CHAPTER IV
RESULTS AND DISCUSSION

4.1 Modelling Hydrogen Pressure Build-Up in the Cups

Hydrogen pressure rise inside the cups which hydrogen transfer through the pipe wall, around the bottom of the cup (edge effect), and diffuse through the cup walls (material effect) were considered was solved by the MATLAB program.

The materials and dimensions of the cups are shown in Table 4.1. The parameters used for modelling the hydrogen accumulation in this case are summarized in Table 4.2. The hydrogen permeability of stainless steel 316, carbon steel 1010, and carbon steel A106-B were obtained from the study of Gunter *et al.* (1987), Gadgeel and Johnson (1979), and Kongvarhodom (2014), respectively. The width of hydrogen diffusion path leaving the cup is 1.662×10^{-4} m from Kongvarhodom (2014) based on hydrogen transfer within the tube. For more detailed information on how the values were determined see Appendix A and B.

Table 4.1 The materials and dimensions of each cup

No.	Materials	Grade	Outer Diameter (mm)	Inner Diameter (mm)	Thickness (mm)	Outer Height (mm)
1	Carbon Steel	1010	6.35	3.861	1.245	25.4
2			6.35	3.048	1.651	25.4
3			12.70	10.211	1.245	25.4
4			12.70	9.398	1.651	25.4
5	Stainless Steel	316	6.35	3.861	1.245	25.4
6			6.35	3.048	1.651	25.4
7			12.70	10.211	1.245	25.4
8			12.70	9.398	1.651	25.4

Table 4.2 Summarized modelling parameters

Parameters	Values							
	Cup 1	**Cup 2**	**Cup 3**	**Cup 4**	**Cup 5**	**Cup 6**	**Cup 7**	**Cup 8**
T_{mean} (K)	382.5	381.2	400.2	397.3	382.5	381.2	400.2	397.3
V (m^3)	1.157×10^{-5}	1.146×10^{-5}	1.334×10^{-5}	1.303×10^{-5}	1.157×10^{-5}	1.146×10^{-5}	1.334×10^{-5}	1.303×10^{-5}
ϕ (mol/m·s·$Pa^{1/2}$)	1.934×10^{-11}							
A (m^2)	8.025×10^{-5}	7.391×10^{-5}	2.129×10^{-4}	2.025×10^{-4}	8.025×10^{-5}	7.391×10^{-5}	2.129×10^{-4}	2.025×10^{-4}
$P_{H_2,i}$ (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)	0.1683							
p_c (m)	0.0200	0.0200	0.0399	0.0399	0.0200	0.0200	0.0399	0.0399
l_{tl} (m)	1.662×10^{-4}							
l_c (m)	6.245×10^{-3}	6.651×10^{-3}	6.245×10^{-3}	6.651×10^{-3}	6.245×10^{-3}	6.651×10^{-3}	6.245×10^{-3}	6.651×10^{-3}
ϕ_c (mol/m·s·$Pa^{1/2}$)	2.638×10^{-11}				2.000×10^{-11}			
t (s)	4.32×10^{7}							

4.1.1 Effect of Cup Materials

The models of hydrogen pressure accumulation with time for all cups, group of carbon steel cups, and group of stainless steel cups are shown in Figures 4.1-4.3.

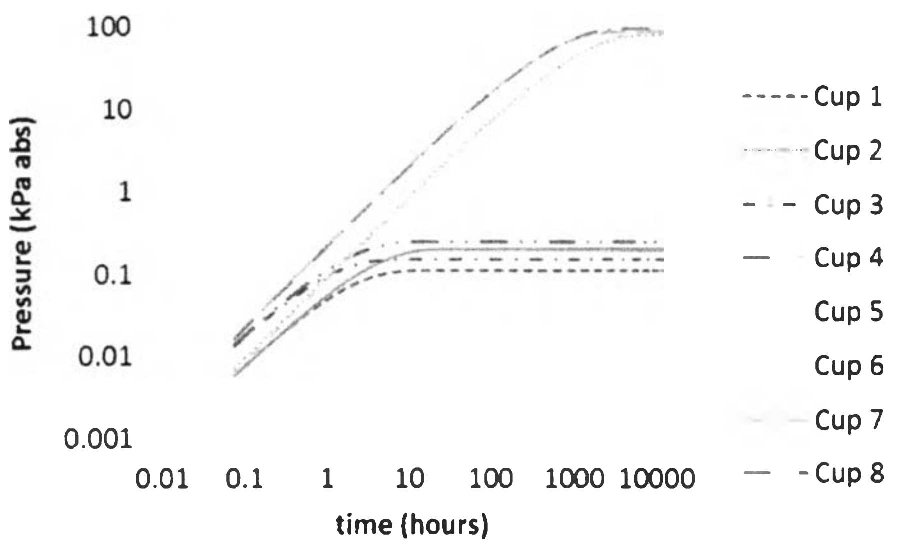

Figure 4.1 Model of hydrogen pressure accumulation inside all cups.

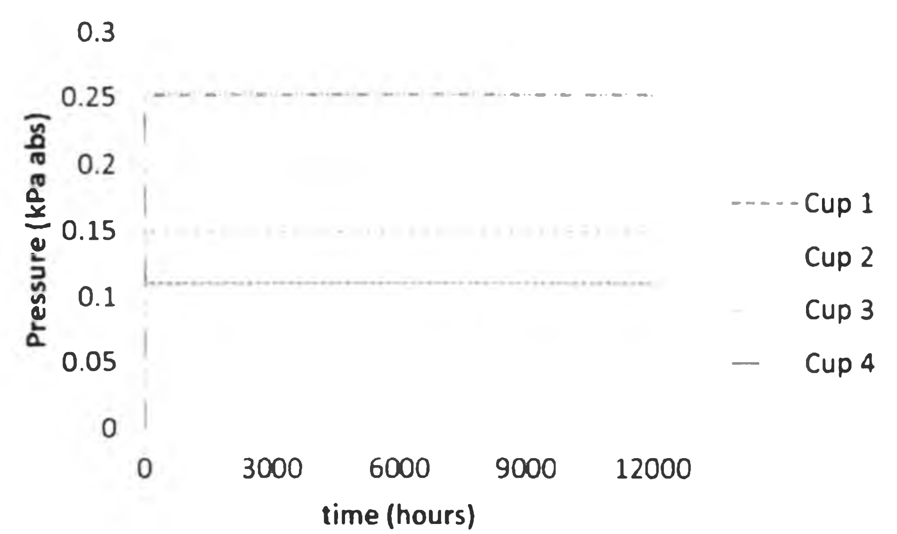

Figure 4.2 Model of hydrogen pressure accumulation inside carbon steel cups.

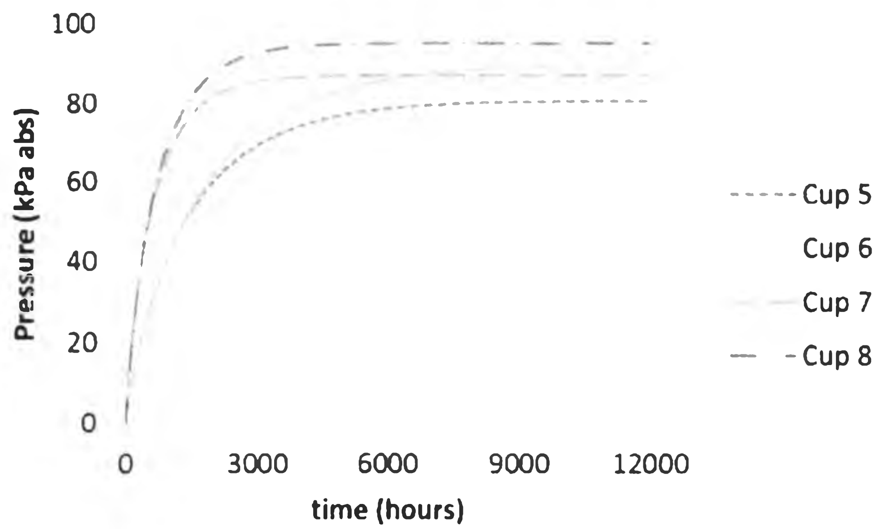

Figure 4.3 Model of hydrogen pressure accumulation inside stainless steel cups.

In order to see the difference of carbon steel cups, the graph of hydrogen pressure accumulation with time is plotted in shorter period of time, 50 hours, as shown in Figure 4.4.

