DIFFUSION KINETICS OF THE CORROSION PROCESS ON TUBE AND DISC ELECTRODES UNDER CONDITIONS OF HEAT TRANSFER IN VISCOUS SOLUTIONS

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It was shown in a previous article [1] that, for corrosive liquids similar to water as regards thermophysical properties, a diffusion-controlled corrosion process taking place in a circular tube might be modeled fairly accurately by one taking place on a rotating disc under the same conditions of heat transfer (or vice versa); for calculating the heat flow at a disc (even for large temperature drops), Keeble's equation may be used in the form

$$Q = 0.468 \cdot \pi a^2 \lambda \omega^{1/2} \cdot \nu^{-1/2} \mathrm{Pr}_{\mathrm{ther}}^{0.39} \cdot \Delta t b \mathrm{m}, \quad (1)$$

where a is the radius of the disc in m; λ the thermal conductivity of the medium in W/(m·deg); ω the angular velocity of the rotating disc in rad/sec; ν the kinematic viscosity in m^2/sec, $\mathrm{Pr}_{\mathrm{ther}}$ the thermal Prandtl criterion; and Δt the temperature difference in degrees.

The aim of the present investigation was to check the applicability of the proposed method of m modeling in the case of far more viscous liquids. For this purpose the corrosion of copper tubes and disc electrodes was checked in a solution with the previous concentration of acid and oxidizing agent (0.1 N HCl + 2 g/liter Fe^{3+}), but thickened by the addition of $CaCl_2$ (530 g/liter). The heat transfer from the copper disc to 98.5% and 50% glycerin and from a steel disc to 96% H_2SO_4 was determined.

Experimental Method

The experimental apparatus and disc samples used were described in earlier papers [1] and [3]. In order to prevent the corrosion of the nonworking surfaces, the carbon steel discs were chemically nickel-plated on the side of the heat carrier (distilled water), and the conical side surface of the discs was coated with polyfluorethylene resin 3M.

In the experiments on measuring the thermal flux we used distilled 98.5% glycerin of the "dynamite" type diluted where necessary with distilled water. The concentration was checked by reference to the density of the solution.

The 96% sulfuric acid was prepared from chemically pure sulfuric acid and chemically pure oleum (fuming sulfuric acid) containing 62% free SO_3.

The thermal flux was determined as before [1] from the slope of the heating or cooling curves for a known thermally-insulated volume of solution at the moment at which this reached the assigned temperature. The correction for thermal losses to the surrounding medium and mechanical heating of the liquid resulting from the rotation of the disc was determined by means of control experiments with the same rates of rotation, but without feeding heat carrier to the inner surface of the disc. The temperature of the solution in the experiments with sulfuric acid and the first experiments with glycerin was measured at a single point in the volume. In additional experiments with viscous glycerin solutions, the temperature was measured at three points in the volume when taking heating and cooling curves and the mean thermal flux determined from the three curves was used in the calculation. The conditions

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TABLE 1. Thermophysical Properties of the Liquids Used in the Experiments on Measuring the Thermal Flux from a Disc

Properties of the solutions	50% glycerin			98.5% glycerin			96% H_2SO_4	
	25°	47,5°	70°	15°	42,5°	70°	25°	60°
Dynamic viscosity, N·sec/m² ·10⁻³ (cP)	5,1 (5,1)	2.65 (2.65)	1.42 (1.42)	2030 (2330)	251 (337)	59 (59)	19.96—24.5 (19.96—24.5)	6.32—8.5 (6.32—8.5)
Specific heat, J/(kg·deg)·10³ (kcal/kg·deg)	3.4 (0.812)	3.36 (0.801)	3,31 (0.79)	2.32 (0.554)	2.44 (0.582)	2.46 (0.587)	1 34—1.5 (0.32—0.36)	1.5 (0.36)
Thermal conductivity, W/(m·deg) (kcal/m·g·deg)	0.424 (0.364)	0.437 (0.375)	0.455 (0.391)	0.288 (0.248)	0.293 (0.252)	0.297 (0.256)	0.27—0.33 (0.23—0.28)	0.34—0.42 (0.29—0.36)
Thermal Prandtl criterion	41	20.4	10.34	1.6410	1950	419	8.15—137	22.5—37.7

