

FIFTH AUSTRALASIAN CONFERENCE

on

HYDRAULICS AND FLUID MECHANICS

at

University of Canterbury, Christchurch, New Zealand

1974 December 9 to December 13

EFFECT OF FLUID OSCILLATIONS ON MASS  
TRANSFER IN POROUS MEDIA WITH  
PARTICULAR REFERENCE TO  
FUEL CELLS

by

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S U M M A R Y

Experiments were performed whereby slightly soluble gases were dissolved in a porous matrix filled with liquid. The liquid in the porous media was caused to sustain purely sinusoidal oscillations and the rate of gas dissolution was measured. Mass transfer enhancements up to 450 per cent greater than experiments without oscillation were obtained. Enhancement was correlated using a functional form suggested by recent theory. Extension of the work to porous electrode fuel cells is considered.

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NOMENCLATURE

A	=	interstitial liquid amplitude
c	=	solute concentration in liquid
D	=	molecular diffusion coefficient of solute
Pe	=	Peclet number, $r_p^2 \omega / D$
$\frac{dP}{dt}$	=	rate of gas pressure change
$r_p$		pore radius in porous media
Q		rate of gas dissolution under pulsatile flow conditions
$Q_s$		rate of gas dissolution without pulsatile flow

Greek

$\omega$		fluid frequency
$\phi$		pore size distribution

INTRODUCTION

It has recently been shown [1, 2, 3] that stationary fluid oscillations applied along the axis of a channel sustaining a concentration gradient induces significant increases in mass transfer. Thus Horn and Kipp [1] considered the theoretical case of a fluid contained between two flat plates oscillating 180° out of phase. When a steady concentration was assumed to exist along the axis, it was shown that a sizeable axial mass transport enhancement could be induced by the oscillating plates. About the same time, Harris and Goren [2] presented a rectilinear solution to the convective-diffusion equation to predict mass transfer increase when small fluid oscillations are applied to a capillary tube connecting two reservoirs of unequal concentration. There was excellent agreement with experiment and mass transfer increases up to 60 times that obtainable by simple molecular diffusion were reported. Later, Rice and Eagleton [3] conducted a similar study and were able to augment mass transfer up to 1100 times that obtainable by molecular diffusion under oscillating flow conditions such that Valensi number ( $r_p^2 \omega / v$ ) was smaller than 0.84. Experimental observations were within a maximum of 6% of theoretical predictions. It is important to note here that only very small fluid oscillations were necessary to produce enormous increases in mass transfer.

On considering the large augmentation obtainable in the above mentioned capillary tube experiments, one inquires into the possible applications of the phenomenon and quite naturally the porous electrode, gas fuel cell springs to mind. Here we have a diffusion limited apparatus whereby fuel ( $H_2$ ) and oxidizer ( $O_2$ ) separately contact a porous matrix (carbon) filled with a conducting solution (say, KOH). When certain catalysts are inbedded in the porous structure of the electrodes the  $H_2$  and  $O_2$  dissolve in the liquid and spontaneously react when the electrodes are electrically coupled to produce current. The limiting current obtainable in the fuel cell is constrained mainly by molecular diffusion and is proportional to it. If we could increase the limiting current, then the number a fuel cells needed for a particular application may be reduced, not to mention the increase in operating ranges possible. While there are other rate limiting steps in fuel cell operation, it appears molecular diffusion may be the most important one.

Our initial experiments were undertaken to see if very small liquid oscillations within a porous matrix contacting a soluble gas could indeed increase the rate of dissolution of the gas (see Figure 1).

