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THE USE OF A CORROSION PROCESS TO OBTAIN MASS TRANSFER DATA

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Abstract—A new technique for measuring mass transfer coefficients has been developed and tested. The method involves corroding copper specimens in dilute hydrochloric acid containing ferric ions. In this system the corrosion rate is controlled by the arrival of ferric ions at the copper surface where they are reduced to ferrous ions, the anodic reaction being the dissolution of copper in a monovalent state as a chloride complex. This system has been tested with a number of specimens including some having a varying mass transfer profile. In all cases the data generated were close to that predicted from the available mass transfer correlations.

INTRODUCTION

IN SITUATIONS where a reaction is controlled by diffusion its rate is related to the concentration driving force (ΔC) and the mass transfer coefficient (K) as shown in Table 1. Relationships between K and other hydrodynamic parameters are expressed in terms of non-dimensional groups as outlined in Table 1. It is important to know both the overall and local values of the mass transfer coefficients. These can be obtained in a number of ways. For relatively simple geometries, such as the rotating disc, theoretical solutions¹ have been available for some time; indeed these preceded experimental confirmation. More recently² analytical solutions have been obtained for more complicated geometries. Mass transfer coefficients are usually determined

TABLE 1. RELATIONSHIPS BETWEEN HYDRODYNAMIC PARAMETERS

Rate = $(D + \epsilon) \frac{dC}{dz}$	Sherwood No. = $Sh = \frac{Kd}{D}$
= $K\Delta C$	Reynolds No. = $Re = \frac{Vd}{\nu}$
	Schmidt No. = $Sc = \nu/D$
$Sh = f(Re Sc)$	Usually $Sh = a Re^x Sc^y$
$K = \frac{D}{d} a Re^x Sc^y$	Rate = $\frac{D}{d} a Re^x Sc^y \Delta C$

d is the tube diameter, K is the mass transfer coefficient, D is the diffusivity of the relevant species, V is the velocity, ν is the kinematic viscosity, ϵ is the turbulent eddy diffusivity, ΔC is the concentration driving force between the surface and the bulk, y is usually 1/3 and x varies between 0.5 and 1 for most geometries, dC/dZ is the concentration gradient.

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U.S. NUCLEAR REGULATORY COMMISSION

In the Matter of Entergy Nuclear Vermont Yankee LLC

Docket No. SD-271 Official Exhibit No. E4-23-VY

OFFERED by: Applicant/Licensee Intervenor _____
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Action Taken: ADMITTED REJECTED ~~WITHDRAWN~~

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experimentally. A large number of techniques have been used but the most widely used are: the dissolving wall method, the limiting current density technique (LCDT) and the analogy with heat transfer.

In the dissolving wall method, a specimen is made of or coated with a material that is sparingly soluble in the test environment. Typical material-environmental combinations which have been used include: transcinamic acid and water,³ benzoic acid in glycerine/water mixtures,⁴ and plaster of Paris in water.⁵ With this technique the surface roughens with time and it is difficult to determine initial smooth values. With solid models it is difficult to reproduce the complex geometries of, for example, tight bends in tubes where both changes in wall thickness and ovality occur. Using coated specimens, ensuring and measuring uniform coating thickness, and making subsequent accurate thickness loss measurements presents problems. Furthermore, with the dissolving wall technique it is possible to induce pure erosion which might be synergistic with the dissolution process.⁶ It is thus essential that the occurrence of any erosion is checked for by using a saturated test solution, with a roughened surface.

With the limiting current density electrochemical technique (LCDT),^{7,8} a single electrochemical reaction is driven at such a potential that its rate becomes diffusion controlled. Either the overall or local mass transfer coefficients can then be calculated from the overall or local limiting current density. The most common reactions are the reduction of the ferricyanide ion⁹ or the deposition of copper.¹⁰ This technique is well suited to a large number of situations, but it does have its drawbacks. Thus the location of a large number of local cathodes, in the bulk cathode, and the suitable positioning of the anode to ensure uniform current distribution, and undisturbed flow present difficulties. Indeed it does appear that certain detailed features have been missed by this technique.¹¹ Furthermore the LCDT has to date been limited to cathodic reactions, so the way mass transfer changes with increasing surface roughness has not been examined for a dissolving surface, although preliminary results for a Cu cylinder dissolving at its LCD have been presented by Gabe.¹²

Mass transfer coefficients can also be obtained from heat transfer data using the analogy between heat and mass transfer,¹³ but these measurements have similar drawbacks to their mass transfer counterparts. Furthermore, the Prandtl number is usually much lower, up to 10, than the Schmidt number counterparts in mass transfer where values are typically 100-3000.

In a number of instances the corrosion rate of metals is controlled solely by diffusion,¹⁴ either of the cathodic reactant to the surface, or of the soluble anodic product away from the surface. An example of the former would be the dissolution of iron, copper or nickel in hydrochloric acid containing ferric ions: the cathodic reaction, the reduction of ferric ions to ferrous ions, is rate controlling.^{15,16} Mild steel corroding in concentrated sulphuric acid is a case¹⁷ where the corrosion rate is governed by the diffusion of the anodic product, soluble ferrous sulphate, away from the surface. Various workers¹⁸ have shown that in such situations the corrosion rate can be predicted from simple mass transfer considerations; or that data from rotating discs or cylinders can be used to predict the corrosion rates in tubes.¹⁹⁻²¹ Ellison and Schmeal²² appeared to have confirmed this approach in a study of carbon steel dissolving in concentrated sulphuric acid. They used both rotating cylinders and flow in tubes, measuring corrosion both electrochemically and by weight loss. Mass transfer predictions were based on known or measured values of the solubility of ferrous sulphate, the diffusivity of ferrous ions and the kinematic viscosity of sulphuric acid. The agreement between measured and predicted values was good.

