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THE SOLUTION OF A CONVECTION–DIFFUSION–REACTION EQUATION ARISING FROM CATHODIC REDUCTION IN A PULSATING CRACK

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SUMMARY

This paper derives the convection–diffusion–reaction equation governing the reaction between the dissolved oxygen in sea-water and the steel walls of a pulsating crack. By the neglect of the diffusion term it is shown that an exact solution of the convection–reaction equation can be obtained. A numerical method for the solution of the complete convection–diffusion–reaction equation is derived by the use of finite differences. The numerical computation of the initial transient and the final periodic steady-state values is also discussed.

KEY WORDS Cathodic Reduction Convection–Diffusion–Reaction Characteristics Finite Differences

INTRODUCTION

One of the major problems affecting the structural integrity of offshore steel structures is corrosion fatigue which results from the interaction of corrosion and cyclic stressing. The rate of growth of corrosion fatigue cracks is strongly influenced by the solution composition in the crack. Experimental measurements of solution composition in the narrow cracks are awkward and consequently theoretical estimates have great potential value. An important factor in the corrosion process is the concentration of dissolved oxygen. Cathodic reduction within a corrosion fatigue crack leads to a depletion of oxygen in the crack resulting in a concentration gradient and mass transport by diffusion. An additional factor is the periodic variation in the displacement of the walls of the crack. As the crack opens the solution at a known concentration enters, and leaves again as the crack narrows. Thus convection is also a factor that must be considered. In summary the whole problem can be seen to be one involving reaction, diffusion and convection.[1,2,3,5]

THE GOVERNING EQUATIONS

We derive the governing equations from a consideration of the appropriate conservation laws. Let a scalar function, c, denote the concentration of the solute carried by the fluid flowing with velocity, $\mathbf{u}$. Applying the conservation law to the solute, contained in a control volume, V, enclosed by a control surface, S, we obtain

$$\frac{\mathrm{d}}{\mathrm{d}t}\int c\,\mathrm{d}V=-\int(\mathbf{J}\cdot\mathbf{n}+qc)\,\mathrm{d}S \tag{1}$$

where $\mathbf{n}$ is the outward unit normal to the control surface, $\mathbf{J}$ is the flux of the solute carried

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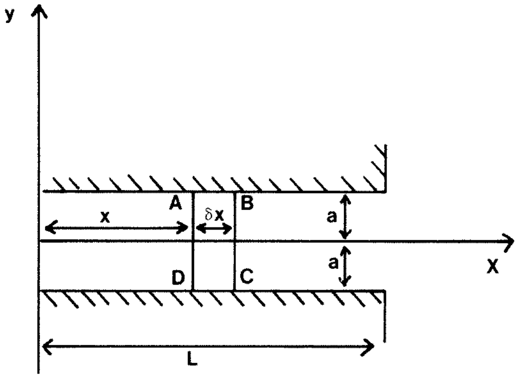

Figure 1. One-dimensional crack representation, length L, width $2a$ and unit depth

across the control surface by convection and diffusion and qc is the rate of removal of the solute by reaction at the control surface, q being constant. The flux, **J**, satisfies the equation

$$\mathbf{J} = c\mathbf{u} - D\nabla c \tag{2}$$

where D is the diffusion coefficient, assumed to be constant.

In this problem we assume that the crack can be represented by the diagram shown in Figure 1. As the crack width is significantly less than the crack length we assume further that the flows are one-dimensional and that edge effects can be ignored.