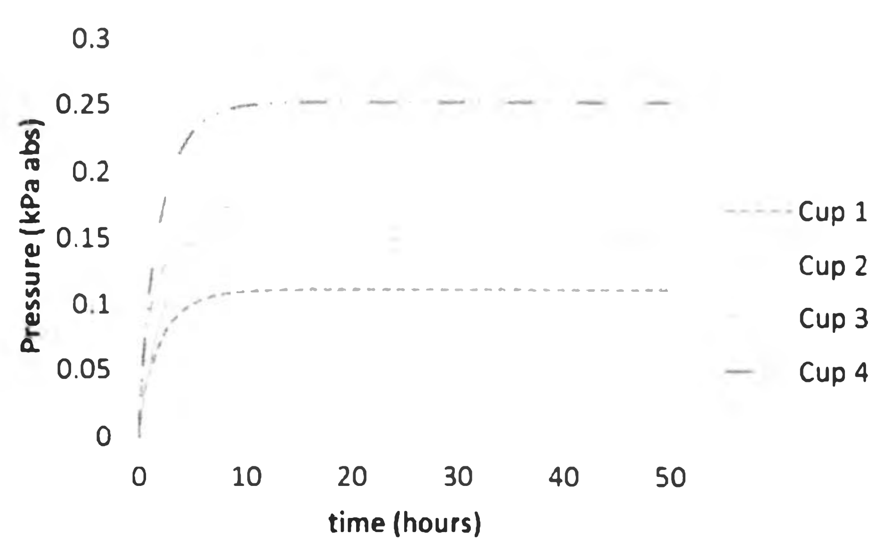

Figure 4.4 Model of hydrogen pressure accumulation inside carbon steel cups in 50 hours.

All of the results are from the modelling only which are the calculation from Equation 3.5. Some parameters are approximate values, so there will be some difference with the results from experiments which will be compared and discussed in detail later in this chapter.

Once the hydrogen gas was introduced into the carbon steel pipe, the pressures in the cups continuously increased until the pressure achieved a steady state value or plateau pressure. The hydrogen accumulation rate in all cups was reported in the form of a line chart in which a total of observed hours was shown in the x-axis while y-axis showed the absolute pressure rises inside the cups.

The effect of cup material, carbon steel and stainless steel, is observed from the Figures 4.1-4.4, which are plots of hydrogen pressure accumulations as a function of time at 5 psig (136 kPa) of hydrogen pressure within the pipe and 300°C. 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 at the temperature of interest. Initially, the hydrogen pressure increased approximately linearly as a function of time. Afterward, there was a tendency for hydrogen accumulation rate to decrease as time increased. However, a comparison of the time axes of Figures 4.3-4.4 shows that the time to steady state, which is the time where pressure in the cup does not alter with time, depends on the material and geometry of cup. The attainment of plateau pressure in carbon steel cups was faster than in stainless steel cups. Moreover, from Figure 4.1, it can be seen clearly that the hydrogen plateau pressure in stainless steel cups were dramatically higher than the plateau pressure in case of carbon steel cups. This is caused by the more rapid diffusion of hydrogen through the carbon steel cup walls – its hydrogen permeability is two orders of magnitude higher. The higher hydrogen permeability caused the last term in Equation 3.5 to increase. The plateau pressure, consequently, decreased.

In addition, the effects of cup geometry for both materials are similar, as displayed in Figure 4.2 and 4.3. The larger cup, which is 1.651 mm thick, yielded the highest hydrogen pressure, followed by the smaller cup of the same thickness. The two thinner cups (1.245 mm thick) showed the lowest plateau pressures. These results indicate that the geometry of the cup also affects significantly the plateau pressure.

4.1.2 Effect of Wall Thickness of Cups

As described previously, the plateau pressure was affected by the geometry of cup. The effect of wall thickness of cups on the hydrogen accumulation can be seen from a comparison of cup 1 with cup 2, cup 3 with cup 4, cup 5 with cup 6, and cup 7 with cup 8 which are presented in Figures 4.5-4.8.

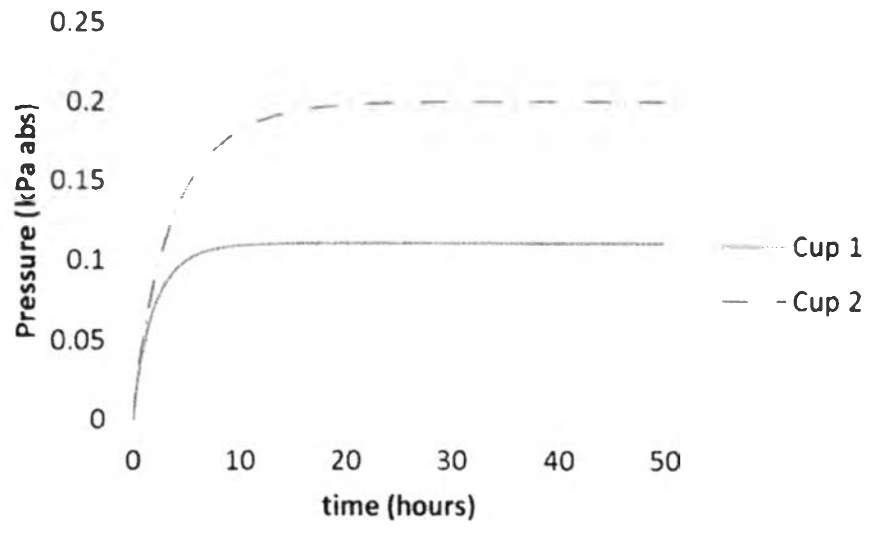

Figure 4.5 Model of hydrogen pressure accumulation inside carbon steel cup 1 and 2.

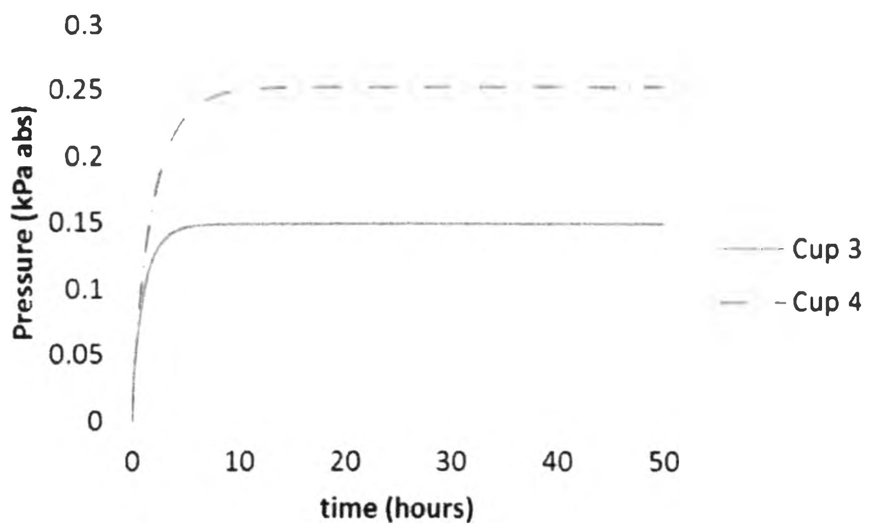

Figure 4.6 Model of hydrogen pressure accumulation inside carbon steel cup 3 and 4.

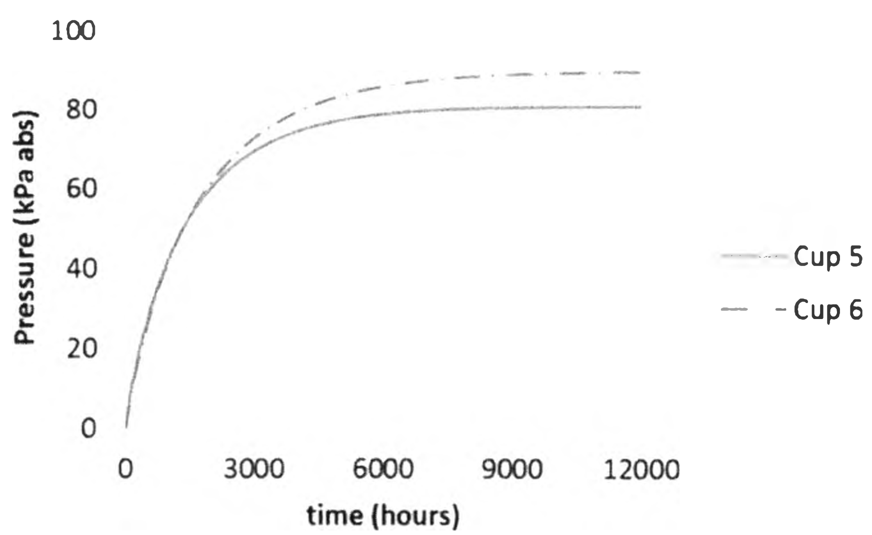

Figure 4.7 Model of hydrogen pressure accumulation inside stainless steel cup 5 and 6.

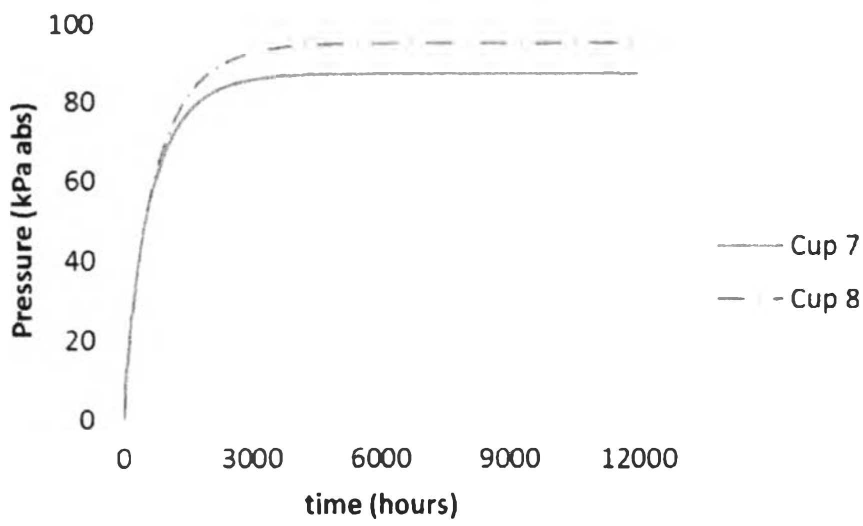

Figure 4.8 Model of hydrogen pressure accumulation inside stainless steel cup 7 and 8.

