface of the heating elements can go as high as 350°C. Therefore, the failure of the heaters by corrosion occurred very fast (within 60 hours), even with the use of stainless steel for the resistance sheath. After repetitive failures, Inconel 625<sup>®</sup> was selected as the construction material for the heating elements. Repassivation of the sheath was scheduled every other month to avoid the development of pits by corrosion on the elements.





Figure III.2: Picture of the entire flow-loop

## III.1.3 The loop

The loop is made of a 4-inch 316 stainless steel pipe. It is 30 meters long and it is thoroughly insulated from the ambient air in the laboratory. The loop is horizontally leveled. In this loop, the gas mixture of water vapor and carbon dioxide flows and condensation of water occurs as this mixture contacts a cooler part of the loop. The condensed water accumulates at the bottom of the pipe and then is moved by the gas phase until it reaches the separator.

# III.1.4 The heat exchangers

Double pipe counter-current heat exchangers are used for the cooling of the gaseous phase. This design was chosen rather than any other since it is easy to implement

on a existing pipe and since the flow profile and heat transfer in the cooling jacket are well known from the literature. The design of the described heat exchanger is given in Figure III.4. Inlet and outlet temperature are monitored both in the pipe and in the cooling jacket. The flow rate of the cooling liquid is also controlled.

# III.1.5 The pump

The pump used for this application is a Moyno Tri-Phase<sup>®</sup> positive displacement progressive cavity liquid pump. The stator is made of rubber and the rotor is made of stainless steel. This liquid pump was adapted to pump wet gas rather than liquids. In the present project, a series of modifications were made after a succession of trials and failures and are worth mentioning:

- A water-lubrication line between the tank and the pump brings the minimum water flowrate needed to lubricate the pump. The pump should always operate with this water-lubrication line to avoid a premature failure of the stator.
- Due to the fact that wet gas is "pumped" rather than water, the shear produced by the rotor on the stator is larger and the temperature reached by the pump is too high for the pump to function properly. As a consequence, the rubber of the stator expands and the shear exerted by the rotor becomes even larger such that the stator can get damaged. In order to keep the temperature low, a cooling device was installed on the lubrication line to cool down the temperature of the water coming from the tank. This lubrication water absorbs the heat produced by the pump and limits the expansion of the stator.

- At larger gas flowrates, the wet gas can carry away the lubrication water contained in the pump faster than it can be added by the lubrication system. Therefore, a recirculation loop was installed between the inlet and the outlet of the positive displacement pump. The preferential path of the water through this recirculation loop allows a longer residence time of the water in the pump.
- Even with such a configuration the heat produced by the shear of the rotor on the stator would lead to the overheating of the seals used on the rotating shaft of the pump. These overheated seals would loose their sealing properties and lead to a leak and the loss of pressure in the system. The cooling of the shaft was done by an external cooling device on the portion of the shaft that is close to the seals. Graphite seals were also used rather than the original seals.

The previously mentioned modifications allow the running of the pump for the pumping of wet gas over a long period of time (more than a week). However, the pump performances prevented any experiments at a temperature higher than 100°C.



Figure III.3: Picture of the modified pump



Figure III.4: Double-pipe counter-current heat exchanger design

The test section is a piece of 4-inch-diameter 316 stainless steel pipe. 4 ports, 2 at the top of the line and 2 at the bottom of the line, are available for the measurement of the corrosion rate by insertion of corrosion monitoring probes. It is surrounded by <sup>1</sup>/<sub>2</sub>-inch-diameter coils. These copper coils represent the cooling device, as shown in Figure III.3.



Figure III.5: Design of the test section (above) and Figure III.6: Picture of the test section and the instrumentation (below)

In order to collect the condensed water without disturbing the flow and the thermodynamic equilibrium in the system, a pressure vessel was connected to the bottom of the separator where the condensed water accumulates. The chamber obtained by closing and opening two valves located before and after the pressure vessel allows the safe collection of condensed water under high pressure and high temperature.

## III.1.8 Operating conditions

The operating conditions for the flow-loop are reported in Table III.1.

	miminum	maximum	
Tank	1 bar	20 bar	
Heaters	0 kW	90 kW	
Pump	1 m/s	8 m/s	
	40°C	100°C	
Cooling device	0 l/min	20 l/min	

Table III.1: operating conditions for the TLC system

# **III.2** Instrumentation and experimental procedure

## III.2.1 Temperature monitoring and control

Temperature is monitored and controlled at the following positions in the system:

 in the tank: a Proportional Integrator Differential (PID) regulator allows the maintenance of the water at a set temperature (+/- 1°C).

- in the gas phase: all around the 30-meter-long loop, thermocouples are installed (at the inlet and outlet of each heat exchanger) to monitor the bulk temperature of the gas phase.
- in the lubrication line: a cooling device is installed on the lubrication line to control the temperature of the lubrication water.
- in the cooling jacket or in the coils around the test section.
- In the heat exchanger: the temperature difference between the inlet and the outlet is monitored. Differential thermocouples are used in this case, allowing an uncertainty of +/- 0.2°C on the difference of temperature.
- at the wall: the wall temperature (or skin temperature) is also monitored by a thermocouple installed in the head of a flush-mounted probe.

## III.2.2 The pressure control and monitoring

The pressure is controlled and monitored in the tank. In order to maintain a constant pressure in the system over large periods of time and even when the condensed water is collected, a pressure regulation valve is installed on the carbon dioxide inlet.

## III.2.3 Flow metering

The flow is monitored both in the gaseous phase and in the cooling liquid. In the gaseous phase, an FMA-900 Series Air Velocity mass flow transducer from Omega<sup>®</sup> is inserted in the pipe after the separator to measure the gas velocity in the driest part of the flow-loop. The transducer is calibrated against air by the company producing the transducer. The reading obtained as an output is given in Standard Cubic Feet per Minute

(SCFM). The sensing part of the transducer is located in the center of the pipe. The cooling liquid volumetric flowrate is also measured on each of the heat exchangers at the inlet of the cooling jacket.

## III.2.4 The condensation rate measurement

Condensation is achieved by the removal of heat from the pipe to the cooling device. Two types of cooling devices were used:

- The double-pipe heat exchanger
- The system of copper coils

The reason behind this double choice is that the heat transfer coefficient is well known from the literature for the double-pipe heat exchanger (in the cooling fluid inside the jacket). Therefore the comparison of the experimental total heat transfer coefficient with the one derived from the developed mechanistic model was possible with such a configuration. In the case of the coils, the heat transfer coefficient between the coils and the pipe is difficult to model and it would not have been possible to compare the experimental results and the theoretical results. On the other hand, the double-pipe configuration would have made difficult the welding of ports for the insertion of the corrosion probes. Therefore, all the experimental results on the corrosion rate were obtained with the coils configuration, the condensation rate being monitored in this case but not predicted.

The experimental procedure is simple: water condenses on the internal wall of the pipe as the cooling liquid flows in the cooling device and removes some heat from the pipe. Both the temperature and the flow rate of the cooling liquid can be modified to vary the heat transfer coefficient on the cooling side. Condensed water is separated from the gas phase in the separator and drains into a 25-liter pressure vessel where it accumulates over time. After a fixed amount of time, the pressure vessel is isolated from the rest of the system by closing a valve and the amount of collected condensed water is measured. It is important to mention here that it was impossible to completely prevent the heat exchanges between the pipe and the ambient air of the laboratory. Even with a large thickness of insulating material, a minimum condensation rate of 0.02 to 0.1 ml/m<sup>2</sup>/s (depending on the temperature of the vapor mixture) would occur without any intentional cooling. This condensation rate will be hereafter called the "natural condensation rate" was measured (in ml/m<sup>2</sup>/s) before the beginning of the cooling and it was subtracted from the total measured condensation rate (in ml/m<sup>2</sup>/s) during cooling.

#### III.2.5 The corrosion rate measurement

The measurement of the corrosion rate represents one of the most challenging aspects of this project. The common electrochemical techniques (Electrical Impedance Spectroscopy or Linear Polarization Resistance) used to measure the corrosion rate failed due to the low conductivity of the condensed water (Sun, 2001). Moreover, at low condensation rate, the discontinuity of the water wetting of the electrochemical probe would have made these measurements impossible. Thus, the techniques used during this study are the Electrical Resistance (ER) measurement and the Coupon Weight Loss (CWL) measurement. Both of these techniques are based on the metal loss measurement (see next paragraph). For both of these techniques, an excellent thermal conductivity between the probe and the pipe and a precise measurement of the skin temperature of the probe are necessary. The reason behind this is that the same thermodynamic and hydrodynamic conditions needed to be achieved on the probe surface and on the pipewall to allow the same condensing conditions. The selected E.R probe is developed by Cormon for the benefit of the company funding the project: TotalFinaElf. This probe, using the Ceion Technology<sup>®</sup>, was tested under flow conditions for the first time at the Institute for Corrosion and Multiphase Technology. The probe has shown its ability to monitor the corrosion rate under dewing conditions and has excellent temperature compensation due to its unique design. Later on, the same probe body as for ER was adapted by the Cormon company to the measurement of CWL according to the design developed at the Institute for Corrosion and Multiphase Technology. This design is to be found in Appendix 1. The design for the E.R probe is not presented here since it is the property of the Cormon company.

The procedure followed for the corrosion rate measurement is as follow: once the system has reached a thermodynamic equilibrium at the desired pressure and temperature, the probe is prepared for insertion into the system. The surface preparation consists of the following steps:

- Removal of any deposit on the surface of the probe by scrubbing
- Washing with diluted phosphoric acid to remove any remaining oxide
- Rinsing of the probe with a large amount of alcohol
- Polishing of the surface

#### Rinsing of the surface of the probe with alcohol

Just after this last step, the probe is inserted in the pipe and mounted flush with the internal wall of the pipe. The probe is then connected to the data acquisition, and the evolution of the wall temperature and the instantaneous metal loss of the sensing element can be monitored with Cormon's lab monitor. At the end of the experiment, the probe is removed and simultaneously washed with a large amount of alcohol. For the ER probe, a picture of the corroding surface is taken. In the case of CWL measurements, the coupon is removed from the probe, weighed, and a picture of the surface is taken.

## III.2.6 More about Electrical Resistance monitoring

The electrical resistance (ER) technique is an "on-line" method of monitoring the rate of corrosion and the extent of total metal loss for any metallic equipment or structure. The ER technique measures the effects of both the electrochemical and the mechanical components of corrosion. It is the only on-line, instrumented technique applicable to virtually all types of corrosive environments. An ER monitoring system consists of an instrument connected to a probe. The probe is equipped with a sensing element (metal or alloy) having a composition similar to that of the process equipment of interest. The electrical resistance of a metal or alloy element is given by:

$$R = \frac{\mathbf{r} \times L}{A} \tag{III.1}$$

r is the resistivity of the element, L is the element length, and A is the cross sectional area. Reduction (metal loss) in the element's cross section due to corrosion will be

accompanied by a proportionate increase in the element's electrical resistance. Practical measurement is achieved using ER probes equipped with an element that is freely "exposed" to the corrosive fluid, and a "reference" element sealed within the probe body.



Figure III.7: Design of the sensing element. (From MetalSamples)

Measurement of the resistance ratio of the exposed element to the protected element is made as shown in Figure III.7. Since temperature changes affect the resistance of both the exposed and protected elements equally, measuring the resistance ratio minimizes the influence of changes in the ambient temperature. Therefore, any net change in the resistance ratio is solely attributable to metal loss from the exposed element once temperature equilibrium is established.

## **III.3** Test matrix

#### III.3.1 Experimentation on the condensation rate

In the field, the conditions encountered vary within the following ranges:

- Gas velocity: 1 to 20 m/s. Above such velocities, the flow regime is no longer stratified but rather annular and TLC is no longer encountered.
- Partial pressure of carbon dioxide: 1 to 20 bar
- Temperature: 40°C to 110°C
- Condensation rate: up to  $5 \text{ ml/m}^2/\text{s}$

In the present study, the following ranges are selected mainly due to the limitations of the gas pump:

- Gas velocity: 2 to 8 m/s.
- Partial pressure of carbon dioxide: 1 to 10 bar
- Temperature: 40°C to 110°C
- Cooling liquid velocity (in the double-pipe heat exchanger): 0 to 0.12 m/s
- The condensation rates to be obtained are dependent on the other parameters and cannot be set, a priori. However, the design of the flow-loop allows the coverage of a range from 0.02 to  $5 \text{ ml/m}^2/\text{s}$ .

# III.3.2 Experimentation on the corrosion rate

The original test matrix run for the corrosion rate measurements is described in Table III.2. The original test matrix was designed to cover the corrosion rate

measurement for 3 temperatures, 3 partial pressures of carbon dioxide, 3 gas velocities, and 3 cooling rates. Some modifications were progressively brought to the test matrix as some intermediate experimental results were obtained and analyzed.

Temperature	Pressure CO2	Vgas	Cooling
( C)	(bar)	(m/s)	
90	2	8	high
90	4	8	high
90	8	8	high
90	4	8	no
70	4	8	no
70	4	8	high
50	4	8	no
50	4	8	low
50	4	8	average
50	4	8	high
50	4	4	high
50	4	2	high

Table III.2: Experimental test matrix for corrosion rate measurement

#### **CHAPTER IV**

## **RESULTS AND DATA ANALYSIS ON THE CONDENSATION RATE**

Within this chapter, experimental condensation rates are reported. For each experiment on the condensation rate that was repeated, the corresponding error bar is plotted along with the corresponding data point. In each case, the error bar represents to the standard deviation.

## **IV.1** Influence of the temperature of the gas phase on the condensation rate

The experimental data obtained with the double-pipe heat exchanger are all plotted against the inlet temperature of the gas phase in Figure IV.1, regardless of the values of other parameters. It can be seen that, whatever the values of the absolute pressure, the partial pressure of carbon dioxide, the cooling liquid flowrate, and the inlet temperature of the cooling liquid are, the condensation rate is strongly dependent on the inlet temperature of the gas phase. Among all parameters, the temperature of the gas phase has a dominant effect on the condensation rate: as the inlet temperature increases, the condensation rate also increases. This can be explained theoretically by the fact that:

- At a higher temperature the amount of water vapor in the gas phase is larger according to the thermodynamics of vapor-liquid equilibrium. The amount of water available for condensation is therefore larger.
- At a higher temperature, the gradient of temperature between the gas bulk and the cooled wall is greater, thus enhancing heat and mass transfer according to

Nusselt's theory of condensation (Nusselt, 1916) modified by Stephan (Stephan, 1992).

The theoretical approach presented in Chapter V offers a better understanding of the multiple and complex influences of the temperature of the bulk on the condensation rate.

The influence of temperature on the condensation rate was also studied by experimentally setting constant all other parameters involved in the condensation process. The experimental results are shown in Figure IV.2 and Figure IV.3. Over a range of temperatures from 50°C to 90°C, the condensation rate increases by a factor 5, both in the absence of cooling or during high cooling. This tends to confirm that over a large range of cooling conditions, identical phenomena occur that involve the temperature of the gas phase. Rather than attempting to correlate the condensation rate to the gas temperature in this chapter, a mechanistic approach of the influence of the temperature on the condensation rate is given in Chapter V. As will be seen later on, it is possible to quite accurately model the influence of the temperature by considering the heat and mass transfer in the gas phase in the presence of a non-condensable gas as the determining phenomeno.



Figure IV.1: Normalized condensation rate as a function of the inlet temperature of the heat exchanger. (1bar<P<11bar), (0.012m/s<Vcooling<0.12m/s). Vgas=3.5 m/s



condensation rate. Gas velocity: 8 m/s, no forced cooling



Figure IV.3: Influence of the bulk temperature of the gas phase on the condensation rate.Gas velocity: 8 m/s, high cooling

#### **IV.2** Influence of the absolute pressure on the condensation rate

At a fixed gas temperature, gas velocity, and cooling liquid temperature and flowrate, the influence of absolute pressure on the condensation rate can be investigated. Figure IV.4 shows that over a wide range of pressures (2 to 8 bar), the absolute pressure does not significantly affect the condensation rate. Theoretically, pressure is involved in the thermodynamic equilibrium of the liquid and vapor phases (see Chapter V for details). The higher the pressure is, the lower is the molar fraction of water vapor present in the gas phase. As a consequence, less water vapor is available for condensation and the condensation rate should decrease. However, pressure is also involved in the heat and mass transfer in the gas phase. At a higher pressure, the heat and mass transfer are enhanced since the phase is denser. This can be better understood by saying that at a higher pressure, the density of the gas is greater and so is the Reynolds number:

$$Re = \frac{\mathbf{r}_g \times V_{gas} \times D}{\mathbf{m}_l} \tag{IV.1}$$

According to Dittus and Boetler (1930), for the case of a turbulent flow in a pipe:

$$\frac{h_{g0} \times D}{I_g} = 0.023 \times Re^{0.8} \times Pr^{0.3}$$
(IV.2)

Thus, the heat transfer coefficient increases in the gas phase as the pressure increases. More heat can be removed from the pipe, which allows a larger condensation of water. Furthermore, the mass transfer coefficient by pure diffusion,  $\boldsymbol{b}_{g0}$ , for a full pipe flow can be estimated using the analogy between heat and mass exchanges, according to which:

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$$\boldsymbol{r}_{g}\boldsymbol{b}_{g0} = \frac{h_{g0}}{Cp_{g}} \times Le^{2/3} \tag{IV.3}$$

In Equation (IV.3), the Lewis number must be defined:

$$Le = \frac{D_w \times \mathbf{r}_g \times C_{pg}}{I_g}$$
(IV.4)

This leads to the conclusion that the mass transfer of water vapor from the gas bulk to the wall increases as the pressure increases. Therefore, the condensation rate should also increase with increasing pressure. These two opposite influences of the pressure on the condensation processes may be the explanation for the fact that no significant change was noticed over the range of pressure studied. The influence of the total pressure on the condensation rate is taken into consideration in the thermodynamic module of the mechanistic model presented in Chapter V. It will be seen that, over the range of temperatures and pressures that were tested, the theory and the experiments agree in demonstrating that the pressure is of little influence.



Gas velocity: 8 m/s, high cooling

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## **IV.3** Influence of the cooling rate on the condensation rate

For the particular case of the double-pipe heat exchanger the experimental results on the influence of the cooling rate can be compared with some previous work from the literature. The experimental results regarding this parameter are reported in Figure IV.5. Four different cooling rates were used: 0, 3, 30, and 66 L/min. For a volumetric flowrate of 0 and 3 L/min, the corresponding flow in the cooling jacket is laminar. For a volumetric flowrate of 30 and 66 l/min, the flow becomes turbulent. From Figure IV.5, it can be clearly seen that, as the flow becomes turbulent in the cooling jacket, the condensation rate is larger but no longer dependent on the cooling rate anymore. This proves that the condensation rate at a higher cooling rate is determined by the heat transfer (and possibly mass transfer) in the pipe rather than in the cooling jacket. At low cooling, this is no longer the case and the condensation rate depends also on the cooling rate. The combined effects of the cooling rate and the temperature on the condensation rate are plotted together on Figure IV.6. The effect of temperature on the condensation rate is dominant at high cooling rates, whereas the effect of the cooling rate is predominant over temperature in the low cooling range.