TABLE 2. Viscosity of the Solutions Employed

Medium	Dynamic viscosity, N·sec/m²·10⁻³(cP)			
	30°	40°	50°	60°
Water	0,8007 (0,8007)	0,656 (0,656)	0,5494 (0,5494)	0,4688 (0,4668)
0,1 HCl + 2 g/liter Fe^{+3}	0,856 (0,856) $d = 1,001$	0,703 (0,703) $d = 0,998$	0,656 (0,656) $d = 0,995$	—
0,1 HCl + 2 g/liter Fe^{+3} + 530 g/liter $CaCl_2$	5,59 (5,59) $d = 1,375$	4,13 (4,13) $d = 1,366$	3,34 (3,34) $d = 1,36$	2,74 (2,74) $d = 1,358$
96%-H_2SO_4	19,1 * (19,1)	11,58 † (11,58)	8,62 (8,62)	6,59 (6,59)

* At 25°C.

† At 41°C.

d Density of the solution at the given temperature.

of the thermal-flux experiments may be seen from the corresponding figures; the properties of the solutions under these conditions, taken from handbook data [4-9], are presented in Table 1.

The corrosion of the heat-transfering discs and tubes was determined in the manner described in [1]. The solution for studying the corrosion of copper samples was prepared from crystalline calcium chloride of chemically pure grade. After determining the calcium concentration trilonometrically, a calculated amount of chemically pure hydrochloric acid and ferric chloride was added to the solution. The concentration of the $FeCl_3$ was also determined trilonometrically.

The conditions for carrying out the corrosion tests on the tubular and disc samples with and without cooling are shown on the corresponding graphs. Table 2 presents the viscosities of the aggressive solutions used, as determined on an Ostwald viscometer, with the viscosity of water for comparison. The corrosion rate was in all cases determined gravimetrically.

Results and Discussion

1. Thermal Flux through the Surface of a Rotating Disc. In view of the great differences in handbook for the thermophysical properties of sulfuric acid (Table 1), Fig. 1 gives the values of thermal flux directly calculated from equation (1) by using the extreme values of ν, λ etc. The experimental points lie within the range of the calculated thermal fluxes. With the heated discs, the thermal flux is somewhat greater than with the cooled discs. The effect of the direction of the thermal flux on its

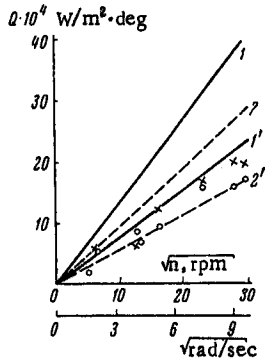

Fig. 1

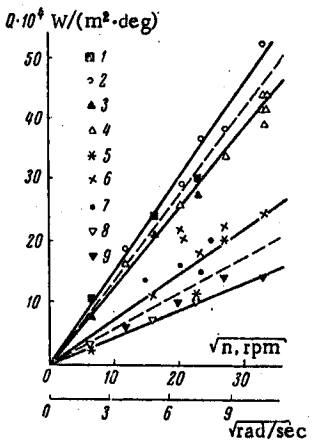

Fig. 2

Fig. 1. Thermal flux from St. 20 discs to 96% sulfuric acid as a function of the rotation rate: 0 signifies acid temperature 60°, disc temperature 25°, + signifies acid temperature 25°, disc temperature 60°; 1, 1') thermal flux calculated from Eq. (1) on substituting the parameters of the liquid corresponding to 60°; 2, 2') the same for 25°.

Fig. 2. Thermal flux from copper discs to 50 and 98.5% glycerin as a function of rotation rate; 50% glycerin: 1) disc at 70 and glycerin at 25°; 2) the same, temperature measured at three points; 3) disc at 25 and glycerin at 70°; 4) the same, temperature measured at three points; 5) disc at 70 and glycerin at 25°; 6) the same, temperature measured at three points; 7) the same, temperature measured at three points with a smaller volume of liquid; 8) disc at 15 and glycerin at 70°; 9) the same, temperature measured at three points.

magnitude is nothing new. For a turbulent flow of water in the tubes, the thermal flux on heating is about 20% greater than on cooling, and for transitional and laminar flow the difference is still greater, owing to the difference in the thermal fields and the consequent changes in the physical properties of the liquid in the boundary layer [10]. In the equations of heat transfer to the tube wall relating to the motion of various liquids, the effect of the direction of the thermal flux is taken into account by special correcting factors [10, 11], which depend on the conditions of motion, the properties of the liquid, the temperature head, the position of the channel in space, and so on.

