THEORETICAL ELUCIDATION ON THE CORROSION TUBE GROWTH MECHANISM OF MILD STEEL IN THE EFFECT OF pH ON OXYGEN CORROSION AT ELEVATED PRESSURES

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ABSTRACT

The major purpose of this paper is the theoretical elucidation of the corrosion tube growth mechanism of mild steel occurred from the effect of pH value and oxygen corrosion at elevated pressure provided by Riggs *et al*. [6]. Based on the Nernst-Planck equation, continuity principle, Green's theorem, Stokes's theorem and the equation of Newton's second law of motion, the mechanism of corrosion tube development can be explained theoretically. The Bernoulli sum is contant at any cross-section of tubular corrosion product. The implication of the present results are theoretically enhanced the formation of corrosion tube mechanism.

I. INTRODUCTION

The increasing number of structures suffering corrosion makes the study of their structural safety of importance. The evaluation of the residual load-bearing capacity based on the quantification of the actual degree of damage and the prediction of its evolution needs the measurement of the steel corrosion rate. Obviously, the study of steel corrosion is very important to the civil or offshore structures.
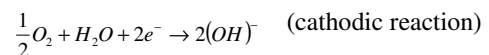
Riggs *et al*. [6] studied the oxygen corrosion of mild steel in brine. They also proposed the corrosion tube growth mechanism of iron mental. This mechanism was cited by Fontana [2]. Although these studies have provided much information on the steel corrosion, there is still theoretical elucidation that has not yet been explored. This paper describes a theoretical study that investigated the effect of pH on oxygen corrosion at elevated pressures for mild steel. The result of this study may be of theoretical support to civil or offshore engineers attempting to employ the corrosion rate of mild steel in reinforced concrete structures.

II. CORROSION TUBE GROWTH MECHANISM

The corrosion process of steel in aqueous media and oxygen is a electrochemical reaction process. The corrosion of the steel is being accomplished by the action of a network of cathodic and anodic cells on the mental surface. Fig. 1 denotes a schematic diagram of the mechanism of oxygen corrosion for an oxygen concentration cell to a mild steel [6]. The basis for corrosion is ascribed to the difference in oxygen concentration. At the anode, oxidation occurs and the area is low in oxygen concentration. This allows a difference in potential to exist due to higher oxygen concentration at the cathode. The chemical theory provides that mental ions enter solution at the anodes of these cells in an amount which is chemically equivalent to the reaction at the cathodes.

When the surface of steel has water and oxygen, both of the anodic reaction of iron ion and the cathodic reaction of oxygen induction with dissolved state have occurred and carried out with constant velocity. The electrochemical mechanism of corrosion reaction on the steal can be expressed as follows:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad \text{(anodic reaction)}$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^- \quad \text{(cathodic reaction)}$$

The entire reaction of corrosion process is the composition of anodic reaction and cathodic reaction. The electric current passes through the electrolyte in the water by the use of a transfer of negative hydroxyl ions, OH^-, toward the anode [4]. Though the transfer of OH^- is a transfer of mass, it is not required to formulate as a diffusion process, because this is correspondingly done by writing the Ohm's law for the electrolyte in the water. The OH^- that arrive at the anodic area electrically neutralize the Fe^{2+} dissolved in water [2], forming a solution of ferrous hydroxide $(Fe(OH)_2)$ as described by the chemical equation (see Fig. 1)
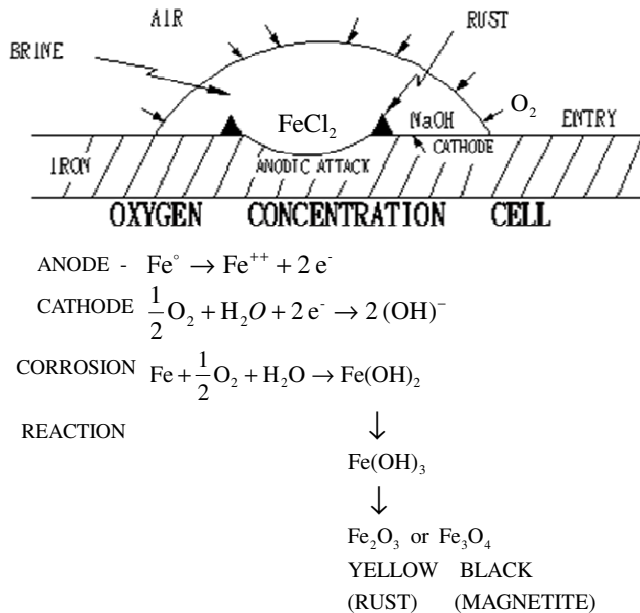
Fig. 1. Mechanism and reaction of oxygen corrosion.