Regarding the computation of the thermal resistance in the cooling jacket, two correlations from the literature for heat transfer in concentric horizontal annuli were considered. For the turbulent case, the correlation used is the Equation IV.2 from Dittus and Boetler (1930) was adapted to the double-pipe geometry. To do so, the Nusselt's and the Reynolds' numbers are estimated using the hydraulic diameter:
$$D_h = \frac{4 \times wetted \ area}{wetted \ perimeter}$$
(IV.5)

In the case where the flow is laminar, the following correlation from Chen et. al. (1946) was used:

$$Nu = 1.02 \times Re^{0.45} \times Pr^{0.5} \times (\frac{D_h}{L})^{0.4} \times Gr^{0.05}$$
(IV.6)

The Reynolds and Nusselt numbers are estimated according to the equivalent diameter  $R_2$  –  $R_1$  ( $R_2$  being the outer radius of the cooling jacket and  $R_1$  the inner one), L is the length of the heat exchanger, and Gr is the Graetz number given by the equation:

$$Gr = Re \times Pr \times \frac{D_h}{L} \tag{IV.7}$$

The comparison of the condensation rates obtained experimentally and the one obtained by using the correlations presented here is given in Chapter V. These correlations are inserted in the heat transfer module of the mechanistic model developed for the prediction of the condensation rate. In the field, the surrounding conditions of the pipeline vary greatly from one line to another. Thus, there is no direct comparison possible between the present experimental results and the condensation rate obtained in the field. However, as a rule of thumb, one can expect that, in the case of a turbulent liquid surrounding (such as sea water or river crossing) and in the absence of coating on the pipe, the condensation rate will be determined by the heat and mass transfer in the gaseous phase. Thus, most of the experimental and modeling work presented here and in the next chapter is focused on the determination of the internal heat and mass transfer in the gas phase.





Figure IV.6: Condensation rate versus inlet temperature for different cooling rates (1 bar<Ptot<10 bar)

# **IV.4** Influence of the gas velocity on the condensation rate

Heat and mass transfer in the gas phase are related to the gas velocity. At a higher velocity, the Reynolds' number is larger and a more turbulent flow is expected. During turbulent flow, the heat and mass transfer from the gas bulk to the pipewall is more important, which respectively increases the water phase change and the amount of water vapor available at the wall for condensation. Figure IV.6 and Figure IV.7 confirm the fact that at a higher gas velocity, the condensation rate is higher, all other experimental parameters remaining constant. The change is more significant at a higher temperature due to the fact that more water vapor is available for condensation in these conditions. In the absence of forced cooling (the only heat exchanges occurring are the unavoidable heat exchanges through the insulation around the cooling coils), the phenomenon is still visible, showing one more time that the heat and mass transfer in the pipe is the key point for the determination of the condensation rate. The influence of the gas velocity is also modeled in the heat and mass transfer module of the mechanistic model presented in Chapter V. The gas velocity is involved in the computation of the Reynolds' number, which, in turn, affects the heat transfer coefficient in the gas phase according to Equation IV.2.

# **IV.5** Discussion

All the experimental results obtained are qualitatively in agreement with the wellestablished theories of thermodynamics, heat and mass transfer in pipes, and condensation. An increase in the gas temperature, in the cooling rate, or in the gas velocity will lead to an increase in the condensation rate. The quantitative prediction of the influence of these parameters on the condensation rate is the subject of the next chapter. The experimental results show a small influence of the total pressure in the system on the condensation rate, which seems to be in disagreement with the laws of thermodynamics. It can be explained by the fact that there are two opposite effects of pressure on the condensation of water vapor in the presence of non-condensable gases: the influence of increasing pressure, which decreases the amount of water vapor available for condensation, seems to be compensated by the influence of heat and mass transfer in the gas phase, which increases at higher pressure. This compensation was observed over a range of pressure from 2 to 8 bar. This compensation may not predominate at lower or at higher pressures.



Figure IV.7: Influence of the gas velocity on the condensation rate. No forced cooling



Figure IV.8: Influence of the gas velocity on the condensation rate. High cooling.

# MECHANISTIC MODEL FOR THE PREDICTION OF THE CONDENSATION RATE IN HORIZONTAL PIPELINES IN THE PRESENCE OF A NON-CONDENSABLE GAS

CHAPTER V

# V.1 Presentation of the modeling work for the condensation rate

The literature review given in Chapter II has shown that, in order to predict how much water vapor condenses at the inner wall of the pipe, one needs to know the heat and mass transfer from the gas bulk to the gas-liquid interface. Further, as the water vapor condenses on the wall, it forms a thin liquid film. The hydrodynamics of this condensed film must be solved to predict its thickness and the velocity profile of the liquid draining on the wall. Once the velocity profile in the condensed liquid film, the temperature profile, and the film thickness are known, the heat transfer through the condensed water can be predicted. The mass transfer of water vapor from the gas bulk to the wall will occur by diffusion and convection. Diffusion is due to a gradient of concentration of water vapor in the gas phase. Thus, the thermodynamics of vapor-liquid equilibrium for a binary mixture (water-carbon dioxide) must be modeled to predict this gradient of concentration. The modeling of the equilibrium requires knowledge of the temperature profile in the gas phase, which comes back to the modeling of the heat and mass transfer in the gas phase. One can easily understand that the hydrodynamic, thermodynamic, and heat and mass transfer equations are coupled for the specific case of condensation in the presence of a non-condensable gas such as carbon dioxide. The following paragraphs are dedicated to the description of the coupling that exists between these equations and their resolution.

# V.2 Description of the temperature profile in the pipe

In the field as well as in the laboratory, the bulk temperature of the gas phase and the temperature of the surrounding of the pipe can be measured. However, the temperature profile between these two boundaries is unknown and needs to be solved. During condensation, a gradient of temperature exists in the gas phase and in the condensed phase, as shown in Figure V.1. This gradient of temperature in the gas phase implies a gradient of partial pressure of carbon dioxide and of water vapor as well: as the temperature decreases closer to the gas-liquid interface, the partial pressure of water vapor also decreases, according to the laws of the thermodynamics applied to a two-phase binary mixture (Peng and Robinson, 1976). Since the total pressure in the pipe remains constant over a cross-section of the pipe, this implies that the partial pressure of carbon dioxide increases next to the gas-liquid interface. The partial pressure profiles are also reported in Figure V.1. At the gas-liquid interface, a "mixing zone" exists due to the shear exerted by the gas phase on the liquid phase. The effect of this mixing zone is to increase the heat and mass transfer close to the gas-liquid interface. In the liquid phase and beyond the mixing zone, the temperature profile is assumed to be linear as it is the case in Nusselt's theory (Nusselt, 1916). A temperature gradient is shown in Figure V.1

between the inner pipe wall and the surrounding. Depending upon the fact that insulation or coating is used on the pipe, this gradient is more or less important. To calculate the temperature at the interface and at the inner wall the heat flux can be written at the wall, which is done in the next paragraph.



**Figure V.1: Schematic of the gas-liquid interface** 

# V.3 Energy balance at the wall

According to Figure V.2, the energy balance at the wall is given by:

$$\dot{q} = \frac{I_{wall}}{l} \times (T_{wall} - T_{ext}) = \frac{I_l}{d} \times (T_i - T_{wall})$$
(V.1)

 $\dot{q}$  is the heat flux through the wall (W/m<sup>2</sup>),  $T_{wall}$  is the wall temperature (K),  $T_i$  is the temperature at the gas-liquid interface (K),  $T_{ext}$  is the temperature of the medium surrounding the pipe (K),  $I_{wall}$  is the conductance of the steel (W/m/K),  $I_l$  is the conductance of the liquid (W/m/K), d is the thickness of the liquid film (m), l is the thickness of the pipe wall (m).



Figure V.2: Schematic of the heat flux at the wall

The double equality in Equation V.1 leads to:

$$\dot{q} = \frac{h_l}{\substack{l+\frac{l}{2}\\wall}} (T_b - T_{ext})$$
(V.2)

$$h_l = \frac{l_l}{d} \tag{V.3}$$

 $h_l$  is the heat transfer coefficient in the condensed film (W/m<sup>2</sup>/K).

### V.4 Energy balance at the gas-liquid interface

At the interface, the heat transfer from the gas phase to the liquid phase can be written as follow:

$$\dot{q} = h_l \times (T_i - T_{wall}) = h_g \times (T_b - T_i) + \dot{m} \times \mathbf{D} h_v(T_i)$$
(V.4)

 $h_g$  is the heat transfer coefficient in the gas phase (W/m<sup>2</sup>/K),  $T_b$  is the bulk temperature of the gas phase (K),  $\dot{m}$  is the condensation rate (kg/m2/s), and  $Dh_v(T_i)$  is the latent energy of vaporization (J/kg). From Equation V.4 it is seen that once the temperature at the interface  $T_i$  is known, the heat flux is known. Moreover, if the heat transfer coefficient in the gas phase,  $h_g$ , can somehow be estimated, the condensation rate can be obtained from Equation V.4. The following paragraphs describe the method to simultaneously compute the temperature at the interface and the condensation rate, since these two variables are coupled.

# V.5 The influence of the heat and mass transfer resistance in the gas phase on the condensation rate

Conservation of mass at the gas-liquid interface implies that, at steady state, the mass flow rate of the gas mixture flowing to the phase interface is condensed and is drawn off as condensate. According to Figure V.3:

$$\dot{m}_l = \dot{m}_g = \dot{m} \tag{V.5}$$

 $\dot{m}_g$  is the gas mass flow rate from the gas bulk to the interface (kg/m<sup>2</sup>/s),  $\dot{m}_l$  is the liquid mass flow rate from the interface to the liquid bulk (kg/m<sup>2</sup>/s), and  $\dot{m}$  is the condensation rate (kg/m<sup>2</sup>/s). According to Figure V.3, the water vapor mass flux in the gas phase can be written as the sum of a convection term and a diffusion term:

$$\dot{m}_{w} = -\mathbf{r}_{g} D_{w} \frac{\partial y_{w}}{\partial r} + y_{w} \times \dot{m}_{g}$$
(V.6)

 $\dot{m}_{w}$  is the mass flux of water vapor in the gas phase,  $y_{w}$  is the bulk mass fraction of water in the gas phase, and  $D_{w}$  is the diffusion coefficient of water vapor in carbon dioxide.



Figure V.3: mass flux and concentration profile at the gas liquid interface

At steady state, the amount of water flowing from the gas phase to the wall is equal to the amount of water condensing at the wall:

$$\dot{m}_w = \dot{m}_l \tag{V.7}$$

According to Equations V.5, V.6, and V.7, one can write that:

$$\dot{m} = -\mathbf{r}_g D_w \frac{\partial y_w}{\partial r} + y_w \times \dot{m}$$
(V.8)

Further, introducing the mass transfer coefficient,  $\beta_g$ , in the previous equation one obtains:

$$\dot{m} = -\boldsymbol{r}_g \, \boldsymbol{b}_g (\, \boldsymbol{y}_w^i - \boldsymbol{y}_w \,) + \boldsymbol{y}_w \times \dot{m} \tag{V.9}$$

 $y_w^i$  is the mass fraction of water vapor in the gas phase at the interface. Equation V.9 can be rewritten as:

$$\dot{m} = \mathbf{r}_g \mathbf{b}_g \frac{y_w^i - y_w}{y_w^i - l} \tag{V.10}$$

According to Equations V.2 and V.10, the energy balance (Equation V.4) takes into consideration the influence of the mass transfer in the gas phase:

$$\frac{h_l}{1 + \frac{h_l \times \boldsymbol{d}_{wall}}{P_{wall}}} (T_i - T_{ext}) = h_g \times (T_b - T_i) - \boldsymbol{r}_g \boldsymbol{b}_g \frac{y_w^i - y_w}{y_w^i - 1} \times \boldsymbol{D} h_v(T_i) \quad (V.11)$$

In order to calculate the temperature at the interface that would satisfy Equation V.11, the heat transfer coefficient in the condensed film,  $h_l$ , the mass fractions,  $y_w^i$  and  $y_w$ , the heat transfer coefficient,  $h_g$ , and the mass transfer coefficient in the gas phase,  $\boldsymbol{b}_g$ , need to be calculated.

# V.6 Coupling of the condensation rate with the thermodynamics of the binary mixture

Assuming that the pressure in the pipe is known, for a binary mixture the mass fraction  $y_{W}^{i}$  depends only on the temperature at the interface if one assumes that the thermodynamic equilibrium is achieved at this specific location. Equating the chemical potentials between the gas phase and the liquid phase leads to the following equation:

$$y_{w}^{i} = \frac{x_{w} \times P_{w}^{sat}(T_{i})}{P \times F_{w}}$$
(V.12)

 $P_w^{sat}(T_i)$  is the vapor pressure of water at the temperature  $T_i$ ,  $x_w$  is the molar fraction of water in the liquid phase (considered equal to 1 in our case), and  $F_w$  is the fugacity coefficient of water in the gas phase. The vapor pressure of water can be calculated using Antoine's equation:

$$ln(P_i^{sat}) = C_1 - \frac{C_2}{t + C_3}$$
(V.13)

 $P_i^{sat}$  is expressed in kPa, and the temperature *t* is in °C. Antoine's coefficient for the binary mixture considered here is given in Table V.1.

 Table V.1: Antoine's coefficient

	C1	C2	C3
Carbon dioxide	n.a	n.a	n.a
water	16.262	3799.89	226.35

The fugacity coefficient can be calculated by choosing an appropriate equation of state such as Peng-Robinson (Peng and Robinson, 1976). The parameters involved in this equation of state have been experimentally determined for the binary mixture of carbon dioxide and water by Fenghour (Fenghour, 1996). This equation of state, experimentally fitted to the binary mixture of concern, has been implemented to this mechanistic model for computation of the condensation rate in order to compute  $y_w^i$  and  $y_w$ .

# V.7 Computation of the heat transfer and mass transfer coefficient in the gas phase

The approach followed here is to consider the flow conditions as a gas-phase-fullpipe flow, and correct the heat and mass transfer obtained in such conditions to take into account the fact that condensation occurs at the wall (Stephan and Laesecke, 1980). For a full pipe flow, the heat transfer coefficient by pure conduction  $h_{g0}$  can be calculated as follows (Dittus and Boetler, 1930):

$$\frac{h_{g0} \times D}{I_g} = 0.023 \times Re^{0.8} \times Pr^{0.3}$$
(V.14)

Further, the mass transfer coefficient by pure diffusion  $\boldsymbol{b}_{g0}$  for a full pipe flow can be estimated using the analogy between heat and mass exchanges, according to which:

$$\boldsymbol{r}_{g}\boldsymbol{b}_{g0} = \frac{h_{g}}{Cp_{g}} \times Le^{2/3} \tag{V.15}$$

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$$Le = \frac{D_w r_g C_{pg}}{I_g} \tag{V.16}$$

*Le* is the Lewis number. The exchange coefficient for pure heat diffusion and mass diffusion are then modified to take into consideration the suction term due to condensation (Stephan and Laesecke, 1980):

$$h_g = h_{g0} + k \times \dot{m} \times C_{pg} \tag{V.17}$$

$$\mathbf{r}_{g}\mathbf{b}_{g} = \mathbf{r}_{g}\mathbf{b}_{g0} + k \times \dot{m} \tag{V.18}$$

k is a correcting factor. k has a value close to 1 if the condensation rates are small. For the mass transfer correcting factor, the value of 1.15 is suggested in the literature (Stephan, 1992).

# V.8 Determination of the heat transfer in the condensed phase at the wall

The heat transfer coefficient in the condensed film  $h_l$  is the remaining unknown in order to solve Equation V.11 to be solved for  $T_i$ . In Chapter II, it has already been mentioned that filmwise condensation occurs on steel. Under certain assumptions, it is possible to determine an analytical expression for the heat transfer coefficient.

# V.8.1 Filmwise condensation theory

As mentioned in the Chapter II, Nusselt (1916) suggested that the condensing of water on a solid plate would form a thin film falling under the influence of gravity. Nusselt made the following additional assumptions:

- The flow in the falling film is laminar
- Inertia forces are neglected. The only forces applied to the liquid are gravity forces, viscous forces and the interfacial shear stress due to the turbulent gas phase.
- The temperature profile in the liquid film is linear.

Under these assumptions, Nusselt derived the condensed film thickness and the heat transfer coefficient for a vertical plate. The author showed that the heat transfer coefficient could be expressed as a function of the temperature difference between the gas phase and the wall. The present work consists of adapting Nusselt's theory to the geometry of a pipe and in modifying it to take into consideration the presence of non-condensable gas.

#### V.8.2 Momentum balance on the condensed film

From the momentum equation applied to the control volume of liquid film dy\*dz (see Figure V.4), and considering that the film thickness is very small compared to the pipe diameter, one can derive the velocity profile in the y and z direction. One considers locally that the curvature of the film is negligible.

According to Nusselt theory, the forces that apply on a control volume of water are:

- the gravity:  $r_l g$
- the internal shear stress:  $\mathbf{m}^2 dw/dy$  where y is the direction perpendicular to the flow and w is the velocity component in the z-direction.
- the pressure forces:  $-\mathbf{r}_g \ sinj$  where j is the circumferential angle



Figure V.4: Cross section of the pipe, control volume for momentum balance

At steady-state, the momentum balance in the *z*-direction reads:

$$\mathbf{m}(T) \times \frac{d^2 w(y, z)}{dy^2} = -(\mathbf{r}_l - \mathbf{r}_g) \times g \times sin \mathbf{j}$$
(V.19)

To solve this equation for w, one needs to know how the temperature in the condensed film is related to the variable y. A linear profile of temperature in the film of thickness d is assumed. The boundary conditions for temperature are:

- the temperature of the saturated liquid at the interface gas-liquid  $T_i$
- The temperature of the wall  $T_{wall}$ .

Thus, the linear temperature profile in the film is given by the equation:

$$T = T_{wall} + \frac{T_i - T_{wall}}{d} \times y \tag{V.20}$$

d is the film thickness at the location considered. In order to simplify the integration of the momentum balance, the following correlation is used for the viscosity:

$$\mathbf{m}(T) = \frac{a}{1+bT} \tag{V.21}$$

a and b are some parameters. Combining Equations V.19, V.20, and V.21, one gets:

$$\frac{a}{1+b\times(T_w+\frac{T_i-T_{wall}}{d}\times y)}\times\frac{d^2w(y,z)}{dy^2} = -(r_l-r_g)\times g\times sinj \qquad (V.22)$$

The boundary conditions are:

- At y = 0, w = 0 (contact with the wall)
- At y = d,  $\frac{dw}{dy} = 0$  (no shear stress at the interface in the *z*-direction)

The analytical solution of this equation is:

$$w(y,z) = \frac{(\mathbf{r}_l - \mathbf{r}_g) \times g \times \sin \mathbf{j}}{A} \times \left[ \left( B \times \mathbf{d} + \frac{C' \times \mathbf{d}}{2} \right) \times y - B \times \frac{y^2}{2} - C' \times \frac{y^3}{6 \times \mathbf{d}} \right]$$
(V.23)

$$A = a \tag{V.24}$$

$$B = l + b \times T_{wall} \tag{V.25}$$

$$C' = b \times T_i - T_{wall} \tag{V.26}$$

Further, one can relate the velocity profile (in the *y*-direction) obtained for the *z*-component of the velocity to the local mass flow rate draining to the bottom of the pipe:

$$\boldsymbol{G}(\boldsymbol{j}) = \int_{0}^{\boldsymbol{d}(\boldsymbol{j})} \boldsymbol{r}_{l} \times w_{l}(\boldsymbol{y}, \boldsymbol{z}) d\boldsymbol{y} = \frac{\boldsymbol{r}_{l}(\boldsymbol{r}_{l} - \boldsymbol{r}_{g}) \times g \sin \boldsymbol{j} \times \boldsymbol{d}^{3}}{A} \times \left(\frac{B}{3} + \frac{5 \times C'}{24}\right) \quad (V.27)$$

G is the mass flow rate of condensed water per unit of length of pipe. Equation V.27 can be differentiated with respect to d:

$$d\mathbf{G}(\mathbf{j}) = \frac{\partial G}{\partial \mathbf{j}} \times \frac{\partial G}{\partial d} dd + \frac{\partial G}{\partial d} dd$$
(V.28)

Thus,

$$d\boldsymbol{G}(\boldsymbol{j}) = D \times \cos \boldsymbol{j} \times \boldsymbol{d}^{3} \times \frac{\partial G}{\partial \boldsymbol{d}} \times d\boldsymbol{d} + 3 \times \boldsymbol{d}^{2} \times D \times \sin \boldsymbol{j} \times d\boldsymbol{d} \qquad (V.29)$$

$$D = \frac{\mathbf{r}_l \times (\mathbf{r}_l - \mathbf{r}_g) \times g \times (\frac{B}{3} + \frac{5 \times C}{24})}{A}$$
(V.30)

# V.8.3 Energy balance on the condensed film

Now applying the energy balance to the control volume  $d^*dz$  in the liquid film (see Figure V.5), one gets:

$$0 = H - (H + dH) + h_g \times dG - \dot{q} \times dz \tag{V.31}$$

*H* is the enthalpy inflow associated with the mass flowrate G and H + dH is the enthalpy outflow associated with the mass flowrate G + dG.