For the control volume, *ABCD*, of unit depth, shown in Figure 1, conservation of mass gives

$$\frac{\mathrm{d}}{\mathrm{d}t}\int \rho a \,\mathrm{d}x = -\int \frac{\partial u}{\partial x} \rho a \,\mathrm{d}x \tag{3}$$

where $u = u(x, t)$ is the fluid velocity, ρ is the fluid density and $a = a(t)$ is half the crack width. As the fluid is assumed to be incompressible this gives

$$u = -\frac{\dot{a}}{a} x \tag{4}$$

Conservation of the solute in the control volume gives

$$\frac{\mathrm{d}}{\mathrm{d}t}\int ca \,\mathrm{d}x = -\int \left(a\frac{\partial J}{\partial x} + qc\right) \mathrm{d}x \tag{5}$$

Here $c = c(x, t)$ is the concentration, $J = J(x, t)$ is the flux and qc is the rate of transfer of the solute to the walls of the crack by cathodic reduction. The equation for the flux is now

$$J = uc - D\frac{\partial c}{\partial x} \tag{6}$$

where D is the diffusion constant.

Equations (4), (5) and (6) lead to a convection–diffusion–reaction equation in the form

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} - u(x, t)\frac{\partial c}{\partial x} - \frac{q}{a(t)} c \tag{7}$$

This equation is to be solved along with the boundary conditions

$$\begin{aligned} c(L, t) &= c_0 \\ \frac{\partial c}{\partial x}(0, t) &= 0 \end{aligned} \tag{8}$$

and the initial condition

$$c(x, 0) = c_0, \qquad 0 \leqslant x \leqslant L \tag{9}$$

The boundary condition at $x = L$ refers to the mouth of the crack at which it is assumed that reservoir conditions hold. The boundary condition at $x = 0$ ensures that the flux along the x-axis is zero at this point, approximately true at a closed end.

It is convenient to put these equations into non-dimensional form with the change of variable

$$m = \frac{c}{c_0}, \qquad T = \frac{D}{L^2} t, \qquad X = \frac{x}{L} \tag{10}$$

In terms of these new variables equation (7) takes the form

$$\frac{\partial m}{\partial T} = \frac{\partial^2 m}{\partial X^2} - U(X, T) \frac{\partial m}{\partial X} - Q(T) m \tag{11}$$

with

$$U(X, T) = \frac{L}{D} u(x, t)$$

$$Q(T) = \frac{b}{a(t)}$$

and

$$b = \frac{L^2}{D} q$$

The corresponding boundary and initial conditions are now

$$\begin{aligned} m(1, T) &= 1 \\ \frac{\partial m}{\partial X}(0, T) &= 0 \\ m(X, 0) &= 1, \qquad 0 \leqslant X \leqslant 1 \end{aligned} \tag{12}$$

On the assumption that the crack width varies periodically, a convenient representation is to take

$$a(t) = a_m (1 - e \cos 2\pi f t) \tag{13}$$

where a_m, e and f are constants. In terms of the non-dimensional variables we have

$$a(T) = a_m (1 - e \cos 2\pi g T) \tag{14}$$

with $g = L^2 f / D$.

THE CHARACTERISTIC SOLUTION OF THE CONVECTION–REACTION EQUATION

In this section we derive a theoretical solution of equation (11) by ignoring the diffusion term. The neglect of the diffusion term may be justified on the grounds that, for typical parameters, the solution of the convection–reaction equation may be regarded as a first approximation to the solution of the convection–diffusion–reaction problem.

We take the convection–reaction equation in the form

$$\frac{\partial m}{\partial T}+U(X,T)\frac{\partial m}{\partial X}+Q(T)m=0 \tag{15}$$

with

$$U(X,T)=-\frac{\dot{a}(T)}{a(T)}X$$

$$Q(T)=\frac{b}{a(T)}$$

$$a(T)=a_m(1-e\cos 2\pi gT)$$

Equation (15) is a linear hyperbolic partial differential equation which must be supplemented by the appropriate Cauchy data. For this example the Cauchy data take the form

$$\begin{aligned} m(X,0)&=1, \qquad 0\leqslant X\leqslant 1\\ m(1,T)&=1, \qquad \frac{n}{g}<T<\frac{(n+\frac{1}{2})}{g} \end{aligned} \tag{16}$$

for $n=0,1,2,\ldots$.