$$Fe^{2+} + 2\,OH^- \rightarrow Fe(OH)_2 \qquad \text{(anode)}$$
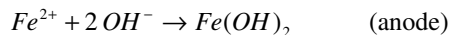
The total cell reaction, summarizing the results of these chemical equations mentioned above, is

$$2\,Fe + 2\,H_2O + O_2 \rightarrow 2\,Fe(OH)_2 \qquad \text{(cell)}$$
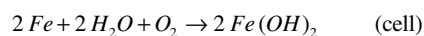
The $Fe(OH)_2$ further reacts with available oxygen and water [2]

$$4\,Fe(OH)_2 + O_2 + 2\,H_2O \rightarrow 4\,Fe(OH)_3 \qquad \text{(anode)}$$
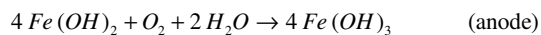
The red rust, $Fe(OH)_3$, constitutes hydrated red rust $(FeOOH + H_2O)$, the final product that precipitates from the solution. Some form $nFe_2O_3 \cdot mH_2O$ (red rust) in advance. Some become Fe_3O_4 (black rust) due to not complete oxidization. Both the red and black rust form rust layer on the steel surface. In any case, the red-rust volume is four times as large as that of steel while the black-rust volume is twice as large [9]. Pitting corrosion (see Fig. 2) is really more dangerous than uniform corrosion due to carbonation. Since the slot effect produced by the pitting corrosion induces stress concentration, this phenomenon will seriously reduce both the ductility and fatigue strength of steel. The reductions of steel strength and ductility definitely influence the structural safety.

Pitting corrosion is a local type of metal corrosion. This means that the corrosion rate of some places of metal is larger than that of the other places. If the region at a small area and an unchanged location is of extremely large metal corrosion then the produced cavity is deep pit. If the metal surface area suffered larger corrosion then the produced cavity is shallow pit.

Fontana [2] illustrated the basic mechanism of crevice or pitting corrosion. The initial position of pitting corrosion is generally located at structural heterogeneities such as medium
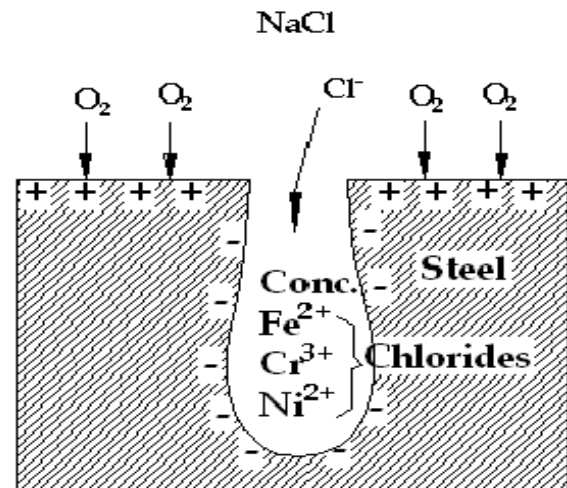

Fig. 2. Steel pitting corrosion.

and depleted oxygen. The growth of pitting corrosion is believely occurred the precipitation of high acid located on the pitting hole. Fig. 2 shows the schematic diagram of occurrence pitting corrosion growth due to metal (M) concurred with Fe^{2+}, Cr^{3+}, and Ni^{2+} in the solution of NaCl. First, since the bottom of pitting is not easily supplied oxygen, the oxidation of the dissolution of metal M is

$$M \rightarrow M^+ + e^- \qquad \text{(oxidation)}$$
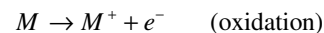
The pitting hole has the highly supplied oxygen surrounding the hole and has the reduction of oxygen to hydroxide ions, i.e. ,

$$O_2 + 2\,H_2O + 4e^- \rightarrow 4OH^- \qquad \text{(reduction)}$$
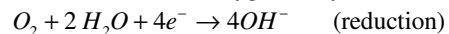
Thus, the surroundings of the pitting hole suffer protect. Meanwhile, for the maintain equilibrium of the electricity of the solution, the Cl^- in the solution concentrates in the pitting hole, The metal chloride and water happen the following chemical reaction:

$$M^+Cl^- + H_2O \rightarrow MOH + H^+Cl^-$$
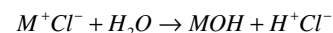
The above chemical reaction indicates that an aqueous solution of a typical metal chloride dissociates into an insoluble hydroxide and a free acid. Hence, the H^+ concentration of the pitting hole increases and makes greater the rate of anodic reaction. Thereafter, the process of the pitting corrosion becomes an auto catalytic phenomenon.