The relationship of hydrogen pressure and time in each couple shows similar results in both materials. The increase of hydrogen pressure inside the cups was approximately linear with time at the beginning of hydrogen accumulation. The rate of accumulation, then, decreased gradually with time. Nevertheless, the thickness of cup affects significantly the time to reach steady state and the plateau pressure at steady state. Figures 4.5-4.8 indicate that the attainment of the plateau pressure was slower when the thickness increased. It is also found that the thinner cup yielded a lower hydrogen pressure accumulation at steady state. These are caused by the decrease of second and the last terms in Equation 3.5, when the thickness increased. In addition, the thinner cup wall allows for higher hydrogen diffusion through the cup wall at a higher rate. However, these results may be affected by the volume that are different in each couple also.

4.1.3 <u>Effect of Size of Cups</u>

The amount of hydrogen accumulated in the cups at steady state and the hydrogen accumulation rate were also affected by the cup size as shown in Figures 4.9-4.12 which are the graphs of hydrogen accumulation inside the cups that are the same in cup material and geometry, except size, with time at 300 °C and hydrogen pressure in carbon steel pipe is 5 psig.

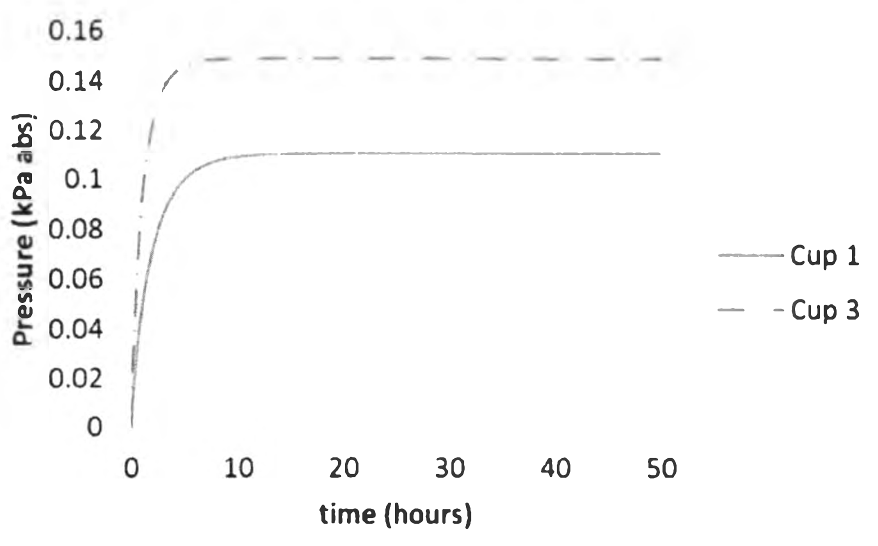

Figure 4.9 Model of hydrogen pressure accumulation inside carbon steel cup 1 and 3.

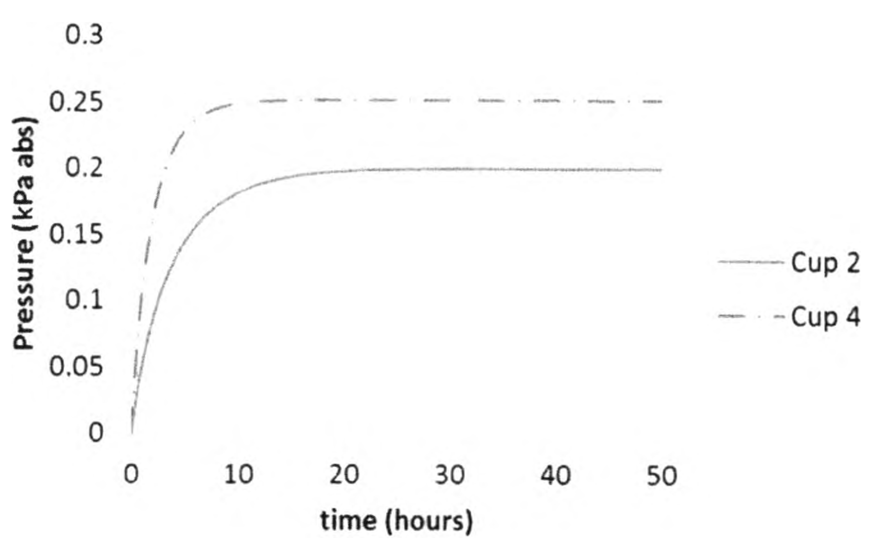

Figure 4.10 Model of hydrogen pressure accumulation inside carbon steel cup 2 and 4.

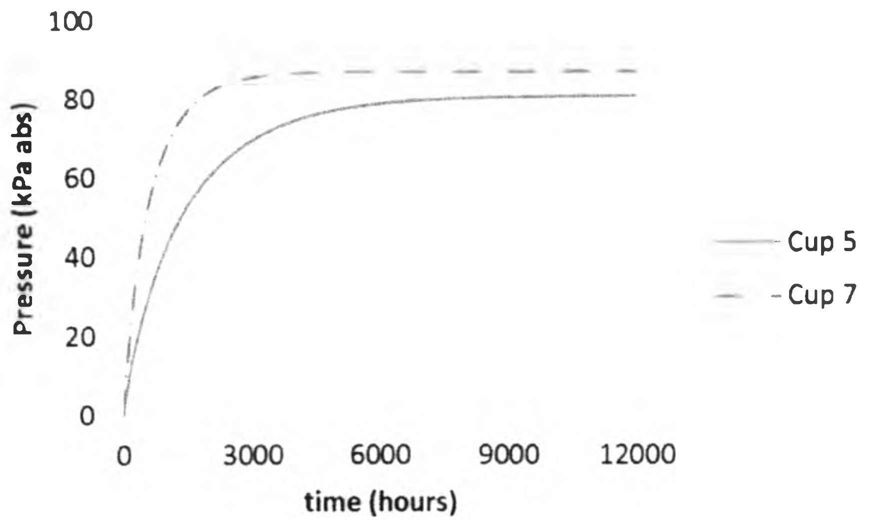

Figure 4.11 Model of hydrogen pressure accumulation inside stainless steel cup 5 and 7.

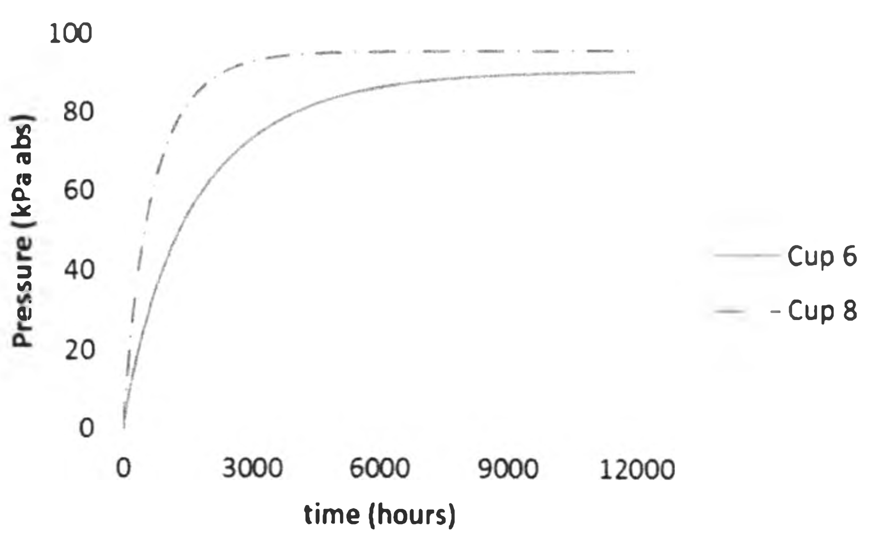

Figure 4.12 Model of hydrogen pressure accumulation inside stainless steel cup 6 and 8.

At the same conditions, as can be seen in Figures 4.9-4.12, the achievement of plateau pressure was faster and the plateau pressure was higher for the larger cup in all couples which are corresponding to thesis of Kongvarhodom (2014) who studied hydrogen accumulation in three different size silver cups. Kongvarhodom reported that the plateau pressure was highest for the large cup, followed by the medium cup and then the small cup. These results were caused by the volume, diffusing area, edge effect and material effect.

From the Ideal Gas Law, the larger cup that has more hydrogen volume will have less hydrogen pressure in the system. However, more volume of the system causes higher mean temperature which makes hydrogen gas more expanded, and results in higher pressure also. By considering these two factors, even if the volume of the larger cup is greater than the smaller cup, it is still almost the same which causes the value of the denominator in Equation 3.5 to be similar. In contrast to mean temperature, the mean temperature in the system of larger cup is much higher than smaller cup. Thus, the numerator in Equation 3.5 is a higher in case of the larger cup. Therefore, the ratio of the mean temperature to volume in the larger cup is higher than the smaller cup.