It is possible to obtain an exact solution to this problem by using the method of characteristics. The characteristic path satisfies

$$a(T)\,\mathrm{d}X+\dot{a}(T)X\,\mathrm{d}T=0$$

which may be integrated to give

$$a(T)X=a(T_0)X_0 \tag{17}$$

with (X_0, T_0) the initial point of the characteristic path.

On this characteristic path the compatibility condition

$$a(T)\,\mathrm{d}m+bm\,\mathrm{d}T=0$$

must hold, which may be integrated to give

$$m=m_0\exp\left(-\frac{bF(T,T_0)}{2\pi g a_m}\right) \tag{18}$$

with

$$F(T,T_0)=\int_{2\pi gT_0}^{2\pi gT}\frac{\mathrm{d}v}{(1-e\cos v)}$$

The expression for $F(T, T_0)$ may also be integrated to give

$$F(T,T_0)=\frac{2}{(1-e^2)^{1/2}}\left\{\tan^{-1}\left[\left(\frac{1+e}{1-e}\right)^{1/2}\tan(\pi gT)\right]-\tan^{-1}\left[\left(\frac{1+e}{1-e}\right)^{1/2}\tan(\pi gT_0)\right]\right\} \tag{19}$$

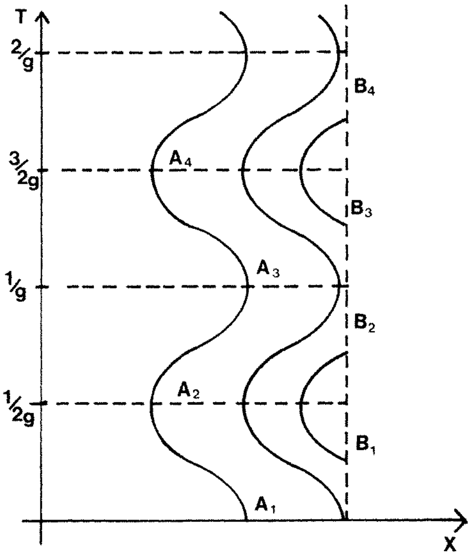

Figure 2. Characteristic paths in the (X, T) plane

There are two types of solution dependent upon the initial point (X_0, T_0) from which the characteristics originate. These two cases divide the (X, T) domain into two regions, illustrated in Figure 2. In region A, illustrated by the characteristic $A_1A_2A_3A_4$, the characteristics originate from the line $T=0$, $0 \leqslant X < 1$, and in region B, illustrated by the characteristics B_1B_2 and B_3B_4, they originate from the line $X=1$, $T>0$.

An integration of equation (2) also yields

$$a(T)X = a(T_0)X_0 \tag{20}$$

showing that the path traced out by a fluid particle is identical to the characteristic path along which the concentration of the solution decreases. This is, of course, only to be expected as the diffusion is zero and the solute is entrained in the fluid.

These two types of solution have fundamentally different properties. In the first type, fluid travelling along the $A_1A_2A_3A_4$ characteristic gives up its solute to the crack walls so that eventually the concentration falls to zero. The solution in region A is therefore in the nature of a transient which steadily decreases to zero. In the second type, the concentration initially has its maximum value, $M=1$, and decays along a characteristic path, such as B_1B_2 or B_3B_4, until the fluid leaves the crack. As the motion of the crack is periodic in nature, fluid will be periodically drawn in and expelled in this region. Further, as the flow is assumed to be one dimensional, the periodicity implies that there will only be the original fluid in the crack at the times $T=0, 1/g, 2/g, \ldots$.

It is also of interest to note that these two fundamentally different types of solution give rise to a discontinuity in the solute concentration across the characteristic separating region A from region B for all $T > 1/g$. This discontinuity, propagated along the characteristic, is an interesting illustration of the nature of the discontinuities that can occur in the solution of linear, as distinct from non-linear, hyperbolic partial differential equations.