Figure V.5: Control volume in the liquid film

$$H = h_l \times \boldsymbol{G} \tag{V.32}$$

$$dH + H = h_l \times (\boldsymbol{G} + d\boldsymbol{G}) \tag{V.33}$$

 $h'_{l}$  is the enthalpy of liquid in the control volume,  $h'_{g}$  is the enthalpy of gas entering the control volume,  $\dot{q}$  is the heat flux absorbed by the solid boundary of the control volume. Thus, the energy balance becomes:

$$(\dot{h_g} - \dot{h_l}) \times dG = \dot{q} \times dz \tag{V.34}$$

With the assumption of a linear temperature profile in the liquid film, we can write

$$\dot{q} = \boldsymbol{I}_l \times \frac{T_i - T_{wall}}{\boldsymbol{d}} \tag{V.35}$$

Combining Equations V.29, V.34, and V.35 one obtains the expression (see Appendix 2):

$$\boldsymbol{d}^{3} \times \frac{d\boldsymbol{d}}{d\boldsymbol{j}} = \frac{K}{3 \times D \times \sin \boldsymbol{j}} - \frac{\cos \boldsymbol{j} \times \boldsymbol{d}^{4}}{3 \times \sin \boldsymbol{j}}$$
(V.36)

$$K = \mathbf{I}_{l} \times \frac{T_{i} - T_{wall}}{\mathbf{D}h_{v}(T_{i})} \times R$$
(V.37)

$$h_{v}(T_{i}) = h_{g}' - h_{l}'$$
 (V.38)

The solution to the differential Equation V.36 is (see Appendix 2):

$$\boldsymbol{d}(\boldsymbol{j}) = \left[\frac{4 \times A \times R \times \boldsymbol{l}_{l} \times (T_{i} - T_{wall}) \times \frac{\int (\sin \boldsymbol{j})^{1/3} d\boldsymbol{j}}{(\sin \boldsymbol{j})^{4/3}}}{\left(B + \frac{15 \times C'}{24}\right) \times ?_{l} \times (?_{l} - ?_{g}) \times g \times ?h_{v}(T_{i})}\right]^{1/4}$$
(V.39)

The corresponding heat transfer coefficient is given by the equation:

$$h_{l}(\boldsymbol{j}) = \frac{\boldsymbol{l}_{l}}{\boldsymbol{d}} = \left[\frac{\left(B + \frac{15 \times C'}{24}\right) \times \boldsymbol{l}_{l}^{3} \times \boldsymbol{?}_{l} \times (\boldsymbol{?}_{l} - \boldsymbol{?}_{g}) \times g \times \boldsymbol{?}h_{v}(T_{i})}{4 \times A \times R \times (T_{i} - T_{wall}) \times \frac{\int (\sin \boldsymbol{j})^{1/3} d\boldsymbol{j}}{(\sin \boldsymbol{j})^{4/3}}}\right]^{1/4}$$
(V.40)

Knowing the temperature at the interface  $T_i$  and at the wall  $T_{wall}$ , the local heat transfer coefficient can be calculated with the last equation.

Solving Equation V.11 for  $T_i$  by an iterative method is now possible since all missing variables have been computed or expressed as a function if  $T_i$ . Knowing  $T_i$ , the local heat transfer coefficient and condensation rate can be calculated around the cross section of the pipe according to Equation V.10 and V.4. However, some additional modeling work is needed to predict the condensation rate along the axial direction.

# V.9 Solving the condensation rate in the axial direction

Besides the energy and mass balance at the interface, one must consider the energy and mass balances on a control volume in the gas phase to determine the change in the water vapor mass fraction as the gas mixture flows along the pipe. For the energy balance, it is assumed that the gas mass flow rate  $\dot{M}_g$  remains constant over a small length of condensing zone ( $\dot{m} \times dA$  is considered negligible compared to  $\dot{M}_g$ ) and also that the bulk temperature can be assumed constant over the elementary control volume considered. According to Figure V.6, dA is the exchange area for a control volume of length dx, one can write that:

$$\dot{M}_g \times C_{pg} \times dT_b = h_{g0} \times dA \times (T_b - T_i) + \dot{m} \times dA \times C_{pg} \times (T_b - T_i)$$
(V.41)

**D**A can be obtained by differentiation of Equation V.41:

$$\mathbf{D}A = \frac{\dot{M}_g \times C_{pg}}{h_{g0} + \dot{m} \times C_{pg}} \times \frac{\mathbf{D}T_b}{(T_b - T_i)}$$
(V.42)



A mass balance over the water vapor gives the relation between the condensation rate and the change in the mass flow rate in the gas phase:

$$\dot{M}_g \times y_{wl} = (\dot{M}_g - d\dot{M}_g) \times (y_{wl} + dy_w) + \dot{m} \times dA \qquad (V.43)$$

The overall mass balance over the gas phase gives:

$$d\dot{M}_g = \dot{m} \times dA \tag{V.44}$$

Replacing Equation V.44 into V.43 and rearranging, one obtains:

$$\frac{dMg}{\dot{M}g} = \frac{dy_W}{y_W - 1} \tag{V.45}$$

After integration between the cross sections 1 and 2, the gas mass flow rate is given by:

$$\mathbf{D}\dot{M}_{g} = \dot{M}_{gl} \times \frac{(y_{w2} - y_{wl})}{(y_{wl} - 1)}$$
 (V.46)

Thus, assuming that the flow and composition are known at cross section 1, the mass flow and the flow composition can be derived from Equation V.44 and V.46,

respectively, at cross section 2, which is located in the pipe such a way that DA verifies Equation V.42. The procedure can be iterated along the whole pipe.





Figure V.7: Stepwise computation along the axial direction of the pipe

The assumptions made here are that the mass flow rate in the gas phase, the bulk temperature, and the total pressure are known. The following procedure allows the calculation of the condensation rate along the pipe. According to the notation in Figure V.7, the following procedure allows the computation of the condensation rate along the pipe and verifies the heat and mass balance on both the liquid and the gas phase:

- 1. Guess the interfacial temperature  $T_i(i)$  in the control volume (*i*) having its inlet interface at the position x(i) in the pipe.  $T_i(i)$  should be within the range between  $T_{ext}$  and  $T_b(i)$ .
- 2. Calculate the corresponding mass fraction at the interface  $y_w^i(i)$ . Peng-Robinson's equation of state (1976) is used.

- Calculate h<sub>g0</sub>, b<sub>g0</sub>, m, h<sub>g</sub>, and b<sub>g</sub> according to Equations V.14, V.15, V.10,
   V.17, and V.18, respectively.
- 4. Calculate the heat transfer coefficient  $h_l(\mathbf{j})$  according to Equation V.40.
- 5. Calculate the new value of  $T_i(i)$  according to Equation V.11. Repeat this procedure until the point of convergence of  $T_i(i)$ .
- 6. Once  $T_i(i)$  has converged, the condensation rate  $\dot{m}$  on control volume (*i*) is given by Equation 10.
- 7. Choose a step for the change of the bulk temperature in the axial direction  $DT_b$  (for example 1°C).
- 8. Calculate the area of condensation corresponding to the change in temperature  $DT_b$  according to Equation V.42. Derive the corresponding position x(i+1) = x(i) + dx(i) of the following inlet cross section for the control volume (i + 1).
- 9. Calculate  $D\dot{M}_{g}$  according to the following equation:

$$\mathbf{D}\dot{M}_{g} = \dot{m} \times \mathbf{D}A \tag{V.47}$$

This equation assures that the amount of water condensed is equal to the amount of water that is removed from the gas phase.Calculate the change of the mass fraction in the gas phase according to the modified Equation V.46:

$$y_{W}(i+1) = y_{W}(i) - \mathbf{D}\dot{M}_{g} \times \frac{(1-y_{W}(i))}{\dot{M}_{g}(i)}$$
(V.48)

10. Iterate from Step 1 on the next control volume (i+1) until the end of the pipe is reached.

## V.11 Comparison between the experimental data and the mechanistic model

The use of a double-pipe heat exchanger allowed the validation of the model by comparison with experimental data. As was already mentioned in Chapter IV, the heat transfer in the cooling jacket is to be found in the specialized literature (Chen, 1946), allowing the validation of the heat and mass transfer in the pipe. As already mentioned while deriving the theory of condensation in pipelines, the model takes into consideration the influence of the gas inlet temperature, the total pressure in the heat exchanger, the area available for condensation, the gas velocity, the inlet temperature of the cooling liquid, and the cooling liquid velocity. The calculated parameters include the local condensation rate in the axial and axis-symmetrical directions, the global condensation rate along the exchanger, the bulk temperature profile in the axial direction, the wall temperature profile in the axial and in the axis-symmetrical direction, and the axial temperature profile in the cooling liquid. According to the liquid velocity, the type of flow (laminar or turbulent) in the cooling liquid is determined and the corresponding correlations are applied. In the gas phase, the flow is always considered as turbulent.

# V.11.1 Comparison of the experimental and calculated data

The accuracy of the calculated data was checked by comparing the calculated condensation rate, the temperature change in the gas phase, and the temperature change in the liquid phase with the experimental values (see Figures V.8, V.9, and V.10). This was done over a range of temperatures from 313K to 363K. Experimental pressures are as high as 11 bars.

In general, the condensation rate is well predicted. Using the least square method, a larger scattering is found in the prediction of the experimental differences of temperature both in the cooling liquid and in the gas phase. However, the scattering applies specifically to the data that were obtained for low cooling rates, showing a poor agreement between the experimental data and the correlation for the computation of the heat transfer coefficient in the cooling jacket for laminar flow. At high cooling rates, the predicted temperature difference is close to the experimental one.



Figure V.8: Calculated condensation rate versus experimental condensation rate (45°C<T<95°C) ,(1bar<P<11bar), (0.012m/s<Vcooling<0.12m/s). Vgas=3.5 m/s.



Figure V.9: Calculated versus experimental temperature drop in the gas phase. (45°C<T<95°C) ,(1bar<P<11bar), (0.012m/s<Vcooling<0.12m/s). Vgas=3.5 m/s.

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Figure V.10: Calculated versus experimental temperature drop of cooling liquid. (45°C<T<95°C) ,(1bar<P<11bar), (0.012m/s<Vcooling<0.12m/s). Vgas=3.5 m/s.

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## V.11.2 Discussion on the modeled data

The theoretical effect of the temperature, the pressure, and the cooling rate on the condensation rate have been compared with the experimental data. Some conclusions can be drawn with respect to the validity of the modeling work:

- The general trend of the predicted values follows the general trend of the experimental data. In particular, the influence of temperature on the condensation rate seems to be accurately predicted.
- At a low pressure (1 bar or less), the model tends to overpredict the condensation rate. This is even more obvious when the temperature increases and becomes closer to the boiling temperature of water at the considered pressure. The theory is based on the fact that mass transfer is the limiting factor in the gas phase. When the gas phase is mainly steam (at low pressure and high temperature), the model based on mass transfer seems to reach its limits and overpredicts the condensation rate due to an overly high mass transfer to the wall. It was not possible to achieve temperatures much higher than 100°C during the experimentation. Thus, it was not possible to confirm the validity of the model at higher pressures and higher temperatures. However, the mechanistic model has been developed to work at higher pressures and temperatures as well.

The present model shows its ability to predict the condensation rate and heat transfer during the cooling of a binary mixture of water vapor and carbon dioxide in a horizontal pipe. This comparison with experimental data was only possible over a temperature range of 313°K to 363°K due to the limiting experimental conditions. The estimation of the heat transfer coefficient in the cooling jacket remains difficult:

correlations from the literature were used (Chen et al. (1946) and Dittus and Boetler (1930)) to determine the heat transfer coefficient in concentric annuli in horizontal pipes. The results are in good agreement with the experimental data for turbulent conditions but less accuracy is obtained for a laminar cooling flow. It is recommended to carefully estimate the heat transfer coefficient of the surrounding for each specific case encountered in the field. In the case where the thermal resistance of the surrounding is low, the thermal and mass transfer resistances in the gas phase are the determining factor and the theory of the model presented in this chapter is more accurate for predicting the condensation rate.

#### **CHAPTER VI**

# RESULTS AND PRELIMINARY DATA ANALYSIS ON THE CORROSION RATE

Within this chapter, experimental corrosion rates are reported. For each experiment on the corrosion rate, the corresponding error bar is plotted along with the corresponding data point. The reader is referred to Appendix 8 for more information about how these error bars are calculated and what they represent.

In the subsequent paragraphs, the influence of the following parameters on the corrosion rate during TLC is studied: the bulk temperature of the gas phase, the temperature of the wall, the partial pressure of carbon dioxide, the gas velocity, the cooling rate, and the condensation rate. Obviously, some of these parameters are independent from each other. For example, the temperature and the partial pressure of carbon dioxide can be set independently. Some others are related: according to Chapter V, the temperature at the wall depends on the bulk temperature, the pressure, and the gas velocity. Each time the influence of one of these parameters on the corrosion rate could be isolated from the influence of the others, it was done so. When a parameter is dependent on others, this dependency is mentioned and explained, and its influence on the corrosion rate is studied.

In parallel, the influence of the studied parameter on the condensation rate is reported alongside the corrosion rate. The reason behind this is to get a deeper understanding of the simultaneous changes occurring in the phenomena of condensation and corrosion as the internal conditions in the pipe change.

#### VI.1 Influence of the bulk temperature of the gas phase on the corrosion rate.

The influence of temperature was studied for different partial pressures (2, 4 and 8 bar) of carbon dioxide and different cooling rates (no forced cooling and high cooling).

# VI.1.1 Influence of the temperature on the corrosion rate without forced cooling

Even if no cooling liquid circulates in the cooling device, "natural condensation" takes place (see Chapter IV) and some corrosion can be observed at the top of the line. In Figure VI.1, the normalized corrosion rates measured by the ER probe are plotted as a function of time for different bulk temperatures, the partial pressure of carbon dioxide being set at 4 bar and the gas velocity being set at 8 m/s. The normalized corrosion rate is defined as the ratio of the corrosion rate considered by the maximum experimental corrosion rate observed during this entire experimental study. In the first hours of experimentation, the curves representing the corrosion rate show a sharp decrease of the corrosion rate at temperatures higher than 70°C. Later, the corrosion rate stabilizes to a constant value. The stabilized corrosion rates and the corresponding condensation rates are reported as a function of the temperature in Figure VI.2. First, as the temperature increases, the corrosion rate increases as well. The maximum corrosion rate is reported at 70°C. The trend is then reversed and the corrosion rate decreases as the temperature increases to 90°C. The condensation rate, however, continues to increase as the temperature increases.

# VI.1.2 Influence of the temperature on the corrosion rate under high cooling

The cooling rate is then increased, keeping all other parameters constant. Once again the corrosion rate is plotted against time on Figure VI.3. This time, the corrosion rate does not show an initial sharp decrease over time. The decrease occurs later and is more progressive. The corrosion rate and condensation rate follow the same trends as reported during "natural condensation": independently from the intensity of cooling, the corrosion rate shows a maximum at 70°C and the condensation rate continuously increases with increasing temperature. However, it can be seen from Figure VI.4 that much higher condensation rates and corrosion rates are obtained under high cooling.

The influence of temperature was studied at different partial pressures of carbon dioxide. The results of the experiments are presented in Figure VI.5. The same trend with a maximum corrosion rate of around 70 or 80°C is observed no matter the partial pressure of the system.

#### VI.1.3 Discussion

These results can be interpreted as follow: at low temperatures (below  $\mathcal{D}^{\circ}C$ ), the corrosion rate increases with temperature according to Arrhenius' law applied to the endothermic reaction of corrosion by CO<sub>2</sub>. This is in agreement with previous works reported in the literature review. In particular, de Waard (1993) reports a temperature dependence of the corrosion rate as follow:

$$CR \sim exp(a - \frac{b}{273 + t})$$
 (VI.1)
However, at a higher temperature (above 80°C), the corrosion rate decreases as temperature increases suggesting that an additional phenomenon occurs for such temperatures. There are at least three possible explanations for this. At a higher temperature, the condensation rate is more important and the condensed liquid film is thicker (see Chapter V). Therefore, the mass transfer of corrosive species through the condensed liquid to the wall may be limiting, which may explain a lower corrosion rate. Another explanation is that, at a higher temperature, the precipitation on the wall of the products of corrosion as an iron carbonate layer may partially protect the metal from further corrosion. According to Van Hunnik (1996), the precipitation rate of iron carbonate increases with temperature, following the Arrhenius' law:

$$PR \sim exp(\mathbf{a} - \frac{\mathbf{b}}{R \times T})$$
(VI.2)

Therefore, at a higher temperature, the phenomenon of precipitation of a scale may predominate over the kinetics of the corrosion reaction and may explain the lower corrosion rates observed. The third explanation could come from the electrochemical reaction. At higher temperatures, and thus, higher corrosion rates, the amount of dissolved iron ions present in the condensed water is greater, increasing the pH of the water. The change in pH may, in turn, change the mechanism of the electrochemical reaction at the wall as was reported by Nesic (1995). Therefore, the corresponding corrosion rate may be smaller even if the temperature is higher. All these assumptions are in agreement with the fact that the corrosion rate should be significantly smaller at low condensation rates, as is clearly observed in Figure VI.5.



Figure VI.1: Corrosion rate vs time on E.R probe (Cormon). Influence of the gas temperature.  $P_{CO2} = 4$  bar, Vgas= 8m/s. No forced cooling





Figure VI.3: Corrosion rate vs time on E.R probe (Cormon). Influence of gas temperature.  $P_{CO2} = 4$  bar,  $V_{gas} = 8$  m/s. High cooling.



P<sub>CO2</sub> = 4 bar, Vgas= 8 m/s, high cooling



at different partial pressures of  $CO_2$  and different cooling rates. $V_{gas} = 8m/s$ 

For all the experiments conducted at a partial pressure of 4 bar and a gas velocity of 8m/s, the experimental corrosion rate and the condensation rate are plotted against the wall temperature (see Figure VI.6). For each wall temperature, the corresponding bulk temperature is reported in Table VI.1.

#### Table VI.1: Wall temperature and bulk temperature of the gas phase

	Bulk temperature (°C)	Wall temperature (°C)
No forced cooling	51	51*
	72	72*
	95	95*
High cooling	51	40
	72	61
	91	81

\* Temperature difference between the bulk and the wall is too small to be measured by the thermocouple

The wall temperature is not an independent parameter since it depends on the total pressure in the system, the cooling rate, the gas velocity, and the bulk temperature. However, it makes sense to study its influence on the corrosion rate, since, in theory, it is the temperature at the wall rather than the one in the gas bulk that should be considered for the prediction of the kinetics of the chemical and electrochemical reactions. The changes in the corrosion rate observed in Figure VI.6 cannot be explained by the influence of the wall temperature alone: for example, at 51°C and under "natural condensation", the corrosion rate is lower than the one data do°C, but at a higher

cooling and a higher condensation rate. Therefore, it can be concluded that both the wall temperature and the condensation rate influence the corrosion rate. For a constant cooling rate, however, Figure VI.6 shows that the influence of the wall temperature on the corrosion rate is similar to the influence of the bulk temperature in the gas phase on the corrosion rate. The explanations for the observed trends are the same as the one given in section VI.1.3.