The larger cup has more hydrogen diffusing area, which is the surface area of pipe under the cup, than the smaller one which means more hydrogen diffuses and accumulates in the cup. Thus, the larger cup has a higher value in the first term of Equation 3.5 than the smaller cup.

The larger cup also has a larger perimeter for hydrogen to transfer around the bottom of the cups (edge effect) which causes the second term of Equation 3.5 to increase and this gives more hydrogen loss from the cup. Moreover, the larger cup also has lower ratio of outer diameter to inner diameter than the smaller cup. The low ratio of outer diameter to inner diameter of larger cup causes the last term of Equation 3.5 to increase, which indicates that it has higher surface area of cup for hydrogen to diffuse through the wall (material effect) and causes more hydrogen loss from the cup as well.

As the result of a thin wall, the hydrogen pressure built-up inside the cups is low. Consequently, the second and last term in Equation 3.5 is low also and then less effective compared to the hydrogen inlet. Therefore, by considering these three factors, the diffusion area in the larger cup is more effective than the other two factors, which means that the larger perimeter (more edge effect) and surface area of cup inside the larger cup (more material effect) are less essential in hydrogen accumulation. The result from volume and these factors, the larger cup yielded the higher plateau pressure than the smaller cup.

4.2 Redesign the Cup

The previous results indicate the plateau pressure of the carbon steel 1010 cups is low. The experiment cannot be set up with these dimension of cups. Their plateau pressures are too low in order to detect the change by the pressure transducer, and the accuracy of pressure transducers that will be used in the experiment is ±1.976 kPa. Consequently, the plateau pressure in carbon steel cups will be 0.12±1.976 to 0.25 ±1.976 kPa which is well more than 100 % deviation. This indicates that the hydrogen plateau pressure in carbon steel cups that are measured by pressure transducers will not be accurate.

Moreover, in the beginning, the cups were planned to be manufactured from stainless steel 316 and carbon steel 1010 tubes at the dimension shown in Table 4.1, but as the cup is very thin, there will be problems with manufacturing, and installing the silver tube on the cup. In addition, the results from the effect of thickness are not good because in each couple of the cups, there is not just the thickness of the cups that are different, but many parameters are different also, and there were problems on ordering the materials required. Thus, the cups were redesigned and modelled with new dimensions and new materials as shown in Table 4.3.

Table 4.3 The new materials and dimensions of each redesigned cup

No.	Materials	Grade	Outer Diameter (mm)	Inner Diameter (mm)	Thickness (mm)	Inner Height (mm)
1	Carbon Steel	1045	21	4	8.5	9.5
2			23	4	9.5	9.5
3			23	6	8.5	9.5
4			25	6	9.5	9.5
5	Stainless Steel	316	11	4	3.5	9.5
6			21	4	8.5	9.5
7			13	6	3.5	9.5
8			23	6	8.5	9.5

The parameters used for modelling the hydrogen accumulation in this case are summarized in Table 4.4. The hydrogen permeability of carbon steel 1045 was obtained from the study of Robertson and Thompson (1980). For more detailed information on how the values were determined see Appendix B and C.

Table 4.4 Summarized new modelling parameters of the cups that were redesigned

Parameters	Values							
	Cup 1	Cup 2	Cup 3	Cup 4	Cup 5	Cup 6	Cup 7	Cup 8
T_{mean} (K)	379.4	379.4	381.1	381.1	379.4	379.4	381.1	381.1
V (m^3)	1.151×10^{-5}	1.151×10^{-5}	1.167×10^{-5}	1.167×10^{-5}	1.151×10^{-5}	1.151×10^{-5}	1.167×10^{-5}	1.167×10^{-5}
ϕ (mol/m·s·$Pa^{1/2}$)	1.934×10^{-11}							
A (m^2)	2.409×10^{-4}	2.692×10^{-4}	2.992×10^{-4}	3.307×10^{-4}	1.228×10^{-4}	2.409×10^{-4}	1.653×10^{-4}	2.992×10^{-4}
$P_{H_2,f}$ (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)	0.1683							
p_c (m)	0.0660	0.0723	0.0723	0.0786	0.0346	0.0660	0.0409	0.0723
l_H (m)	1.662×10^{-4}							
l_c (m)	13.5×10^{-3}	14.5×10^{-3}	13.5×10^{-3}	14.5×10^{-3}	8.5×10^{-3}	13.5×10^{-3}	8.5×10^{-3}	13.5×10^{-3}
ϕ_c (mol/m·s·$Pa^{1/2}$)	2.578×10^{-11}				2.000×10^{-13}			
t (s)	4.32×10^{7}							

The hydrogen pressure accumulation with time for all redesigned cups, group of redesigned carbon steel cups, and group of redesigned stainless steel cups are shown in Figures 4.13-4.15 using the parameters in Table 4.4.

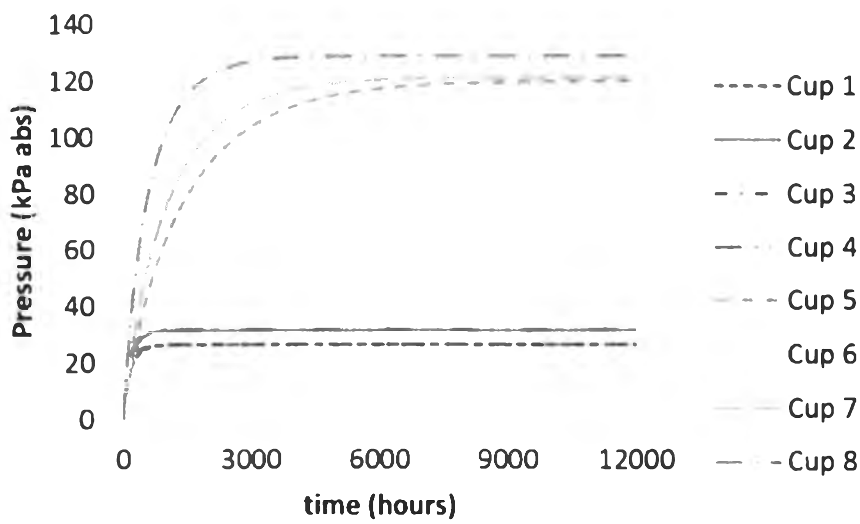

Figure 4.13 Model of hydrogen pressure accumulation inside all redesigned cups.

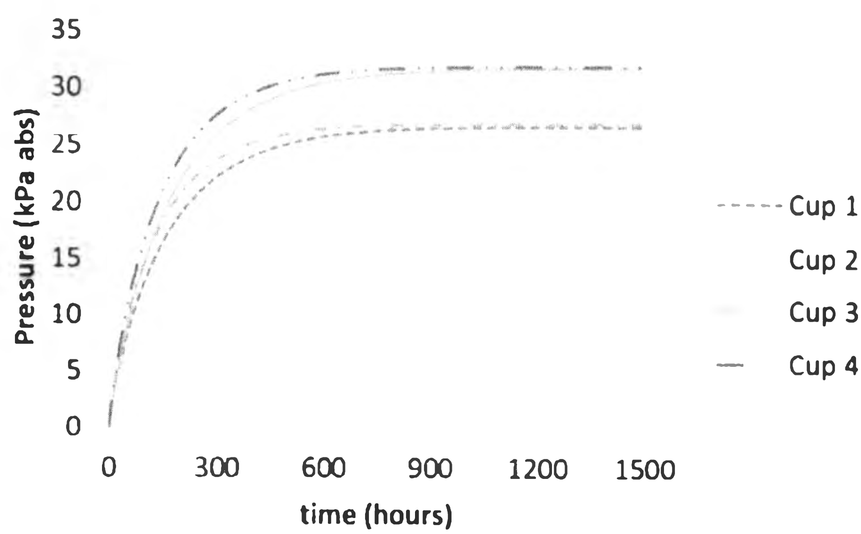

Figure 4.14 Model of hydrogen pressure accumulation inside redesigned carbon steel cups in 1500 hours.

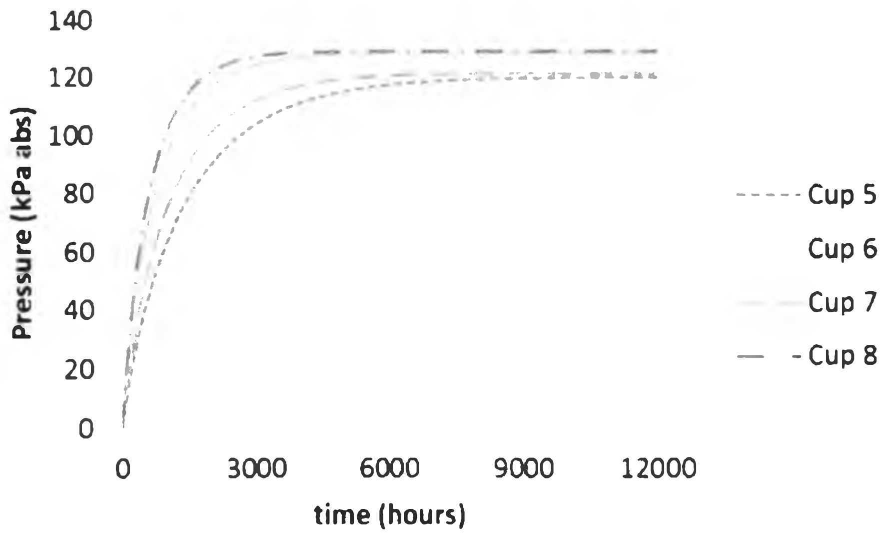

Figure 4.15 Model of hydrogen pressure accumulation inside redesigned stainless steel cups.