A FINITE-DIFFERENCE SOLUTION OF THE CONVECTION–DIFFUSION–REACTION EQUATION

We consider here the solution of equation (11) subject to the conditions given in equations (12) and (14). The solution of this equation by finite differences is awkward because of the dominant nature of the convective term. A first attempt at the solution, with a standard central difference approximation to the convective term, had to be abandoned as the method produced negative values for the concentration which in no way corresponded to the reality of the physical situation.[1] One method of proceeding is to use a flux discretization scheme also described in Reference 1. The problem is overcome in this paper by using an upwind approximation to the convective term, with forward or backward differences dependent upon the direction of fluid flow.

The failure of the standard central difference approximation has been shown to result from the dominance of the convective term and has been discussed by Siemieniuch and Gladwell[4] for explicit finite difference schemes. An analysis of the implicit method of solution used here has produced similar results.

In our approximation of equation (11) a Crank–Nicolson type of method was used, the first step being to take the right-hand side as the mean of its values at the two time levels T and $T+\Delta T$

$$\begin{aligned}\frac{\partial m}{\partial T}=&\frac{1}{2}\left(\frac{\partial^2 m}{\partial X^2}-U(X,T)\frac{\partial m}{\partial X}-Q(T)m\right)_{T=(j+1)k}\\ &+\frac{1}{2}\left(\frac{\partial^2 m}{\partial X^2}-U(X,T)\frac{\partial m}{\partial X}-Q(T)m\right)_{T=jk}\end{aligned}\tag{21}$$

where $k=\Delta T$ and $j=0,1,2,\ldots$.

The time derivative is now approximated by a forward difference, the diffusion term by a central difference and the convective term by either a forward or backward difference depending upon the sign of $U(X,T)$.

For $U(X,T)<0$, the convective term is approximated by a forward difference and we have

$$A_{i,j+1}M_{i+1,j+1}+B_{i,j+1}M_{i,j+1}+C_{i,j+1}M_{i-1,j+1}=D_{i,j}\tag{22}$$

where

$$A_{i,j+1}=\frac{1}{2}\left(r-\frac{k}{h}U_{i,j+1}\right),\qquad C_{i,j+1}=-\tfrac{1}{2}r,$$

$$B_{i,j+1}=1+r-\frac{k}{2h}U_{i,j+1}+\frac{k}{2}Q_{j+1},$$

$$\begin{aligned}D_{i,j}=&\frac{1}{2}\left(r-\frac{k}{h}U_{i,j}\right)M_{i+1,j}+\frac{1}{2}rM_{i-1,j}\\ &+\left(1-r+\frac{k}{2h}U_{i,j}-\frac{k}{2}Q_j\right)M_{i,j}\end{aligned}$$

which holds for $i=0,1,\ldots,N-1$ with

$$M_{i,j}=M(ih,jk)=M(X,T),\qquad r=k/h^2$$
$$h=\Delta X\quad\text{and}\quad k=\Delta T.$$

From a consideration of the boundary conditions we can determine values for

$M_{-1,j+1}$, $M_{-1,j}$, $M_{N,j+1}$, $M_{N,j}$ and so obtain a tri-diagonal system of N equations which can be solved for the unknowns $M_{i,j+1}$, $i=0, 1, \ldots, N-1$.

For $U(X, T)>0$, the convective term is approximated by a backward difference and we now have

$$A_{i,j+1}M_{i+1,j+1}+B_{i,j+1}M_{i,j+1}+C_{i,j+1}M_{i-1,j+1}=D_{i,j} \tag{23}$$

with

$$A_{i,j+1}=-\tfrac{1}{2}r, \qquad C_{i,j+1}=-\frac{1}{2}\left(r+\frac{k}{h}U_{i,j+1}\right),$$

$$B_{i,j+1}=1+r+\frac{k}{2h}U_{i,j+1}+\frac{k}{2}Q_{j+1},$$

$$D_{i,j}=\frac{1}{2}rM_{i+1,j}+\frac{1}{2}\left(r+\frac{k}{h}U_{i,j}\right)M_{i-1,j}$$

$$+\left(1-r-\frac{k}{2h}U_{i,j}-\frac{k}{2}Q_j\right)M_{i,j}$$

holding for $i=0, 1, \ldots, N-1$.