There are a number of pieces of evidence that such a simple approach does not always work, especially for geometries where the mass transfer is non-uniform, possibly leading to effects based on separation of anodic and cathodic areas. For example La Que²³ showed that the response of rotating iron and copper alloy discs in sea water was radically different. In the case of iron discs the outer region tended to remain unattacked while the centre corroded (differential aeration); with the copper alloy the centre remained relatively unattacked with the outer regions being attacked, due to increased mass transfer and/or turbulence there.

Bignold *et al.*²⁴ examined the erosion-corrosion rate of carbon steel in pure water between 100 and 180°C using an orifice geometry. It was found that the erosion-corrosion rate varied in proportion to the mass transfer coefficient raised to a power which varied between 1 and 3, depending on the pH and temperature.

This paper describes corrosion tests carried out to examine the feasibility of using a corrosion process to determine overall and local mass transfer coefficients, especially on geometries where this is non-uniform.

EXPERIMENTAL METHOD

Analysis and forms of the experimental materials are given in Table 2. All solutions were made from reagent grade chemicals and de-ionized water. Testing was performed in a polyvinylidene fluoride (PVDF) flow loop.¹¹ 17.5 l of the test solution was premixed in the 20 l glass-reinforced PVDF tank and brought to the right conditions in the bypass circuit. The solution was then circulated through the test specimen using a PVDF centrifugal pump with a Hastalloy C shaft. The exposure times were chosen to ensure that the concentration of the ferric ion remained approximately constant and that an equal amount of dissolution occurred under each flow condition. Average ferric concentrations during the test were calculated from the initial values and the metal loss data. The flow rates were measured using calibrated rotameters, and the temperature was controlled to $\pm 0.25^\circ\text{C}$.

Hydrodynamic entry lengths of either 36 or 52 tube diameters preceded these orifice type specimens (Fig. 5). No significant difference between these two conditions could be found. These entry lengths are much greater than those recommended by Ross²⁵ and the longer length is only slightly less than the 56 tube diameters recommended in BS 1042,²⁶ for flow measuring orifices. The impinging jet electrode test cell included both large, small and multihole jets.

A number of different measuring techniques were used to monitor specimen dimensional changes, including the following.

(a) Digital bore measuring equipment (Dia-test) utilizing a curved measuring head and cone to convert radial to longitudinal motion which is measured by a linear transducer. Resolution is $1\ \mu\text{m}$ on a smooth surface but repeatability on a rough surface is limited by the precision to which the head can be positioned down the tube ($\pm 0.25\ \text{mm}$).

(b) Digital micrometer (Moore and Wright) resolution $1\ \mu\text{m}$.

(c) Metallographic examination using both optical and scanning electron microscopy for local dimensional changes and surface morphology.

(d) Weight loss.

The value of the diffusion coefficient of ferric ion in 0.1 N HCl at 50°C was estimated to be $1.2 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}$. This is the lower range of values measured by Case²⁷ for ferrous ion diffusion in 0.1 N HCl, which surprisingly, the evidence³⁸ suggests is similar to ferric ion diffusion: it is higher than the value extrapolated from Russian work¹⁹ using Wilkes rule. (Diffusion coefficient \times dynamic viscosity/absolute temperature is a constant which gives $0.85 \times 10^{-5}\ \text{cm}^2\ \text{s}^{-1}$). The kinematic viscosity of 0.1 N HCl containing $2\ \text{g}\ \text{l}^{-1}$ ferric ion added as FeCl_3 was on the basis of available evidence taken to be $0.005534\ \text{cm}^2\ \text{s}^{-1}$ at 50°C, i.e. that of water.

TABLE 2. ANALYSIS OF EXPERIMENTAL MATERIALS (wt %)

	C	Si	Mn	P	S
Carbon steel: 1" o.d. $\frac{1}{2}$ " i.d. tube	0.11	0.17	0.53	0.01	0.02
Copper: 1" o.d. $\frac{1}{2}$ " i.d. tube	Cu	Fe			
	99.9	0.1			

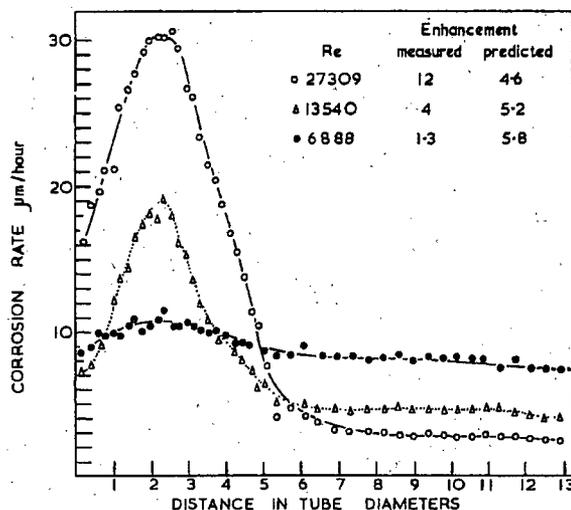


FIG. 1. Corrosion rate profiles of carbon steel specimens downstream of an orifice tested in oxygenated 0.1 N HCl + 1 M NaCl at 50°C.

EXPERIMENTAL RESULTS

Initial tests using the orifice geometry

A number of tests were carried out on steel specimens corroding in either oxygenated acidified 1 M NaCl or 0.1 N HCl containing 2 g l^{-1} ferric ion both at 50°C since previous work had suggested diffusion control in these systems. An orifice

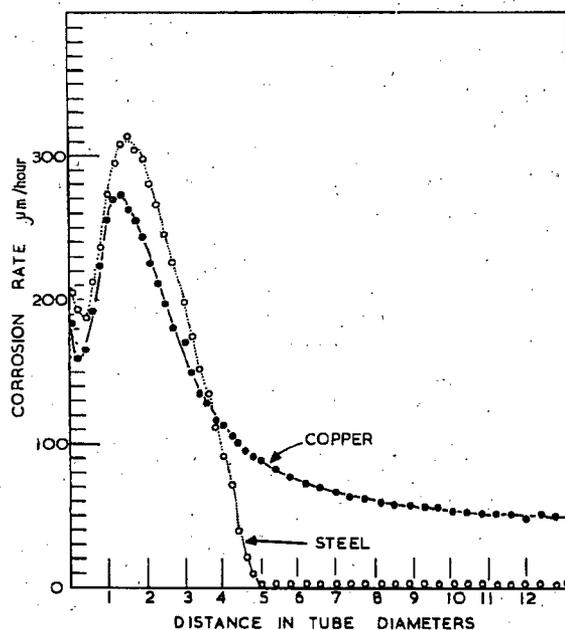


FIG. 2. Corrosion rate profiles downstream of an orifice after testing in 0.1 N HCl initially containing $2 \text{ g l}^{-1} \text{ Fe}^{3+}$ at Re of 27 309 and d/d_o of 2.67, not corrected for different average C_s .