The influence of the condensation rate on the corrosion rate is studied later on in this chapter. It is interesting to mention here that, as the normalized condensation rate increases above 0.11, the corresponding corrosion rates are 2 to 3 times higher, all other parameters remaining almost constant (see Figure VI.7).



Figure VI.6: Condensation rate and corrosion rate as a function of the wall temperature  $P_{CO2} = 4$  bar, Vgas = 8m/s. No forced cooling and high cooling



and different condensation rates.  $P_{CO2} = 4bar$ , Vgas = 8m/s.

#### VI.3 Influence of the partial pressure of carbon dioxide on the corrosion rate.

The influence of the partial pressure of carbon dioxide was studied at 50, 70, and 90°C. At 90°C, the corrosion rate was studied under natural condensation and at high cooling. The experimental results regarding the corrosion rate and the condensation rate are plotted in Figure VI.8 and Figure VI.9, respectively. From Figure VI.8 it can be seen that the partial pressure has little influence on the corrosion rate, both at 50°C and at 90°C without cooling. On the other hand, at 70°C and at 90°C with high cooling, the influence of the partial pressure of carbon dioxide is more significant. As the partial pressure doubles, the corrosion rate increases 40% at 70°C and more than 110% at 90°C. Comparatively, de Waard's correlation (de Waard, 1993) predicts a 60% increase of the corrosion rate as the partial pressure of carbon dioxide doubles.

Furthermore, it is interesting to note that, at 50°C and at 90°C without cooling, Figure VI.9 shows relatively low condensation rates, whereas for higher temperatures, the condensation rates are more significant. Thus, it appears from the comparison between Figure VI.8 and Figure VI.9 that the corrosion rate is sensitive to a change in partial pressure of carbon dioxide at high condensation rates but is insensitive to such a change at low condensation rates. This observation can be explained as follows: at low condensation rates, it may be easier to saturate, or even supersaturate, the condensed liquid with the products of corrosion, thus increasing the pH, and somehow, slowing down the kinetics of the reaction of corrosion by CO<sub>2</sub>.



Figure VI.8: Influence of the partial pressure of carbon dioxide on the corrosion rate.  $V_{gas} = 8m/s$ .





At higher condensation rates, the buffering of the pH of the solution by iron ions may be impossible and the pH might be more sensitive to the change in partial pressure of carbon dioxide. In Chapter VII, the change in pH and its influence on the corrosion rate during TLC is modeled according to Nesic's electrochemical model (Nesic, 1995).

### VI.4 Influence of the gas velocity on the corrosion rate.

The influence of gas velocity on the corrosion was studied over a range from 2 to 8 m/s. It was studied both at a gas temperature of 90°C and 50°C. The experimental results of the corrosion rate versus time are plotted in Figure VI.10 and VI.11, respectively. At high temperature, the stabilized corrosion rate does not seem to be significantly affected by the change of gas velocity. On the other hand, at 50°C, a sudden change of the corrosion rate is observed as the gas velocity drops from 4 to 2 m/s.

It appears that gas velocity does not have a direct effect on the corrosion rate, but rather on the condensation rate, which, in turn, may affect the corrosion rate. This is clearly demonstrated by Figure VI.12 where both the condensation rate and the corrosion rate are reported as a function of the gas velocity: at 90°C as well as at 50°C, the condensation rate drops as the gas velocity decreases from 8 to 2 m/s. Mass transfer in the gas phase is less important for a less turbulent flow (low velocities). Therefore, less water is available for condensation at the wall and less heat is removed, preventing the phase change of the water vapor. Meanwhile, the corrosion rate the condensation rate below a certain critical value.



Influence of the gas velocity.  $P_{\rm CO2}$  = 8 bar, high cooling, Tbulk = 90 °C.





Figure VI.12: Influence of the gas velocity on the condensation rate and on the corrosion rate. High cooling,  $P_{CO2} = 8$  bar

The study of the influence of the condensation rate on the corrosion rate, in general, and of the existence of a critical condensation rate, in particular, represents the topic of the following section.

## VI.5 Influence of the condensation rate on the corrosion rate.

The condensation rate during TLC has been thoroughly studied in Chapter V. This study demonstrates that the condensation rate is dependent on all other parameters without exception. However, it appears from the previously reported experimental data that the role of the condensation rate is central in the determination of the corrosion rate during TLC. Therefore, its influence on the corrosion rate is studied here. In the previous section, it was reported that it is in the lower range of condensation rates that a significant influence of the condensation rate on the corrosion rate can be observed. Thus, the influence of the condensation rate was studied at 50°C, where lower condensation rates occur. It was possible to change the condensation rate by an order of magnitude, only by changing the temperature of the pipewall a few degrees. The results of these experiments are reported in Figure VI.13 where it can be seen that the normalized corrosion rate jumps from a steady value of 0.14 to 0.34 as the normalized condensation rate crosses a threshold in the range of 0.02 to 0.043. This confirms the existence of a threshold for the condensation rate that was already observed while studying the influence of the temperature and of the gas velocity.



Altogether, the experiments showed:

- An increase of the normalized corrosion rate from 0.14 to 0.32 at 50° C as the normalized condensation rate increases from 0.015 to 0.11 by applying an intentional cooling
- An increase of the normalized corrosion rate from 0.14 to 0.3 at 50° C as the normalized condensation rate increases from 0.03 to 0.06 by changing the gas velocity
- An increase of the normalized corrosion rate from 0.14 to 0.34 at 50° C as the normalized condensation rate increases from 0.02 to 0.04 by changing the wall temperature

Therefore the critical condensation rate at  $50^{\circ}$  C is experimentally found to be between 0.03 and 0.04, and the corresponding increase in the corrosion rate is around 150%.

The concept of a critical condensation rate is in agreement with the theory of a corrosion rate controlled by the level of saturation of the condensed water by the products of corrosion. At high condensation rates, the bulk of the condensed water may never become saturated. In this case, the corrosion rate would not be dependent on the condensation rate, since no significant change in pH can occur by an increase of the iron ion concentration. At low condensation rates, the water is more likely to become supersaturated with the products of corrosion. In this case, the corrosion rate would be affected by a higher pH and a lower availability of corrosive species in solution. If the temperature is high enough, the formation of a scale of iron carbonate may be possible, which could further decrease the corrosion rate. In-between these two situations of corrosion, a transition regime may exist, where the pH of condensed water changes

rapidly with small perturbations of the primary parameters. Therefore, the sensitivity of the corrosion rate to the condensation rate, the wall temperature, and the partial pressure of carbon dioxide would be greater. This theory may explain the sudden jumps in the corrosion rate observed by changing the normalized condensation rate from 0.02 to 0.04 and the wall temperature from 49 to 51°C. A model for the determination of the pH of condensed water and its influence on the electrochemical reactions at the wall during TLC is presented in the following chapter.

#### VI.6 Other experimental results

#### VI.6.1 Reproducibility of the results

In order to gain some confidence in the corrosion rates obtained with the ER probes from Cormon, one specific test was repeated 5 times as the probe was aging and each time a new probe was used. The conditions set for the reproducibility test are:

- $T_{gas} = 50^{\circ}C$
- $P_{C02} = 4 \text{ bar}$
- $V_{gas} = 8m/s$
- High cooling rate

This base test was found to give a mean normalized corrosion rate of 0.312 with a standard deviation of 0.023. The maximum corrosion rate measured is 9% higher than the average corrosion rate and the minimum corrosion rate reported is 8% lower than the

average corrosion rate. The experimental results for this reproducibility test are reported in Table VI.2.

# Table VI.2: Reproducibility of the results with ER probe (Cormon)

Experimental conditions:  $T_{gas} = 50^{\circ}C$ ,  $P_{CO2} = 4$  bar,  $V_{gas} = 8$ m/s, high cooling \*Normalized corrosion rate =  $\frac{\text{corrosion rate}}{\text{maximum corrosion rate}}$ 

Test	ER Probe	Normalized
		corrosion rate
#1	#1	0.32
#2	#1	0.32
#3	#2	0.28
#4	#2	0.30
#5	#3	0.34

#### VI.6.2 Influence of the position of the probe

During the experimentation, the probe can be either flush-mounted to the inner pipewall or a 4-millimeter gap can be left between the surface of the probe and the surface of the pipe, forming an artificial cavity in the wall. When it is not in its flush-mounted configuration, the probe is referred to as the "cavity" probe (see Figure VI.14).



Figure VI.14: Schematic of the flush-mounted and "cavity" probes

Experiments were run simultaneously with a flush-mounted and a "cavity" probe. The results of the experiments show that different corrosion rates occur at the wall depending on the position of the probe. In Figure VI.15, it can be seen that higher corrosion rates are measured by the flush-mounted probe for temperatures lower than 80°C. However, as the temperature increases above 80°C, the corrosion rate monitored by the "cavity probe" becomes greater than the one measured by the flush-mounted probe. It is quite possible that the condensation rate in the cavity is lower according to the fact that the hydrodynamics of the condensed water is different. Water that condenses in the cavity can remain in the cavity for a longer time. Therefore, its level of saturation can be higher, which would explain the lower corrosion rates observed for temperature lower than 80°C. At a higher temperatures, the condensation rate may be so high both on the "cavity" probe and on the flush-mounted probe that no significant difference of the corrosion rate is observed. As the temperature increases further, a protective scale is more likely to form on the probes. The temperature measured by the flush-mounted probe for a gas bulk temperature of 101°C is 4°C higher than the temperature measured by the "cavity" probe. This may explain why the rate of corrosion of the flush-mounted probe is lower at higher temperatures.

This set of experiments shows the importance of the hydrodynamics of the condensed water on the corrosion rate during TLC. Also, it was noticed after experimentation that the corroding element on the flush-mounted probe would show a much more irregular surface than the corroding element on the "cavity probe". Some cavities and crevices were observed on the former that could not be visually noticed on the latter. It is possible that the flush-mounted probe suffered flow-enhanced corrosion at

a faster rate than the "cavity probe" due to its preferential exposition to the shear exerted by the gas phase.

#### VI.6.3 Comparison between ER and coupon weight loss measurement

The corrosion rate was measured by two different techniques during 3 experiments. The corrosion rate according to the Electrical Resistance (ER) measurements and according to the Coupon Weight Loss (CWL) measurements are reported in Figure VI.16. In general the two measuring techniques show the same trend. The corrosion rates obtained by CWL measurements are smaller than the corrosion rates obtained with the flush-mounted ER probe. However, they are in good agreement with the measurement obtained with the ER "cavity probe". It is important to mention that the surface of the coupon is much flatter than the surface of the ER probe. Therefore, flowenhanced corrosion is more likely to occur on the ER probe than on the coupons. This could explain the better agreement on the corrosion rate obtained between the "cavity" probe and the coupon, since both are less sensitive to the shear of the gas phase. No pit or crevice was visually observed on the coupons after experimentation. Also, it is possible that the calibration of the flush-mounted probe was less precise than the calibration of the "cavity" probe. These probe are calibrated by the company Cormon and very little information is given regarding the techniques and constants of calibration used. Therefore, it is quite possible that the difference in the values measured comes from a less accurate calibration on one of the probes.

The visual inspection of the coupon confirmed the preferential formation of a scale at higher temperatures (see Figure VI.17). The iron carbonate scale is black in color

and more difficult to remove as the temperature increases. At 50°C, there is no obvious presence of a deposit on the coupon.

#### VI.7 Summary

The amount of information collected experimentally and the number of assumptions made to explain the observed phenomena are quite important. Therefore, a summary of the main phenomena observed is given here:

- At high condensation rates as well as at low condensation rates, the corrosion rate increases with temperature until its reaches a maximum around 70-80°C. Then, the corrosion rate decreases as the temperature increases, which can be explained by the formation of a partially protective scale of iron carbonate on the wall. This scale slows down further corrosion by limiting the transport of corrosive species to the wall.
- The partial pressure of carbon dioxide does not seem to influence the corrosion rate at low condensation rates, but it has a significant effect at high condensation rates. It is possible that at low condensation rates, the iron ions produced by the corrosion reaction buffer the pH of the condensed water, slowing down the kinetics of the corrosion reaction.
- The change in gas velocity showed no direct effect on the corrosion rate, except when this change would lead to a decrease of the normalized condensation rate below 0.03. It was concluded that the condensation rate affects the corrosion rate, the former being affected by the gas velocity.

• A sudden increase in the corrosion rate was observed at 50°C as the normalized condensation rate crosses a threshold of 0.03-0.04. Once again, the assumption was made that the products of corrosion may buffer the pH of the condensed water at low condensation rates. As the condensation rate increases, the concentration of iron ions decreases and the corrosion reaction may no longer be affected by the change in the chemistry of the condensed water. It was also mentioned previously that at higher condensation rates, the thickness of the condensed film might limit the mass transfer of corrosive species to the wall, thus reducing the corrosion rate.





Figure VI.16: Comparison of the corrosion rates obtained with ER measurements and CWL measurements. P<sub>CO2</sub> = 8bar, Vgas = 8m/s, high cooling



 $T_{gas} = 50^{\circ}C$ 

 $T_{gas} = 70^{\circ}C$ 

 $T_{gas} = 90^{\circ}C$ 

Figure VI.17: Pictures of corroded coupons: presence of a scale at higher temperatures

#### CHAPTER VII

# MODELING OF THE INFLUENCE OF MASS TRANSFER AND CHEMISTRY AT THE WALL ON THE CORROSION RATE DURING TOP-OF-THE LINE CORROSION

# VII.1 Presentation of the modeling work for the prediction of the corrosion rate

During TLC, the chemistry of the condensed water is well known since the only species present in solution are the dissolved carbonic acid, the products of its dissociation (protons, bicarbonate and carbonate ions), and the products of corrosion (iron ions). However, their concentrations, or more precisely, their profiles of concentration in the condensed water at the wall, are one key point for the determination of the corrosion rate. At the top of the line, in the absence of any inhibitors, the formation of a protective, or at least partially protective, scale is the only way to prevent rapid corrosion of the carbon steel pipe. Thus, the saturation or supersaturation of the condensed water with iron carbonate must be predicted accurately to determine under which conditions a scale is going to form, and if it does form, what protection against further corrosion it will provide to the pipe. The prediction of concentration profiles of the corrosive species and of the products of corrosion in the condensed liquid is not an easy task. First, the hydrodynamics of the condensed liquid must be determined. The hydrodynamics will change significantly depending on where the condensation takes place around the internal circumference of the pipe. At the very top of the line (within few degrees of inclination from the vertical line), the gravity and the surface tension forces intervene and set the

shape and the flowing pattern of the condensed water (Gertsmann, 1967). This is no longer valid as the water flows down the circumference of the pipe in a filmwise manner, according to Nusselt's theory (1916).

Once the hydrodynamics are determined, proper boundary conditions at the gascondensed liquid interface and at the wall must be chosen to obtain the concentration profile of species. The boundary condition at the wall implies the coupling between the transport of species and the electrochemical reactions taking place at the wall.

### VII.2 Mass transfer model in the condensed liquid

# VII.2.1 Liquid velocity profile around the circumference of the pipe

Where the gravity forces and shear forces determine the hydrodynamics of the condensed liquid film, the liquid velocity parallel to the wall is given by Equation V.23:

$$w(y,z) = \frac{(\mathbf{r}_{l} - \mathbf{r}_{g}) \times g \times \sin \mathbf{j}}{A} \times \left[ \left( B\mathbf{d} + \frac{C' \times \mathbf{d}}{2} \right) \times y - B \times \frac{y^{2}}{2} - C' \times \frac{y^{3}}{6 \times \mathbf{d}} \right] \quad (V.23)$$

From this equation, it is possible to derive the liquid velocity in the direction perpendicular to the wall by using the continuity equation applied to a control volume of the condensed liquid. This derivation is presented in Appendix 3 and leads to the velocity v(y, z) in the radial direction.

Where the surface tension forces and the gravity forces determine the hydrodynamics of the condensed water, several flow regimes may occur (Gertsmann, 1967). The growth of droplets, wavy films, and ridges becomes possible within a few

degrees of inclination from the vertical line. In this area, Gertsmann reports an average film thickness on the underside surface of a horizontal plate to be:

$$\boldsymbol{d} = \left(\frac{\boldsymbol{s}}{g \times (\boldsymbol{r}_l - \boldsymbol{r}_g)}\right)^{l/2}$$
(VII.1)

s is the surface tension coefficient, g is the gravity constant,  $r_l$  is the liquid density and  $r_g$  is the gas density. This averaged thickness will be used to determine the condensed film thickness at the very top of the pipeline.

#### VII.2.2 Boundary conditions for the dissolved carbon dioxide

The boundary condition at the interface between gas and condensed liquid is derived from the thermodynamic equilibrium. The concentration of carbon dioxide that dissolves in water can be determined when the partial pressure of carbon dioxide in the gas phase is known. According to Henry's law for infinite dilution, one can write:

$$y_i \times P = H_i \times m_i$$
 (VII.2)

*P* is the total pressure in the system (atm),  $y_i$  is the molar fraction of species i at the interface,  $m_i$  is the molality of species i at the interface (mol/kg), and  $H_i$  is the Henry's constant of species i (atm.kg/mol).  $H_i$  depends on the temperature and the total pressure of the system according to the following equation:

$$\ln H_i = \ln H_i^T + v_i^\infty \times \frac{(P - P_w^{sat})}{RT}$$
(VII.3)

 $H_i^T$  is the temperature dependent term of Henry's coefficient (atm.kg/mol),  $v_i^{\infty}$  is the partial molar volume of molecular solute at infinite dilution (cm<sup>3</sup>/mol),  $P_w^{sat}$  is the vapor pressure of pure solvent (atm), R is the gas constant (R = 8.314 J/mol/K) and T is the absolute temperature (K). The value sought is the concentration at the interface, which can be written as

$$C_i^e = m_i \times \boldsymbol{r}_w = \frac{y_i \times P \times \boldsymbol{r}_w}{H_i}$$
(VII.4)

 $C_i^e$  is the concentration of species i at the interface (mol/m<sup>3</sup>), and  $r_w$  is the density of water, considered to be equal to 984.5 kg/m<sup>3</sup> in this case. The computation of  $H_i^T$  relies on experimental data. According to Edwards et al (Edwards, 1978), Henry's coefficient can be correlated to the temperature as follow:

$$\ln H_{i}^{T} = \frac{B_{1}}{T} + B_{2} \times \ln T + B_{3} \times T + B_{4}$$
(VII.5)

The values of the constants  $B_i$  (i = 1,2,3, and 4) for the dissolution of carbon dioxide in water are given in Appendix 4.

At the wall, the boundary condition for the determiantion of the species concentration is the flux of consumption of carbon dioxide due to the electrochemical reaction with the steel. Many models and correlations are available in the literature for the computation of the reaction rate. Among them, the most commonly used is de Waard's semi-empirical model (1993). As it was already mentioned in the literature review, according to de Waard, the reaction rate is given by Equation II.1. At the wall, the species move only by diffusion since the liquid velocity is null. Thus, the boundary condition is given by:

$$D_{AB} \times \frac{\partial C}{\partial y}\Big|_{y=0} = W \times \left[ 5.8 - \frac{1710}{273 + t} + 0.67 \times \log(P_{CO_2}) \right]$$
(VII.6)

 $D_{AB}$  is the diffusivity of carbon dioxide in water (m<sup>2</sup>/s), **W** is a conversion factor that converts mm/yr into kmol/m<sup>2</sup>/s, and *C* is the concentration of carbon dioxide (kmol/m<sup>3</sup>). Equation VII.6 is a non-linear differential equation and must be solved for the concentration of carbon dioxide, which is the only unknown at a fixed temperature and total pressure.

