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ABSTRACT

Two dimensional diffusion of hydrogen atoms in a membrane has been analysed. The hydrogen atoms are assumed to be generated in a circular area on one side of the membrane and detected in a circular region on the opposite side. The average flux on the detection side has been calculated as a function of membrane thickness and detection area and compared with the prediction from the conventional one-dimensional solution. The applicability of the latter increases with decreasing thickness to detection area ratio. Recommendations are given for reliable utilisation of the one-dimensional analysis.

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INTRODUCTION

Measurement of hydrogen diffusion and trapping in metals is most commonly made using a permeation technique. Hydrogen atoms are generated on one side of the membrane by electrochemical reduction of hydrogen ions or water molecules (or by gaseous adsorption and dissociation of hydrogen gas molecules) and detected on the opposite side through the effect on the oxidation current at constant applied potential (or through change in pressure of a vacuum system as a consequence of recombination).

The analysis of diffusivity and trapping is based largely on the application of Fick's Law[1] and on the theory of McNabb and Foster[2]. An important assumption in these analyses is that the movement of atoms through the material can be described by one-dimensional transport equations. The premise is that lateral diffusion of hydrogen can be neglected. Clearly, this is intuitively valid if the membrane thickness is very much less than the radius of the monitoring area. However, no specific recommendation for an acceptable ratio of area to thickness is available when designing appropriate test systems. This becomes important when measuring transport in ferritic steels of high diffusivity for which thick specimens may be necessary. In order to provide some guidance, analysis of hydrogen transport in two dimensions has been made. For simplicity, the analysis has been confined to steady-state but the conclusions would be expected to be more generally applicable.

MATHEMATICAL MODEL

The geometry of the system is described in Figure 1. The exposed area on the charging side is circular with radius d and the area exposed on the oxidation side has radius b. The membrane thickness is defined by the parameter a.

The equation describing steady-state transport in this system is

$$D\frac{\partial^2 C}{\partial r^2} + \frac{D}{r}\frac{\partial C}{\partial r} + D\frac{\partial^2 C}{\partial z^2} = 0 \qquad (1)$$

The boundary conditions are

$$\begin{aligned} z = 0 \qquad & 0 \le r \le d \qquad & C = C_0 \\ & d < r < \infty \qquad & C = 0 \end{aligned} \qquad (2)$$

and

$z = a$	$0 \le r \le b$	$C = 0$	
	$b < r < \infty$	$C = 0$	(3)

For ease of mathematical analysis it is convenient to convert equation (1) to a dimensionless form using $Z = z/d$, $R = r/d$ and $u = C/C_0$. Thus

$$\frac{\partial^2 u}{\partial R^2} + \frac{1}{R}\frac{\partial u}{\partial R} + \frac{\partial^2 u}{\partial Z^2} = 0 \tag{4}$$

and the transformed boundary conditions using $h = a/d$ and $c = b/d$ are given by

$Z = 0$	$0 \le R \le 1$	$u = 1$	
	$1 < R < \infty$	$u = 0$	(5)
$Z = h$	$0 \le R \le c$	$u = 0$	
	$c < R < \infty$	$u = 0$	(6)

The assumption that the concentration of hydrogen is zero at the surface immediately adjacent to the charging and oxidation areas assumes rapid recombination and removal of hydrogen molecules from this surface. There is uncertainty about the rate of this process in practical situations but the assumption that it is rapid and the concentration is zero would represent a conservative approach for this analysis since the lateral flux would be enhanced.

The method of solution is given in the Appendix. The average flux over the oxidation area of the membrane, $F_{AV}(c)$, was calculated from equation (A.9) using Simpsons rule. An upper limit for the integral of 100 gave convergent values for the average flux.

RESULTS AND DISCUSSION

The important parameter from the perspective of measurement is the flux of hydrogen atoms on the oxidation side of the membrane. In practice, the total flux is measured and the average flux is estimated by dividing by the area of the oxidation surface. Hence, in evaluating the effect of thickness on the validity of the one-dimensional treatment it is most relevant to compare the average flux derived from the two dimensional analysis with the flux predicted from the one dimensional analysis. The latter is defined at steady state by $J_{1D} = -1/h$ where J_{1D} is the normalised flux in dimensionless units.