FIG. 4. Corrosio

geometry was used non-uniform.

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Initial test results are shown in Fig. 2. The predicted enhancement stream of the peak by copper seems entire actual rates in accordance dissolution of the smoother and more evidence of the draw

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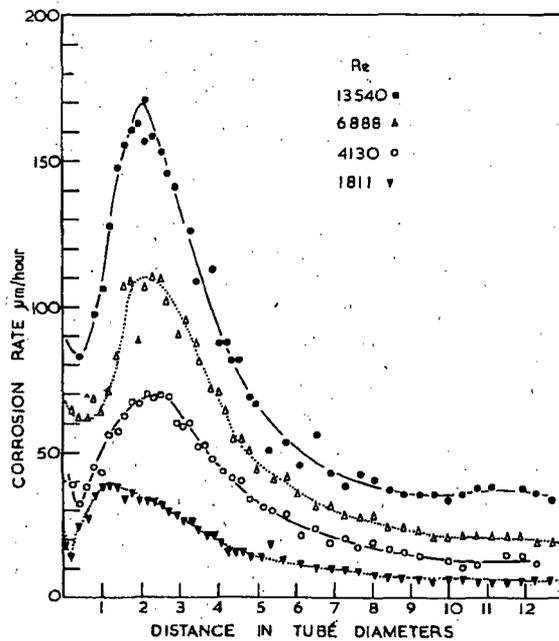


Fig. 4. Corrosion rate profile downstream of an orifice, copper specimens tested in acid ferric chloride solution at 50°C.

geometry was used because its mass transfer characteristics are well defined and non-uniform.

Results for the oxygenated acidified NaCl solution are shown in Fig. 1. The profiles are interesting in that the peak rates downstream of the orifice appear to be controlled by diffusion since the peak rates increase as the Reynolds number is raised to the power of 0.7 or 0.8. Further downstream the rates of dissolution decrease with increasing flow rate, and this was an unexpected result. This causes the enhancement (i.e. the ratio of peak loss rate to the downstream asymptotic rate) to increase with increasing velocity which is exactly the opposite of mass transfer predictions.¹¹ It must be concluded that this metal environment combination is unsuitable for producing mass transfer data.

Initial test results for both copper and steel specimens in the acid FeCl_3 solution are shown in Fig. 2. Again it is clear that iron is not suitable, since a much higher than predicted enhancement factor is produced, apparently by iron dissolution downstream of the peak being inhibited in some way. However, as shown in the discussion, copper seems entirely suitable since it produces an enhancement factor, profile and actual rates in accord with mass transfer predictions. The morphology of the dissolution of the two metals was notably different (Fig. 3) with copper being smoother and more crystallographic than the steel which was rougher, with some evidence of the drawing process influencing the attack.

The effect of flow velocity on corrosion downstream of an orifice

The effect of flow velocity ($0.035\text{--}1.18\text{ m s}^{-1}$) on corrosion downstream of an orifice was examined. Typical corrosion rate profiles are shown in Fig. 4. Clearly the corrosion rate reaches a peak at about two tube diameters downstream of the orifice then slowly decays to what is probably close to the fully developed turbulent flow by

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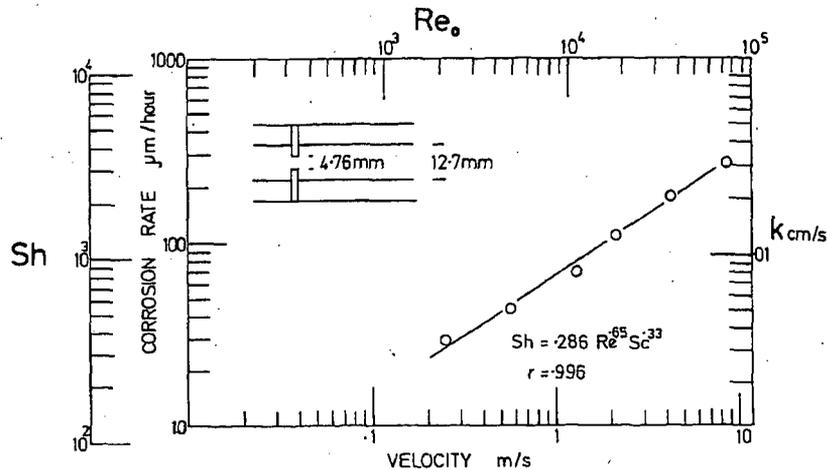


FIG. 5. Correlation of peak corrosion rate following an orifice and orifice Reynolds number, for copper specimens tested in acid ferric chloride solution at 50°C.

the end of the specimen. In general the specimen did not develop pronounced roughening although scallops (shallow smooth craters) did develop on some specimens tested at the higher Reynolds numbers after prolonged exposure especially in the region of highest mass transfer.