#### VII.2.3 Numerical solution for the transport of species in condensed water

It was decided to develop a code to solve the transport phenomena involved in the condensed liquid boundary layer for the specific case of filmwise condensation of water with an electrochemical reaction at the wall. This paragraph reports the numerical methods used for the simulation of the phenomena involved during corrosion under filmwise condensation. Some numerical results are also reported for the validation of the model.

As previously mentioned, the theories used for the modeling of the Top-Of-The line Corrosion are as follow:

- Filmwise condensation according to Nusselt's theory for the hydrodynamics
- Charge transfer limitation of the electrochemical reaction at the wall according to de Waard's semi-empirical model

 Vapor-liquid thermodynamic equilibrium at the interface between the condensed liquid and the vapor phase

The model of simulation allows the resolution of a transient two-dimensional flow and can solve the heat and mass transfer in these two dimensions. The velocity profile is analytically calculated according to Nusselt's theory of filmwise condensation. For the specific case of corrosion under filmwise condensation the model solves:

- The convection of species as the water flows down around the circumference of the inner pipe wall to the bottom of the pipe where it accumulates.
- The convection and diffusion of species in the radial direction within the condensed liquid
- The species depletion or formation at the wall according to the corrosion process.
   The equation giving the corrosion rate at the wall is discretized in order to be coupled to the equations of transport of species within the film.
- The species concentration at the interface between the gas and the liquid phase depending on the temperature at this interface, the total pressure, and the partial pressure of carbon dioxide.

The discretization methods used to obtain the concentration profile in the film are:

- The upwind scheme for the computation of the convective termThe central difference scheme for the computation of the diffusive term
- The two-dimensional Tri-Diagonal Matrix Algorithm (TDMA) with line-by-line computation for the resolution of the system of linearized equation.

The discretization methods of the differential equations obtained from the mass balance and the meshing of the falling film are reported in Appendix 5. Before comparing the code against the experimental data, it must be confirmed that there is no error induced by the numerical methods used. The following techniques were used to validate the numerical simulation:

- The comparison of the results obtained by convergence of the transient model when it reaches steady-state and the results of the steady-state model. By definition, the two solutions should be exactly identical.
- The comparison of the results obtained with grid refinement. The results should not differ significantly when the grid becomes sufficiently refined.
- The computation of the mass balance on each control volume of the grid. The conservation of mass on each of these control volumes should be maintained.

The model successfully passed these tests. The results of these comparisons are available in Appendix 6.

# VII.3 Preliminary numerical results for the mass transfer model and their comparison with experimental data

Having validated the numerical work, it is now possible to analyze the results of simulation. For the real-case study, the following conditions were used:

- Temperature at the wall: 90°C
- Total pressure: 5 bar, partial pressure of carbon dioxide: 4 bar
- Film thickness: obtained from the filmwise condensation model or Equation (VII.1)
Film depth: 0.15 meter (length of the circumference between the top and the bottom of the pipe for a 4-inch pipe)

### VII.3.1 Concentration profile in the condensed film at the top of the line

At the top of the line, the condensed water is supposed to be quasi-stagnant, which means that convection in the condensed liquid can be neglected. The transport of corrosive species happens by diffusion only. With the model presented in section VII.2, it is possible to study the influence of the thickness of the film on the corrosion rate. In Figure VII.1, the steady-state corrosion rate at the wall is reported as a function of the film thickness for the conditions of simulation mentioned above. It is seen from the graph that diffusion through the condensed film influences the corrosion rate. Thicknesses up to 6 mm are reported. This corresponds to the radius of the droplet when its weight forces it to detach from the wall. It is important to mention here that diffusion of corrosive species does not change the corrosion rate significantly when the film thickness is smaller than 200 microns. With the conditions of simulation reported previously and without taking into consideration the mass transfer limitation, the computed normalized corrosion rate is 6.2. For a film thickness of 200 microns, the normalized corrosion rate becomes 5.9 corresponding to a decrease of 5%. A decrease of more than 50% is seen for thicknesses close to the departure radius of the droplet. According to the test made in the laboratory, at 90°C and a partial pressure of 4 bar, the experimental corrosion rate at the top of the line is almost two orders of magnitude smaller. Therefore, it is not possible to explain the observed low corrosion rates only by taking into consideration the mass transfer limitation in the condensed droplet.



for stagnant condensed water (no convection). T =90°C,  $P_{\rm CO2}$  = 4 bar

#### VII.3.2 Concentration profile around the circumference of the pipe

As the condensed water departs from the top of the line and flows down the circumference of the pipe, the convection is no longer negligible, and the transport of corrosive species in the condensed film occurs both in the radial and axis-symmetrical directions. In order to understand the evolution of the carbon dioxide concentration at the pipewall as the condensed water flows down the circumference of the pipe, the code is run for a two-dimensional simulation and the convective terms are taken into consideration. The film thickness is obtained from the filmwise condensation theory, which gives film thicknesses between 50 and 200 microns over the range of condensation rates studied in the present work (up to 5  $ml/m^2/s$ ). At the inlet (the very top of top of the line), water saturated with carbon dioxide is considered. This assumption is acceptable for such a small film thickness according to the simulation presented in section VII.3.1. The concentration profiles along the circumference appear as presented in Figure VII.2. The concentration at the wall decreases as the water flows down the circumference of the pipe. The change of concentration between the top and the bottom of the pipe is around 10% for these simulated conditions. These results are in agreement with the observations obtained from the field (Gunaltun, 1999), showing the main corroded area to be at the top of the line and some less severe corrosion on the sidewalls. However, the corresponding corrosion rates remain above 25 mm/yr and mass transport, taking into consideration the convective terms, still does not explain the corrosion rates observed by experimentation.



Figure VII.2: Simulated concentration profile of carbon dioxide in the condensed film at different depth of the film. Concentration at the inlet of the film: equilibrium with gas phase. Steady-state

## VII.4 Modeling of the combined influence of the mass transport of species and of the change in chemistry of the condensed water on the corrosion rate

### VII.4.1 Phenomena occurring at the wall and in the condensed liquid

As corrosion takes place, iron ions are released into the condensed water. As a consequence, the chemistry of the water in the vicinity of the wall may change significantly and may affect further corrosion processes. In what follows, the present model is used to solve the concentration profile of iron ions in the condensed film. Of particular interest is the concentration of iron ions at the wall, which may change the pH at the wall significantly, and therefore modify the corrosion rate. The boundary conditions used to determine the iron ion concentration profile into the condensed film are as follow:

- At the wall, the net flux of iron ions released in the condensed water is equal to the corrosion rate minus the precipitation rate.
- At the gas-liquid interface, the concentration of iron ions is assumed to be equal to 0 ppm in the newly condensed water.

Figure VII.3 gives a schematic of the source, sink, and transport of iron ions in the condensed water at the top of the line:

• Production of iron by the corrosion reaction. The rate of production is given by the electrochemical model developed by Nesic (1995). The reason for the choice of Nesic's model rather than deWaard's correlation is explained later on.

• Diffusion of iron ions takes place due to the gradient of concentration that exists between the pipewall where iron ions are produced and the gas-liquid interface where iron ions are diluted by the freshly condensed water



Figure VII.3: Transport, source, and sink of iron ions during TLC

- Iron is also removed from the vicinity of the internal pipewall at the top of the line by discharge of the condensed water, this latter draining down the circumference of the pipe at a rate equal to the condensation rate
- If the saturation of the water is reached, these iron ions combine with carbonate ion to form iron carbonate:

$$Fe^{2+} + CO_3^{2-} \to FeCO_3$$
 (VII.8)

Iron carbonate is a solid that deposits on the surface of the pipe. As mentioned in the literature review, the work done by Van Hunnik (1996) can be used here to determine the precipitation rate. According to Equation II.3, the precipitation rate is  $(in \text{ kmol/m}^2/s)$ :

$$\boldsymbol{F}_{p} = e^{\frac{-E_{a}}{RT}} \times K_{sp} \times (s-1)(1-\frac{1}{s})$$
(VII.7)

$$s = \frac{[Fe^{2+}][CO_{3}^{2-}]}{K_{sp}}$$
(II.4)

In order to determine the iron ion concentration at the wall, a mass balance on a control volume of condensed water near to the wall is needed.

### VII.4.2 Solving the mass conservation for iron ions in the condensed water

Figure VII.4 represents a control volume of thickness  $d_c$  and the corresponding iron ions fluxes near to the wall:



Figure VII.4: Control volume in the condensed water at the wall

A material balance applied to the condensed water gives:

$$\frac{d(V[Fe^{2+}]_{wall})}{dt} = \mathbf{F}_c \times A_c - \mathbf{F}_p \times A_p - \mathbf{F}_d \times A_d - A_{co} \times \dot{m}_c \times [Fe^{2+}]_{wall} \quad (VII.8)$$

*V* is control volume (m<sup>3</sup>),  $[Fe^{2+}]_{wall}$  is the concentration of iron ions at the wall (kmol/m<sup>3</sup>),  $F_c$  is the corrosion rate (kmol/m<sup>2</sup>/s),  $A_c$  is the area where corrosion takes place (m<sup>2</sup>),  $F_p$  is the precipitation rate (kmol/m<sup>2</sup>/s),  $A_p$  is the area where precipitation takes place (m<sup>2</sup>),  $F_d$  is the diffusion rate (kmol/m<sup>2</sup>/s),  $A_d$  is the area through which diffusion takes place (m<sup>2</sup>),  $\dot{m}_c$  is the discharge rate at the wall (m<sup>3</sup>/m<sup>2</sup>/s),  $A_{co}$  is the condensation area (m<sup>2</sup>), and  $d_c$  is the thickness of the control volume (m). If one assumes that the area of corrosion, precipitation, diffusion and condensation are equal, Equation VIII.8 becomes:

$$\frac{d([Fe^{2+}]_{wall})}{dt} = \frac{1}{\boldsymbol{d}_c} \times \left[ \boldsymbol{F}_c - \boldsymbol{F}_p - \boldsymbol{F}_d - \dot{\boldsymbol{m}}_c \times [Fe^{2+}]_{wall} \right] \quad (\text{VII.9})$$

<u>.</u>

For the specific case of quasi-stagnant condensed water at the top of the line, the iron ions concentration profile in the film is linear since diffusion is the only phenomenon occurring in the bulk of the condensed liquid film. Thus,

$$\boldsymbol{F}_{d} = D \times \frac{\boldsymbol{D}C}{\boldsymbol{d}} = \frac{[Fe^{2+}]_{wall}}{\boldsymbol{d}}$$
(VII.10)

**d** is the thickness of the condensed liquid film as determined by Equation VII.1.

#### VII.4.3 Computational procedure for the corrosion rate

Equation VII.9 can be discretized in time as follow:

$$[Fe^{2+}]_{t+dt} = [Fe^{2+}]_t + \frac{Dt}{d} \times \left[F_c(t) - F_p(t) - F_d(t) - \dot{m} \times [Fe^{2+}]_t\right]$$
(VII.11)

The procedure for computation of the corrosion rate is as follow:

- 1. Compute the pH at the wall and the chemistry of condensed water in the absence of iron ions.
- 2. Determine the corresponding corrosion rate according to Nesic's model (1995).
- 3. Determine the corresponding precipitation rate according to Van Hunnik's model (1996). If the saturation level is not reached, the precipitation rate is equal to 0.
- 4. Determine the corresponding diffusion rate according to Equation VII.10.
- 5. Calculate the amount of iron present in the solution after a time step  $\Delta t$  according to Equation VII.11. Over this time step, the corrosion rate, the precipitation rate, and the diffusion rate are considered to be constant.
- 6. Iterate in time from the second step until convergence on the iron ion concentration is reached. The corresponding corrosion rate is then read.

### VII.4.4 Preliminary computational results and discussion

It is now possible to determine the concentration of iron ion at the wall and see its effect on the corrosion rate. The concentration of iron ion at the wall has been computed as a function of the condensed film thickness for a gas temperature of 90°C, a partial pressure of carbon dioxide of 4 bar and a normalized condensation rate of 0.03 (see Figure VII.5). Clearly, the iron ion concentration changes significantly with the film thickness. For small film thicknesses the transport of corrosive species to the wall is not limiting and the concentration of iron ions at the wall increases with increasing film thickness. This is due to the fact that diffusion of iron ions from the wall to the bulk is slower for a larger thickness of film, leading to a higher gradient of corrosive between the wall and the bulk. For greater film thicknesses, the transport of corrosive

species to the wall becomes limiting. Thus, the flux of iron ions released at the wall by the corrosion reaction is smaller and the concentration of iron ions at the wall decreases with increasing film thicknesses.

Once the iron ion concentration at the wall is known, the equation of dissolution of carbon dioxide, the equation of electroneutrality, and the equations of dissociation of carbonic acid can be solved to obtain the corresponding pH at the wall. The pH at the wall is given in Figure VII.6 as a function of the film thickness. Taking into consideration the concentration of iron ions at the wall leads to a higher pH, as expected.

The effect of the pH at the wall on the corrosion rate cannot be taken into consideration by the deWaard's equation (deWaard, 1993) without the use of some empirical correcting factors. In order to keep the present model as mechanistic as possible, Nesic's electrochemical model (1995) was used to compute the corrosion rate according to the changes in chemistry in the condensed water. The reader should refer to Nesic's model (1995) to better understand the coupling that exists between the pH of the water at the wall and the corresponding corrosion rate. The results of simulation for  $T_{gas}$  = 90°C,  $P_{CO2}$  = 4 bar and a normalized condensation rate of 0.03 are plotted in Figure VII.7 along with the corrosion rates obtained in section VII.3.1 (corrosion rate without the influence of the local pH and iron concentration). Even if the computed corrosion rates are significantly lower when the chemistry of the condensed water in the vicinity of the wall is taken into consideration, they are still an order of magnitude larger than the experimental one.



Figure VII.5: Simulated concentration of species at the wall as a function of the condensed film thickness.  $T_{gas} = 90^{\circ}C$ ,  $P_{CO2} = 4$  bar



Figure VII.6: Simulated pH at the wall as a function of the condensed film thickness  $T_{gas}$  = 90°C,  $P_{CO2}$  = 4 bar



Figure VII.7: Simulated corrosion rate as a function of the condensed film thickness  $T_{gas}$  = 90°C,  $P_{CO2}$  = 4 bar

### VII.5 Intermediate computational results and comparison with experimental data

VII.5.1 Influence of the temperature

Parameters of simulation and corrosion rates are listed in Table VII.1.

## Table VII.1: Experimental and theoretical corrosion rates Influence of the temperature.

Exp. CR: normalized experimental corrosion rate Theo. CR: normalized theoretical corrosion rate

Temperature	Pressure	Gas velocity	Normalized	Exp. CR	Theo. CR
( °C)	(bar)	(m/s)	Condensation rate		
41	8	8	0.10	0.32	1.20
58	8	8	0.17	0.50	1.78
77	8	8	0.69	0.54	2.46

Experimental and theoretical corrosion rates, as well as the corrosion rate according to de Waard's model (without considering the chemistry at the wall), are also plotted against the temperature in Figure VII.8. In general, the corrosion rate is overpredicted by both of the models. Including the influence of concentrations and pH at the wall in the model allows decreasing the difference obtained between the experimental and predicted corrosion rate. This is particularly true at high temperature. The present model shows an increase in the corrosion rate as the temperature increases above 80°C, whereas the experimental corrosion rate decreases above such temperature. The overprediction of the corrosion rate is due to the fact that the formation of a scale that could protect the metal from further corrosion is not taken into consideration.



Influence of temperature.  $P_{CO2} = 8$  bar.

### VII.5.2 Influence of the partial pressure of carbon dioxide

Table VII.2 includes the parameters of simulation and the corresponding experimental and theoretical corrosion rates. The results are also plotted in Figure VII.9 where it can be seen that the trend is well predicted by the present model. Once again, the model overpredicts the corrosion rate over the range of pressures covered. The explanation comes from the fact that the formation of a protective scale and is influence on the corrosion rate is not taken into consideration in the present model.

# Table VII.2: Experimental and theoretical corrosion rates Influence of the pressure

Exp. CR: normalized experimental corrosion rate Theo. CR: normalized theoretical corrosion rate

Temperature	Pressure	Gas velocity	Normalized	Exp. CR	Theo. CR
( °C)	(bar)	(m/s)	Condensation rate		
78	2	8	0.60	0.10	0.96
79	4	8	0.56	0.26	1.58
77	8	8	0.69	0.54	2.46

VII.5.3 Influence of the condensation rate

The influence of the condensation rate according to the present model is shown in

Figure VII.10. The corresponding parameters of simulation are reported in Table VII.3.

# Table VII.3: Experimental and theoretical corrosion rates Influence of the condensation rate

Exp. CR: normalized experimental corrosion rate Theo. CR: normalized theoretical corrosion rate

Temperature	Pressure	Gas velocity	Normalized	Exp. CR	Theo. CR
( °C)	(bar)	(m/s)	Condensation rate		
51	4	8	0.200	0.420	1.020
48	4	8	0.042	0.320	0.960
52	4	8	0.020	0.140	1.040
51	4	8	0.004	0.140	1.020

The overprediction of the corrosion rate is explained the same way as in sections VII.5.1 and VII.5.2. In addition, Figure VII.10 shows that, according to the present model, the influence of the temperature on the corrosion rate at low condensation rates is predominant: experimentally, as the normalized condensation rate increases from 0.02 to 0.04, the corresponding wall temperature drops from 52°C to 48°C. Accordingly, the predicted normalized corrosion rate decreases from 1.04 to 0.96. Experimentally, an increase in the corrosion rate from 0.14 to 0.32 was observed, suggesting that at low condensation rates, the influence of the condensation rate on the corrosion rate is predominant rather than the influence of temperature. It appears that the sensitivity of the model to the change in condensation rate is not sufficient.

### VII.5.4 Discussion of the theoretical results

Clearly, neither the influence of the hydrodynamics, nor the influence of the chemistry of the condensed water is sufficient to predict the corrosion rate during TLC. Even if the prediction of corrosion rate is much less conservative when the saturation of the condensed water by-products of corrosion is taken into consideration, the theoretical results still overpredict the experimental ones, sometimes by an order of magnitude. Therefore, it is necessary to take into account the formation of a scale that deposits on the metal surface and partially prevents further corrosion. An approach for the modeling of the influence of an iron carbonate scale on the corrosion rate is developed in what follows.



Figure VII.9: Comparison of the experimental and theoretical corrosion rates. Influence of the partial pressure of carbon dioxide. $T_{gas} = 90^{\circ}C$ 



Influence of the condensation rate.  $T_{gas}$  = 50°C,  $P_{CO2}$  =4 bar

### VII.6 Influence of the precipitation of an iron carbonate scale

In order to predict the corrosion rate under scaling conditions, it must be determined in which conditions the scale is likely to form. In the case where a scale would form, the rate of formation must be determined. Then, as the scale precipitates on a corroding surface, it is important to determine if the precipitation rate is fast enough to compete with the corrosion rate so that the scale would actually remain attached to the metal surface. Corrosion under a growing iron carbonate scale is possible as is clearly demonstrated in the work published by Nesic (2002). In this case, the formation of a scale does not lead to the protection of the metallic surface. The physical properties of the scale, and particularly its porosity, are some key parameters for the prediction of the protectiveness offered by the iron carbonate scale. According to some experimental data, Pots (2000) reports that the formation of a partially protective scale correlates well with the ratio of the precipitation rate to the corrosion rate in the absence of a scale, namely the scaling tendency ST:

$$ST = \frac{Calculated \ precipitation \ rate}{Calculated \ corrosion \ rate}$$
(VII.12)

Above a scaling tendency of 0.5, Pots experimentally obtained partially protective scales. A semi-empirical approach is attempted in the following paragraph: the scaling tendency is first determined by taking into consideration the local species concentrations at the wall as calculated before. Then, the superficail porosity K is inserted into the mass balance equation to account for the presence of an iron carbonate scale, allowing the

prediction of the corrosion rate in the presence of a partially protective scale. The superficial porosity is then correlated with the scaling tendency.