Viscosity is the most sensitive of all the properties of the liquid to temperature (Table 1), and for very viscous liquids we may expect that the direction of the thermal flux will have a considerable influence on the heat transfer of the disc. As a particularly viscous liquid we chose glycerin, the thermophysical properties of which have been thoroughly studied. The results of the measurements are presented in Fig. 2. The broken straight line in each case corresponds to the thermal flux calculated by Eq. (1), using a temperature half-way between that of the wall and the liquid. The experimental points for heating lie above this straight line and those for cooling below it. The continuous lines give the calculated relationship between the thermal flux and the angular velocity of the discs, using the disc temperature as the determining value in the equation. For the heat transfer to 50% glycerin the experimental points lie on these straight lines to within 2 to 19%. In experiments with 98% glycerin the spread is greater: 2 to 18% for cooling and 3 to 50% for heating. This is associated, however, especially in the latter case, to the fact that the rotating disc did not agitate the viscous solution enough. The temperature varies in a different manner with time in different parts of the volume, as indicated by the difference in the slopes of the local cooling and heating curves for the three points of temperature measurement. In some experiments we took a volume of glycerin about 30% smaller than in the rest, and this slight change in conditions (the temperature change in the volume being uniform) proved sufficient to reduce the spread in the experimental points to a level of 1.8 to 30%.

The results indicate that, when using the theoretical equation (1), the effect of the direction of heat flow on the heat transfer from the disc to the viscous liquid is automatically taken into account (with a reasonable accuracy) if the determining temperature is taken as that of the wall. Hence, even for viscous liquids (with substantial temperature heads), the rate of flow in the tube and the angular velocity of the disc equivalent to one another in respect of heat transfer may be determined by identifying Eq. (1) with the equation of heat transfer between a liquid and a tube given in [11].

2. Corrosion of Disc and Tubular Samples under Isothermal Conditions. Under isothermal conditions, the corrosion of copper discs and tubes in an acid solution of ferric chloride with added calcium chloride (Fig. 3) is expressed at 30° by the equations

$$K_d = 2.8 + 3.41\ n^{0.5} \tag{2}$$

$$K_t = 33 + 23\ v, \tag{3}$$

where K_d and K_t are the corrosion rates of the disc and tube in g/m²·h, v is the rate of flow in m/sec, and n is the rate of rotation of the disc in rpm; at 60° the expressions are

$$K_d = 4.3 + 5.9\ n^{0.5}, \tag{4}$$

$$K_t = 36 + 62.4\ v. \tag{5}$$

The equations linking the linear flow rate (tube) and angular velocity (disc) equivalent from the corrosion point of view may be obtained by comparing Eqs. (2) and (3) and also (4) and (5). Introducing the values of $\sqrt{\nu}$ for 30 and 60° into these equations, we have finally

$$v = \Delta c + 0.73\sqrt{\nu n} \tag{6}$$

for 30° and

$$v = \Delta c' + 0.66\sqrt{\nu n} \tag{7}$$

for 60°.

In order to find the theoretical equivalence relationships for the same conditions in accordance with [12], we must know the diffusion coefficient of the agent which, by its presence on the surface of the metal, determines the rate of the corrosion process (in the present case the Fe^{3+} ion). For this purpose we measured the limiting cathode current to a platinum rotating-disc electrode in the solution

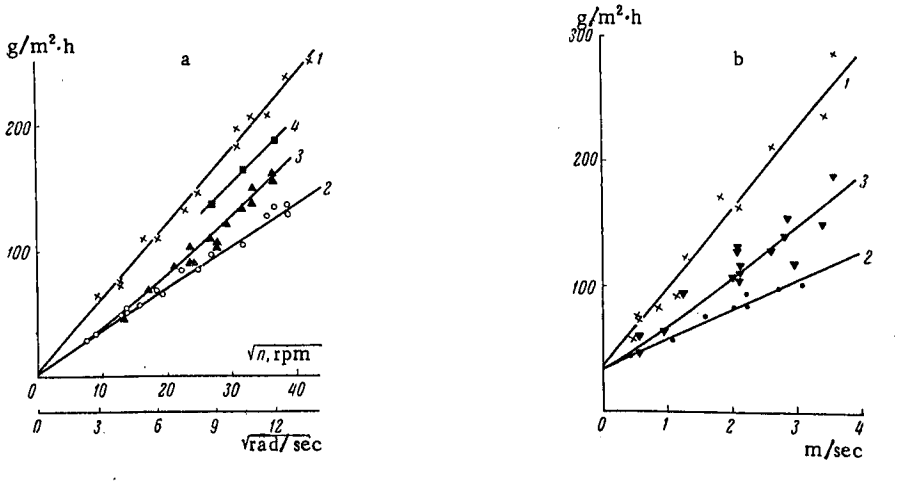

Fig. 3. Corrosion of copper discs in a solution of 0.1 N HCl + 2 g/liter Fe^{3+} + 530 g/liter $CaCl_2$ as a function of the rate of rotation (a), and the corrosion of copper tubes in the same solution as a function of flow rate (b). 1) Temperature of solution and metal 60°; 2) temperature of solution and metal 30°; 3) temperature of solution 60°, temperature of metal 30°; 4) temperature of solution and metal 50°.