In this case, the plateau pressure inside carbon steel 1045 cups were in the range of 26 to 31 kPa. Consequently, the hydrogen pressure at steady state that will be detected by pressure transducer will be 26±1.976 to 31±1.976 kPa which is not more than 7.6 % deviation. This value of deviation is acceptable and the results from the experiment that will use the redesigned cups will be more accurate than the original cup design.

4.2.1 Effect of Cup Materials

The effect of cup materials, carbon steel and stainless steel, is observed from the Figures 4.16-4.17, which are plots of hydrogen pressure accumulations as a function of time for comparing cup 1 with cup 6, and cup 3 with cup 8.

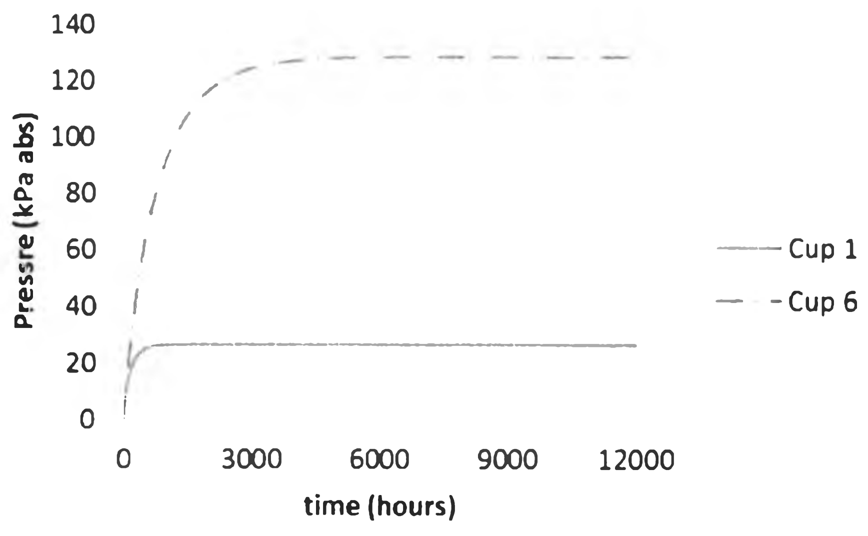

Figure 4.16 Model of hydrogen pressure accumulation inside carbon steel cup 1 and stainless steel cup 6.

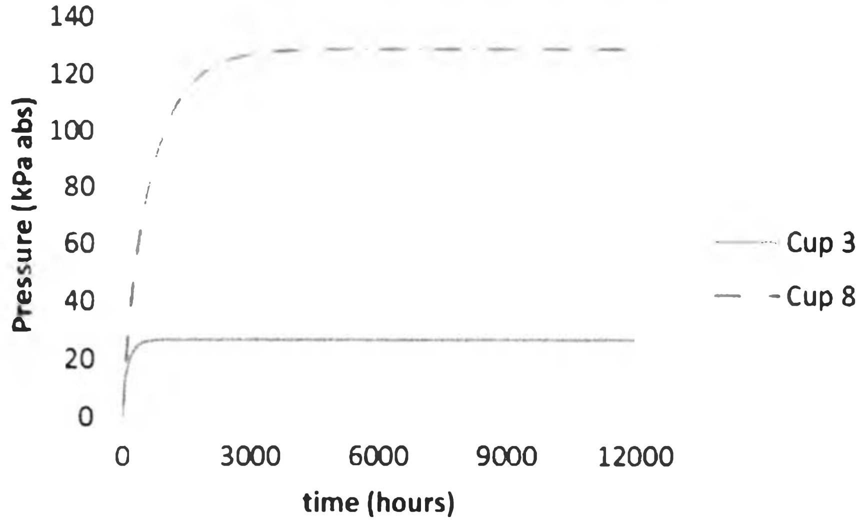

Figure 4.17 Model of hydrogen pressure accumulation inside carbon steel cup 3 and stainless steel cup 8.

It is apparent from these figures that the effect of material is the same as the previous seen. The hydrogen accumulation rate of carbon steel cups was higher, but its plateau pressure was dramatically lower than stainless steel cups due to its hydrogen permeability being two orders of magnitude higher.

4.2.2 Effect of Wall Thickness of Cups

In these redesigned cups as can be seen in Figures 4.18-4.21, the hydrogen pressure at steady state was higher in the thicker cups, but there was a deviation of the achievement of plateau pressure inside the cups. For the carbon steel cup, the cups that are thinner yielded a faster establishment of steady state, in contrast to the stainless steel cups, the attainment of plateau pressure in the thicker cup was higher than the thinner one. These results are caused by the material effect and the edge effect.

For the stainless steel cup that has low hydrogen permeability, there is hydrogen transfer around the bottom of the cup more than diffusion through the cup wall which means that the edge effect controls the rate of hydrogen going out from the cup. As the thickness increases, the perimeter of cup also increases, and results in higher edge effect. Consequently, the thicker cup allows for higher hydrogen transfer around the bottom of the cup at a higher rate acheives the hydrogen pressure at steady state faster than the thinner cup.

In contrast, the carbon steel cup that has high hydrogen permeability, there is more hydrogen diffusion through the cup wall than transfer around the bottom of the cup which means that the material effect plays more important role than the edge effect, and it increases as the thickness decreases. Therefore, the thinner cup wall allows for higher hydrogen diffusion through the cup wall at a higher rate reaches the steady state faster than the thicker cup.

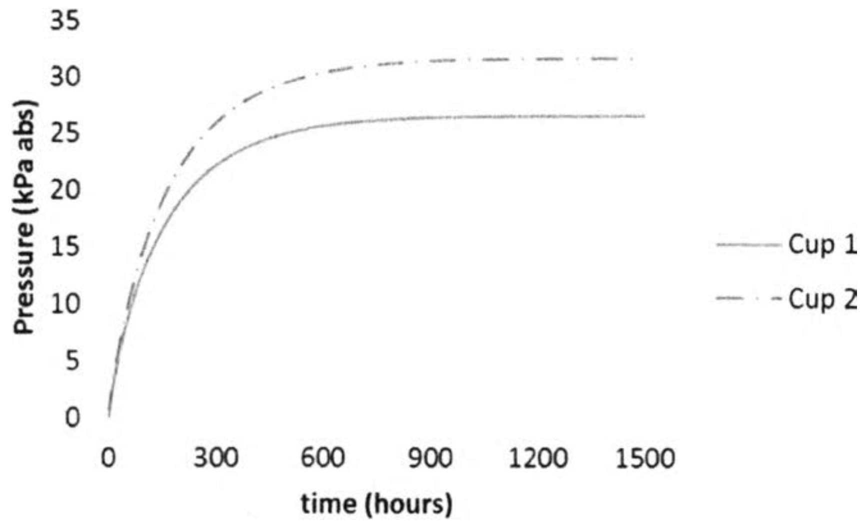

Figure 4.18 Model of hydrogen pressure accumulation inside carbon steel cup 1 and 2.

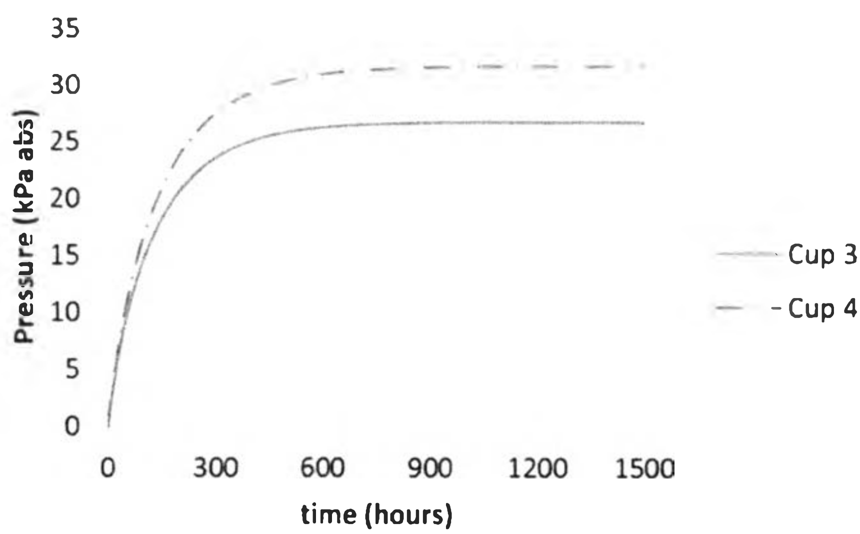

Figure 4.19 Model of hydrogen pressure accumulation inside carbon steel cup 3 and 4.