Once again, by considering the boundary conditions, a tri-diagonal system of N equations for the unknowns $M_{i,j+1}$, $i=0, 1, \ldots, N-1$, can be obtained.

THE COMPUTATIONS

Numerical solutions were obtained for both the characteristic and finite difference methods of solution. Typical parameter values for the problem were taken as $L=1$ cm, $a_m=5{\cdot}25\,.\,10^{-3}$ cm, $e=0{\cdot}3$, $f=0{\cdot}1$ Hz, $D=1{\cdot}4\,.\,10^{-5}$ cm^2/sec and $q=1{\cdot}3\,.\,10^{-3}$ cm^2/sec. From these values the non-dimensional frequency of oscillation is obtained as $g\approx 7142{\cdot}9$.

Numerical solutions of the convection–diffusion–reaction equation, obtained with a mesh length $\Delta X=0{\cdot}05$ and a step length $\Delta T=0{\cdot}7\,.\,10^{-5}$, are shown in Figure 3. With this value

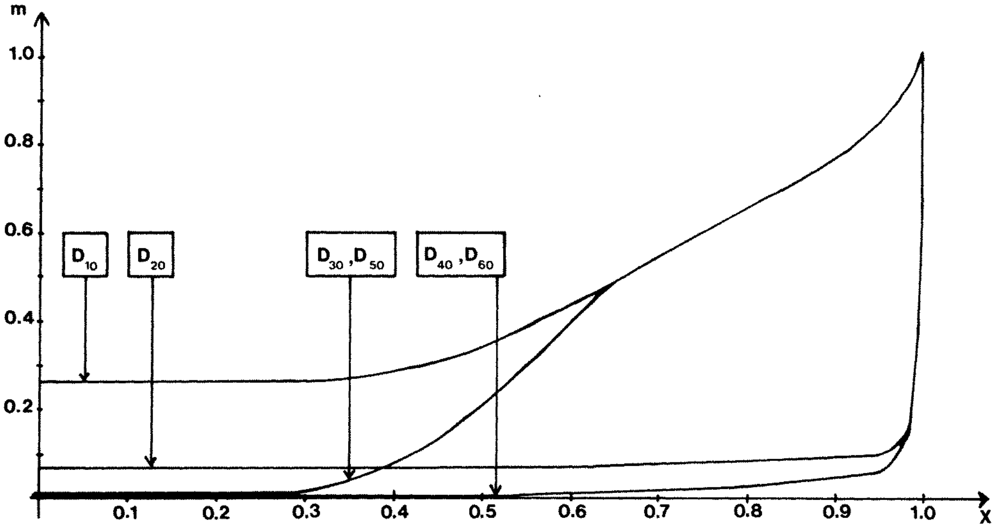

Figure 3. Numerical solutions of the convection–diffusion–reaction equation

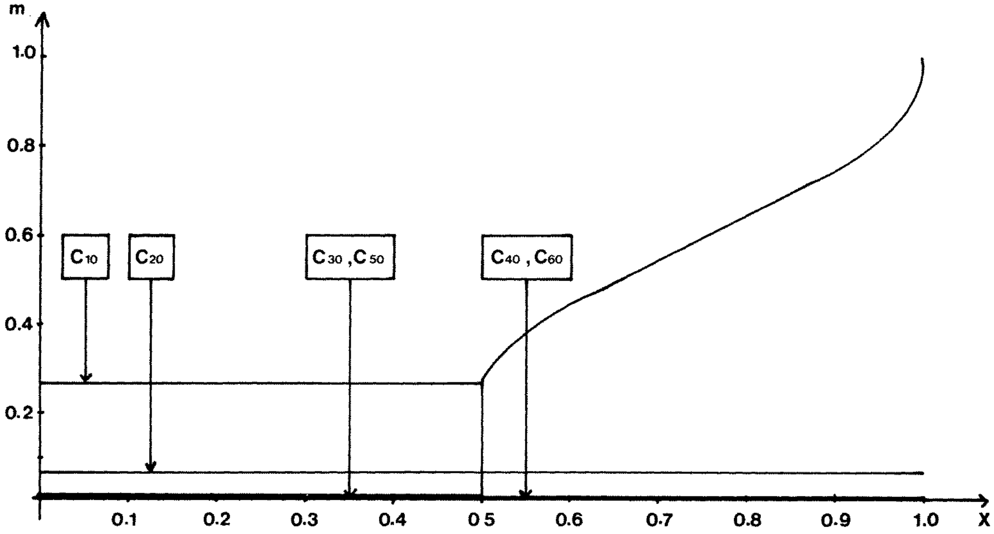

Figure 4. Numerical solution of the convection–reaction equation

for a time step there are 20 steps per cycle. The values of the concentration shown at $D_{10}, D_{20}, D_{30}, \ldots,$ are the values after $10, 20, 30, \ldots,$ time steps respectively. These computations show that the nature of the solution is similar to that of the convection–reaction equation in that both solutions have an initial transient which eventually decays to give a periodic steady-state solution. The accuracy of these computations was checked by reducing the mesh and step lengths, the results of which showed agreement, in general, to two places of decimals.

Numerical solutions for the convection–reaction equation, using the characteristic method of solution, are shown in Figure 4 using a compatible notation. The path of the discontinuity, obtained by setting $X_0 = 1$, $T_0 = 0$ in equation (17), is

$$X = \frac{1-e}{1-e\cos(2\pi gT)} \tag{24}$$

which, for the parameters used here, gives a maximum penetration of $X = 0{\cdot}5$.

Of great practical interest is the periodic steady-state solution after the initial transient has died away. In this problem the periodic steady-state is achieved to sufficient accuracy quite rapidly, after only 30 time steps, as shown by the computations in Figure 3. For a problem with different parameter values, however, the transient may take much longer to decay and will consequently require proportionately greater computing time. For the present problem it was found that time required to compute the periodic steady-state solution could be significantly reduced by the simple expedient of replacing the initial condition in equation (12) by

