Modelling Hydrogen Permeation in a Hydrogen Effusion Probe for Monitoring Corrosion of Carbon Steels

P. Santiwiparat[1], T. Rirksomboon[2,3], F. R. Steward[1], D. H. Lister[1], W. G. Cook[1]

[1]Department of Chemical Engineering, University of New Brunswick, Fredericton, New Brunswick, Canada
(p.santiwiparat@unb.ca)
[2]The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand
[3]Center of Excellence on Petrochemical and Materials Technology, Bangkok, Thailand

A Master's Level Submission

Summary

Hydrogen accumulation inside carbon steel and stainless steel devices shaped like cylindrical cups attached to a pipe containing hydrogen gas was modelled with MATLAB software. Hydrogen transfer around the bottom of the cups (edge effect) and diffusion through the cup walls (material effect) were accounted for. The variation of hydrogen pressure with time was similar for both materials, but the hydrogen plateau pressures in stainless steel cups were significantly higher than those in carbon steel cups. The geometry of the cup also affected the plateau pressure inside the cup.

1. Introduction

There are several techniques for monitoring corrosion rate. One of them employs the Hydrogen Effusion Probe (HEP), which has been developed by the Centre for Nuclear Energy Research (CNER) at the University of New Brunswick. It is a device that infers pipe thinning rate by measuring the quantity of hydrogen produced by the corrosion reaction at the inner surface of the pipe; the hydrogen effuses through the pipe wall and accumulates in a chamber on the outside of the pipe wall, resulting in a pressure rise. The rate of pressure increase measured by the HEP is proportional to the corrosion and can be used to calculate the rate of metal loss. The current HEP uses a silver cup as the chamber for the collection of the hydrogen gas, which silver has very low hydrogen permeability. A vacuum pump relieves the pressure periodically to allow for quasi-continuous operation [1], making the system inconvenient and expensive for long term measurement. Cups made of a material permeable to hydrogen would achieve plateau pressures that depended on the corrosion rates to be measured, raising the possibility of simpler and cheaper devices.

Among industrial materials, stainless steel and carbon steel are of interest. They are readily available and easy to machine. Both have a moderate hydrogen permeability (although that of stainless steel is two orders of magnitude lower than that of carbon steel at 300°C), which means that it is conceivable to make the cups with these materials for operation in the corrosion monitoring system without the requirement of a vacuum pump [2,3].

A model of hydrogen accumulation inside the cups arising from a mathematical computation of diffusion was developed from Sievert's Law. The model is capable of accurately predicting the pressure rise and plateau pressure inside the cups. The purpose of this work is to investigate the effect of different cup materials, stainless steel and carbon steel, and of cup geometry on the hydrogen accumulation inside the cups. The results will aid future designs of HEP.

2. Modelling

Hydrogen transfer through the pipe wall, around the bottom of the cup (edge effect), and diffuse through the cup walls (material effect) were considered.

2.1 Model Derivation and Model Parameters

Hydrogen transfer around the bottom of a silver cup was studied by Kongvarhodom [1]. For the relatively permeable materials stainless steel and carbon steel, a model of hydrogen diffusion and accumulation inside the cups was developed from a combination of Sievert's Law and the Ideal Gas Law. The effects of hydrogen transfer around the bottom of the cups and diffusion through the cup walls on the accumulation inside the cups are described as shown in Equation 1, in which the second and the last terms represent the edge effect and the material effect.

$$\frac{dP}{dt} = \frac{RT_{mean}}{V}\left(\left(\frac{2\pi\phi A(P_{H_{2,f}}^{1/2} - P_{H_{2,p}}^{1/2})}{\ln(r_{p,o}/r_{p,i})\pi D_{p,o}}\right) - \frac{p_c l_H \phi P_{H_{2,p}}^{1/2}}{l_c} - \frac{2\pi\phi_c h_{in} P_{H_{2,p}}^{1/2}}{\ln(r_{c,o}/r_{c,i})}\right) \quad (1)$$

P is pressure rise inside the cup (Pa) over the test time t (s) ; V is total hydrogen gas volume (m^3); R is ideal gas constant (m^3·Pa/mol·K); T_{mean} is mean absolute temperature (K); A is the diffusing area, which is the outer surface area of pipe under the cup (m^2); ϕ is the permeability of A106-B carbon steel pipe material (mol/m·s·Pa$^{1/2}$); $P_{H_{2,f}}$ is the feed side partial pressure of hydrogen, which is the hydrogen pressure inside the pipe (Pa); $P_{H_{2,p}}$ is the permeate side partial pressure of hydrogen, which is the hydrogen pressure inside the cup (Pa); $r_{p,o}$ is the outer radius of pipe (m); $r_{p,i}$ is the inner radius of pipe (m); $D_{p,o}$ is the outer diameter of pipe (m); p_c is the perimeter of cup (m); l_H is the width of hydrogen diffusion path leaving the cup (m); l_c is the length of diffusing element which is the thickness of cup wall and silver solder around the cup (m); ϕ_c is the permeability of cup material (mol/m·s·Pa$^{1/2}$); $r_{c,i}$ is the inner radius of cup (m); $r_{c,o}$ is the outer radius of cup (m); and h_{in} is the inner height of cup (m).