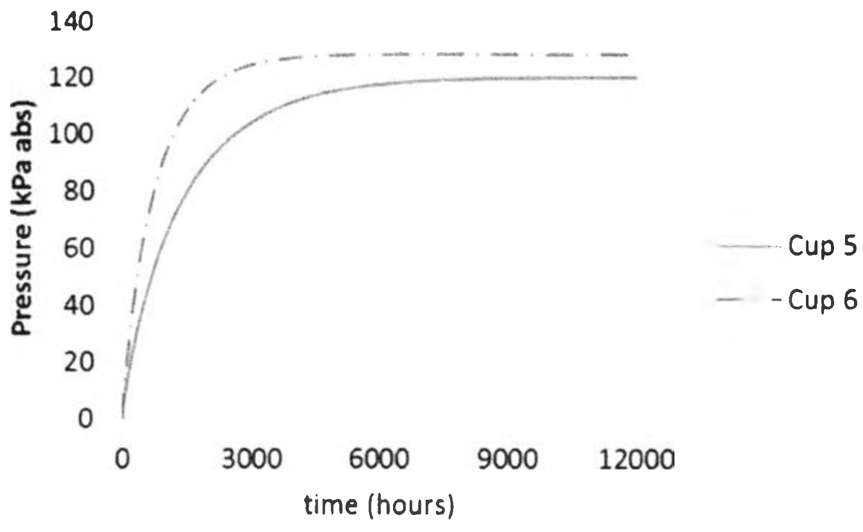

Figure 4.20 Model of hydrogen pressure accumulation inside stainless steel cup 5 and 6.

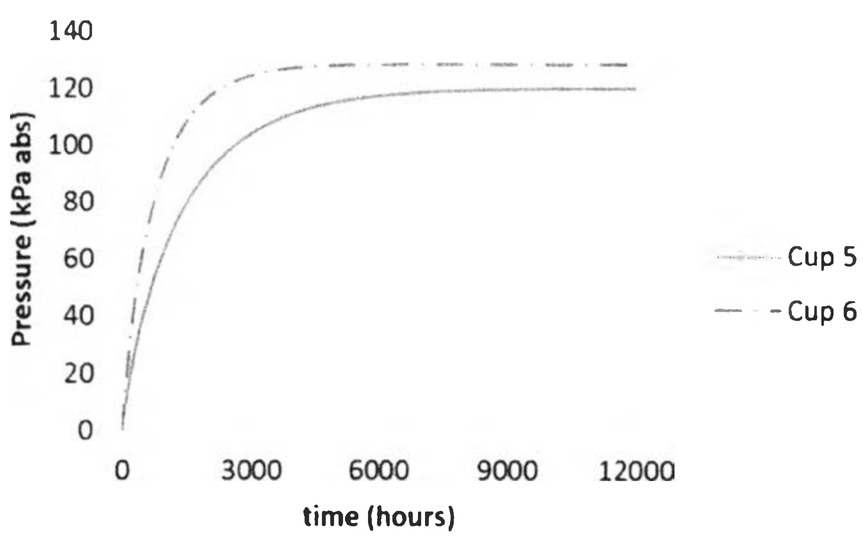

Figure 4.21 Model of hydrogen pressure accumulation inside stainless steel cup 7 and 8.

4.2.3 Effect of Size of Cups

The effect of the size of the cups is similar to the previously designed cups. The hydrogen accumulation rate was faster and the plateau pressure was higher for the larger cup in all couples as shown in Figures 4.22 – 4.25 due to volume, diffusing area, edge effect and material effect.

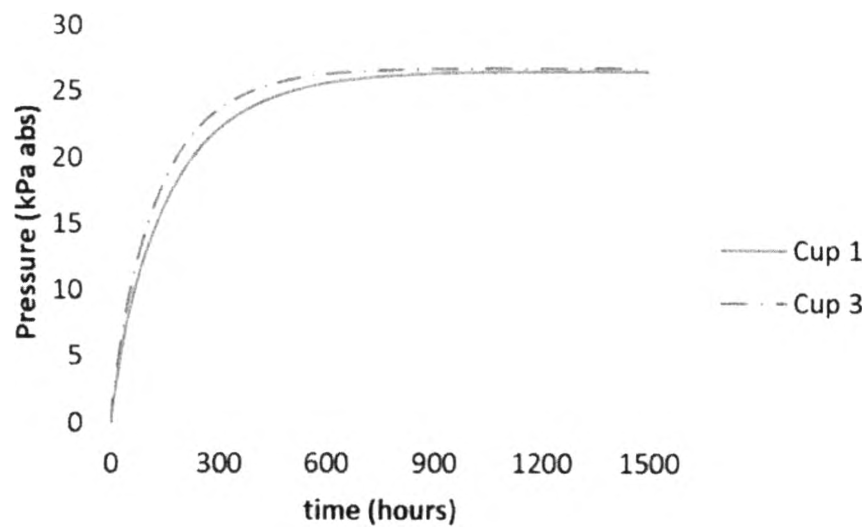

Figure 4.22 Model of hydrogen pressure accumulation inside carbon steel cup 1 and 3.

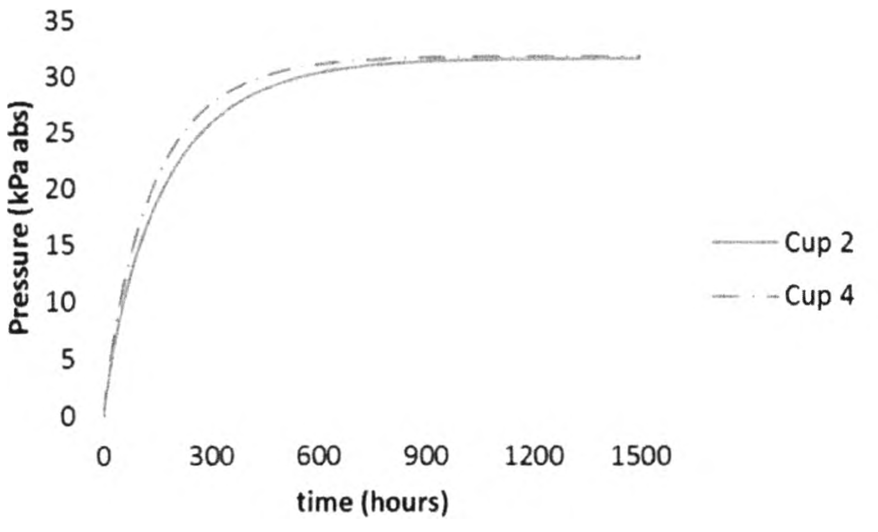

Figure 4.23 Model of hydrogen pressure accumulation inside carbon steel cup 2 and 4.

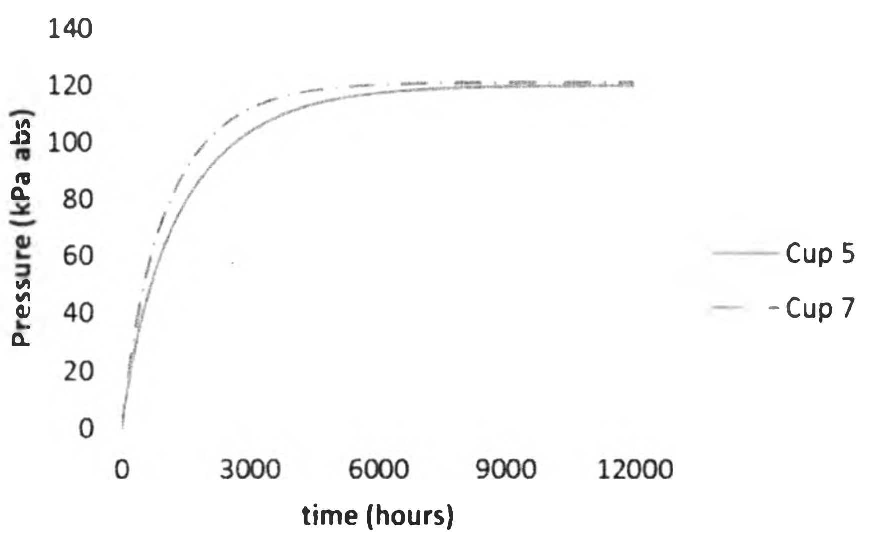

Figure 4.24 Model of hydrogen pressure accumulation inside stainless steel cup 5 and 7.