in question at 30 and 60°C [16]. The diffusion coefficients calculated from the Levich equation [13] were $1.34 \cdot 10^{-10}$ m²/sec for 30° and $2.55 \cdot 10^{-10}$ m²/sec for 60°. Finally the theoretical equivalence equations of v and n for 30 and 60° respectively take the form

$$v = 0.63\sqrt{vn}, \tag{8}$$

$$v = 0.56\sqrt{vn}. \tag{9}$$

The empirical Eqs. (6) and (7) differ from the theoretical Eqs. (8) and (9) in respect to the free terms Δc and $\Delta c'$ which are independent of the motion of the medium. The appearance of these is associated with the existence of the corresponding terms in Eq. (2) to (5), and (as already noted [14]) is explained by the fact that, owing to natural convection, the corrosion process takes place even in the absence of forced circulation. Equations (8) and (9), however, only consider forced circulation and therefore have no free terms. In addition to this, the appearance of the free term may be associated with subsidiary corrosion processes taking place at the surface of the disc or tube, the rate of such processes being independent of the motion of the liquid [15]. Taking this into account and comparing the empirical and theoretical formulas without considering the free terms, we may conclude that data relating to the corrosion of rotating discs enable us to calculate the internal corrosion of a tubular conduit theoretically for various rates of flow of a viscous medium to an accuracy no worse than 15%.

3. Corrosion of Heat-Transferring Disc and Tubular Samples. This may be expressed (Fig. 3) by curves lying between the 30 and 60° isotherms, respectively described by the equations:

$$K_d = 2.8 + 2.63\ n^{0.57}, \tag{10}$$

$$K_t = 33 + 33.1\ v^{1.11} \tag{11}$$

If we compare the right-hand sides of these equations and disregard the free terms (the causes of which are no doubt the same as in the case of thermal-equilibrium conditions), we obtain the following equivalence relation for the v and n of heat-transferring samples:

$$v = 0.51\sqrt{vn}. \tag{12}$$

It was noted in [1] that the equivalence relation remained practically the same under heat-transfer conditions as under conditions of thermal equilibrium. The extent to which this is still true in the present case may be judged from Table 3. The second column gives the corrosion rates of heat-transferring discs for four arbitrarily-chosen angular velocities according to Eq. (10), and the fourth column gives the experimental values of corrosion rate for heat-transferring tubular samples in the case of flow rates which, according to the theoretical equation (8), are equivalent to the disc angular velocities chosen. The difference between the corresponding values is no greater than 18.5%.

The results confirm the possibility of quantitatively modeling a diffusion-controlled corrosion process in a tubular conduit with a heat-transferring wall by means of rotating heat-transferring discs in aggressive media with very varying viscosities.

CONCLUSIONS

1. We have shown that the Keeble equation is applicable for calculating the thermal flux from a rotating disc to a viscous liquid under conditions involving a large temperature drop.

TABLE 3. Comparison of Calculated and Experimental Corrosion Rates of Heat-Transferring Samples

Angular velocity of disc, rpm	Corrosion rate according to (10), K_1, g/m²·h	Equivalent velocity of flow from (8), m/sec	Experimental corrosion rate, K_2, g/m²·h	$\frac{K_2 - K_1}{K_2}$, %
100	36.3	1.27	43	18.5
400	80.4	2.54	93	16.7
900	126.9	3.81	145	14.3
1250	153	4.48	174	13.7

2. We have shown that it is possible to model the corrosion of the inner walls of a tube passing a turbulent flow of viscous solution by means of rotating discs in a region of laminar flow, both in the presence and absence of a thermal flux (heat flow) through the wall.

3. In order to find the rate of rotation of the heat-transferring disc equivalent (as regards corrosion) to a given linear flow velocity in a heat-transferring tube, we may, to a fair accuracy, use the equivalence equation corresponding to isothermal conditions.

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