It was assumed that the corrosion rate was equal to the limiting current density for ferric ion reduction and, substituting in Faraday's law, the rate of ferric ion reduction is given by:

$$\text{rate of Fe}^{3+} \text{ reduction} = \text{rate of Cu corrosion} \times \text{Cu density} \times \frac{\text{at. wt of Fe}}{\text{at. wt of Cu}}$$

The mass transfer coefficient could then be obtained as well as the Sherwood number. Figures 5 and 6 show the measured and derived quantities and their variation with velocity for both peak and fully developed flow. The correlation

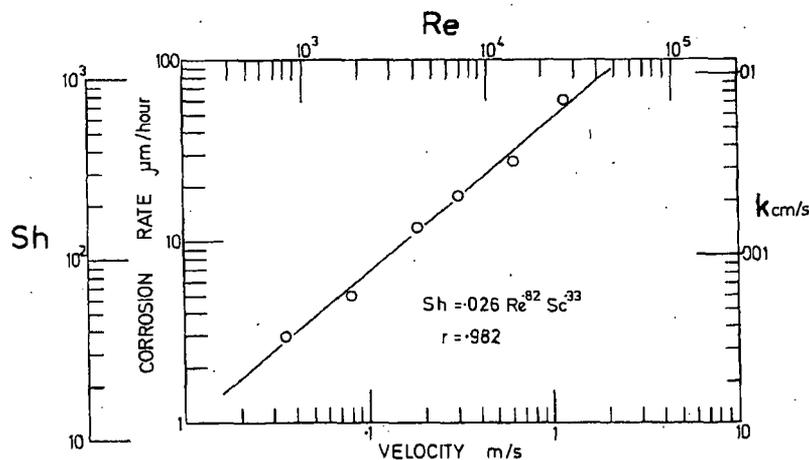
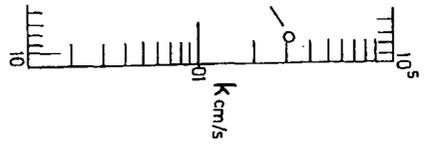


FIG. 6. Correlation of fully developed corrosion rate with Reynolds number for copper specimens tested in acid ferric chloride solution at 50°C.



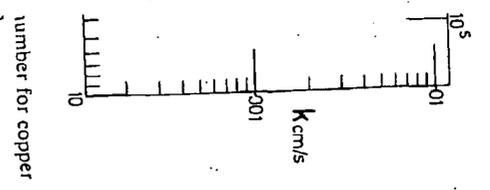
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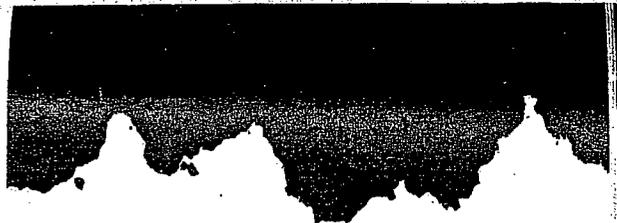
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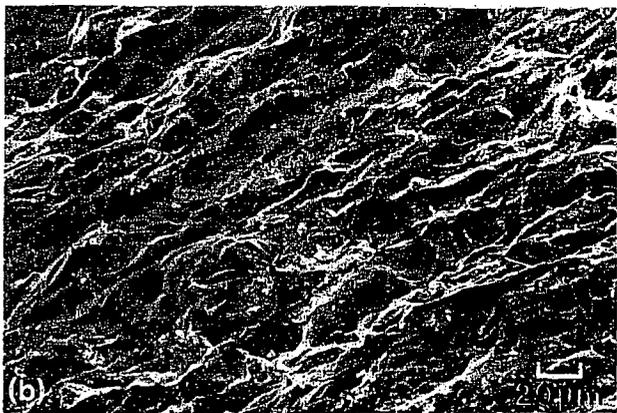
number for copper



(a)



(c)



(b)



(d)

FIG. 3. Morphology of attack on copper and steel specimens in 0.1 N HCl containing $2 \text{ g l}^{-1} \text{ Fe}^{3+}$ at 50°C.