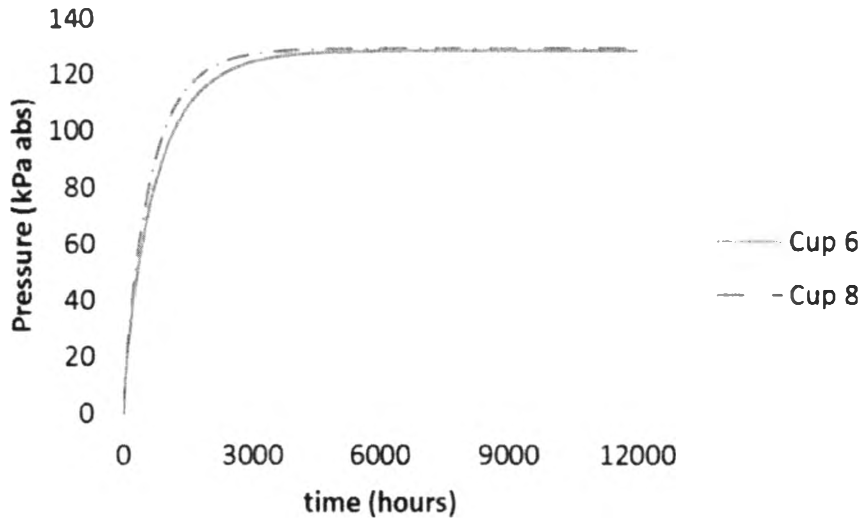

Figure 4.25 Model of hydrogen pressure accumulation inside stainless steel cup 6 and 8.

4.3 Response Time

The response time is also an important factor. After equilibrium or pressure reached steady state, if somethings happen to the system and result in changing in corrosion rate, the device should be able to detect the changing as soon as possible.

In this section, the hydrogen pressure in the carbon steel pipe is changed to half, twice, quarter and 1.5 times of the initial hydrogen pressure in the pipe (5 psig). The hydrogen gas pressure that is changed can be used to refer to the changing in corrosion rate in the plant. This will give an idea of how a real-time process monitor might work.

The prediction of hydrogen pressure rises inside all the cups in case of changing hydrogen pressure in the carbon steel pipe after the steady state was achieved are shown in Figures 4.26 – 4.33 which IHPF is Initial Hydrogen Pressure on the Feeder side.

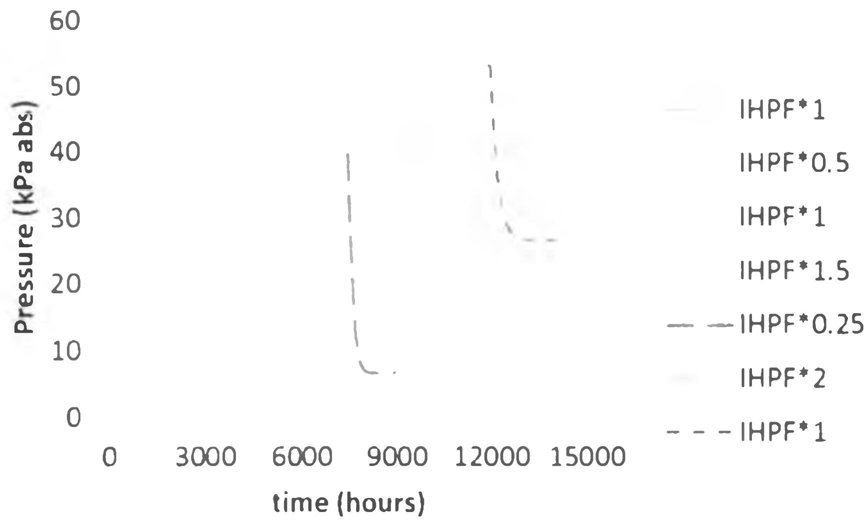

Figure 4.26 Model of hydrogen pressure accumulation inside carbon steel cup 1 when initial hydrogen pressure is changed after steady state was achieved.

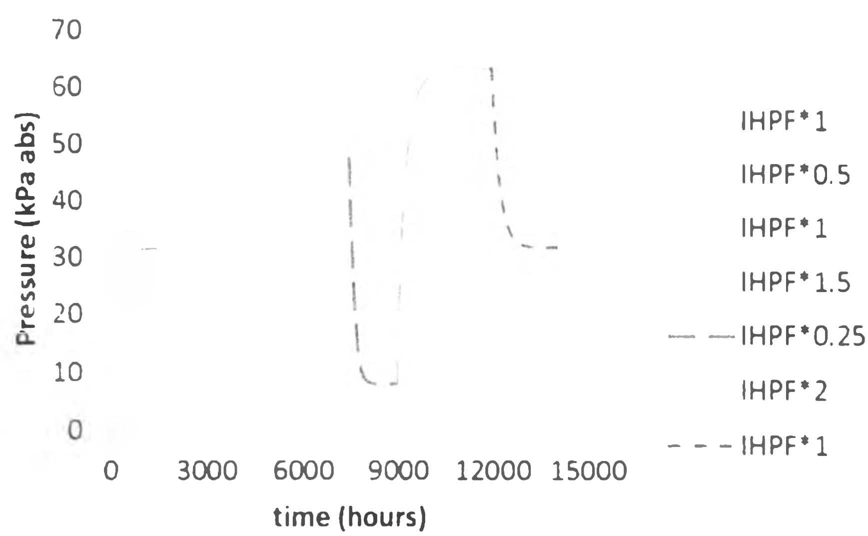

Figure 4.27 Model of hydrogen pressure accumulation inside carbon steel cup 2 when initial hydrogen pressure is changed after steady state was achieved.

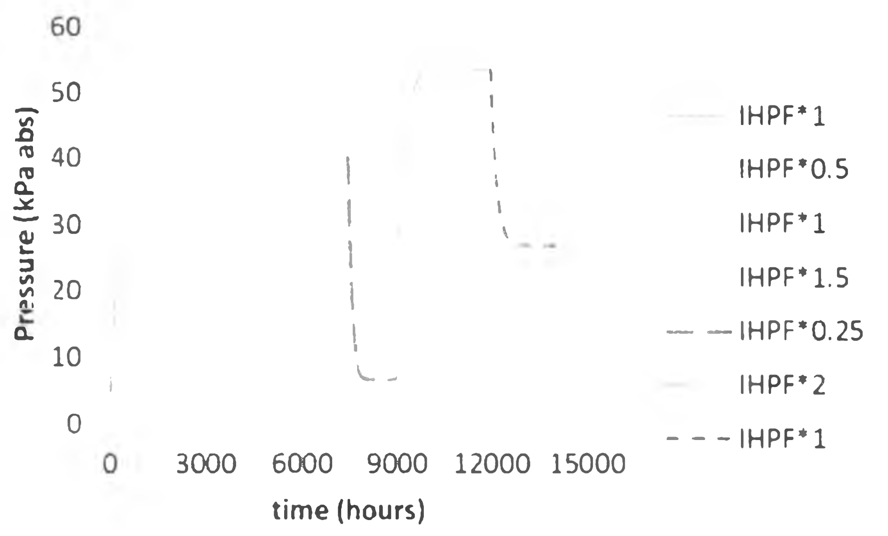

Figure 4.28 Model of hydrogen pressure accumulation inside carbon steel cup 3 when initial hydrogen pressure is changed after steady state was achieved

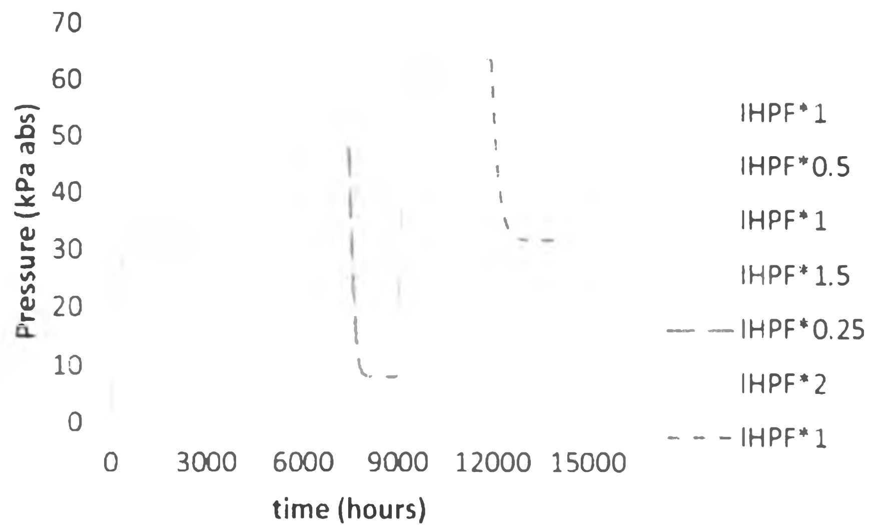

Figure 4.29 Model of hydrogen pressure accumulation inside carbon steel cup 4 when initial hydrogen pressure is changed after steady state was achieved.