The point of chemical review of oxygen corrosion of mild steel in brine has been introduced. Now the mathematical model of corrosion tube of steel in oxygen and water is described as follws.

The general form of partial differential equation, i.e., the Nernst-Planck equation, that relates these factors to a three-dimensional transport process can be written as [3,5]

$$\frac{\partial C_j}{\partial t} = D\nabla^2 C_j - V \cdot D C_j + R + Z_j U_j F \nabla \cdot (C_j \nabla \phi) \qquad (1)$$

where C_j is the bulk concentration of ion j (mol/m^3), D is the

diffusion coefficient (m^2/s), V is the flow velocity (m/s), R is the reaction rate or Boltzmann's constant in RT, T is the absolute temperature (K), z_j is the valance of ion j , U_j is the mobility of ion j, F is the Faraday's constant (96500 coulombs/equivalent), ϕ is the electrostatic potential, t is the time, ∇ is the nabla (or del) operator, and ∇^2 is the Laplacean operator.

The term on the left of Eq. (1) is the contribution accumulation due to diffusion, convection, reaction rates and migration. The first term on the right of Eq. (1) is the contribution of molecular transport due to diffusion. The second and third terms are the contribution due to convection and reaction rates, respectively. The last term is the contribution due to migration.

Riggs *et al.* [6] pointed out that extremely severe localized corrosion is evidenced in the form of filament or whisker growth at very high pH levels. It was interesting to note that these filaments are at actually hollow tubes on steel surface due to oxygen (aerobic) corrosion at elevated pressures. For the oxygen corrosion of steel in water, the contribution of diffusion in water is small at the potentials normally used in oxygen corrosion and can safely be neglected. Likewise the contribution due to convection can be ignored, because it is unlikely that there are appreciable temperature gradients to cause convection [8].The contribution of reaction rate of steel due to oxygen dissolved in water is also small and can disregarded with safety. Only the third term is of most importance in the electrochemical in nature for the corrosion process of steel in aqueous media and oxygen. If one considers both the steady flow,i.e., $\frac{\partial C_j}{\partial t}=0$ and the constant concentration, i.e., C_j=constant, then Eq. (1) reduces to

$$\nabla^2\phi = 0 \qquad (2)$$

Eq. (2) means that the electrostatic potential is satisfied the Laplace equation.

Since the physical phenomenon of mass transport is described by the Nernst-Planck equation which can be applied to calculate ionic movements, it should be obeyed the principle of mass conservation. The equation of continuity primarily represents the principle of mass conservation. With this notion one can introduce the equation of continuity as follows.
The general continuity equation of compressible fluid in unsteady flow [1] is

$$\frac{\partial \rho}{\partial t}+\nabla \cdot \rho\ V_c =0 \qquad (3)$$

where ρ is the iron rust density, $Vc = u\vec{i} + v\vec{j} + w\vec{k}$ is the corrosion velocity vector, in which $\vec{i}$, $\vec{j}$, and $\vec{k}$ are the unit vectors in the x, y, and z-axes, respectively, and $\nabla = \vec{i}\frac{\partial}{\partial x}+\vec{j}\frac{\partial}{\partial y}+\vec{k}\frac{\partial}{\partial z}$ is the del (or nabala) operator.