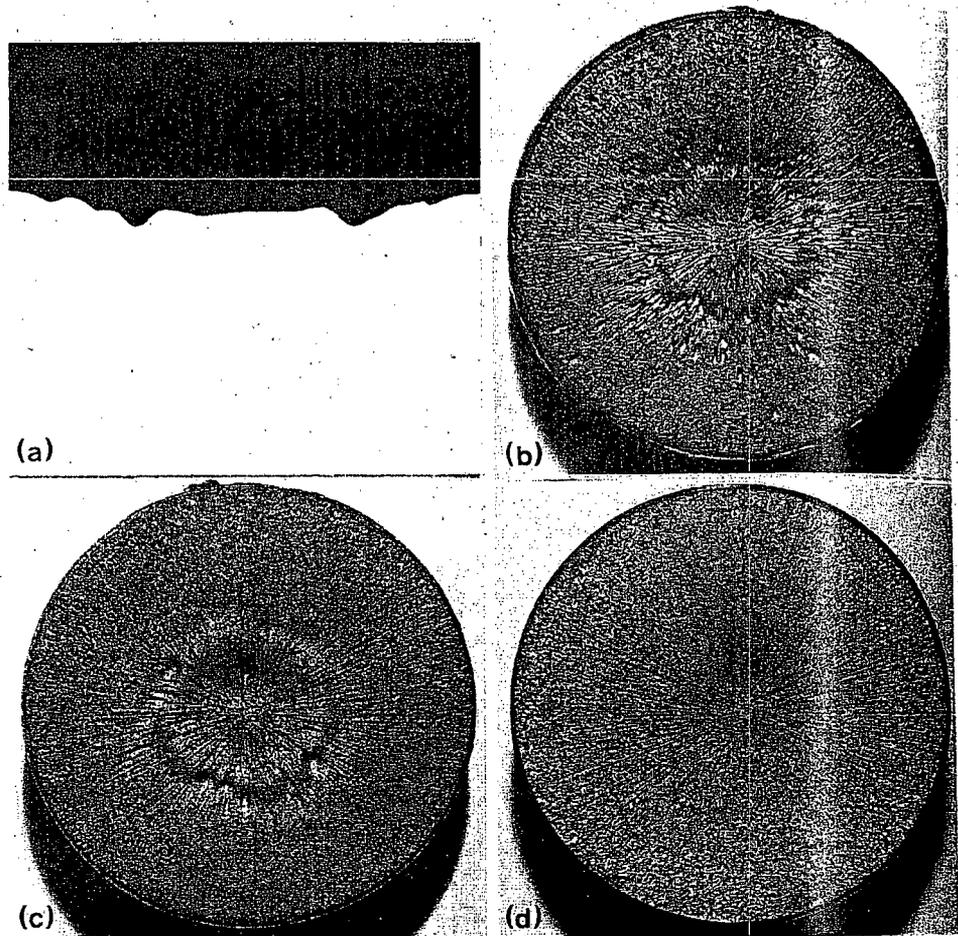


FIG. 10. Attack produced by small jet on 25.5 mm dia. copper specimens using acid ferric chloride solutions. (a) and (b) Cross section and surface morphology at a Re of 49 000. (c) Surface morphology at Re s between 15 000 and 25 000. (d) Surface morphology below a Re of 15 000.

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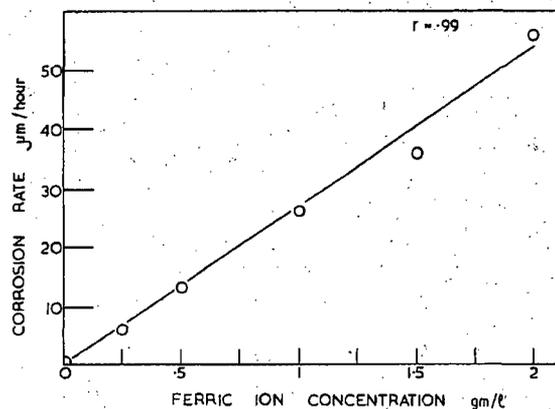


FIG. 7. Effect of ferric ion concentration on corrosion rate of copper; large jet impinging on 25.4 mm dia. specimen at a Re of 10000.

equations for the two situations were then obtained assuming a dependency on $Sc^{1/3}$ as is usual; the equations were:

$$\begin{aligned} Sh_{\text{peak}} &= 0.286 Re^{0.65} Sc^{0.33} \\ Sh_{\text{fully developed}} &= 0.026 Re^{0.82} Sc^{0.33} \end{aligned}$$

Enhancement factors, i.e. the ratio of peak to fully developed rates were also obtained, after much longer exposure times, when the concentration of ferric ions had been reduced significantly.

The effect of concentration driving force and reactions involved

The effect of ferric ion concentration on the corrosion of copper in 0.1 N HCl at 50°C was examined using the large diameter impinging jet at a Reynolds number of 10000. This geometry was used because the specimens are very simple, the corrosion is uniform thereby allowing weight loss measurement and finally because the concentration driving force will stay constant as a result of the small amount of metal loss. Average corrosion rates are plotted against ferric ion concentration in Fig. 7. Clearly there is no corrosion without ferric ions present and the rate is proportional up to a concentration of 2 g l⁻¹ which was the level used in this work.

To find if copper was dissolving as a monovalent or a divalent species static tests were performed in which copper was potentiostatically held in 0.1 N HCl at the potential at which it dissolved in the ferric containing solution. In all cases a Faradaic comparison of weight loss and total charge passed, i.e.

$$\text{wt loss (g)} = \frac{\text{at. weight} \times \text{charge passed (C)}}{\text{number of electrons involved (n)} \times \text{Faraday (F)}}$$

indicating a value of n within 10% of 1, i.e. copper was dissolving as a monovalent ion in agreement with other workers.^{28,29}

The effect of velocity using large impinging jet

The effect of flow velocity on corrosion was examined using this geometry because it causes uniform corrosion under laminar flow where the mass transfer rate is dependent on the square root of the Reynolds number. Velocities in the range 0.075 to 2.5 m s⁻¹ were examined, the results obtained are shown in Fig. 8. In this and other jet experiments it was the jet diameter that was used to calculate both Re and

specimens using acid ferric
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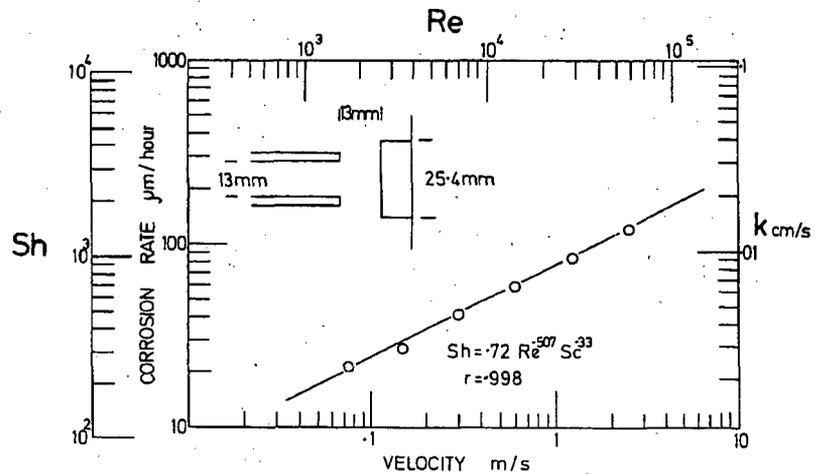


FIG. 8. Correlation curve for large jet impinging onto 25.4 mm dia. copper specimens tested in acid ferric chloride solution at 50°C.

Sh. It was noted in these tests that the surface did not roughen and actually appeared smoother after testing. The equation correlating mass transfer and Reynolds number was:

$$Sh = 0.72 Re^{0.507} Sc^{0.33}$$

The effect of velocity using a multi jet nozzle

This was examined because we wanted to look at a geometry which was uniformly highly turbulent and which had a known mass transfer dependency. Velocities over the range 0.1–7 m s⁻¹ were used.