THEORETICAL CONSIDERATIONS

In the capillary tube experiments [2, 3] mentioned previously, the convective-diffusion equation

$$(1) \quad \frac{\partial c}{\partial t} + v \frac{\partial c}{\partial x} = D \left( \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial x^2} \right)$$

was solved under quasi-steady conditions by assumming a functional form

$$(2) \quad c(r,x,t) = \bar{c}(x) + C_{+1}(r)e^{i\omega t} + C_{-1}(r)e^{-i\omega t}$$

using a purely sinusoidal rectilinear velocity of the form

$$(3) \quad v(r,t) = u_{+1}(r)e^{i\omega t} + u_{-1}(r)e^{-i\omega t}$$

which satisfies the Navier-Stokes equation and is driven by an applied pressure gradient which is also purely sinusoidal.

The solution obtained is too complex to present here, but for the case when  $r_p^2\omega/D < 1$  an asymptotic relationship was obtained which showed that the ratio of mass transfer rate under pulsing to the unpulsed (molecular diffusion) case was given by the simple expression

$$(4) \quad Q/Q_s = 1 + \frac{1}{384} (Ar_p\omega/D)^2$$

A liquid filled porous matrix is more complex than a simple capillary tube, owing to the circuitous and tortuous passages, not to mention the irregular pore sizes. However, the above simple relationship suggests a very important dimensionless group. Hence we assume the mass transfer enhancement obtainable when a soluble gas contacts an oscillating liquid in a porous matrix may depend as

$$(5) \quad (Q/Q_s - 1) = K(Ar_p\omega/D)^n$$

and set out to find a value for K and n which will allow at least an engineering estimate of the expected mass transfer enhancement. Note, one expects that K and n are positive since

$$(6) \quad \lim_{\omega \rightarrow 0} Q = Q_s$$

$$A \text{ or } \omega \rightarrow 0$$

Further, in the porous matrix of a fuel cell the pore size would be order  $1\mu$ , hence even for large frequencies  $r_p^2\omega/D = Pe < 1$  as required to use the asymptotic form in equation (4).

#### EXPERIMENTAL SET UP

Figure 1 shows a schematic of the experimental rig. Distilled water was used as the absorption media filling the inside of a porous bronze cartridges. Two cartridges were used, both with approximately equal voidage of 0.1. The cartridge measured 100 mm long (only 89 mm of length was exposed to the dissolving gas) with inner diameter 48 mm and outer diameter 54 mm. Experiments of air flow versus pressure drop through the bronze cartridges were used to estimate average flow pore size. Pore radius for coarse and fine cylinders were estimated to be 1.0 and .7 microns, respectively. The porous cylinders are sold in the trade as Bronze Filter Cartridges and were supplied by Nilsen Sintered Products (Australia).

Both pulsed and unpulsed experiments were initiated by filling the inside of the cartridge with distilled water while gas ( $CO_2$  or  $O_2$ ) was applied to the outside of the cylinder. Pulsations were applied to the gas phase by raising and lowering a mercury filled reservoir as shown in Figure 1. Except for the motor-cam pulser, the entire apparatus was immersed in a constant temperature bath and held at  $25 \pm 1.0^\circ C$  for  $CO_2$  dissolution and  $75 \pm 2.0^\circ C$  for  $O_2$  dissolution. The liquid movement needed to induce mass transfer was observed by way of a precision bore, 1 mm diameter capillary tube leading from the liquid phase. Mass transfer rates for pulsed and unpulsed experiments were taken to be proportional to the slope of the pressure versus time curve when linearity is obtained. Thus

$$(7) \quad Q/Q_s = (dP/dt)/(dP/dt)_s = \text{constant}$$

was used to calculate mass transfer enhancement as the ratio of mass flux under pulsations to flux unpulsed. Figure 2 shows that after a few minutes the pressure-time curves becomes linear, hence can be used to compute gas dissolution rate. The results shown for pulsed and unpulsed experiments are presented as pressure change relative to a constant initial charge pressure of 50 inches water. As can be seen, absolute mass rates are not necessary, only the ratio of the two slopes. The mass transfer enhancement is obvious, owing to the much steeper slope of the pulsed pressure change curve. Pressure drop-off in the gas compartment during a pulsed experiment was obtained by momentarily stopping the pulse generator and reading gas pressure. A single data point,  $Q/Q_s$ , thus required order of two hours experimental work.

