Extension of the Corrosion Analyzer to Multiphase Flow Conditions

Interim Report

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December 21, 2011

Introduction

The objective of this task was to extend the Corrosion Analyzer to predict corrosion behavior under multiphase flow conditions. Further, the extension has been designed in such a way that the necessary parameters that characterize multiphase flow can be obtained from OLGA in cases when an aqueous film exists on the inner surface of pipeline.

Background

In general, the Corrosion Analyzer is a comprehensive program that allows users to predict corrosion potential, repassivation potential (i.e. to predict the presence of localized corrosion) and rates of general corrosion in multicomponent chemical systems. However, the existing version of the Corrosion Analyzer (V3.2) can be used in one-phase flow only. This is because the mass transfer coefficients predicted in OLI software are applicable only to one-phase flow. It is therefore necessary to generalize the mass transfer formulation to multiphase flow if our goal is to use Corrosion Analyzer to predict corrosion in water-gas, water-oil, and water-oil-gas systems.

We will show below that the above goal is achievable by using hydrodynamic properties computed in existing software packages (such as OLGA). Specifically, the predicted shear stress under water films, that may cover the inner surface of pipes, is used.

Mass-transfer in OLI's models

In accordance with the principles of heterogeneous kinetics the rate of the m-th electrochemical reaction can be presented in the following form (in the units of current density):

$$i_m = i_m(E, c_{ks}, T_s, P) \tag{1}$$

where i_m is the current density that corresponds to m-th reaction, E is the metal potential, c_{ks} (k= 1,2…) are the surface concentrations of the species that determine the rate of the reaction, T_s is the surface temperature, and P is the pressure.

However, we measure and, accordingly, need to calculate the following function:

$$i_m = i_m(E, c_{k0}, T_0, P) \tag{2}$$

where the index 0 refers all values to the bulk of solution.

A transition from Equation (1) to Equation (2) can be obtained by solving the equations of mass and heat transfer, which allow us to find c_{ks} and T_s as functions of c_{k0} and T_0.

In the OLI model, we neglect the difference between the surface and bulk temperatures (i.e. $T_s \approx T_0$). It is also assumed that the rate of the m-th reaction depends only on a single ion with the concentration, c_s, i.e.

$$i_m = nFkc_s^p \tag{3}$$

were p is the order of the electrochemical reaction. In the absence of homogenous chemical reaction, in the first approximation, we have $i_m \propto (c_0 - c_s)$ and, accordingly

$$\frac{i_m}{i_{m,0}} = \left(1 - \frac{i_m}{i_{m,\lim}}\right)^p \tag{4}$$

where

$$i_{m,0} = nFkc_0^p \tag{5}$$

is the activation current density (i.e. partial current density in the absence of diffusion limitations) and

$$i_{m,\lim} = nFk_m c_0 \tag{6}$$

is the limiting current density (i.e. partial current density at the absence of kinetic limitations). Here, k_m is the mass transfer coefficient of the m-th reaction. In a particular case when the order of the electrochemical reaction is p = 1, Equation (4) has a simple analytical solution

$$i_m = \frac{i_{m,\lim} i_{m,0}}{i_{m,\lim} + i_{m,0}} \tag{7}$$

It is evident that at $i_{m,0} \ll i_{m,\lim}$ we have $i_m \approx i_{m,0}$ and at $i_{m,0} \gg i_{m,\lim}$ we have $i_m \approx i_{m,\lim}$.

It follows from Equations (5)-(7) that the problem of describing mass transfer effects on the rate of corrosion reduces to the calculation of mass transfer coefficients. The OLI software calculates the mass transfer coefficients, k_m, for rotating disk electrode (laminar flow), rotating cylinders (turbulent flow) and single phase flow in a straight pipe (turbulent flow). It is clear that first two cases have no relations with the corrosion in pipelines. In the third case (single phase turbulent flow in straight pipe) mass transfer coefficients are estimated via empirical Berger and Hau (1977) [1] relations:

$$Sh = 0.0165 \, Re^{0.86} \, Sc^{0.33} \tag{8}$$

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where $Sh = \dfrac{kd}{D}$, $Re = \dfrac{Vd}{\upsilon}$ and $Sc = \dfrac{\nu}{D}$ are Sherwood Reynolds and Schmidt numbers correspondingly. Here V is the average fluid velocity, d – is the diameter of the pipe, D is the diffusion coefficient and ν is the kinematic viscosity.