Attack on the specimen was fairly uniform but some effect of jet interaction, leading to surface roughening, could be seen. The results are shown in Fig. 9 and the correlation equation obtained is:

$$Sh = 0.195 Re^{0.65} Sc^{0.33}$$

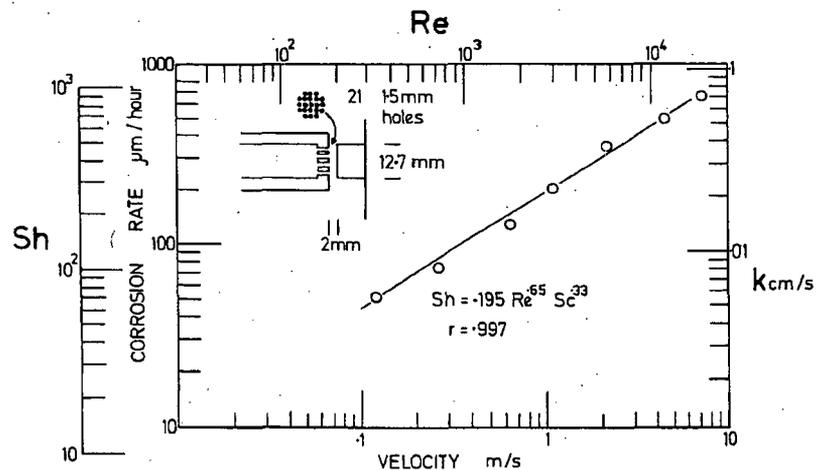


FIG. 9. Correlation curve for multihole turbulent jet impinging onto 12.7 mm dia. copper specimens tested in acid ferric chloride solution at 50°C.

Tests using a single small jet

A limited number of tests were performed using a 3 mm dia. jet impinging onto a 25.4 mm dia. specimen at a distance of 3 mm. These tests were carried out to see if the corrosion profile mirrored the known mass transfer profile. A cross section through a specimen tested at high Reynolds number is shown in Fig. 10a. The pattern of attack was similar in all cases but clear trends depending on the Reynolds number were noted: relatively uniform attack with little surface roughening up to 3 mm from the centre, a peak in the corrosion rate between 4 and 5 mm from the centre, the relative magnitude of which increased with Reynolds number, and finally a region of slowly decaying attack with radial distance. Above a Re of approx. 25 000 small scallops developed everywhere except the central region (Fig. 10b). Between values of Re 15 000–25 000 larger craters developed. In the region of peak mass transfer (Fig. 10c) below a Re of 15 000 no scallops developed, only radial flow lines (Fig. 10d). On some specimens the central region appeared to be undercut by the developing peak.

DISCUSSION

There are a number of criteria, both qualitative and quantitative, which need to be satisfied before a corrosion reaction can be said to be simply dependent on the rate of mass transfer. These are:

1. The corrosion rate should be proportional to the concentration driving force (ΔC) and be zero when this is zero, i.e. no cathodic reactant or a saturated solution.
2. For a reaction that is controlled by the rate of the cathodic reduction the rate should be independent of the metal (with due allowance for the differences in atomic weight, density and the number of electrons involved in the transfer).
3. The corrosion rate profile should be similar to the mass transfer profile.
4. Peaks, plateaux and enhancement factors should be the correct function of the Reynolds number.
5. Actual corrosion rates should be close to those predicted from reliable existing mass transfer correlations.

From the practical viewpoint it would be desirable for the concentration driving force to be constant or easily measurable, that the chemicals involved should be relatively benign and that production components, e.g. mild or low alloy steels, could be tested. Unfortunately steel in either ferric or oxygenated acid chloride solutions behaved anomalously and was thus rejected, but is nevertheless worthy of mechanistic interest. Mild steel in sulphuric acid remains a possibility, but has so far been rejected on the basis of the hazards involved in handling large quantities of concentrated sulphuric acid.

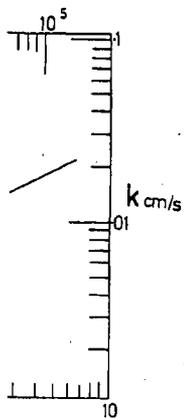
Copper corroding in acid ferric chloride solutions appears to corrode in accordance with mass transfer expectations. Before examining in detail the criteria to test this it is appropriate to review briefly the available mass transfer data of the specimens used in this investigation. These have recently been reviewed in detail.¹¹

For the case of fully developed turbulent flow in a straight pipe there is a large choice of correlations. The best known is the Chilton–Colburn analogy³⁰ with heat transfer:

$$Sh_{fd} = 0.023 Re^{0.8} Sc^{0.33}$$

Probably the most detailed experimental study of mass transfer is by Berger and Hue³¹ using the LCDT. It was suggested that for values of $Sc > 10$

$$Sh_{fd} = 0.0165 Re^{0.86} Sc^{0.33}$$

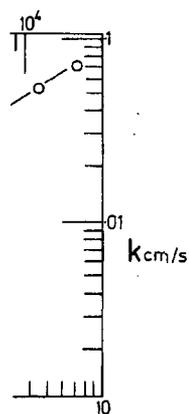


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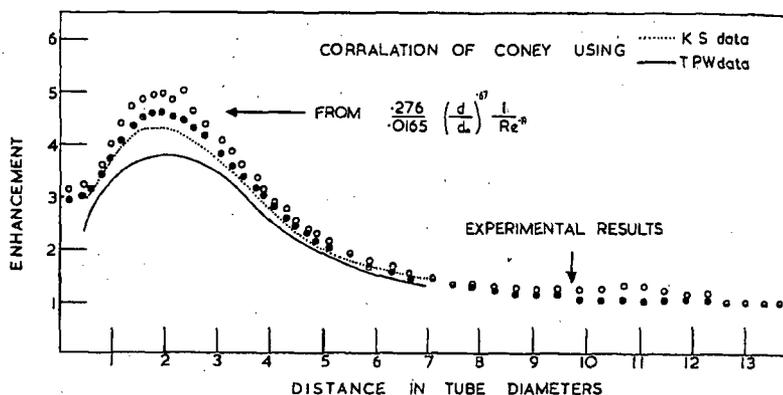


FIG. 11. Comparison of degree of enhancement downstream of an orifice with Coney's correlation using the heat transfer data of Krall and Sparrow and the mass transfer data of Tagg, Patrick and Wragg; copper specimen tested in acid ferric chloride solution at 50°C and a Reynolds number of 27309.