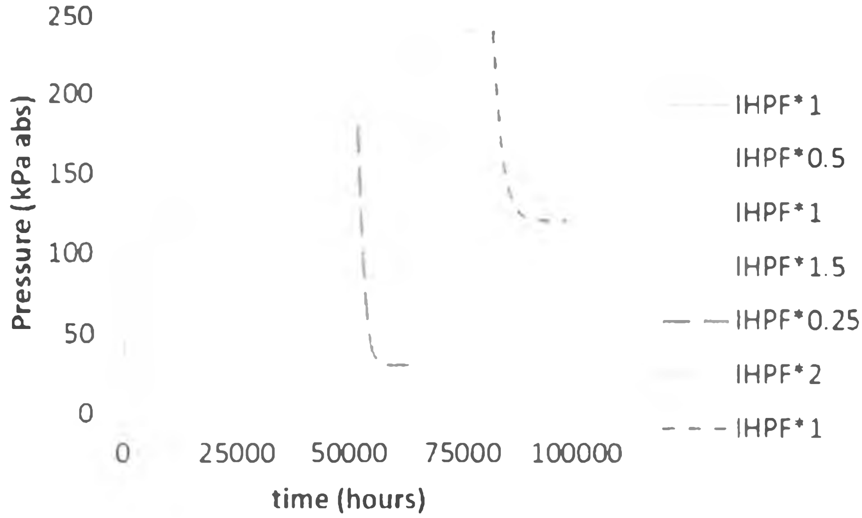

Figure 4.30 Model of hydrogen pressure accumulation inside stainless steel cup 5 when initial hydrogen pressure is changed after steady state was achieved

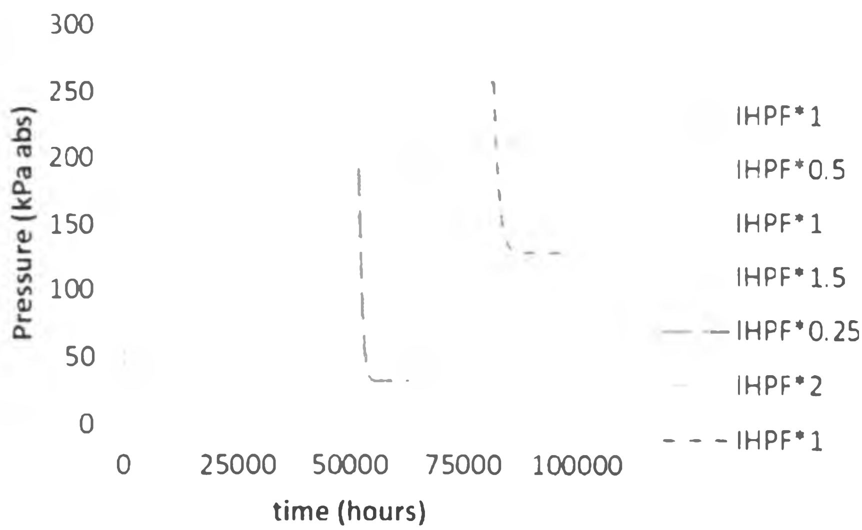

Figure 4.31 Model of hydrogen pressure accumulation inside stainless steel cup 6 when initial hydrogen pressure is changed after steady state was achieved

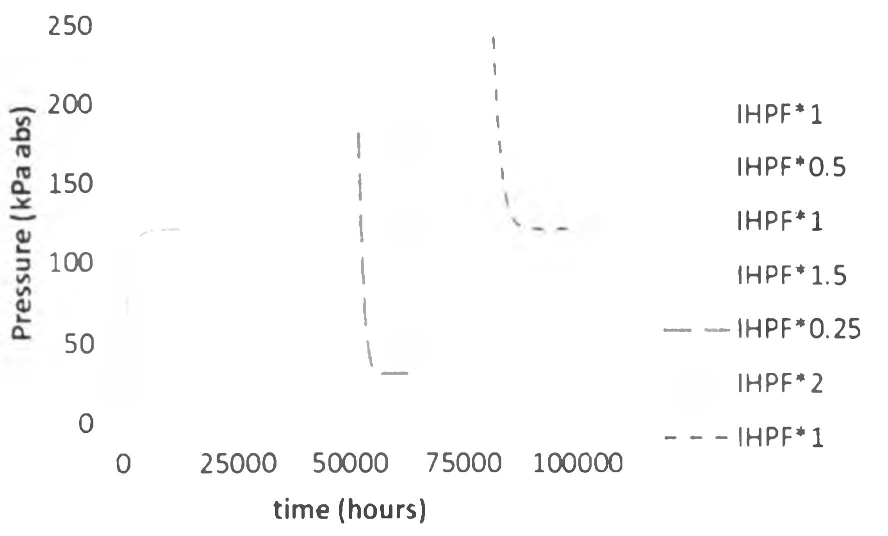

Figure 4.32 Model of hydrogen pressure accumulation inside stainless steel cup 7 when initial hydrogen pressure is changed after steady state was achieved.

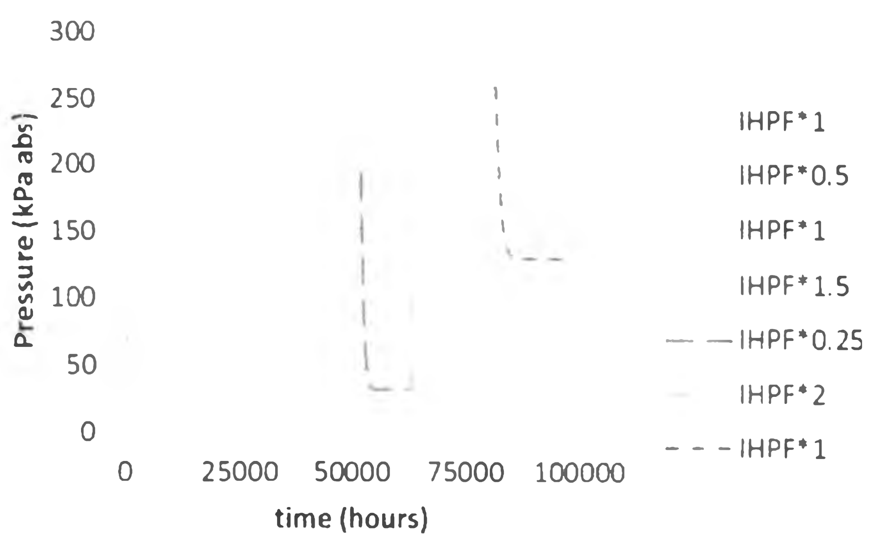

Figure 4.33 Model of hydrogen pressure accumulation inside stainless steel cup 8 when initial hydrogen pressure is changed after steady state was achieved

The results indicated that the initial pressure decreases, the time taken to achieve steady state decreases. The carbon steel cup can respond to the changes faster than the stainless steel cup which means that the carbon steel cup can monitor the changes better than the stainless steel cup. The decrease in size of the cup leads to a shorter response time to observe the changes. Furthermore, the faster detection of changes appears when there is the reduction in wall thickness of carbon steel cup, and the increase in wall thickness of the stainless steel cup.

4.4 Comparison Modelling Results with the Experimental Results

In 2014, Kongvarhodom did an experiment on hydrogen accumulation inside the stainless steel 316 cup at the 6.35 mm outer diameter with a wall thickness of 1.245 mm. The cup was attached on the outer surface of a carbon steel pipe by silver solder with an edge of 0.5 cm. These dimensions of the cup are the same as cup 5 in the first design described in this work. Consequently, to compare the modeling result with the literature experimental result, both results are presented in Figures 4.34.

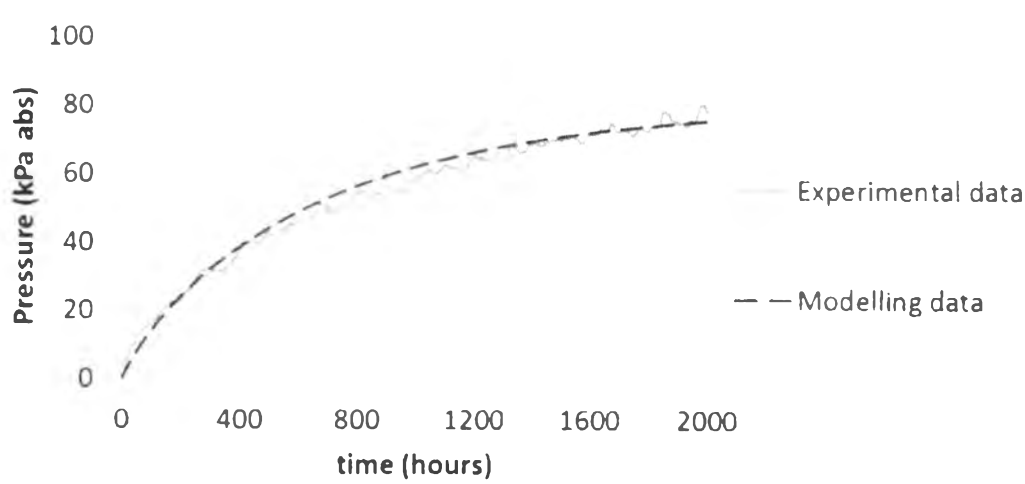

Figure 4.34 Comparison of the results from experiment in thesis of Kongvarhodom (2014) with the result from modelling in this work.

As shown in Figure 4.34, at the same condition, hydrogen accumulation inside the cup predicted from the model agrees well with the experimental result reported in the thesis of Kongvarhodom (2014). However, a small deviation of the modelling and experimental results was found. This may be attributed to the estimate of the width of the hydrogen diffusion path leaving the cup, some parameters are approximate values; the length of silver tubing outside and inside the furnace, the length of silver solder, and furnace temperature: and also the assumptions made for the model: no hydrogen diffusion through silver tubing, fitting, pressure transducer, tee, and valve, no hydrogen diffusion through the top and corner of the cup, and half of hydrogen that go to the edge of cup comes into the cup.