The case of carbonic acid reduction (which is important for CO_2 corrosion in oil and gas pipelines) requires a special treatment because reduction of H_2CO_3

$$H_2CO_3 + e^- \rightarrow 0.5H_2 + OH^- \tag{9}$$

which is complicated by the homogeneous reaction:

$$CO_2 + H_2O \Leftrightarrow H_2CO_3 \tag{10}$$

In this case, i_{lim} in OLI's software is calculated via the expression (Nesic et al. (1996) [2]

$$i_{H_2CO_3,lim} = -D\left(\frac{dc_{H_2CO_3}}{dy}\right)_{y=0} = DFc_{CO_2,0}\sqrt{D_{H_2CO_3}K_{H_2CO_3}k^f_{H_2CO_3}} \tag{11}$$

where $K_{H_2CO_3}$ is the equilibrium constant of Reaction (10) and $k^f_{H_2CO_3}$ is the constant of the forward Reaction (10) and where y is the distance from the metal surface.

It is easy to check that Equation (11) is the result of a solution of the transport equation for carbonic acid in a motionless liquid:

$$D_{H_2CO_3}\frac{d^2c_{H_2CO_3}}{dy^2} = k^f_{H_2CO_3}c_{CO_2,0} - k^b_{H_2CO_3}c_{H_2CO_3} \tag{12}$$

with the boundary conditions:

$c_{H_2CO_3} = 0$ at $y = 0$ and $c_{H_2CO_3} = c_{H_2CO_3,0}$ at $y = \infty$.

Accordingly, Equation (11) can be used only in the case when the diffusion layer is so thin that the turbulent effects cannot influence mass transport.

Turbulent Mass-Transfer in the Absence of Chemical Relations

Usually, mass transfer near the electrode surface in a turbulent boundary layer is considered on the basis of a generalized Fick's law [3]

$$j = -(D + D_t)\frac{dc}{dy} \tag{13}$$

where j is the diffusion flux density at the wall, c is the concentration of diffusing species, D_t is the eddy (turbulent) diffusion coefficient and y is the distance from the wall.

It can be shown that the ratio

$$\frac{D_t}{v} = f(y^+) \tag{14}$$

where v is the kinematic viscosity of the electrolyte and

$$y^+ = \frac{y}{v}\sqrt{\frac{\tau_0}{\rho}} \tag{15}$$

is the dimensionless distance from the wall. Here, τ_0 is the shear stress at the metal surface and ρ is the density of the electrolyte.

Usually the eddy diffusion coefficient is described by a power function: $D_t \propto y^3$ or $D_t \propto y^4$. It can be easily proven that there are no linear or quadratic terms in the expansion of the function f in Equation (14) [4]. Up to now the most accurate description of the eddy diffusion coefficient is given by Wasan et al (1963) [5].

$$\frac{D_t}{v} = \frac{4A_1(y^+)^3 - 5A_2(y^+)^4}{1 - 4A_1(y^+)^3 + 5A_2(y^+)^4} \quad \text{for } y^+ \leq 20, \text{ where } A_1 = 1.0972\times10^{-4} \text{ and } A_2 = 3.295\times10^{-6}$$

$$\tag{16}$$

$$\frac{D_t}{v} = \frac{y^+}{2.5} - 1 \quad \text{for } y^+ \geq 20$$

In order to obtain all results in an analytical form, we will describe eddy diffusivity by the power function (with a power equal to 3):

$$\frac{D_t}{v} = b(y^+)^3 \quad \text{at } y^+ \leq 20, \text{ where } b = 8.75\times10^{-4} \tag{17}$$

The value of the empirical parameter b is chosen from the requirement that Equation (17) yields the same value of eddy difusivity at $y^+ = 20$ (on the border of the so called logarithmic region), as Equation (16).