The parameters used for modelling the hydrogen accumulation in this case are summarized in Table 1. The hydrogen permeability of stainless steel 316, carbon steel 1010, and carbon steel A106-B pipe material, were obtained from the studies of Gunter *et al.* [4], Gadgeel *et al.* [3], and Kongvarhodom [1], respectively. The width of hydrogen diffusion path leaving the cup at the cup-pipe interface is 1.662×10^{-4} m from Kongvarhodom [1] based on modelling hydrogen transfer within the tube. The total hydrogen gas volume, diffusing area (i.e., outer surface area of the pipe under the cup), and perimeter of cup were calculated from equations developed in the study of Kongvarhodom [1]. The inner height was calculated by Equation 2 where h is the outer height of cup (m).

$$h_{in} = h - \left(\sqrt{r_{p,o}^2 - r_{c,i}^2} - \sqrt{r_{p,o}^2 - r_{c,o}^2}\right) \quad (2)$$

Table 1 Summarized modelling parameters

Parameters	**Values**							
	Cup 1	**Cup 2**	**Cup 3**	**Cup 4**	**Cup 5**	**Cup 6**	**Cup 7**	**Cup 8**
Material	Carbon Steel 1010				Stainless Steel 316			
$D_{c,o}$×10^{-3} (m)	6.35	6.35	12.70	12.70	6.35	6.35	12.70	12.70
$D_{c,i}$×10^{-3} (m)	3.86	3.05	10.21	9.40	3.86	3.05	10.21	9.40
T_{mean} (K)	382.5	381.2	400.2	397.3	382.5	381.2	400.2	397.3
V×10^{-5} (m^3)	1.16	1.15	1.33	1.30	1.16	1.15	1.33	1.30
ϕ (mol/m·s·Pa$^{1/2}$)	1.934×10^{-11}							
A×10^{-5} (m^2)	8.03	7.39	21.29	20.25	8.03	7.39	21.29	20.25
$P_{H_2,f}$ (Pa)	136302.1							
$P_{H_2,p}$ (Pa)	0 (Initial hydrogen pressure inside the cup)							
$r_{p,o}$ (m)	8.414×10^{-2}							
$r_{p,i}$ (m)	7.818×10^{-2}							
$D_{p,o}$ (m)	0.168							
p_c (m)	0.0200	0.0200	0.0399	0.0399	0.0200	0.0200	0.0399	0.0399
l_H (m)	1.662×10^{-4}							
l_c×10^{-3} (m)	6.25	6.65	6.25	6.65	6.25	6.65	6.25	6.65
ϕ_c (mol/m·s·Pa$^{1/2}$)	2.638×10^{-11}				2.000×10^{-13}			
thickness×10^{-3} (m)	1.25	1.65	1.25	1.65	1.25	1.65	1.25	1.65
h (m)	25.40×10^{-3}							
h_{in}×10^{-3} (m)	25.36	25.35	25.32	25.29	25.36	25.35	25.32	25.29
t (s)	4.32×10^7							

3. Results and Discussion

The modelled hydrogen pressure accumulations with time for all cups, for the group of carbon steel cups and for the group of stainless steel cups are shown in Figures 1-3. The conditions are 5 psig (136 kPa) of pipe hydrogen pressure and 300°C.