### VII.6.1 Material balance in the presence of a protective scale

The role of a protective scale can be simplified by considering that part of the corroding surface is now covered by the products of corrosion, and on a covered site, no further corrosion occurs. On the uncovered surface, only corrosion occurs. If one considers that the scale covers a percentage (1-K) of the corroding surface, K being greater than or equal to 0 and smaller than or equal to 1, the material balance presented in Equation VII.9 becomes:

$$\frac{d([Fe^{2+}])}{dt} = \frac{1}{d} \times \left[ K \times \mathbf{F}_c - (1-K) \times \mathbf{F}_p \right] - K^{1.5} \times \mathbf{F}_d - \dot{m}_c \times [Fe^{2+}]$$
(VII.13)

The discretized form of this Equation VII.13 is:

$$[Fe^{2+}]_{t+dt} = [Fe^{2+}]_t + \frac{Dt}{d} \left[ KF_c(t) - (1-K)F_p(t) - K^{1.5} \times F_d(t) - \dot{m}_c \times [Fe^{2+}]_t \right]$$

This represents Equation VII.14. The diffusion term is multiplied by the porosity at the power 1.5 according the theory of diffusion in porous electrodes (Newman, 1991). Following the same computational procedure as the one developed for the prediction of the corrosion rate in the absence of a protective scale, the chemistry of the water can be derived in time. The procedure converges to give the corrosion rate at steady state in the presence of a protective scale.

The parameter K is determined for each of 17 experiments run over a wide range of temperatures, partial pressures of carbon dioxide, and condensation rate. K is found by trial and error so that Equation V.14 converges to give the corresponding experimental corrosion rate.

### VII.6.3 Correlation between the superficial porosity *K* and the scaling tendency

In section VII.5.3, it has been mentioned that at a low temperature, according to the experimental data collected, the corrosion rate depends more on the condensation rate than on the temperature. This phenomenon is neither explained by the mass transfer of species nor by the chemistry of condensed water at the wall. Thus, it may be related to the protectiveness of the scale. The precipitation rate calculated with the conditions at the wall has been plotted in Figure VII.11 as a function of the condensation rate for two temperatures (50°C and 90°C), the partial pressure of carbon dioxide remaining constant and equal to 4 bar. The corresponding scaling tendencies are also plotted in Figure VII.12. From these two graphs it can be seen that the scaling tendency is not very dependent on the condensation rate at high temperatures. At low temperature however, this dependency is much stronger. In particular, the scaling tendency never goes below a value of 0.8 at higher temperatures whereas it can drop to values as low as 0.1 at low temperatures. It can be concluded that, according to Pots' criterion of a critical scaling tendency of 0.5 (2000), at a fixed low temperature, the conditions can be changed from protective to non-protective by increasing the condensation rate. Also, the scaling tendency seems to be a reliable way to predict the protectiveness of the scale in the case

of TLC. Therefore, a correlation between the superfical porosity K and the scaling tendency was derived. The results are plotted in Figure VII.13 where it can be seen that K decreases sharply above a scaling tendency of 0.6, which is in fair agreement with the results obtained by Pots (2000). It is interesting to mention that in a range from 0.4 to 0.7 for the scaling tendency, the values of the superficial porosity tend to be greater than the values observed at lower scaling tendencies, which is counter-intuitive. It is believed that within this range a partially protective scale forms. This scale may be responsible for the development of localized attack by galvanic effect, which may provoke an increase in the overall corrosion rate. The artificial increase in the superficial porosity within the range of scaling tendencies from 0.4 to 0.7 may be a consequence of this localized attack. The reported range is in good agreement with the results obtained by Sun (2002).

If the bulk concentrations rather than the wall concentrations are considered, and the mass balance is applied over the entire condensed film rather than over a control volume at the wall, the superficial porosity K is found to correlate in a stepwise manner with the scaling tendency (see Figure VII.14). The coverage of the total corroding area by the protective scale is found to be around 70% for scaling tendencies below 0.7 and around 90% for scaling tendencies above 0.7. If the scaling tendency is close to 1, the coverage can be as high as 98%.



Figure VII.11: Simulated precipitation rate as a function of the condensation rate.  $P_{CO2} = 4$  bar



Figure VII.12: Scaling tendency as a function of the condensation rate.  $P_{CO2} = 4$  bar



of the scaling tendency. Wall concentrations



of the scaling tendency. Bulk concentrations

#### CHAPTER VIII

### CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE STUDIES

During this project of research, the phenomena involved during Top-of-the-Line Corrosion (TLC) have been extensively studied both experimentally and theoretically. Based on the results from the experiments and from the mechanistic models developed, the following conclusions and recommendations are made.

Its was experimentally determined that the corrosion rate during TLC increases with temperature until its reaches a maximum around 70 - 80°C. Above that temperature the decrease in the corrosion rate is attributed to the formation of a partially protective iron carbonate scale.

For condensation rates lower than a certain threshold value, the partial pressure of carbon dioxide did not seem to influence the experimental corrosion rates. At higher condensation rates, a significant influence of the partial pressure on the corrosion rate was measured. This is explained by the fact that, at low condensation rates, the products of corrosion buffer the pH of the condensed water.

The gas velocity did not influence the corrosion rate directly. However, the condensation rate was found to be dependent upon the gas velocity. Therefore, the gas velocity can affect the corrosion rate by modifying the condensation rate.

At low temperatures, as the condensation rate crosses a threshold, a rapid increase in the corrosion rate was observed. This was attributed to a change in the pH of the condensed water as the condensation rate increases above a threshold. A mechanistic model was developed in order to predict the condensation rate on the inner wall of a horizontal pipeline in the presence of a non-condensable gas. The model was tested against experimental data obtained for the condensation rate. A good agreement between the experimental and theoretical condensation rates was obtained.

The same mechanistic model was improved in order to determine the combined effects of chemistry at the wall and mass transfer limitation in the condensed liquid. Numerical results show that the mass transfer of the corrosive species can become a limiting step in the process of corrosion as the liquid film thickness increases.

The protectiveness of a deposited scale was correlated to the scaling tendency. It was found that the protection offered to the metal by the scale sharply decreases below a scaling tendency of 0.7. In a range of scaling tendencies from 0.4 to 0.7, the results reported tend to validate the hypothesis of a partially protective scale. A non-uniformly deposited scale may lead to localized corrosion by galvanic effect and increase the overall corrosion rate (Sun, 2002).

As a result of this project of research, the Institute for Corrosion and Multiphase Technology now possesses a unique flow-loop for the study of the phenomena of corrosion occurring at the top of the inner wall of a horizontal pipelines. The perspectives of study of the phenomena of corrosion with this piece of equipment are broad. In particular, this facility offers the opportunity to study the corrosion of pipelines under dewing conditions in presence of acetic acid. Moreover, the efficiency of a new generation of inhibitors, called volatile inhibitors, can be verified and quantified by slightly modifying the flow-loop developed for this project. Some further experimentation can be done that complements the present work:

- The critical condensation rate can be experimentally studied as a function of the primary parameters (temperature, total pressure, partial pressure of carbon dioxide, and gas velocity).
- The stability of the protective scale under shear at higher gas velocity can also be studied. There is a strong interest from the oil and gas industry in the determination of the critical flowrate in wet gas pipelines, above which the deterioration of protective scales occurs.

Furthermore, the model developed provides a useful tool for the design of further experimentation. It will be used to develop the test matrix for the set of experiments on the combined effect of  $CO_2$  and acetic acid.

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### LIST OF SYMBOLS

### Latin letters

Symbol	Name	SI-Units
A	cross section of the sensing element	$m^2$
A	surface area	$m^2$
$A_p$	pre-exponential factor	1/s
CR	corrosion rate	mm/yr
$C_{pg}$	specific heat of the gas at constant pressure	J/kg/K
$C_{pl}$	specific heat of the liquid phase at constant pressure	J/kg/K
D	inside diameter of the pipe	m
D, D <sub>w</sub>	diffusivity of water vapor in carbon dioxide	$m^2/s$
dL	elementary length of pipe	m
dQ	heat loss	W
$E_a$	activation energy	J/kg
F	correcting factor for the corrosion rate	(-)
g	gravitational constant	m/s <sup>2</sup>
$G_{\scriptscriptstyle W}$	condensation rate	kg/m <sup>2</sup> /s
Н	enthalpy inflow	J/kg
H <sub>i</sub>	Henry's constant of species i	atm.kg/mol
H <sub>e0</sub>	external (external wall to surrounding) convection coefficient	W/m <sup>2</sup> /K
H <sub>i0</sub>	internal (inner wall to effluents) convection coefficient	W/m <sup>2</sup> /K
H <sub>th0</sub>	global heat transfer coefficient (pipe+coating+ insulation)	W/m <sup>2</sup> /K
h <sub>l</sub>	heat transfer coefficient in the liquid film	W/m <sup>2</sup> /K

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h <sub>g</sub>	heat transfer coefficient in the gas phase	W/m <sup>-</sup> /K
$h_w$	heat transfer coefficient in the gas wall	W/m <sup>2</sup> /K
h	local heat transfer coefficient	W/m <sup>2</sup> /K
$\overline{h}$	global heat transfer coefficient	W/m <sup>2</sup> /K
$h_{l}^{'}$	enthalpy of liquid	J/kg
$h_{g}^{'}$	enthalpy of gas	J/kg
j	diffusive flux	kg/m2/s
Κ	correcting factor for corrosion rate	(-)
K <sub>sp</sub>	product of solubility	mol/l
l	thickness of the pipewall	m
L	length of pipe considered	m
L	length of sensing element	m
ṁ	condensation rate	kg/m <sup>2</sup> /s
$\dot{m}_{g}$	mass flux of water vapor in the gas phase	kg/m <sup>2</sup> /s
$\dot{m}_l$	mass flux of water (liquid phase)	kg/m <sup>2</sup> /s
$\dot{M}_l$	total mass flow rate of condensed water	kg/s
$\dot{M}_{g}$	mixture mass flow rate	kg/s
$P_{CO2}$	partial pressure of carbon dioxide	bar
$P_{v}$	vapor pressure	Pa
$P_{g}$	gas pressure	Pa
P <sub>s</sub>	saturation pressure	Pa
Р	total pressure	Pa
PR	precipitation rate	kmol/m <sup>3</sup> /s
$\dot{q}$	heat flux through the wall	W/m <sup>2</sup>

$q_l$	heat flux in the liquid phase	180 W/m <sup>2</sup>
$q_g$	heat flux in the gas phase	W/m <sup>2</sup>
R	ideal gas constant	J/mol/K
R	resistance of the sensing element	ohm
$R_0$	reference radius	m
S	supersaturation level	mol/l
ST	scaling tendency	(-)
t	temperature	°C
$T_{ext}, T_A$	ambient external temperature	K
$T_b$	temperature in the bulk	K
$T_F$	fluid temperature at the center line	K
$T_i$	temperature at the interface	K
$T_{sat}$	temperature at saturation	K
$T_w$	temperature at the wall	K
$U_0$	overall heat transfer coefficient	W/m <sup>2</sup> /K
v	liquid velocity in the axial direction	m/s
W	liquid velocity in the axis-symmetrical direction	m/s
V	volume of solution	m <sup>3</sup>
V <sub>gas</sub>	gas velocity	m/s
x	coordinate	m
Уь	vapor mass fraction in the bulk	(-)
УI	vapor mass fraction at the interface	(-)
Z.	coordinate in the direction of the flow	m
Symbol	Name	SI-Units
--------------------	--	------------------------
$\boldsymbol{b}_g$	mass transfer coefficient in the gas phase	m/s
d	thickness of the momentum boundary layer in the liquid	m
$?h_v$	specific enthalpy of vaporization	J/kg
$?h_v^*$	corrected enthalpy of vaporization	J/kg
j	circumferential angle	-
$oldsymbol{F}_{c}$	corrosion rate	kmol/m <sup>2</sup> /s
$F_d$	diffusion rate	kmol/m <sup>2</sup> /s
$oldsymbol{F}_p$	precipitation rate	kmol/m <sup>2</sup> /s
? <sub>l</sub>	thermal conductivity of the liquid phase	W/K/m
? <sub>g</sub>	thermal conductivity of the gas phase	W/K/m
?wall	thermal conductivity of the pipewall	W/K/m
m <sub>l</sub>	dynamic viscosity of the liquid phase	kg/s/m
?	resistivity of the sensing element	ohm/m
? <sub>g</sub>	density of the gas phase	kg/m <sup>3</sup>
? <sub>l</sub>	liquid density	kg/m <sup>3</sup>
?w	water density	kg/m <sup>3</sup>
S	surface tension coefficient	N/m

# Others

Symbol	Name	SI-Units
[Fe <sup>2+</sup> ] <sub>supersat</sub>	iron concentration under supersaturation	mol/l
[Fe <sup>2+</sup> ] <sub>wall</sub>	concentration of iron ions at the wall	kmol/m <sup>3</sup>





# **DERIVATION OF EQUATIONS V.32 AND V.35**

According to Equation V.27:

$$\boldsymbol{G}(\boldsymbol{j}) = \boldsymbol{D} \times \sin \boldsymbol{j} \times \boldsymbol{d}^3 \tag{A2.1}$$

$$D = \frac{\mathbf{r}_{l} \times (\mathbf{r}_{l} - \mathbf{r}_{g}) \times g \times (\frac{B}{3} + \frac{5 \times C'}{24})}{A}$$
(A2.2)

 $\boldsymbol{G}$  is differentiated with respect to  $\boldsymbol{d}$ :

$$d\mathbf{G}(\mathbf{j}) = \frac{\partial G}{\partial \mathbf{j}} \times \frac{\partial G}{\partial \mathbf{d}} + \frac{\partial G}{\partial \mathbf{d}}$$
(A2.2)

$$d\mathbf{G}(\mathbf{j}) = D \times \cos \mathbf{j} \times \mathbf{d}^{3} \times \frac{\partial G}{\partial \mathbf{d}} \times d\mathbf{d} + 3 \times \mathbf{d}^{2} \times D \times \sin \mathbf{j} \times d\mathbf{d}$$
(A2.4)

$$d\mathbf{G}(\mathbf{j}) = D \times \cos \mathbf{j} \times \mathbf{d}^{3} \times \frac{\partial G}{\partial \mathbf{d}} \times d\mathbf{d} + 3 \times \mathbf{d}^{2} \times D \times \sin \mathbf{j} \times d\mathbf{d}$$
(A2.4)

Applying the energy balance:

$$d\mathbf{G} = \mathbf{I}_{l} \times \frac{T_{sat} - T_{w}}{\mathbf{d} \times \mathbf{D}h_{v}} \times \mathbf{R} \times d\mathbf{j} = \frac{K}{\mathbf{d}} d\mathbf{j}$$
(A2.5)

$$K = \mathbf{I}_{l} \times \frac{T_{sat} - T_{w}}{\mathbf{D}h_{v}} \times R \tag{A2.6}$$

Combining the two previous equations, one obtains:

$$\frac{K}{d}dj = D \times \cos j \times d^3 \times \frac{\partial G}{\partial d} \times dd + 3 \times d^2 \times D \times \sin j \times dd$$
(A2.7)

This equation can be re-written as:

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$$\partial G = 1^2$$
  $\nabla$  (12.3)

$$\frac{K}{d}\frac{dj}{dd} = D \times \cos j \times d^3 \times \frac{\partial G}{\partial d} + 3 \times d^2 \times D \times \sin j$$
(A2.8)

Since d is dependent on the only variable j, one can write:

$$\frac{d\mathbf{j}}{d\mathbf{d}} = \frac{\partial G}{\partial \mathbf{d}} \tag{A2.9}$$

Thus,

$$\left(\frac{K}{d} - D \times \cos j \times d^{3}\right) \times \frac{dj}{dd} = 3 \times d^{2} \times D \times \sin j$$
(A2.10)

$$\frac{d\boldsymbol{d}}{d\boldsymbol{j}} = \frac{\left(\frac{K}{\boldsymbol{d}} - \boldsymbol{D} \times \cos \boldsymbol{j} \times \boldsymbol{d}^{3}\right)}{3 \times \boldsymbol{d}^{2} \times \boldsymbol{D} \times \sin \boldsymbol{j}}$$
(A2.11)

$$\boldsymbol{d}^{3} \times \frac{d\boldsymbol{d}}{d\boldsymbol{j}} = \frac{K}{3 \times D \times \sin \boldsymbol{j}} - \frac{\cos \boldsymbol{j} \times \boldsymbol{d}^{4}}{3 \times \sin \boldsymbol{j}}$$
(V.32)

Proceeding to the change of variable

$$Y = d^4 \tag{A2.12}$$

$$\frac{dY}{dj} = 3 \times \boldsymbol{d}^3 \times \frac{d\boldsymbol{d}}{dj}$$
(A2.14)

One obtains:

$$\frac{1}{4}\frac{dY}{dj} = \frac{K}{3 \times D \times \sin j} - \frac{\cos j \times Y}{3 \times \sin j}$$
(A2.15)

$$\frac{\sin \mathbf{j}}{4} \times \frac{dY}{d\mathbf{j}} + \frac{\cos \mathbf{j}}{3} \times Y = \frac{K}{3 \times D}$$
(A2.16)

This is a first order differential equation with non-constant coefficients. Solving the linear equation (without the RHS term):

$$\frac{\sin \mathbf{j}}{4} \times \frac{dY}{d\mathbf{j}} + \frac{\cos \mathbf{j}}{3} \times Y = 0 \tag{A2.17}$$

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Thus,

$$\ln Y = -\frac{4}{3} \times \ln|\sin \mathbf{j}| + C \tag{A2.18}$$

C is a constant. This can also be written as:

$$Y = A \times (\sin \mathbf{j})^{-4/3} \tag{A2.19}$$

Solving the differential equation with the RHS term, one obtains:

$$\frac{dY}{d\mathbf{j}} = -\frac{4}{3}A \times \cos \mathbf{j} \times (\sin \mathbf{j})^{-7/3} + \frac{dA}{d\mathbf{j}} \times (\sin \mathbf{j})^{-4/3}$$
(A2.20)

Injecting this expression into the original differential equation, one gets:

$$\frac{dA}{dj} = \frac{4 \times K}{3 \times D} \times (\sin j)^{1/3}$$
(A2.21)

$$A = \int \frac{4 \times K}{3 \times D} \times (\sin \mathbf{j})^{1/3} d\mathbf{j}$$
(A2.22)

Thus,

$$Y = \frac{\int \frac{4 \times K}{3 \times D} \times (\sin \mathbf{j})^{1/3} d\mathbf{j}}{(\sin \mathbf{j})^{4/3}}$$
(A2.23)

$$\boldsymbol{d} = \left(\frac{4 \times K}{3 \times D} \times \frac{\int (\sin \boldsymbol{j} \ )^{1/3} d\boldsymbol{j}}{(\sin \boldsymbol{j} \ )^{4/3}}\right)^{1/4} \tag{V.35}$$