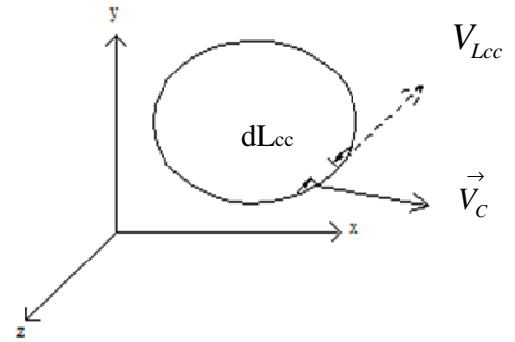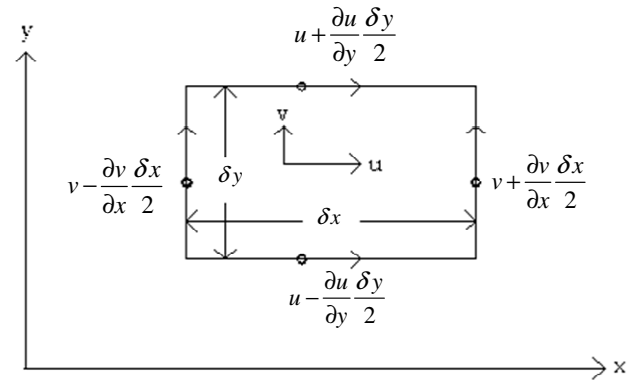Assume that iron rust is an incompressible fluid, i. e., $\nabla \times V_c = 0$,

Fig. 3. Line integral.
Fig. 4. Circulation of corrosion velocity around elementary rectangle.

and the iron rust is a homogeneous material i. e. , ρ =constant. Consider the steady flow, then Eq. (3) becomes

$$\nabla \cdot V_c = 0 \qquad (4)$$

Eq.(4) is the continuity equation for incompressible fluid and steady flow.

Consider the tangential component V_{Lcc} of a corrosion velocity vector V_c. The corrosion circulation, Γ, is taken the line integral of V_{Lcc} around a closed curve [7] (see Fig.3), i.e.,

$$\Gamma = \oint V_{Lcc}dL_{cc}$$
$$= \oint_{Lcc} (udx + vdy + wdz) \qquad (5)$$

where dx, dy and dz are, respectively, the projections of the element of curve L_{cc} in the x , y and z directions, and L_{cc} is the closed circuit of the border of a curved surface of arbitrary shape.

With the aid of Fig. 4, the corrosion circulation around an elementary rectangle with sides parallel to the axes x and y can be expressed in terms of

$$\delta \Gamma = (u-\frac{\partial u}{\partial y}\frac{\delta y}{2})\ \delta x+(v+\frac{\partial v}{\partial x}\frac{\delta x}{2})\delta y-(u+\frac{\partial u}{\partial y}\frac{\delta y}{2})\delta x-(v-\frac{\partial v}{\partial x}\frac{\delta x}{2})\delta y$$
$$= (\frac{\partial v}{\partial x}-\frac{\partial u}{\partial y})\delta x\delta y \qquad (6)$$

If Eq. (6) for the corrosion circulation is now divided by the area of the rectangle and the latter is allowed to approach zero as a limit, it will be clear that

$$\lim_{\delta x \delta y \to 0} \frac{\delta \Gamma}{\delta x \delta y} = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} = \zeta \qquad (7)$$

where ζ is the corrosion vorticity in the z direction.

Let $\delta s = \delta x \delta y$, where s is the surface. Then Eq. (7) becomes

$$\lim_{\delta s \to 0} \frac{\delta \Gamma}{\delta s} = \omega_n \qquad (8)$$

where ω_n is the corrosion vorticity. This means that the limiting value of the corrosion circulation per unit area about any curve must equal the component of the vorticity about an axis normal to the limiting plane of the corrosion circulation. A general mathematical theorem cooperated with the names of Green and Stokes supports the same relationship to a bounded surface as the theorem of Gauss used in conjunction with continuity principle supports to a bounded region of space, and is stated in terms of the same continuous and single-valued functions and their derivatives [7]:

$$\oint (\overline{P}dx + \overline{Q}dy + \overline{R}dz)$$
$$= \iint_s \left[(\frac{\partial \overline{R}}{\partial y} - \frac{\partial \overline{Q}}{\partial z})\frac{\partial x}{\partial n} + (\frac{\partial \overline{P}}{\partial z} - \frac{\partial \overline{R}}{\partial x})\frac{\partial y}{\partial n} + (\frac{\partial \overline{Q}}{\partial x} - \frac{\partial \overline{P}}{\partial y})\frac{\partial z}{\partial n} \right] ds \qquad (9)$$

Herein the term on the left of Eq. (9), when $\overline{P}$, $\overline{Q}$, and $\overline{R}$ are replaced by the corrosion velocity components u, v, and w, will be recalled from Eq. (5) to state with the corrosion circulation around the closed curve L_{cc}. The term on the right of Eq. (9), in turn, will be found to be the integral of the normal component of the corrosion vorticity over the surface bounded by the curve. In another way,

$$\Gamma = \iint_s \omega_n dS = \iint_s \left(\xi \frac{\partial x}{\partial n} + \eta \frac{\partial y}{\partial n} + \zeta \frac{\partial z}{\partial n} \right) dS \qquad (10)$$

where ξ, η, and ζ are the corrosion vorticity in the x, y, and z directions, respectively.