The values of J_{1D} and $F_{AV}(c)$ calculated as a function of membrane thickness are given in

Table 1 for membranes with identical charging and oxidation areas (c = 1). The values given for $F_{AV}(c)$ are convergent to the number of decimal places shown.

The results show that for ratios of the radius of the charging surface to membrane thickness of 10 to 1 or greater the error associated with the use of the one dimensional analysis is less than 5%. Even at a smaller ratio of 5:1 corresponding to a thicker membrane the error is only 10%. The magnitude of these errors is probably acceptable for most applications though clearly it is desirable to minimise them.

An approach to reducing the errors is to utilise a smaller oxidation surface. The influence of the radius of the oxidation area on the calculated flux for a range of membrane thicknesses is given in Table 2. It can be observed that reducing the radius to just 90% of that of the charging surface gives considerably improved accuracy of the one-dimensional solution. It should be noted that with increased thickness of membranes the radius of the oxidation surface has to be correspondingly reduced to maintain acceptably low errors. For example, Table 2 shows that for a membrane with a normalised thickness of 0.4 the radius of the oxidation surface must be less than 70% of that of the charging surface to maintain errors below 5%.

CONCLUSIONS

Errors in the conventional analysis of hydrogen permeation measurements can occur when the ratio of the membrane thickness to radius of the charging surface is increased.

The source of the error is associated with lateral diffusion of hydrogen atoms which is not accounted for in the conventional analysis based on one-dimensional transport. Nevertheless, the errors are less than 5% provided the ratio of the radius of the charging surface to membrane thickness is greater than 10 to 1.

The errors can also be reduced by using apparatus where the oxidation area has a smaller radius than the charging area.

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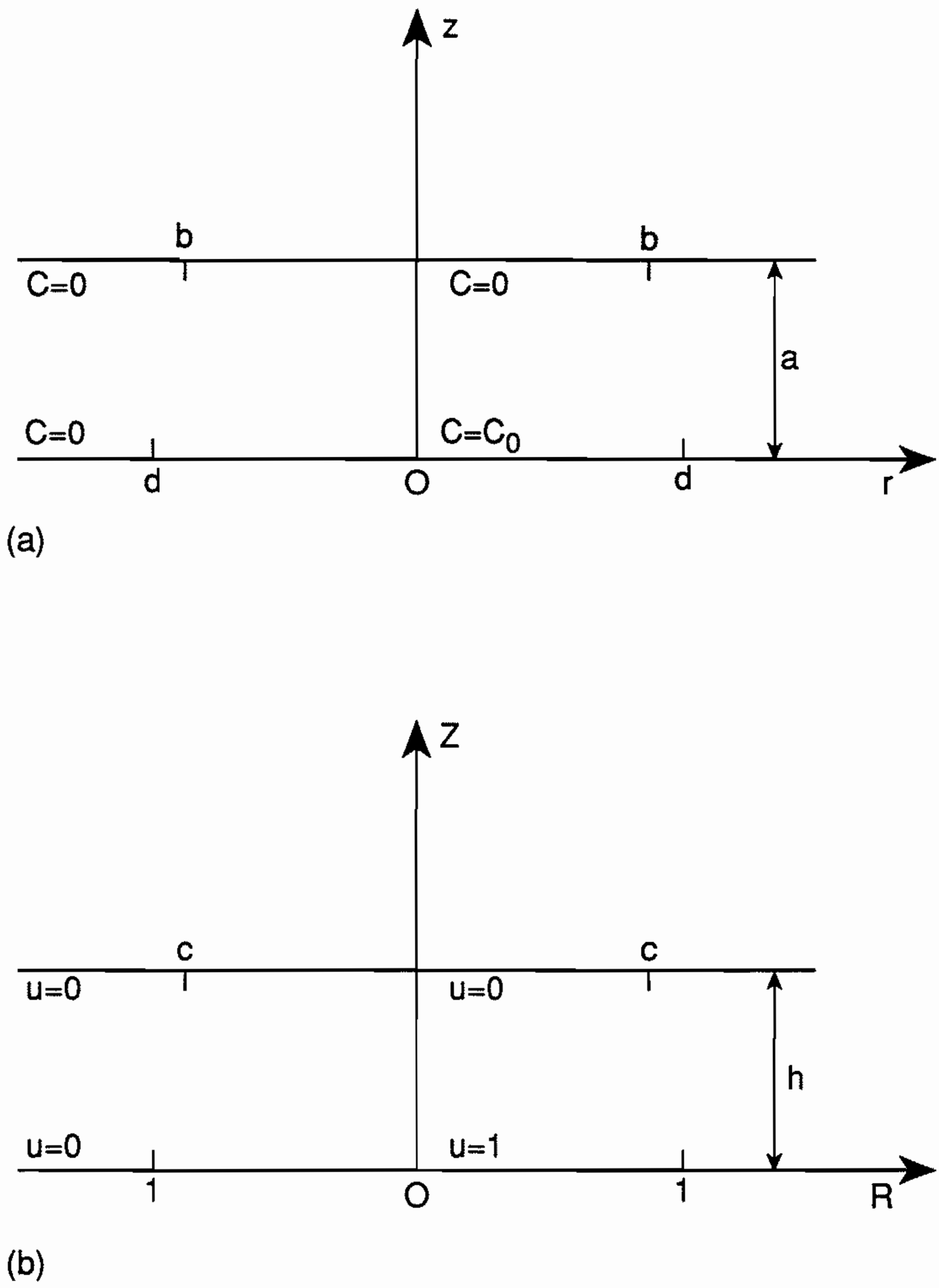