EXPERIMENTAL RESULTS

Frequencies ranging from .05 to .2 cps were applied to the gas phase. The amplitude of water in the capillary tube ranged from .32 to 3.5 inches. This suggests that water amplitude within the porous bronze matrix contacting the gas phase ranged from approximately  $.176 \times 10^{-5}$  to  $1.93 \times 10^{-5}$  inches, very small displacements indeed.

Mass transfer enhancements for  $\text{CO}_2$  or  $\text{O}_2$  dissolving in water using two porous materials of different pore size are correlated in Figure 3. As mentioned earlier, theory suggests a functional form given by equation (5) and the parameters  $n$  and  $K$  are estimated from Figure 3 to give

$$(8) \quad Q/Q_S = 1 + 1000 (Ar_p \omega / \mathcal{D})^{1/2}$$

This correlation is recommended for estimation purposes only.

No doubt representing the porous media with a single pore size is erroneous. If a pore size distribution can be obtained, a more accurate representation would be

$$(9) \quad Q/Q_S = 1 + K \int_0^\infty (Ar_p \omega / \mathcal{D})^n \phi(r_p) dr_p / \int_0^\infty \phi(r_p) dr_p$$

where  $\phi(r_p)$  is the pore size distribution. In this way, a proper accounting of each pore size contribution to mass enhancement is obtained.

CONCLUSIONS

It has been found experimentally when a soluble gas contacts an oscillating liquid confined within a porous media that significant increases in mass transfer are obtainable. In this work, interstitial fluid amplitude-frequency product of order  $5 \times 10^{-5}$  cm/sec produced mass transfer increases above that obtainable through molecular diffusion by as much as 450 per cent. Applications to fuel cell technology are envisaged with a view to increasing the limiting currents obtainable.

ACKNOWLEDGEMENTS

Special thanks to Mick Brisbane and Gail Geronomos of the Chemical Engineering Laboratory, University of Queensland for building and operating the apparatus used in this work. Stimulating discussions with Professor M.H.I. Baird, McMaster University, Canada on enhanced mass transfer under pulsatile conditions are gratefully acknowledged.