# DERIVATION OF THE LIQUID VELOCITY V(Y,Z)

$$w(y,z) = \frac{(\mathbf{r}_{l} - \mathbf{r}_{g}) \times g \times \sin \mathbf{j}}{A} \times \left[ \left( B \times \mathbf{d} + \frac{C \times \mathbf{d}^{2}}{2} \right) \times y - B \times \frac{y^{2}}{2} - C \times \frac{y^{3}}{6} \right]$$

$$= \mathbf{D} \times \sin \frac{z}{R} \times \left[ \left( B \times \mathbf{d} + \frac{C' \times \mathbf{d}}{2} \right) \times y - B \times \frac{y^{2}}{2} - C' \times \frac{y^{3}}{6 \times \mathbf{d}} \right]$$

$$\mathbf{D} = \frac{(\mathbf{r}_{l} - \mathbf{r}_{g}) \times g \times \sin \mathbf{j}}{A}$$
(A3.1)

*z* is defined as:

$$z = R \times j$$

For the condensed liquid, the continuity equation can be written as:

$$\frac{dv(y,z)}{dy} = \frac{dw(y,z)}{dz}$$
(A3.2)

Thus,

$$\frac{dv(y,z)}{dy} = \frac{\mathbf{D}}{R} \times \cos\frac{z}{R} \times \left[ \left( B \times \mathbf{d} + \frac{C' \times \mathbf{d}}{2} \right) \times y - B \times \frac{y^2}{2} - C' \times \frac{y^3}{6 \times \mathbf{d}} \right] + \mathbf{D} \times \sin\frac{z}{R} \times \frac{d\left[ \left( B \times \mathbf{d} + \frac{C' \times \mathbf{d}}{2} \right) \times y - B \times \frac{y^2}{2} - C' \times \frac{y^3}{6 \times \mathbf{d}} \right]}{d\mathbf{d}} \times \frac{d\mathbf{d}}{dz}$$
(A3.3)

According to Equation V.32,

$$\frac{dd}{dz} = \frac{1}{R} \frac{dd}{dj} = \frac{1}{R} \left( \frac{K}{3 \times D \times \sin j \times d^3} - \frac{\cos j \times d}{3 \times \sin j} \right) = \frac{t}{d^3} - \mathbf{y} \times d$$
(A3.4)

$$\boldsymbol{t} = \frac{1}{R} \left( \frac{K}{3 \times D \times \sin \boldsymbol{j}} \right) \tag{A3.5}$$

$$\mathbf{y} = \frac{1}{R} \left( \frac{\cos \mathbf{j}}{3 \times \sin \mathbf{j}} \right) \tag{A3.6}$$

Thus,

$$\frac{dv(y,z)}{dy} = \frac{\mathbf{D}}{R} \times \cos\frac{z}{R} \times \left[ \left( B \times \mathbf{d} + \frac{C' \times \mathbf{d}}{2} \right) \times y - B \times \frac{y^2}{2} - C' \times \frac{y^3}{6 \times \mathbf{d}} \right]$$
(A3.7)  
+  $\mathbf{D} \times \sin\frac{z}{R} \times \left[ \left( B + \frac{C'}{2} \right) \times y + C' \times \frac{y^3}{6 \times \mathbf{d}^2} \right] \times \left( \frac{\mathbf{t}}{d^3} - \mathbf{y} \times \mathbf{d} \right)$   
$$\frac{dv(y,z)}{dy} = \mathbf{D} \left[ \left( B + \frac{C'}{2} \right) \times \left( \frac{\mathbf{d}}{R} \times \cos\frac{z}{R} + \left( \frac{\mathbf{t}}{d^3} - \mathbf{y} \times \mathbf{d} \right) \times \sin\frac{z}{R} \right) \times y - \left( \frac{B}{2 \times R} \cos\frac{z}{R} \right) \times y^2$$
  
+  $C' \left( \left( \frac{\mathbf{t}}{6 \times \mathbf{d}^5} - \frac{\mathbf{y}}{6 \times \mathbf{d}} \right) \times \sin\frac{z}{R} - \frac{1}{6 \times \mathbf{d} \times R} \times \cos\frac{z}{R} \right) \times y^3 \right]$ (A4.8)

If we integrate the previous equation with respect to y,

$$v(y,z) = \mathbf{D} \times \left[ \left( B + \frac{C'}{2} \right) \times \left( \frac{\mathbf{d}}{R} \times \cos\frac{z}{R} + \left( \frac{\mathbf{t}}{d^3} - \mathbf{y} \times \mathbf{d} \right) \times \sin\frac{z}{R} \right) \times \frac{y^2}{2} - \left( \frac{B}{2 \times R} \cos\frac{z}{R} \right) \times \frac{y^3}{3} + C' \left( \left( \frac{\mathbf{t}}{6 \times \mathbf{d}^5} - \frac{\mathbf{y}}{6 \times \mathbf{d}} \right) \times \sin\frac{z}{R} - \frac{1}{6 \times \mathbf{d} \times R} \times \cos\frac{z}{R} \right) \times \frac{y^4}{4} \right] + cste \qquad (A4.9)$$

The boundary condition at y = 0 is v = 0. Thus, cste = 0. The final expression for v(y,z) is:

$$v(y,z) = \mathbf{D} \times \left[ \left( B + \frac{C'}{2} \right) \times \left( \frac{\mathbf{d}}{2 \times R} \times \cos \frac{z}{R} + \frac{1}{2} \left( \frac{\mathbf{t}}{d^3} - \mathbf{y} \times \mathbf{d} \right) \times \sin \frac{z}{R} \right) \times y^2 - \left( \frac{B}{6 \times 2 \times R} \cos \frac{z}{R} \right) \times y^3 + C' \left( \left( \frac{\mathbf{t}}{24 \times \mathbf{d}^5} - \frac{\mathbf{y}}{24 \times \mathbf{d}} \right) \times \sin \frac{z}{R} - \frac{1}{24 \times \mathbf{d} \times R} \times \cos \frac{z}{R} \right) \times y^4 \right]$$
(A3.10)

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$$\boldsymbol{D} = \frac{(\boldsymbol{r}_l - \boldsymbol{r}_g) \times g \times sin\boldsymbol{j}}{A}$$
(A3.1)

$$D = \frac{\mathbf{r}_{l} \times (\mathbf{r}_{l} - \mathbf{r}_{g}) \times g \times (\frac{B}{3} + \frac{5 \times C'}{24})}{A}$$
(A3.11)

$$K = \mathbf{I}_{l} \times \frac{T_{i} - T_{wall}}{\mathbf{D}h_{v}} \times R \tag{A3.12}$$

$$\boldsymbol{t} = \frac{1}{R} \left( \frac{K}{3 \times D \times \sin j} \right) \tag{A3.5}$$

$$\mathbf{y} = \frac{1}{R} \left( \frac{\cos \mathbf{j}}{3 \times \sin \mathbf{j}} \right) \tag{A3.6}$$

# COMPUTATION OF HENRY'S COEFFICIENTS FOR THE CARBON DIOXIDE - WATER VAPOR BINARY MIXTURE

According to Edwards et al (Edwards, 1978), Henry's coefficient and temperature as follow:

$$\ln H_i^T = \frac{B_1}{T} + B_2 \times \ln T + B_3 \times T + B_4$$

For carbon dioxide, in a range of 0-250°C:

$$B_1 = -6789.04$$
  
 $B_2 = -11.4519$   
 $B_3 = -0.010454$   
 $B_4 = 94.4914$ 

# ALGORITHM AND NUMERICAL METHODS FOR THE RESOLUTION OF THE MASS TRANSFER IN A FALLING FILM WITH AN ELECTROCHEMICAL REACTION AT THE BOUNDARY

#### A5.I Scope of the algorithm

The algorithm presented here solves the mass transfer equations in a laminar film using the finite-difference method. The scope and limitations of the program are:

- Two-dimensional equations
- Cartesian coordinates
- Non uniform grid
- Constant density of the liquid, constant thermal conductivity of the solvent
- Temperature dependence of the other physical parameters such as diffusivity
- The flow field is known analytically (according to Nusselt's theory)
- Linear temperature profile (according to Nusselt's theory)

#### A5.II Equations describing the system and their discretization

#### A5.II.1 General form of the equations

To solve the temperature and concentration profile in a boundary layer where convection and diffusion take place a two-dimensional control volume  $Dy^*D_z$  is considered (see Figure A5.1). The point P is included in the control volume and is also part of the mesh covering the entire domain of interest. The control volume is delimited by four interfaces n, s, e, and w located between the point P and its direct neighbors N, S, E, and W respectively.



Figure A5.1: Control volume in the laminar film.

If the density of the considered fluid is constant, the continuity equation over the control volume is:

$$\frac{\partial(\mathbf{r}v)}{\partial y} + \frac{\partial(\mathbf{r}w)}{\partial z} = 0$$
 (A5.1)

v is the velocity component in the y direction and w is the velocity component in the z direction. At steady state, the balance on a variable of interest F can be written as:

$$\frac{\partial J_y}{\partial y} + \frac{\partial J_z}{\partial z} = S \tag{A5.2}$$

$$J_{y} = \mathbf{r}v\mathbf{F} - \mathbf{G}\frac{\partial \mathbf{F}}{\partial y}$$
(A5.3)

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$$J_z = \mathbf{r}w\mathbf{F} - \mathbf{G}\,\frac{\partial \mathbf{F}}{\partial z} \tag{A5.4}$$

 $J_y$  is the total flux (convection and diffusion) in the y direction,  $J_z$  is the total flux in the z direction, S is the source term that includes any chemical reaction, G is the diffusion coefficient of the variable F, and r is the density of the fluid considered. In order to achieve the complete linearization of the equations describing the system, one supposes that the source term can be linearized with respect to F:

$$S = S_c + S_p F_P \tag{A5.5}$$

Sc and Sp are two constants, Sc being chosen negative. Also, we define  $J_e$  as the diffusion term through the interface e of the control volume or, more simply:

$$J_e = \int J_y dz$$
 over the interface e (A5.6)

Similarly,

$$J_w = \int J_y dz$$
 over the interface w

$$J_n = \int J_z dy$$
 over the interface n (A5.8)

$$J_s = \int J_z dy$$
 over the interface s (A5.9)

The convection terms through the interfaces of the control volume are defined as:

$$F_e = (\mathbf{r}u)_e \mathbf{D}z$$
 over the interface e (A5.10)

$$F_W = (\mathbf{r}u)_W \mathbf{D}z$$
 over the interface w (A5.11)

$$F_n = (\mathbf{r}v)_n \mathbf{D}y$$
 over the interface n (A5.12)

$$F_s = (\mathbf{r}v)_s \mathbf{D}y$$
 over the interface s (A5.13)

The discretization of Equation A5.1 and A5.2 respectively gives:

$$F_e - F_w + F_n - F_s = 0 (A5.14)$$

$$J_e - J_w + J_n - J_s = (S_c + S_p \boldsymbol{F}_P) \boldsymbol{D} \boldsymbol{y} \boldsymbol{D} \boldsymbol{z}$$
(A5.15)

If Equation A5.14 is multiplied by  $F_P$  and then subtracted from Equation 15, one obtains the following equation:

$$(J_e - F_e F_P) - (J_w - F_w F_P) + (J_n - F_n F_P) - (J_s - F_s F_P) = (S_c + S_p F_P) D_y D_z$$
  
This represents Equation A5.16. Each  $(J_i - F_i F_P)$  term has to be linearized with respect to  $F_P$  and  $F_I$ .

#### A5.II.2 Linearization of convection and diffusion terms

A linearized form of equation (5) can be written as:

$$a_P \boldsymbol{F}_P = a_E \boldsymbol{F}_E + a_W \boldsymbol{F}_W + a_N \boldsymbol{F}_N + a_S \boldsymbol{F}_S + b \tag{A5.17}$$

 $a_P$ ,  $a_E$ ,  $a_W$ ,  $a_N$ ,  $a_S$ , and b are some coefficients to be determined. To calculate these coefficients, one needs to determine a linear expression for the diffusion and convection terms.

#### A5.II.2.i A linear expression for the diffusion term.

For computation of the diffusion term, the assumption that the profile of F is linear between two points on the grid is made. Also, the diffusion coefficient G will be calculated at the interface i (i = e, w, n, and s) between the two grid points considered.



Figure A5.2: Typical grid point cluster with control volume interface.

For example, the discretized form of the diffusion term between the points E and P, with respect to the notation used in Figure 2, is given by:

$$\left(\boldsymbol{G}\,\frac{\partial\boldsymbol{F}}{\partial\boldsymbol{x}}\right)_{\boldsymbol{e}} = \frac{\boldsymbol{G}_{\boldsymbol{e}}(\boldsymbol{F}_{\boldsymbol{E}} - \boldsymbol{F}_{\boldsymbol{P}})}{(\boldsymbol{d}\boldsymbol{x})_{\boldsymbol{e}}} \tag{A5.18}$$

 $G_e$  is the diffusion coefficient (with respect to F) calculated at the interface e and x the direction of interest. If one considers a two-dimensional grid, the linearization of the diffusion term reads:

$$\left(\boldsymbol{G} \frac{\partial \boldsymbol{F}}{\partial x}\right)_{i} = \frac{\boldsymbol{G}_{i}(\boldsymbol{F}_{I} - \boldsymbol{F}_{P})}{(\boldsymbol{d}x)_{i}}, I = E \text{ and } N \text{ and } i = e \text{ and } n \text{ respectively}$$
(A5.19)

$$\left(\boldsymbol{G} \; \frac{\partial \boldsymbol{F}}{\partial x}\right)_{i} = \frac{\boldsymbol{G}_{i}(\boldsymbol{F}_{P} - \boldsymbol{F}_{I})}{(\boldsymbol{d}x)_{i}}, \text{ I} = \text{W} \text{ and S and } i = \text{w} \text{ and s respectively}$$
(A5.20)

A5.II.2.ii The linear expression for the convection term.

A simple scheme used for the linearization of the convection term is the upwind scheme: the value of F at the interface i is equal to the value of F at the grid point on the upwind side of the face i. For example, for the interface e,

$$\boldsymbol{F}_{\boldsymbol{e}} = \boldsymbol{F}_{\boldsymbol{P}} \quad if \quad \boldsymbol{F}_{\boldsymbol{e}} > 0 \tag{A5.21}$$

$$\boldsymbol{F}_{\boldsymbol{e}} = \boldsymbol{F}_{\boldsymbol{E}} \quad if \quad \boldsymbol{F}_{\boldsymbol{e}} < 0 \tag{A5.22}$$

If ||A, B|| denotes the greater of A and B, then between the point P and its neighbor I:

$$(\mathbf{r}_{u}\mathbf{F})_{i}\mathbf{D}x_{i} = F_{i}\mathbf{F}_{i} = \mathbf{F}_{P} || F_{i}, 0 || - \mathbf{F}_{I} || - F_{i}, 0 ||$$
 (A5.23)

In this case, I = E or N and i = e or n respectively. The convection term in the other direction is expressed in the same manner:

$$(\mathbf{r} u \mathbf{F})_i \mathbf{D} x_i = F_i \mathbf{F}_i = \mathbf{F}_i || F_i, 0 || - \mathbf{F}_P || - F_i, 0 ||$$
 (A5.24)

In this case, I = W or S and i = w or s, respectively. At this point, it is possible to give the completely linearized form of Equation A5.16 by substituting the linearized form of the convection and diffusion into this same equation.

# A5.II.2.iii Coefficients $a_P$ and $a_I$ for I = E, W, N, and S.

Comparing Equations A5.16 and A5.17 and after computation, one finds:

$$a_I = D_i + || - F_i, 0 ||$$
 for I = E and N (A5.25)

$$a_I = D_i + ||F_i, 0||$$
 for I = W and S (A5.26)

$$a_P = a_E + a_W + a_N + a_S - S_p \times \mathbf{D} \mathbf{x} \mathbf{D} \mathbf{y}$$
(A5.27)

$$b = S_c \times \mathbf{D} x \mathbf{D} y \tag{A5.28}$$

 $D_i$  is defined as:

$$D_i = \frac{G_i Dx_i}{(dx)_i} \tag{A5.29}$$

The reader can refer to the work done by Patankar (Patankar, 1972) for a more detailed computation of the coefficients.

## A5.III Numerical methods for solving the equations of the system

#### A5.III.1 One dimensional case: Thomas algorithm

The nomenclature of Equation A5.17 is modified by introducing 3 consecutive aligned points j 1, j, and j+1 of the grid and the values of F at 3 consecutive points (see Figure A5.3). With this new nomenclature, Equation A5.15 can be written as:

$$a_{j}F_{j} = b_{j}F_{j+1} + c_{j}F_{j-1} + d_{j}$$
 j = 1, 2,..., N (A5.30)

The coefficients in Equation A5.30 are expressed by:

$$a_{j} = b_{j} + c_{j} - Sp_{j} \times \mathbf{D}y_{j}\mathbf{D}z$$

$$b_{j} = D_{j+1} + ||-F_{j+1}, 0|| = \frac{2\mathbf{D}z \times \mathbf{G}_{j+1}}{(\mathbf{D}y)_{j+1} + (\mathbf{D}y)_{j}} + ||-(\mathbf{r}v)_{j+1} \times \mathbf{D}z, 0||$$

$$c_{j} = D_{j} + ||F_{j}, 0|| = \frac{2\mathbf{D}z \times \mathbf{G}_{j}}{(\mathbf{D}y)_{j-1} + (\mathbf{D}y)_{j}} + ||(\mathbf{r}v)_{j} \times \mathbf{D}z, 0||$$

$$d_{j} = Sc_{j} \times \mathbf{D}y_{j}\mathbf{D}z$$
(A5.31)



Figure A5.3: Typical grid point cluster with control volume interface.

According to the boundary conditions,  $F_0$  is a known value or can be expressed as a function of  $F_1$  and  $F_2$ . Thus for j = 1 in Equation A5.16,  $F_1$  can be expressed as a function of the only variable  $F_2$ . If one applies Equation A5.30 at the next step, one gets  $F_2$  as a function of  $F_1$  and  $F_3$ . Substituting  $F_1$  by the expression obtained at the step (j = 1),  $F_2$  can be expressed as a function of only  $F_3$ . Iterating this method, a set of equation having the following form is obtained:

$$F_{j} = P_{j}F_{j+1} + Q_{j}$$
 j = 1, 2,..., N (A5.32)

For j = 1,  $P_1$  and  $Q_1$  are known since  $a_i$ ,  $b_1$ ,  $c_1$ , and  $d_i$ , are known from the boundary conditions. If  $P_{j-1}$  and  $Q_{j-1}$  are known, then

$$F_{j-1} = P_{j-1}F_j + Q_{j-1}$$
(A5.33)

can be substituted in Equation 11 to give:

$$a_{j}F_{j} = b_{j}F_{j+1} + c_{j}(P_{j-1}F_{j} + Q_{j-1}) + d_{j}$$
 (A5.34)

Equating Equation A5.32 to Equation A5.34, P<sub>i</sub> and Q<sub>i</sub> can be found as:

$$P_{j} = \frac{b_{j}}{a_{j} - c_{j}P_{j-1}}$$
(A5.35)

$$Q_{j} = \frac{d_{j} + c_{j}Q_{j-1}}{a_{j} - c_{j}P_{j-1}}$$
(A5.36)

These recurrence relations can be used to calculate the  $P_j$  and  $Q_j$  coefficients for j = 1, ...,N. The method is used in a backward substitution manner at the other end of the grid, where the second boundary condition applies and give an additional equation between  $F_{n-1}$  and  $F_n$ . For example, if this equation reduces to  $b_n = 0$  (case where  $F_n$  is known and equal to a constant), then  $F_n = Q_n$  and  $F_{n-1},...,F_1$  are obtained from a successive resolution of the set of Equations A5.32.