$$m(X, 0) = 0, \qquad 0 \leqslant X \leqslant 1 \tag{25}$$

This is of course the exact steady-state solution of the convection–reaction problem at the minimum crack width, and is consequently a first approximation to the steady-state solution of the convection–diffusion–reaction problem at the minimum crack width. Using this idea, with the parameters given here, our calculations showed that the periodic steady-state solution could be obtained after 10 time steps instead of the 30 time steps required with the original boundary conditions.

CONCLUSION

From an assumption of one-dimensional flow this paper has derived the convection–diffusion–reaction equation governing the reaction between the dissolved oxygen in sea-water and the steel walls of a pulsating crack.

By neglecting the diffusion term an exact solution, using the method of characteristics, has been obtained, and it has been shown that the solution space is divided into two regions separated by a discontinuity. In one of the regions the solution decays steadily to zero and in the other region the solution is of a periodic steady-state nature.

A numerical method for the solution of the complete convection–diffusion–reaction equation has also been obtained by the use of finite-difference approximations. Solutions have been computed for typical parameter values, which show that the steady-state solution is periodic in nature after the initial transient has decayed. An alternative initial condition has also been used which has enabled the periodic steady-state solution to be calculated more efficiently.

From the results in this paper it is possible to speculate on the mechanism of fracture for a steel structure vibrating in a salt-water solution. Once an initial crack has appeared, sea-water will enter and corrosion will commence. At the closed end of the crack there will be little corrosion because of the depletion in the dissolved oxygen. Further cyclic stressing will increase the length of the corrosion fatigue crack, more sea-water will be drawn in, and the corrosion process will continue. It would seem likely that these two mechanisms will operate in this sequential fashion until complete fracture occurs.

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