Figure 1 Definition of the geometry of the system and boundary conditions in (a) dimensional and (b) non-dimensional forms.

Table 1

Effect of thickness on flux measured (charging and oxidation areas equal)
Normalised radius of charging area = 1.

Normalised radius on oxidation side c	Normalised thickness h	Typical membrane dimensions		Charging surface radius: thickness ratio d/a	Average flux from two-dimensional analysis $F_{AV}(c)$	Flux from one-dimensional analysis J_{1D}	Error
		Radius of charging surface d mm	Membrane thickness a mm				
1	0.001	10	0.01	1000	-9.91×10^2	- 1000.0	0.9%
1	0.01	10	0.1	100	-9.90×10^1	- 100.0	1.0%
1	0.02	10	0.2	50	-4.937×10^1	- 50.0	1.3%
1	0.05	10	0.5	20	-1.951×10^1	- 20.0	2.5%
1	0.1	10	1.0	10	- 9.534	- 10.0	4.9%
1	0.2	10	2.0	5	- 4.547	- 5.0	10.0%
1	0.4	10	4.0	2.5	- 2.056	- 2.5	22%
1	0.8	10	8.0	1.25	-8.208×10^{-1}	- 1.25	52%
1	1.0	10	10.0	1	-5.811×10^{-1}	- 1.0	72%

Table 2
Effect of size of oxidation area on flux measured for a range of membrane area to thickness ratios

Normalised radius on oxidation side	Normalised thickness	Typical membrane dimensions			Average flux from two-dimensional analysis	Flux from one dimensional analysis	Error
		Radius of charging area	Radius of oxidation area	Membrane thickness			
c	h	d mm	b mm	a mm	$F_{AV}(c)$	J_{1D}	
Effect on thin membrane							
1.0	0.02	10	10	0.2	- 49.4	- 50	1.2%
0.9	0.02		9		- 49.9	- 50	0.2%
Effect on intermediate thickness membrane							
1.0	0.1	10	10	1.0	- 9.534	- 10	4.9%
0.95	0.1		9.5		- 9.845	- 10	1.6%
0.9	0.1		9		- 9.944	- 10	0.6%
0.5	0.1		5		- 9.975	- 10	0.25%
1.0	0.2	10	10	2.0	- 4.547	- 5	10.0%
0.9	0.2		9		- 4.847	- 5	3.2%
Effect on thicker membrane							
1.0	0.4	10	10	4.0	- 2.055	- 2.5	22%
0.9	0.4		9		- 2.218	- 2.5	12.7%
0.7	0.4		7		- 2.398	- 2.5	4.3%
Oxidation on area greater than charging area							
2.0	0.1	10	2	1.0	- 2.475	- 10	304%