#### A5.III.2 Two-dimensional case: Thomas algorithm and line-by-line method

Considering a two-dimensional grid as presented in Figure A5.4, one chooses a line j and considers the neighboring points of line j-1 and j+1 to be known from the previous iteration (or from the initial patch at the first step). According to Equation A5.30, the problem drops from a two-dimensional to a one-dimensional equation that can be solved with the Thomas algorithm previously described. In two dimensions, Equation A5.30 is given by:

$$a_{i,j}F_{i,j} = b_{i,j}F_{i,j+1} + c_{i,j}F_{i,j-1} + e_{i,j}F_{i+1,j} + f_{i,j}F_{i-1,j} + d_{i,j}$$
(A5.37)

The coefficients are defined as follow

$$\begin{cases} a_{i,j} = b_{i,j} + c_{i,j} + e_{i,j} + f_{i,j} - Sp_{i,j} \times \mathbf{D}y_{i,j}\mathbf{D}z_{i,j} \\ b_{i,j} = \frac{2\mathbf{D}z_{i,j}\mathbf{G}_{i+1,j}}{(\mathbf{D}y)_{i+1} + (\mathbf{D}y)_{i}} + // - (\mathbf{r}v)_{i+1,j}\mathbf{D}z_{i,j}, 0 // \\ e_{i,j} = \frac{2\mathbf{D}y_{i,j}\mathbf{G}_{i,j+1}}{(\mathbf{D}z)_{i,j+1} + (\mathbf{D}z)_{i,j}} + // - (\mathbf{r}w)_{i,j+1}\mathbf{D}z_{i,j}, 0 // \\ c_{i,j} = \frac{2\mathbf{D}z_{i,j}\mathbf{G}_{i,j}}{(\mathbf{D}y)_{i-1} + (\mathbf{D}y)_{i}} + // (\mathbf{r}v)_{i,j}\mathbf{D}z_{i,j}, 0 // \\ f_{i,j} = \frac{2\mathbf{D}y_{i,j}\mathbf{G}_{i,j}}{(\mathbf{D}z)_{i,j-1} + (\mathbf{D}z)_{i,j}} + // (\mathbf{r}w)_{i,j}\mathbf{D}z_{i,j}, 0 // \\ d_{i,j} = Sc_{i,j} \times \mathbf{D}y_{i,j}\mathbf{D}z_{i,j} \end{cases}$$
(A5.38)



If one chooses to move line-by-line in the direction z, Equation A5.37 can be written in the form of Equation A5.30:

$$a_{i,j}\mathbf{F}_{i,j} = b_{i,j}\mathbf{F}_{i,j+1} + c_{i,j}\mathbf{F}_{i,j-1} + D_{i,j}$$
(A5.39)

$$a_{i,j} = b_{i,j} + c_{i,j} - Sp_{i,j} \times ?y_{i,j} ?z_{i,j}$$
(A5.40)

$$D_{i,j} = e_{i,j}^0 F_{i+1,j}^0 + f_{i,j}^0 F_{i-1,j}^0 + d_{i,j}$$
(A5.41)

The subscript 0 indicates that the values are obtained from the previous iteration (or from a patched value at the first iteration). One can alternate the directions in which the Thomas algorithm is applied to bring the information from the boundaries to the inside points of the grid. However, faster convergence is obtained in the direction where the coefficients are larger.

#### A5.IV Application of the numerical methods to the TLC model

#### A5.IV.1 Description of the system and meshing

The problem to be solved is a two-dimensional steady-state mass transfer ( $\mathbf{F} = C$  where *C* represent the concentration of the species considered) with convection and diffusion in the y-direction and only convection in the z-direction. The surface representing a falling liquid film on a wall needs to be meshed. The assumption that the wall is a vertical smooth plate is made. The thickness of the film varies with the z coordinate as shown in Figure A5.5. The boundary condition assumed at the gas-liquid interface is that thermodynamic equilibrium applies. Thus, temperature and concentration are constant at the interface as long as steady state is achieved in the gas phase. At the wall, the corrosion rate is set equal to the flux of species to the wall according to the steady-state assumption.

#### A5.IV.2 Equations of the system

Applying Equation 6 to the variable concerned, that is, the concentration of the species in solution, one gets:

$$a_{i,j}C_{i,j} = b_{i,j}C_{i,j+1} + e_{i,j}C_{i,j-1} + e_{i,j}C_{i+1,j} + f_{i,j}C_{i-1,j} + d_{i,j}$$
(A5.42)

One needs to determine the parameters  $F_i$  and  $D_i$  for the case where F = C. According to the expression of the coefficients  $a_{i,j}$ ,  $b_{i,j}$ ,  $c_{i,j}$ ,  $e_{i,j}$ , and  $f_{i,j}$ , the parameters to be computed or defined are:  $v_{i,j}$ ,  $w_{i,j}$ ,  $G_{i,j}$ ,  $Dy_{i,j}$ , and  $Dz_{i,j}$ .



Convection and Diffusion

Figure A5.5: Meshing of the liquid film

An arbitrary computational step has to be determined in both directions. The step value in the y-direction is:

$$\boldsymbol{D}_{y_{i,j}} = \frac{\boldsymbol{d}_{min}}{20} \tag{A5.43}$$

 $d_{min}$  is the minimum value of the film thickness all around the circumference of the pipe. In the z-direction the step is:

$$\boldsymbol{D}_{z_{i,j}} = \boldsymbol{d}_{min} \tag{A5.44}$$

With this double choice of computational steps, the dimensions of the cell remain within one order of magnitude one from the other.



Figure A5.6: Control volume with two-dimensional fluxes.

The sign of v(i, j) and w(i, j) is defined according to the convention adopted in Figure A5.6 where the dimensions of a cell are described. In chapter V and Appendix 4, the equations describing the flow field were obtained. These are expressed as follow:

$$v(y,z) = \mathbf{D} \times \left[ \left( B + \frac{C'}{2} \right) \times \left( \frac{\mathbf{d}}{2 \times R} \times \cos \frac{z}{R} + \frac{1}{2} \left( \frac{\mathbf{t}}{d^3} - \mathbf{y} \times \mathbf{d} \right) \times \sin \frac{z}{R} \right) \times y^2 - \left( \frac{B}{6 \times 2 \times R} \cos \frac{z}{R} \right) \times y^3 + C' \left( \left( \frac{\mathbf{t}}{24 \times \mathbf{d}^5} - \frac{\mathbf{y}}{24 \times \mathbf{d}} \right) \times \sin \frac{z}{R} - \frac{1}{24 \times \mathbf{d} \times R} \times \cos \frac{z}{R} \right) \times y^4 \right]$$
(A4.10)

and

$$w(y,z) = \frac{(\mathbf{r}_l - \mathbf{r}_g) \times g \times \sin\frac{z}{R}}{A} \times \left[ \left( B\mathbf{d} + \frac{C' \times \mathbf{d}}{2} \right) \times y - B \times \frac{y^2}{2} - C' \times \frac{y^3}{6 \times \mathbf{d}} \right] \quad (V.22)$$

*y* is the distance to the wall and *z* is the coordinate in the flow direction. *d* is chosen to be equal to the film thickness (at the position *z*) computed according to Nusselt's theory:

$$\boldsymbol{d} = \left[\frac{4 \times A \times R \times \boldsymbol{l}_{l} \times (T_{sat} - T_{w}) \times \frac{\int (\sin \boldsymbol{j})^{l/3} d\boldsymbol{j}}{(\sin \boldsymbol{j})^{4/3}}}{\left(\frac{15 \times C'}{24}\right) \times ?_{l} \times (?_{l} - ?_{g}) \times g \times ?h_{v}(Tsat)}\right]^{l/4}$$
(V.35)

In the previous equations, we can express y and z at the grid point (i, j) as follow:

$$y = d - \sum_{k=1}^{j-1} Dy_{i,k} + \frac{Dy_{i,j}}{2}$$
(A5.45)

$$z = \sum_{k=1}^{i-1} \mathbf{D}_{z_{k,j}} + \frac{\mathbf{D}_{z_{i,j}}}{2}$$
(A5.46)

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In the case that F = C, then  $G = D_{Aw}$  where  $D_{Aw}$  is the conductivity of water and depends only on the temperature. Thus,

$$G_{i,j} = \frac{2? z_{i,j} D_{Aw}}{? y_{i,j-1} + ? y_{i,j}}$$
(A5.47)

# VALIDATION OF THE CFD CODE FOR THE MODELING OF MASS TRANSFER IN A FALLING FILM WITH AN ELECTROCHEMICAL REACTION AT THE BOUNDARY

#### A6.I Comparison of the steady-state solution and the transient solution

The validation of this model was done with an imaginary case of filmwise condensation. The film thickness and the film depth were chosen so that the number of control volumes in the grid is smaller than 1000. In a real case, the thickness of the film is of the order of magnitude of one hundred microns whereas the depth of the film (from the top of the line to the bottom of the line) is around 15 cm (for a 4 inch pipe). Thus, one dimension is 1500 times larger than the other one, which renders a visual presentation of the results of simulation quite difficult. For the validation presented here, the thickness of the film was chosen equal to 10 microns and the depth was chosen equal to 60 microns. The total number of control volumes is 600 and the dimensions of a control volume are 1 micron by 1 micron. Moreover, the flux of consumption of species at the wall was chosen so that a large gradient of concentration occurs rapidly in the film. One more time, such a flux of consumption does not correspond to a realistic rate for the reaction of corrosion by CO<sub>2</sub>. At the initial time step, the film is saturated everywhere with carbon dioxide at equilibrium with the gas phase. The temperature was set at 363 K, the total pressure at 5 bar, and the partial pressure of carbon dioxide in the gas phase at 4 bar. The same case

will be used for the other types of validations. Figure A6.1 shows the converged transient two-dimensional profile of carbon dioxide concentration in the condensed film. Figure A6.1 can be compared to Figure A6.2, which was obtained without solving the transient term (steady-state solution). One can notice that these 2 profiles are identical. The corresponding numerical values are exactly identical. The transient model shows its ability to converge to a steady-state solution.

#### A6.II Grid refinement

For the same case, the steady-state concentration profile was solved using two type of meshing:

- A 1  $\mu$ m x 1  $\mu$ m control volume grid
- A 0.5 μm x 0.5 μm control volume grid

The results of the two simulations are compared in Figure A6.3. The concentration profiles in the x-direction (thickness of the film) at a depth of 10, 20, 30, 40, 50, and 60 microns are reported for the two different grids. It can be seen that these profiles match for each depth of film considered. Figure A6.4 gives the relative error made on the concentration of carbon dioxide by switching from one grid to the other. The relative error is never bigger than 2 percent, which is an acceptable number. The model is shown to give reproducible results, as the grid is sufficiently refined.



Figure A6.1: Transient concentration profile of dissolved carbon dioxide in a 10 **m** thick film. Total pressure: 5 bar , PCO<sub>2</sub>: 4 bar, T= 363 K. Corrosion at the wall (x=0). Saturation at the interface gaz-liquid (x =10) and in the entire film at time t=0.



Figure A6.2: Steady-state concentration profile of dissolved carbon dioxide in a 10 microns thick film. Total pressure: 5 bar , PCO2: 4 bar, T= 363 K. Corrosion at the wall (x=0). Saturation at the interface gaz-liquid (x=10)



Figure A6.3: comparison of concentration profile in the film at different depth and for 2 grids. First grid: 0.5mm x 0.5mm, second grid: 1 mm x 1 mm



Figure A6.4: Relative error on the concentration between grid 1 and 2

#### A6.III Computation of the mass balance on each control volume

The mass balance was computed with the simulated results obtained with the 0.5  $\mu$ m x 0.5  $\mu$ m control volume grid. The results of this computation are shown in FigureA6.5. The maximum error on the mass balance is of the order of 10e-24 kmol/m<sup>2</sup>/s, which is a negligible error. Therefore, it can be concluded that the modeling work satisfies the mass balance on each of the control volumes of the grid.



Figure A6.5: Mass balance on each control volume of the grid (120x20 nodes) 1 node: 0.5mm x 0.5mm

## **COMPUTATION OF THE pH**

# OF THE CONDENSED WATER

#### **IN ABSENCE OF IRON IONS**

When in contact with water, carbon dioxide dissolves:

$$CO_{2(g)} \Leftrightarrow CO_{2(aq)}$$
 (A7.1)

When dissolved in solution, carbon dioxide is hydrated to give:

$$CO_{2(aq)} + H_{2}0 \Leftrightarrow H_{2}CO_{3}$$
(A7.2)

which dissolves in two steps:

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \tag{A7.3}$$

$$HCO_3^- \Leftrightarrow H^+ + HCO_3^-$$
 (A7.4)

The corresponding constants of equilibrium for the reactions A7.1, A7.2, A7.3, and A7.4 are:

$$K_{sol} = \frac{[CO_2]}{P_{CO_2}} \tag{A7.5}$$

$$K_{hy} = \frac{[H_2 CO_3]}{[CO_2]}$$
(A7.6)

$$K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$
(A7.7)

$$K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^{-}]}$$
(A7.8)

The values of these constants are given elsewhere (Nesic, 2001). The partial pressure of carbon dioxide in the system is a given parameter. Thus, there are 5 unknowns among which the proton concentration. One additional equation is needed to solve the system of 5 equations and 5 unknowns. This equation is correspond to the electroneutrality of the solution:

$$[H^{+}] = [HCO_{3}^{-}] + 2[CO_{3}^{2-}] + [OH^{-}]$$
(A7.8)

Using Newton-Raphson's technique, it is possible to solve the system of equations for  $[H^+]$  and calculate the pH in absence of iron ions.

#### **EXPERIMENTAL UNCERTAINTY ANALYSIS**

# A8.I Uncertainty of the measurement on the corrosion rate due to the type of instrumentation

The instrumentation used to measure the corrosion rate are the Cormon ER probes including Ceion Technology. According to Cormon company: "the measurements are virtually unaffected by other process variables such as temperature, hydrostatic pressure, impact loading (slugging), or flow regimes" <sup>(1)</sup>. More precisely, for a 1 mm-thick sensor, the resolution of the sensor is  $5 \times 10e-6$ . This means that the minimum measurable change in the element thickness is 5 nanometers. The lowest corrosion rate experimentally measured was above 0.01 mm/yr. Since the stabilized corrosion rate was measured over a period of time of at least 12 hours, the minimum metal loss measured during experimentation was around 13.5 micrometers.

Thus, the relative error  $\varepsilon$  due to the sensitivity of the instrumentation is:

$$e = \frac{5 \times 10^{-9}}{13.5 \times 10^{-6}} = 3.7 \times 10^{-5} = 0.04\%$$
(A8.1)

The temperature effects are compensated to a relative error of  $\pm -10e-6/°C$ . The change in hydrostatic pressure is compensated to  $\pm -10e-6/20$  Bar. Thus, the error of measurement due to these 2 parameters is smaller than resolution of the sensor for the experimental conditions achieved (temperature is measured within  $\pm -0.5°C$  and pressure is measured within  $\pm -0.5$ psig).
## A8.2 Uncertainty of the measurement on the corrosion rate based on the theory of Electrical Resistance measurements

The sensing element of an ER probe is represented in Figure A8.1:



Figure A8.1: ER sensing element

The electrical resistance of the sensing element is given by:

$$R = \frac{\mathbf{r} \times L}{h \times \mathbf{d}} \tag{A8.2}$$

*R* is the electrical resistance (Ohm), r is the electrical resistivity (Ohm.m), *L* is the sensor length (m), *h* is the sensor thickness (m), and *d* is the sensor width (m). The corrosion rate is obtained from the metal loss:

$$CR = 1000 \times \frac{Dh}{Dt} \tag{A8.3}$$

*CR* is expressed in mm/yr, and the time interval Dt is expressed in year. Combining Equations A8.2 and A8.3, one obtains:

$$CR = \frac{1000 \times L}{Dt \times d} \times D(\frac{r}{R})$$
(A8.4)

The resistivity and the resistance are dependent on the temperature. The other system variables (total pressure, partial pressure of carbon dioxide, and gas velocity) do not affect these two variables in a significant manner. *L* and *d* are not significantly affected by the change of temperature (coefficient of linear expansion around  $1.2 \times 10e-5/^{\circ}C$  for CS 1020) or other system parameters. Thus, the absolute uncertainty in the measurement of the corrosion rate as a result of uncertainties in the system variables can be expressed as follow:

$$\frac{\boldsymbol{d}(CR)}{CR} = \left[\frac{\partial(CR)}{\partial T}\right] \frac{\boldsymbol{d}T}{CR}$$
(A8.5)

According to Equation A8.4:

$$\frac{\boldsymbol{d}(CR)}{CR} = 2 \times \left[\frac{\partial(CR)}{\partial \boldsymbol{r}} \times \frac{\partial(\boldsymbol{r})}{\partial T} + \frac{\partial(CR)}{\partial R} \times \frac{\partial(R)}{\partial T}\right] \frac{\boldsymbol{d}T}{CR}$$
(A8.6)

The dependences of  $\mathbf{r}$  on T, and R and T are obtained from the literature <sup>(1,2)</sup>:

$$\mathbf{r} = 6.01 \times 10^{-10} \times T - 7.97 \times 10^{-8}$$
(A8.7)

$$\frac{1}{R}\frac{\partial R}{\partial T} = 0.4\% = 0.004$$
 (A8.8)

Equation A8.4 is equivalent to:

$$\frac{\boldsymbol{d}(CR)}{CR} = \frac{2000 \times L}{\boldsymbol{D}t \times \boldsymbol{d} \times R} \left[ \frac{\partial(\boldsymbol{r})}{\partial T} - \frac{\boldsymbol{r}}{R} \frac{\partial(R)}{\partial T} \right] \times \frac{\boldsymbol{d}T}{CR}$$
(A8.9)

After substitution and simplification:

$$\frac{\boldsymbol{d}(CR)}{CR} = \frac{2000 \times h}{\boldsymbol{D}t} \times \left(\frac{6.01 \times 10^{-10}}{6.01 \times 10^{-10} \times T - 7.97 \times 10^{-8}} - 0.004\right) \times \frac{\boldsymbol{d}T}{CR}$$
(A8.10)

The error on the temperature is within  $\pm -0.5^{\circ}$ C, and *h* measures around 1mm. Therefore,

$$\frac{d(CR)}{CR} = \pm \frac{1}{Dt \times CR} \times \left( \frac{6.01 \times 10^{-10}}{6.01 \times 10^{-10} \times T - 7.97 \times 10^{-8}} - 0.004 \right)$$
(A8.11)

The previous formula is applied to some experimental conditions. For example, for a 4day test at 314°K, the relative error on the corrosion rate is 8%. At 350°K, for a 4-day test, the relative error is 2%.

## A8.3 Standard deviation on the measurement of the corrosion rate

Due to the nature of the experiments, it was not possible to repeat each experimental points many times and obtain a standard deviation for the measured corrosion rates. However, a mentioned on page 130, one experiment was repeated 5 times. More detailed statistical analysis on these experiments is offered here:

Mean	0.312
Standard Error	0.01019804
Standard Deviation	0.02280351
Sample Variance	0.00052
Range	0.06
Minimum	0.28
Maximum	0.34
Confidence Level(95.0%)	0.02831435

 Table A8.1: Statistical analysis on experimental data (see page 130)

The standard deviation of around 8% of the mean obtained here builds our confidence in the goodness of the experimental results. This standard deviation is reported as an error bar for each data point representing the corrosion rate to support the conclusions that the author draws throughout this document.

(1): <u>http://www.cormon.com/catalog/techpres.htm</u>

(2): CRC Handbook of Chemistry and Physics, 79<sup>th</sup> Edition 1998-1999