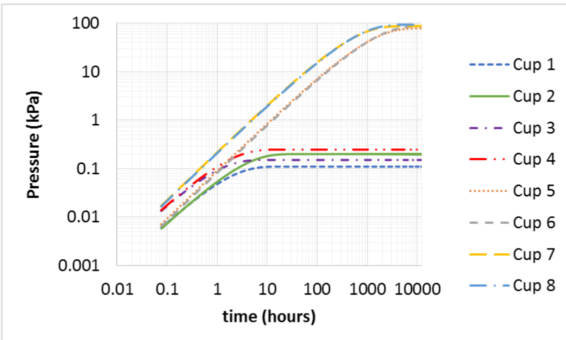

Figure 1 Model of hydrogen pressure accumulation inside all cups

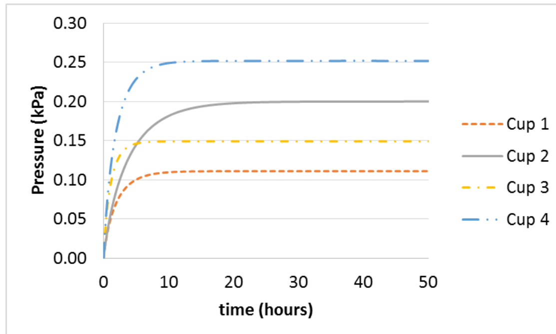

Figure 2 Model of hydrogen pressure accumulation inside carbon steel cups

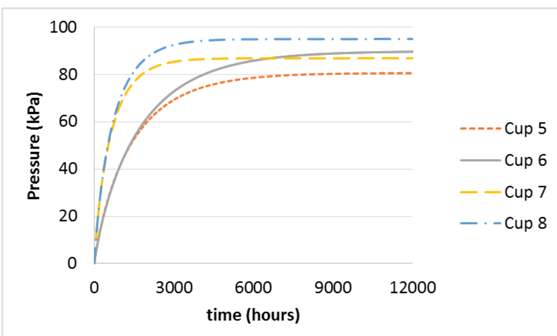

Figure 3 Model of hydrogen pressure accumulation inside stainless steel cups

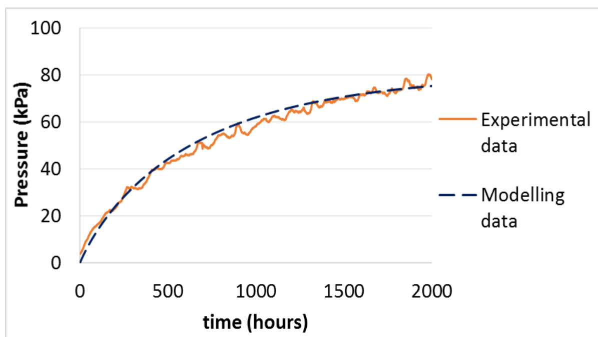

Figure 4 Comparison of the results from experiment in thesis of Kongvarhodom [1] with the result from modelling in this work

Once the hydrogen gas was introduced into the carbon steel pipe, the pressure in the cups continuously increased until steady-state values or plateau pressures were achieved. The effect of the cup materials, carbon steel and stainless steel, is observed in Figures 1-3. It is apparent from these figures that the trend of the variation of hydrogen pressure in the cups with time was similar for the two materials, although the magnitudes were different. The time to steady state (the plateau pressure) depends on the material and geometry of the cup. The attainment of plateau pressure in carbon steel cups was faster than in stainless steel cups and the plateau pressure dramatically lower. These are caused by the more rapid diffusion of hydrogen through the carbon steel cup walls – its hydrogen permeability is two orders of magnitude higher than stainless steel. The higher permeability gives a higher value for the last term in Equation 1. The plateau pressure, consequently, decreased.

At the same conditions, the result from modelling an experiment reported in the thesis of Kongvarhodom [1] is shown in Figure 4, which shows good agreement with the experimental result.

The effects of cup geometry for the two materials are similar, as displayed in Figures 2 and 3. The larger cup, which is 1.651 mm thick, yielded the highest hydrogen pressure rise, followed by the smaller cup of the same thickness. The two thinner cups (1.245 mm thick) showed the lowest plateau pressures. These results indicated that the geometry of the cup also affects significantly the plateau pressure.

4. Conclusion

The hydrogen accumulation inside the cups depends on the cup material and geometry. The variation of hydrogen pressure in the cups with time was similar for the two materials at the temperature of interest; however, the hydrogen plateau pressures in the stainless steel cups were higher than those in the carbon steel cups. This was due to the difference in diffusion rate of hydrogen through the two materials; the permeability through stainless steel is two orders of magnitude lower than through carbon steel. The hydrogen accumulation inside both materials raises the possibility of a self-moderating pressure design due to the significantly higher hydrogen permeability than silver.

5. References

[1] C. Kongvarhodom, “Measurement of hydrogen diffusion through carbon steel under different operating conditions associated with the development of a hydrogen effusion probe to measure metal corrosion rates”, The University of New Brunswick, 2014.

[2] D.M. Grant, D.L. Cummings, and D.A. Blackburn, “Hydrogen in 316 steel — diffusion, permeation and surface reaction”, *Journal of Nuclear Materials*, Vol. 152, Iss. 2-3, 1988, pp.139-145.

[3] V. Gadgeel, and D. Johnson, “Gas-phase hydrogen permeation and diffusion in carbon steels as a function of carbon content from 500 to 900 K”, *Journal of Materials for Energy Systems*, Vol. 1, Iss. 2, 1979, pp.32-40.

[4] W.D. Gunter, J. Myers, and S. Girsperger, “Hydrogen: Metal membranes”, *Hydrothermal Experimental Techniques*, Wiley-Interscience: New York, USA, 1987, pp.100-120.