For the case of an orifice the mass transfer profile downstream is of the form shown in Fig. 11. The peak occurring at approximately two tube diameters downstream has been correlated to the orifice Reynolds number Re_o by both heat transfer work (Krall and Sparrow)³² and mass transfer (Tagg, Patrick and Wragg)³³, the latter workers using a nozzle.

$$Sh_{\text{peak}} = 0.27 Re_o^{0.67} Sc^{1/3}$$

The degree of enhancement, i.e. how much the peak exceeds the fully developed tube value can be obtained by dividing the peak equation by the Berger and Hue equation, i.e.:

$$\frac{Sh_{\text{peak}}}{Sh_{fd}} = \frac{0.27}{0.0165} \left[\frac{d}{do} \right]^{2/3} \frac{1}{Re^{0.19}}$$

i.e. it increases with the degree of restriction and decreasing Reynolds numbers.

The actual enhancement profile downstream of the orifice has been described empirically by Coney.³⁴ Using the data of Refs 32 and 33 he obtained

$$\frac{Sh_x}{Sh_{fd}} = 1 + Ax \left[1 + Bx \left(\frac{Re_o^{0.66}}{0.0165 Re^{0.86}} - 21 \right) \right]$$

where Ax and Bx are empirical constants which vary with distance from the orifice and are given in tabular form in Ref. 11. For single jets impinging vertically on to a specimen at a small nozzle-to-specimen distance the profile is of the type shown in Fig. 12.³⁵ With multiple turbulent jets the position is more complicated but there is general agreement³⁵ that mass transfer is proportional to $Re^{0.66}$.

We can now examine the criterion listed previously for determining whether the corrosion reaction, that of copper in acid $FeCl_3$, is controlled by the rate of mass transfer, in this case of ferric ions to the surface.

Figure 3 shows that copper does not corrode without ferric ions being present and the rate is proportional to ferric ion concentration when they are present. It should be mentioned that in other circumstances, especially with anodic polarization, the diffusion of copper ions away from the surface can be rate controlling.³⁶ When the

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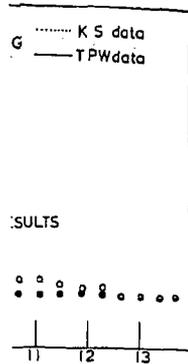
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distance from the orifice impinging vertically on to a surface of the type shown in Fig. 10 is complicated but there is

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conditions being present and are present. It should be noted that periodic polarization, the controlling factor.³⁶ When the

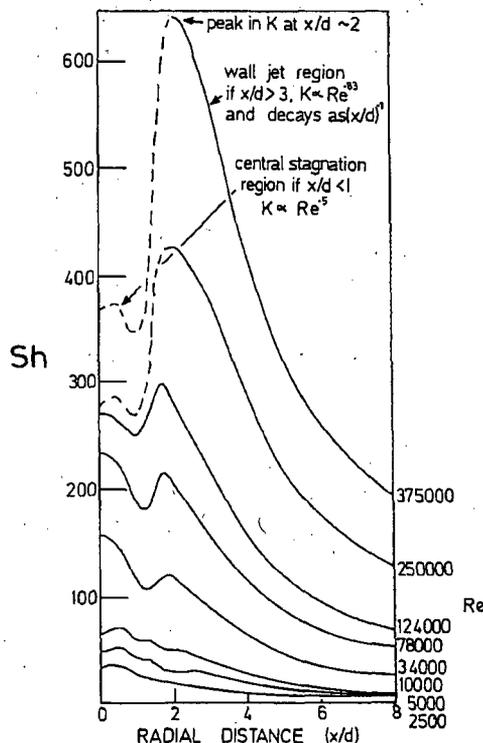


Fig. 12. Mass transfer from impinging small jet at small jet-to-specimen distances showing characteristic secondary peaks ($Sc = 0.8$) (Martin).

data from Fig. 5 and similar results for a Ni specimen were corrected for different average concentration driving forces, and for the electrons involved in the reaction, the peak dissolution rates were similar, in agreement with the second criterion. This is in spite of the fact that steel does not fulfill all the criteria for diffusion controlled mass transfer.

In Fig. 11 we have plotted a typical set of results for the corrosion enhancement profile downstream of an orifice against the predicted curve of Coney; the agreement is good. Similarly the complex profiles obtained with a single small diameter jet on a large specimen (Fig. 10) are very similar to the available mass transfer profiles (Fig. 12).

In Table 3 we have compared the Reynolds number dependency obtained for each of the four geometries in this investigation with the available data; again the agreement is good. The effect of Reynolds number on the degree of enhancement downstream of an orifice is compared to the predicted effect in Fig. 13; again the fit is close.