APPENDIX

Two dimensional analysis of steady state diffusion in a slab

We consider the steady diffusion through a slab of thickness a shown in Figure 1 which shows cylindrical co-ordinates with origin at O. The region $z = 0$, $r < d$ is maintained at constant concentration, and zero concentration is maintained in $z = 0$, $r > d$. The face $z = a$ is assumed to be at zero concentration. In this appendix the concentration distribution which satisfies these boundary conditions is determined. It is convenient to use scaled variables given by

$$R = r/d, \qquad Z = z/d, \qquad u = C/C_0$$

in equation (1) which then becomes

$$\frac{\partial^2 u}{\partial R^2} + \frac{1}{R}\frac{\partial u}{\partial R} + \frac{\partial^2 u}{\partial Z^2} = 0 \tag{A.1a}$$

with conditions

$$u = 0 \qquad Z = h = (a/d) \tag{A.2a}$$

$$u = 1 \qquad R \leq 1 \quad Z = 0 \tag{A.3a}$$

$$u = 0, \qquad R > 1 \quad Z = 0 \tag{A.4a}$$

We shall use the Hankel transform defined as

$$\bar{u}\,(p) = \int_0^\infty u(r)\, r\, J_0(pr)\, dr \tag{A.5}$$

with its corresponding inverse

$$u\,(r) = \int_0^\infty \bar{u}(p)\, p\, J_0(pr)\, dp. \tag{A.5a}$$

We multiply (A.1a) by $rJ_0(pr)$ and integrate with respect to r between the limits 0 and infinity. On using (A.5) this gives

$$\frac{d^2\bar{u}}{dZ^2} - p^2\bar{u} = 0 .$$

The solution of this equation which satisfies conditions (A.2a) is

$$\bar{u} = A\,(\sinh(pZ) - \tanh(ph)\cosh(pZ)) . \qquad \text{(A.6)}$$

On Z = 0 we use (A.3a) and (A.4a) together with (A.5) to give

$$\bar{u} = \int_0^\infty u\,R\,J_0(pR)\,dR = \int_0^1 R\,J_0(pR)\,dR = \frac{1}{p}J_1(p) .$$

Thus the constant A in (A.6) is given by

$$A = \frac{-\coth(ph)}{p} J_1(p)$$

and (A.6) becomes

$$\bar{u} = \frac{-\coth(ph)}{p} J_1(p)\,(\sinh(pZ) - \tanh(ph)\cosh(pZ)) .$$

Using (A.5a) the solution to the problem is therefore

$$u\,(R,Z) = \int_0^\infty (\cosh(pZ) - \coth(ph)\sinh(pZ))\,J_1(p)\,J_0(pR)\,dp. \qquad \text{(A.7)}$$

Direct differentiation of (A.7) and some reduction gives

$$\left(\frac{\partial u}{\partial Z}\right)_{Z=h} = -\int_0^\infty p\,\mathrm{cosech}(ph)\,J_1(p)\,J_0(pR)\,dp \qquad \text{(A.8)}$$

which is an expression for the flux on Z = h as a function of R.

It is desirable to obtain an expression for the average flux $F_{AV}(c)$ over a circle of radius c at Z = h. This is given by the total flux over the circle divided by the area of the circle.

The flux through an annular ring of width dR at Z = h is

$$2\pi R dR \left(\frac{\partial u}{\partial Z}\right)_{Z=h}$$

so the total flux through a circle of radius c is

$$2\pi \int_0^c \left(\frac{\partial u}{\partial Z}\right)_{Z=h} . RdR$$

or

$$-2\pi \int_0^c \int_0^\infty p \operatorname{cosech}(ph)\, J_1(p)\, J_0(pR)\, dp\, .\ \ RdR$$

on using (A.8). Using the known result

$$\int_0^c R\, J_0(pR)\, dR \;=\; \frac{c}{p}\, J_1(pc)$$

the total flux becomes

$$-2\pi c \int_0^\infty \operatorname{cosech}(ph)\, J_1(p)\, J_1(pc)\, dp .$$

The required average flux is therefore

$$F_{AV}(c) \;=\; \frac{-2}{c} \int_0^\infty \operatorname{cosech}(ph)\, J_1(p)\, J_1(pc)\, dp . \qquad \text{(A.9)}$$