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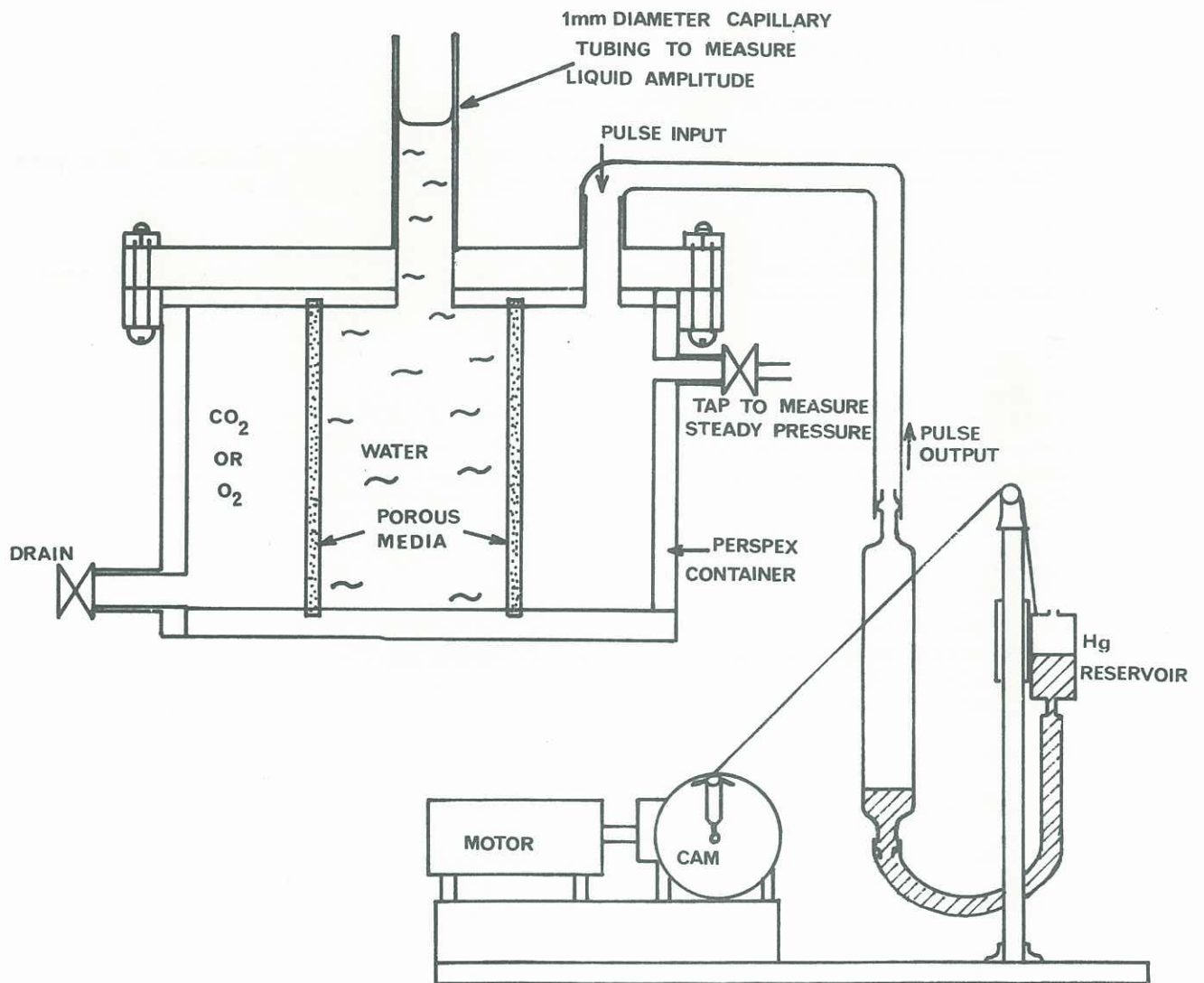