Suppose that the corrosion vorticity vector is

$$\vec{\omega} = \xi \vec{i} + \eta \vec{j} + \zeta \vec{k} \qquad (11)$$

The following counterpart of the continuity equation occurs:

$$\nabla \cdot \vec{\omega} = div \ \vec{\omega} = \frac{\partial \xi}{\partial x} + \frac{\partial \eta}{\partial y} + \frac{\partial \zeta}{\partial z} = 0 \qquad (12)$$

In the same fashion as a corrosion stream line is tangent to the corrosion velocity vector, a corrosion vortex line can be made visible as tangent to the corrosion vorticity vector at every point; the differential equation of such a corrosion vortex line can be written as
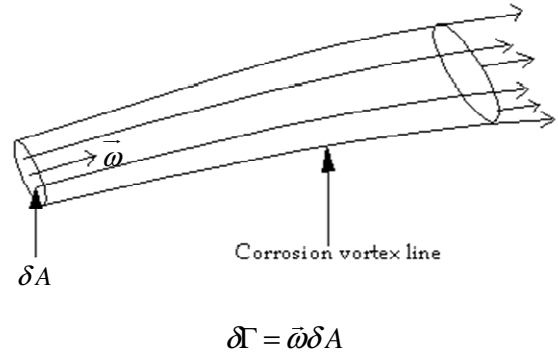

$$\delta \Gamma = \vec{\omega} \delta A$$

Fig. 5. Corrosion vortex tube.

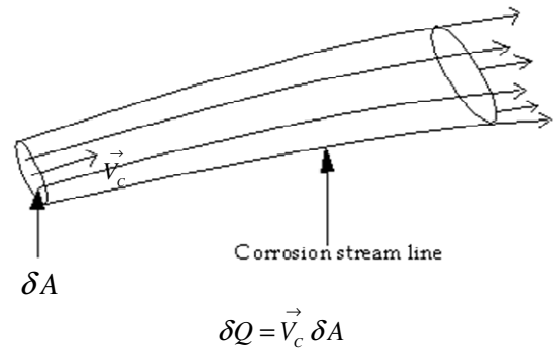$$\delta Q = \vec{V_c} \delta A$$

Fig. 6. Corrosion stream tube.

$$\frac{dx}{\xi} = \frac{dy}{\eta} = \frac{dz}{\zeta} \qquad (13)$$

A group of corrosion vortex lines may then be supposed to bound a corrosion vortex tube (see Fig. 5) just like corrosion stream lines bound a corrosion stream tube (see Fig. 6). From Figs. 5 and 6, we have , respectively,

$$\Gamma = \vec{\omega}A \qquad (14)$$

and

$$Q = \vec{V_c}A \qquad (15)$$

where Γ is the corrosion circulation, $\vec{\omega}$ is the corrosion vorticity vector, A is the cross-sectional area of corrosion vortex or stream tube, Q is the corrosion discharge, and $\vec{V_c}$ is the corrosion velocity vector.