Integration of Equation (13) [by taking into account Equations (15) and (17)] with the boundary condition $c = c_s$ at $y^+ = 0$ yields:

$$j = \frac{(c - c_s)}{\left\{ \int\limits_0^{(bScy^+)^{1/3}} \frac{dz}{1 + z^3} \right\}} \sqrt{\frac{\tau_0}{\rho}} Sc^{-2/3} \tag{18}$$

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The integral in Equation (18) converges very quickly. Thus, the difference between this integral and its limiting value

$$\int_0^\infty \frac{dz}{1+z^3} = \frac{2\pi}{3\sqrt{3}} \approx 0.827 \tag{19}$$

is less than 3 % at $(bSc)^{1/3} y^+ = 3.7$ which corresponds $y^+ \approx 4$ at $Sc = 10^3$ and $b = 8.75 \times 10^{-4}$. Accordingly, we have

$$j = \frac{3\sqrt{3}}{2\pi} b^{1/3} \sqrt{\frac{\tau_0}{\rho}} Sc^{-2/3} (c_0 - c_s) \tag{20}$$

where c_0 is the bulk concentration of the species. Finally, for the mass transfer coefficient we have

$$k = \frac{3\sqrt{3}}{2\pi} b^{1/3} \sqrt{\frac{\tau_0}{\rho}} Sc^{-2/3} \approx 0.0791 \sqrt{\frac{\tau_0}{\rho}} Sc^{-2/3} \tag{21}$$

In the case of one-phase flow the shear stress at the metal surface, τ_0, can be found from the relation [6]:

$$\tau_0 = \frac{f}{2} \rho V^2 \tag{22}$$

where V is the average fluid velocity in the pipe an f is the friction coefficient. If for f we will use the simplest empirical Blasius relation for round smooth tubes [6]:

$$f = \frac{0.079}{Re^{1/4}} \tag{23}$$

the dimensionless relation for mass transfer coefficient will have the form

$$Sh = \frac{kd}{D} = 0.0157 Re^{0.875} Sc^{1/3} \tag{24}$$

which practically coincides with the empirical Berger and Hau relation (see Equation(8).

However, in the case of multiphase flow it is impossible to use the Blasius relation because presence of gas and oil fractions definitely influences the shear stress at the metal surface even under water film. In this case for calculating mass transfer coefficients we will use Equation (21) assuming that the value of shear stress at the metal surface under the liquid film will be provided by OLGA software. In accordance with the OLGA 5 User Manual the variable TAUWWTA yields "water-film-average wall shear stress" and namely this value will be used instead of τ_0 in Equation (22). It is important to note that the approach described above can be used only if there is a liquid film on the metal surface inside the oil or gas pipeline. In accordance with the OLGA

5 User Manual such information is provided by the parameter WCWALL, which is defined as 1 if there is a continuous water film at the wall.

Turbulent Mass-Transfer with Chemical Reaction

As mentioned above, the very important case of CO_2 corrosion is complicated by the chemical Reaction (9). Accordingly, a generalization of the above method for a homogenous chemical reaction will be obtained here.

In the case of a first-order chemical reaction with the rate constant, K, the equation of mass transfer has the form:

$$\frac{dc}{dy}\left\{(D+D_t)\frac{dc}{dy}\right\} = K(c_0 - c) \tag{25}$$

with the boundary conditions

$$c = c_s \quad \text{at} \ \ y = 0, \qquad c = c_0 \quad \text{at} \ \ y \to \infty \tag{26}$$

By using a dimensionless distance from the metal surface, y^+, it is possible to rewrite Equation (26) in the form:

$$\frac{dc}{dy^+}\left\{[Sc^{-1} + b(y^+)^3]\frac{dc}{dy^+}\right\} = K(c_0 - c)\frac{\rho v}{\tau_0} \tag{27}$$

By using the method of asymptotic correction and the so called algebraic method [7, 8] it is possible to show that the ratio $X = k/k^+$, where k is the mass transfer coefficient and k^+ is mass transfer coefficient calculated at the absence of chemical reactions [for example, via Equation (21)] satisfy approximately the following cubic equation:

$$X^2 - \frac{1}{X} = M \tag{28}$$

where

$$M = \frac{KD}{(k^+)^2} = \frac{(k^*)^2}{(k^+)^2} \tag{29}$$

and

$$k^* = \sqrt{KD} \tag{30}$$

is the mass transfer coefficient calculated at the absence of turbulent pulsations (in a motionless solution).

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We will not provide here the derivation of Equation (28) because this derivation is relatively complicated and because we will compare the approximate solution of this equation (which can be considered as a interpolation formulas) with the numerical solution of Equation (27) that has been done by Vieth et al. (1963) [9].