FIG 1 SCHEMATIC OF APPARATUS

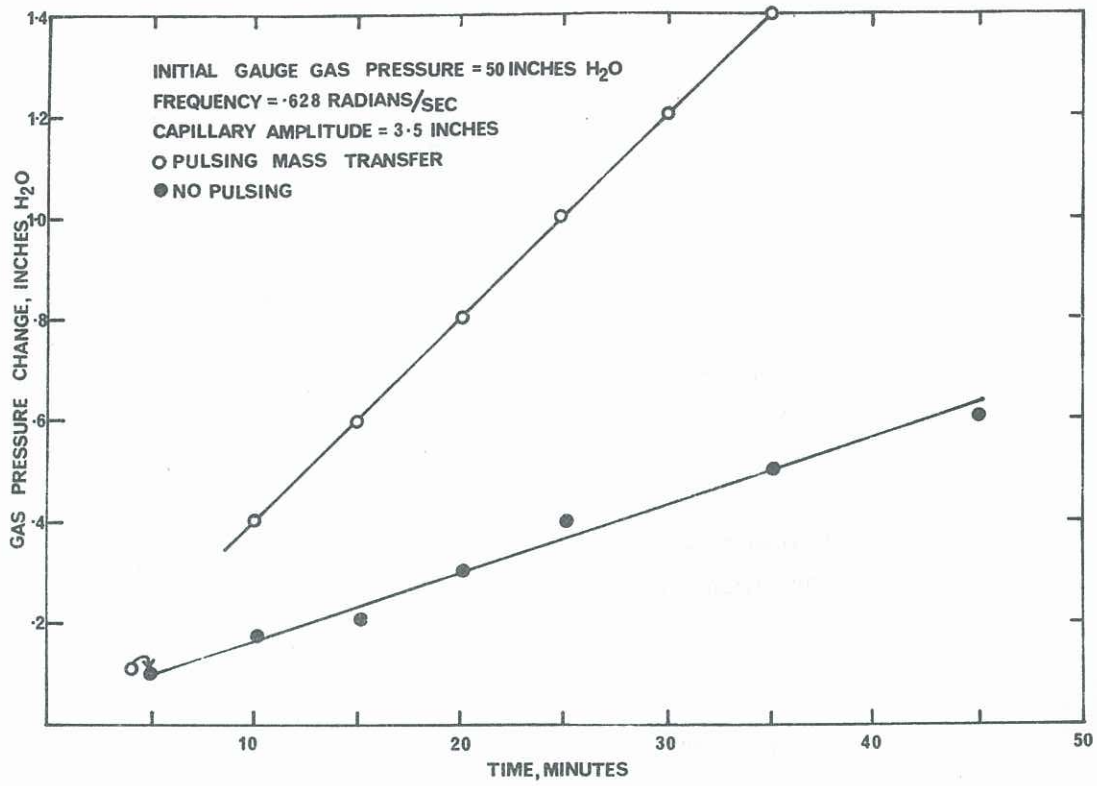


FIG 2 SAMPLE DATA USED FOR COMPUTING  $Q/Q_s$ , COURSE PORE

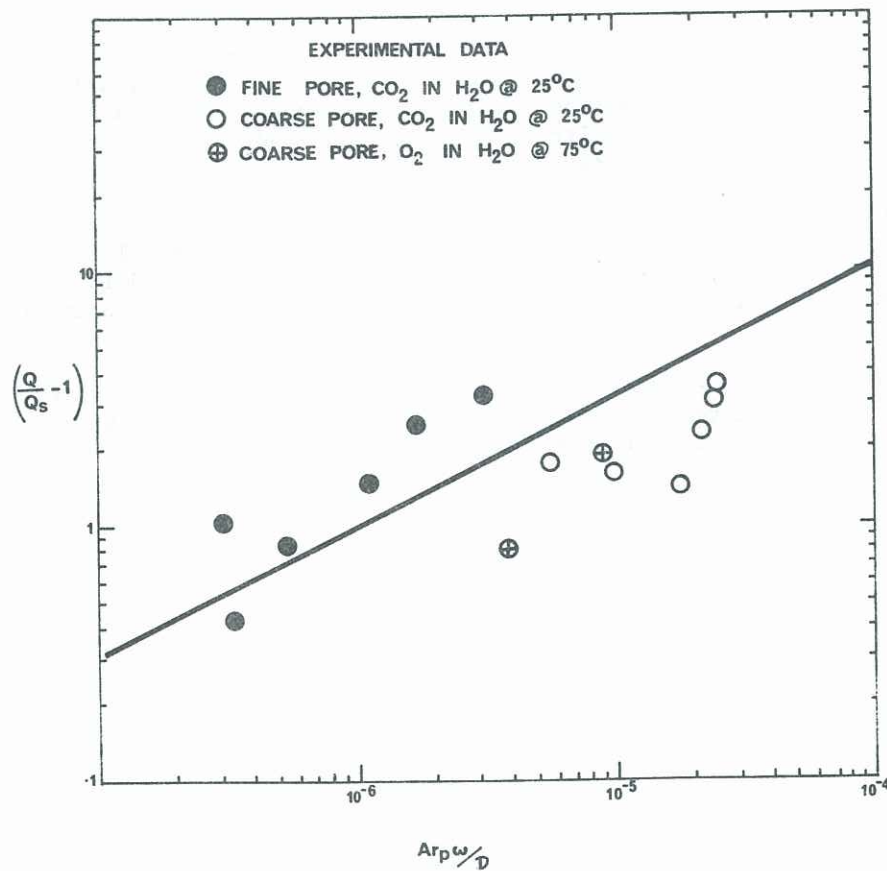


FIG 3 CORRELATION OF ENHANCED MASS TRANSFER RESULTS