Fig. 7 shows a corrosion tube growth mechanism. At the interface between the pit and the adjacent surface, iron hydroxide forms due to interaction between the OH^- produced by the cathodic reaction and the pit corrosion product. This is furthermore oxidized by the dissolved oxygen in the solution to $Fe(OH)_3$, Fe_3O_4, Fe_2O_3 and other oxides. This "rust" rim grows in the form of a tube as shown in Fig. 7.
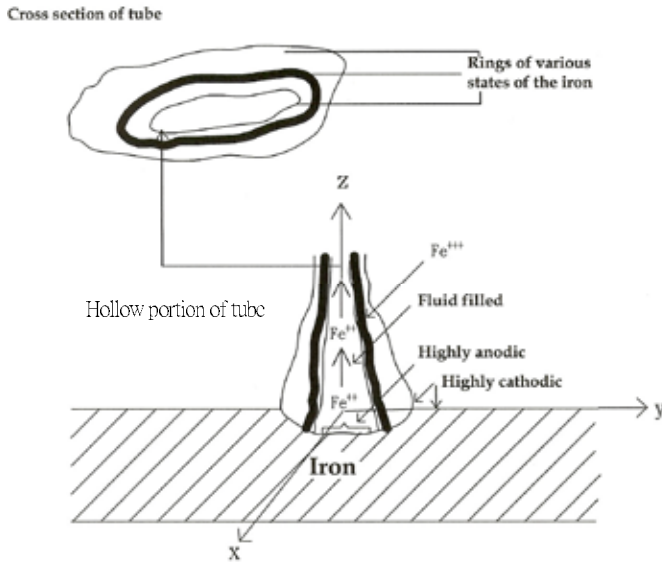
Fig. 7. Corrosion tube growth mechanism.

III. DISCUSSION

In the case of the electrochemical phenomenon of corrosion process of steel in aqueous media and oxygen, the electric potential, ϕ, is a scalar function. In addition, the existence condition of irrotational flow is $\bar{\omega} = \nabla \times V_c = 0$, i.e., $\Gamma = 0$. Then one may find a scalar function, ϕ, such that $V_C = \nabla \phi$. Consider a function $\Phi = \phi + i\psi$, where $\phi(x, y, z, t)$ is the potential function, $\psi(x, y, z, t)$ is the stream function, and $i = \sqrt{-1}$. If the corrosion flow is continuity, then both the ϕ and ψ are satisfied the Laplace equation, i.e., $\nabla^2 \phi = 0$ (see Eq. (2)) and $\nabla^2 \psi = 0$.

For steady flow, one may obtain the Bernoulli sum from the Navier-Stokes equation [1]

$$\frac{V_c^2}{2g} + z + \frac{P}{\gamma} = \text{constant} \tag{16}$$

where $\frac{V_c^2}{2g}$ is the kinetic energy head, z is the elevation (or potential energy head in gravitational fluid) and $\frac{P}{\gamma}$ is the pressure head, P is the gas (oxygen) pressure, in which g is the gravitational acceleration, $\gamma = \rho g$ is the unit weight of iron rust. It is worthy to point out that Eq. (16) is suitable for both the potential and stream functions in two- and three- dimensions. Moreover, the potential function is perpendicular to the stream function.

For convenience, consider two-dimensional flow as shown in Fig. 8. The ψ and ϕ in Fig. 8 represent the stream and potential functions, respectively. Let a_ψ and a_ϕ be the acceleration rates of corrosion in the directions of stream and potential functions, respectively. Then one has

$$a_\psi = \frac{dV_\psi}{dt} = \frac{\partial V_\psi}{\partial t} + \frac{\partial V_\psi}{\partial \psi}\frac{d\psi}{dt} = \frac{\partial V_\psi}{\partial t} + \frac{\partial(V_\psi^2/2)}{\partial \psi} \tag{17}$$

$$a_\phi = \frac{dV_\phi}{dt} = \frac{\partial V_\phi}{\partial t} + \frac{\partial V_\phi}{\partial \phi}\frac{d\phi}{dt} \tag{18}$$

Consider a small element of stream line as shown in Fig. 9. The P and ΔA denote that the pressure acts on the stream tube and ΔA is the cross-sectional area of stream tube, respectively. Using the equation of Newton's second law of motion, one obtains the equilibrium force

$$F_\psi = -\frac{\partial P}{\partial \psi} - \gamma \frac{\partial z}{\partial \psi} \tag{19}$$

Since acceleration $a_\psi = \dfrac{F_\psi}{\rho}$, one obtains from Eqs. (17) and (19)

$$\frac{\partial V_\psi}{\partial t} + \frac{\partial(V_\psi^2/2)}{\partial \psi} = -\frac{1}{\rho}\frac{\partial}{\partial \psi}(P + \gamma z) \tag{20}$$

Similarly, one obtains

$$\frac{\partial V_\phi}{\partial t} + V_\phi \frac{\partial V_\phi}{\partial \psi} = -\frac{1}{\rho}\frac{\partial}{\partial \phi}(P + \gamma z) \tag{21}$$

For irrotational flow, one knows

$$\bar{\omega} = \frac{\Gamma}{A} = \frac{\partial V_\psi}{\partial \phi} - \frac{\partial V_\phi}{\partial \psi} = 0 \tag{22}$$