We will obtain an approximate solution of Equation (29) by using the simplest iteration method. Rewriting Equation (29) in the form $X = \sqrt{1/X + M}$ and choosing as a zero approximation X=1 we will have in the fist approximation

$$X = \frac{k}{k^+} = \sqrt{1+M} \tag{31}$$

which yield results that coincide with the results of numerical calculations [9] with great accuracy. Accordingly, there is no practical need to continue the iteration process. It is evident that at M→0 we have X ≈ 1. On the other hand at M→∞ we have X ≈ M$^{1/2}$. It means that Equation (31) can be considered as an interpolation formulas between the evident limiting cases.
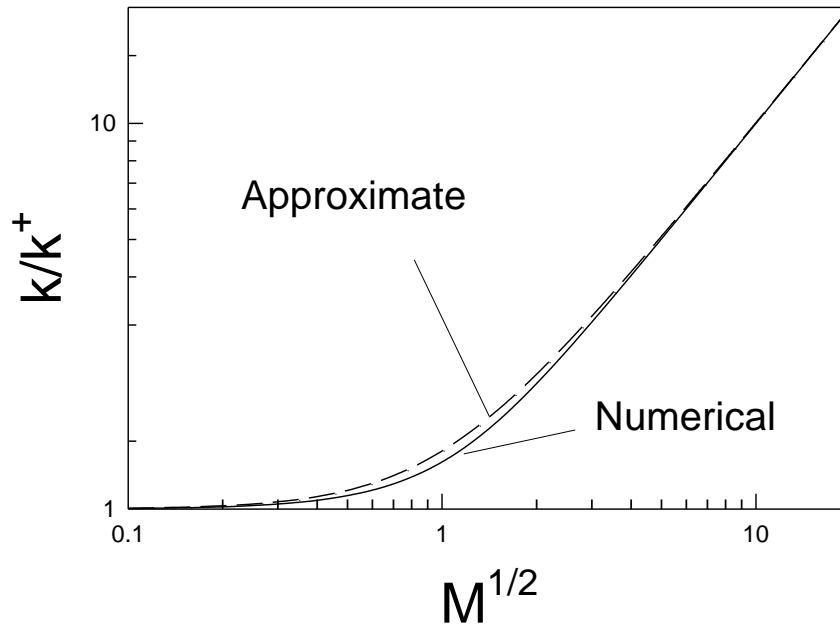

Figure 1. Comparison of values obtained from the approximate solution (Equation (31)) and numerical solution

It is important to note that Equation (31) can be rewritten in the forms:

$$k = \sqrt{(k^+)^2 + (k^*)^2} \tag{32}$$

or

$$i_{\text{lim}} == \sqrt{(i_{\text{lim}}^d)^2 + (i_{\text{lim}}^k)^2} \tag{33}$$

where i_{lim}^d is the limiting current calculated in the absence of chemical reactions and i_{lim}^k is the limiting current density calculated in a stagnant electrolyte.

Numerical calculations show that Equations (32) and (33) can be used not only in the case of the first order chemical reaction but also in the case of chemical reactions with an arbitrary order. The only difference is that in the last case the mass transfer coefficient calculated in the motionless solution, k^*, can be calculated not via Relation (30) but can be found as the solution of the following equation

$$D\frac{d^2c}{dy^2} = Kf(c_0 - c) \tag{34}$$

where f is an arbitrary function which satisfies the evident boundary condition $f \to 0$ at $y \to \infty$ (in the bulk of the solution, the concentration reaches its equilibrium value). Solution of the differential Equation (34) leads to the following relation [instead of Relation (30)]

$$k^* = \sqrt{2DK \int_{c_s}^{c_0} f(c_0 - c)dc / (c_0 - c_s)^2} \tag{35}$$

It is evident, that at $f(c_0 - c) = c_0 - c_s$ (first order reaction) Equations (30) and (35) yield the same results.

Conclusion

The method described above allows us to generalize the Corrosion Analyzer for the parts of oil and gas pipelines that are covered by water films so that the general corrosion rates, corrosion and repassivation potentials can be predicted if the value of shear stress under this water film is known. The shear stress value can be obtained from the OLGA software.

References

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