Finally, to compare actual corrosion rates with predicted rates we have chosen the peak following the orifice, for which if we equate the corrosion rate to the product of the mass transfer rate and the concentration driving force and include factors to get the corrosion rate in $\mu\text{m h}^{-1}$, with D in $\text{cm}^2 \text{s}^{-1}$, d in cm and ΔC in g cm^{-3} , we obtain:

$$CR (\mu\text{m h}^{-1}) = 0.276 \frac{D}{d} (Re_w)^{0.67} Sc^{1/3} x \Delta C \times \frac{10000}{\rho_{cu}} \times 60 \times 60 \times \frac{63.54}{55.85}$$

TABLE 3. OBSERVED AND PREDICTED REYNOLDS NUMBER DEPENDENCY

Geometry	Observed (this work)	Data range ¹¹	Best value
Single large nozzle	0.507	—	0.5
Multiple jet	0.65	0.6-0.76	0.66
Peak downstream of orifice	0.65	0.6-0.82	0.67
Fully developed turbulent tube	0.82	0.8-1	0.86

Predicted and measured corrosion rates are compared in Table 4. There is clearly a systematic overestimation of the corrosion rate by about 12%; but a very high correlation ($r = 0.998$) between measured and predicted rates. This suggests that one of the parameters used to estimate the corrosion rate is in error. The most likely candidate is the diffusion coefficient of ferric ions. The corrosion rate is proportional to $D^{0.67}$ and as outlined earlier the range of rates is between 0.85 and $1.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ but we are checking this as it could clearly lead to errors much larger than we have found. A different value of D would also lead to the constant in the correlation equations which have been obtained being modified.

A number of criteria were suggested to test if the corrosion rate of copper in acid FeCl_3 solutions was simply related to the mass transfer of ferric ions. These criteria have all been found to hold. Thus we have another method of measuring mass transfer rates on a dissolving surface. Since this work was completed it has come to the authors attention that Gregory and Riddiford³⁷ used the corrosion of zinc in an iodine-containing solution in their study of mass transfer to a rotating disc. However the general validity of the method was not apparently tested, for example, for use on specimens having a non-uniform mass transfer profile.

We are using this technique to examine the enhancement of mass transfer in 180° bends at Reynolds numbers between 10^3 and 10^5 . Preliminary results for bends with a bend-to-tube diameter ratio of 6 suggest enhancement factors of between 1.3 and 1.8. Future work will use models of real bends with a bend-to-tube diameter ratio of one.

The changes in surface roughness observed in these tests are worth examining. In general there is much less surface roughening with the development of scallops than has been observed with the chemical dissolution technique.⁵ With the small jet impinging on the large specimen the effect of Reynolds number on this was very marked: above Re of 25 000 small scallops developed everywhere except the central stagnation zone, between 15 000 and 25 000 larger scallops developed but only in the

TABLE 4. COMPARISON OF MEASURED AND PREDICTED PEAK CORROSION RATES FOLLOWING ON ORIFICE

Orifice Reynolds number	Measured corrosion rate ($\mu\text{m h}^{-1}$)	Predicted corrosion ($\mu\text{m h}^{-1}$)	% error
73 151	271	312	+15
36 145	180	196	+12
18 503	111	125	+11
11 188	69	89	+22
4819	44	49	+10
2151	29.5	33	+11

DEPENDENCY

range ¹¹	Best value
—	0.5
6-0.76	0.66
6-0.82	0.67
8-1	0.86

Table 4. There is clearly a 12% error; but a very high correlation. This suggests that one of the most likely errors is in the corrosion rate. The most likely error on rate is proportional to the square of the error in d and Re . The error in d is 0.85 and $1.4 \times 10^{-5} \text{ cm}^2$ is much larger than we have seen in the correlation.

The rate of copper in acid ferric chloride solutions. These criteria for the method of measuring mass transfer coefficients. It has come to be recognized that it has come to be recognized that the corrosion of zinc in an acid solution on a rotating disc. However, the error for example, for use on a rotating disc.

of mass transfer in 180° bends with results for bends with radii of between 1.3 and 1.5 tube diameter ratio of 1.3 and 1.5.

is worth examining. In the presence of scallops than in the absence of scallops. With the small jet diameter on this was very similar except the central jet diameter but only in the region of peak mass transfer.

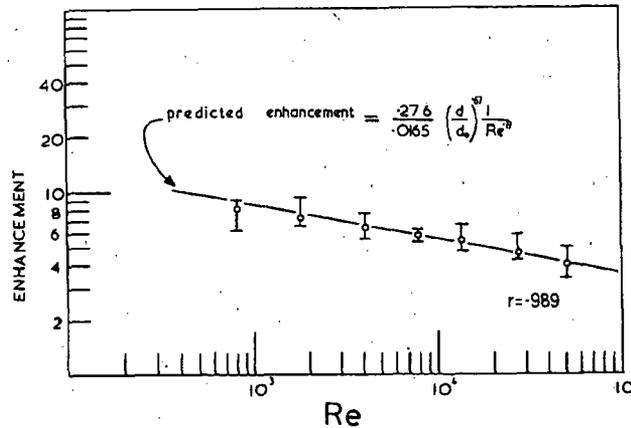


Fig. 13. Effect of Reynolds number on maximum enhancement downstream of an orifice. Range and average of data points shown. Copper specimens tested in acid ferric chloride solution.

region of peak mass transfer, below Re of approx. 15 000 no scallops developed, only radial flow lines. This was not studied in detail with the orifice geometry but scallops were only observed on specimens tested at the higher Reynolds numbers, and only occurred in the region of maximum mass transfer; they were not accounted for in the correlation equation or in the measured enhancement factors. The corrosion rate profiles of steel in both acidified FeCl_3 and oxygenated acidified NaCl are both practically and theoretically interesting. Corrosion reactions involve the occurrence of both an anodic and a cathodic reaction. One possible reason for the higher than predicted enhancement is that these reactions become localized on the surface, i.e. the anodic dissolution reaction occurs at the region of maximum mass transfer and the cathodic reduction of ferric to ferrous ions occurs further downstream. These ideas are clearly speculative and are currently being examined.

CONCLUSIONS

1. A new technique has been developed to measure mass transfer coefficients from a dissolving surface, which involves the corrosion of copper in acid FeCl_3 solutions.
2. Not all metal environment systems in which the corrosion rate is diffusion controlled produce a corrosion rate profile which is directly related to the mass transfer profile. It is speculated that this is the result of the separation of anodic and cathodic areas.
3. Developing roughness in this technique is less than in the chemical dissolution technique, and appears to be a function of Reynolds number or more probably the rate of mass transfer.

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