From Eq. (18), it is very obvious that $\dfrac{\partial V_\psi}{\partial \phi} = \dfrac{\partial V_\phi}{\partial \psi}$. Thus, Eqs. (20) and (21) canbe rewritten as

$$\frac{\partial V_\psi}{\partial t} + \frac{1}{\rho}\frac{\partial}{\partial \psi}\left(\frac{\rho_{vc}^2}{2} + P + \gamma z\right) = 0 \tag{23}$$

$$\frac{\partial V_\phi}{\partial t} + \frac{1}{\rho}\frac{\partial}{\partial \phi}\left(\frac{\rho_{vc}^2}{2} + P + \gamma z\right) = 0 \tag{24}$$

For steady and irrotational flow from Eqs. (23) and (24), one has the Bernoulli sum as described in the following :

$$\frac{\rho_{vc}^2}{2} + P + \gamma z = \text{constant} \tag{25}$$

The physical meaning of Eq. (25) is that the Bernoulli sum at any cross-section of tubular corrosion product is constant. Furthermore, the accelerated rate of steel corrosion in the tubular growth (see Fig. 7) is occurred from the difference in oxygen concentration of cell (the anode being low in oxygen and the cathode being high in oxygen).
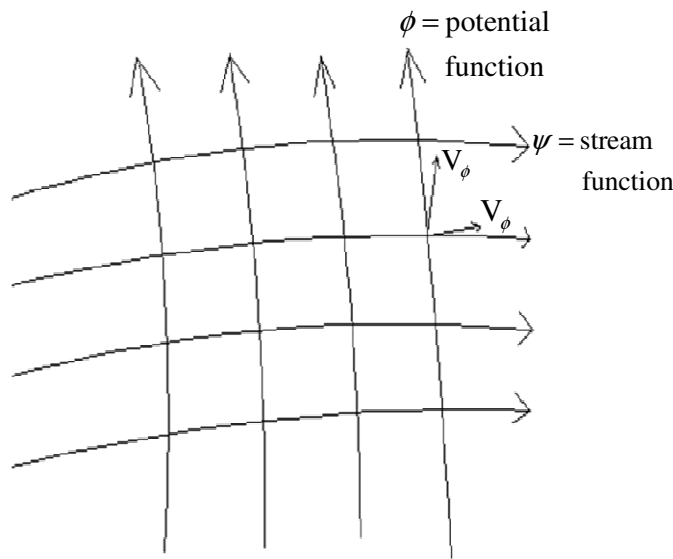
ϕ = potential function

ψ = stream function

Fig. 8. Potential function perpendicular to stream function (flow net).

$$\cos\theta = \frac{\partial z}{\partial \psi} = \frac{dz}{d\psi}$$
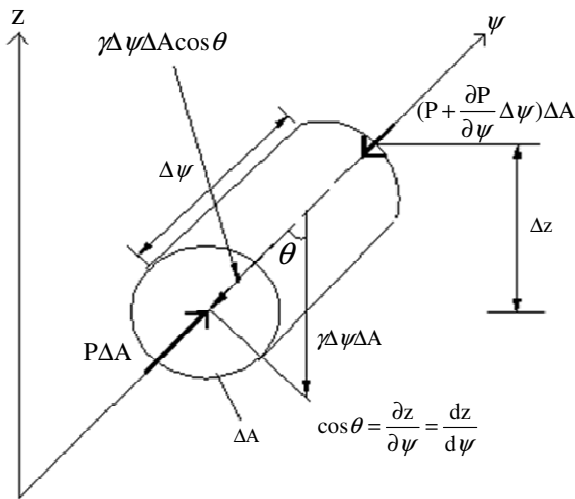
Fig. 9. Motion of Newton's second law.

IV. CONCLUSIONS

In this present work, the theoretical elucidation for the corrosion tubular growth mechanism of mild steel subjected to the effect of pH and oxygen corrosion at elevated pressures has been described. According to the Nernst-Planck equation, continuity equation, Green's theorem, Stokes's theorem and the equation of Newton's second law of motion, the mechanism of tubular growth development may be explored theoretically. The mechanism of the tubular corrosion product is a type of oxygen concentration cell. The tubular corrosion product is arised from the oxygen difference between the anode and the cathode area. The Bernoulli sum at any cross-section of the tubular corrosion product is constant.

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