

CHAPTER IV

RESULTS AND DISCUSSIONS

The results of this research will be reported into 2 parts, as follows:

1) The findings of the appearances on surface of the corroded Al and CS specimens were carried out to identify forms of corrosion that taken place. The results were identified by visual observation, photographs of the specimens after immersion in corrosive solution, and by investigation of the corroded surfaces under the SEM operations, micrographs with magnification of x 60 to x 600. Such micrographs could show characteristics of corrosion produced by various corrosive solutions, such as CH₃OH + DMM, CH₃OH + DMM + HCl, CH₃OH + HCl, PE + HCl, PE + DMM + HCl, etc., in detail.

2) The effects of various factors, such as the exposure temperature, concentration of DMM in corrosive solution, etc., on corrosion rates(C.R.) of the corroded Al and CS specimens were analyzed. The corrosion rates were calculated in 2 system units; milligrams/sq. decimetre/ day, mdd, and mils/year, mpy, (1 mil = 1/1000 inch).

On reporting, the corrosion results obtained by the other corrosive medias, such as H₂O, HCl in H₂O, Hg in cyclohexane were also reported in comparison to that obtained by the interested corrosive solutions. Such comparison would provide results to support others.

Identification of Forms of Corrosion on Al and CS Specimens

Calculation of corrosion rate in section 4.2 appeared that the corrosion rate of CS specimens was somewhat low in comparison to that of the Al specimens, which its corrosion rate was high. Such a low corrosion rate of CS specimens was obviously leading to incorrect conclusion, therefore it was better to examine the characteristics of the appearances on those surfaces together with the corrosion rates. Agreement on both corrosion rates and characteristics on corroded surface would make the experimental results more correctly. Findings of corrosion forms were identified by visual observation on Al and CS specimens, photographs and by photomicrographs of those specimens with magnification of x 60 to x 600 on SEM

1. Compositions of Tested Specimen

Because the ability to resist corrosion of each elements is not the same, therefore, various compositions of the specimens should be examined. Awareness of those compositions will make discussion of corrosion result in subsection easier. Table 4.1 shows those compositions of carbon steel specimens used in the test. Both kind of specimens were analysed compositions by the vacuum spectrometer.

Tested specimen shown in table 4.2 had aluminium 98.231 %. The remaining compositions were exhibited higher % weight of Mg and Si than the others, then this aluminium should be combined to series 6xxx, but it was surprising why there was high elemental iron in it.

Table 4.1 Various compositions of carbon steel tested specimen

Element	symbol	% weight Test specimen	Commercial std.specimen
Iron	Fe	# 1	# 2
Carbon	C	0.208	0.061
Silicon	Si	0.203	
Manganese	Mn	1.275	0.291
Phosphorus	P	0.016.0.001	
Sulphur	S	0.020	0.012
Copper	Cu	0.321	0.053
Nikel	Ni	0.085	0.026
Chromium	Cr	0.102	0.037
Molybdenum	Mo	0.003	0.005
Aluminium	Al	0.001	0.001
Titanium	Ti	0.003	0.002
Tin	Sn	0.015	
Lead	Pb	0.006	0.001
Vanadium	V		

Table 4.2 Various composition of aluminium tested specimen

Element	symbol	% weight
Aluminium	Al	# 1
Silicon	Si	0.361
Iron	Fe	0.581
Copper	Cu	0.118
Titanium	Ti	0.015
Manganese	Mn	0.057
Magnesium	Mg	0.523
Nickel	Ni	0.010
Zinc	Zn	0.078
Chromium	Cr	0.016
Lead	Pb	0.010

2. Surface Preparation of Al and CS Specimens Before Testing

Surface preparation of metal specimen as mentioned in chapter 3 included finishing with No.120 abrasive paper and degreasing with mixture of 1:1 methanol to ether. The appearances on the CS and Al specimen surfaces were shown in Figure 4.1 and 4.2 respectively. Both kinds of metal surfaces revealed their smooth and polished surfaces, whereas the photomicrographs of CS specimen surface were shown in Figures 4.3 and 4.4 as well as Figure 4.5 showing that of Al specimens. A lot of scratches rubbed by sand on abrasive paper were appeared on surface of CS specimens scanned by SEM. Small black pits on the surface shown on photomicrograph were not valuable to pay attention to because they were resulted from impacts on each other during scrubbing process

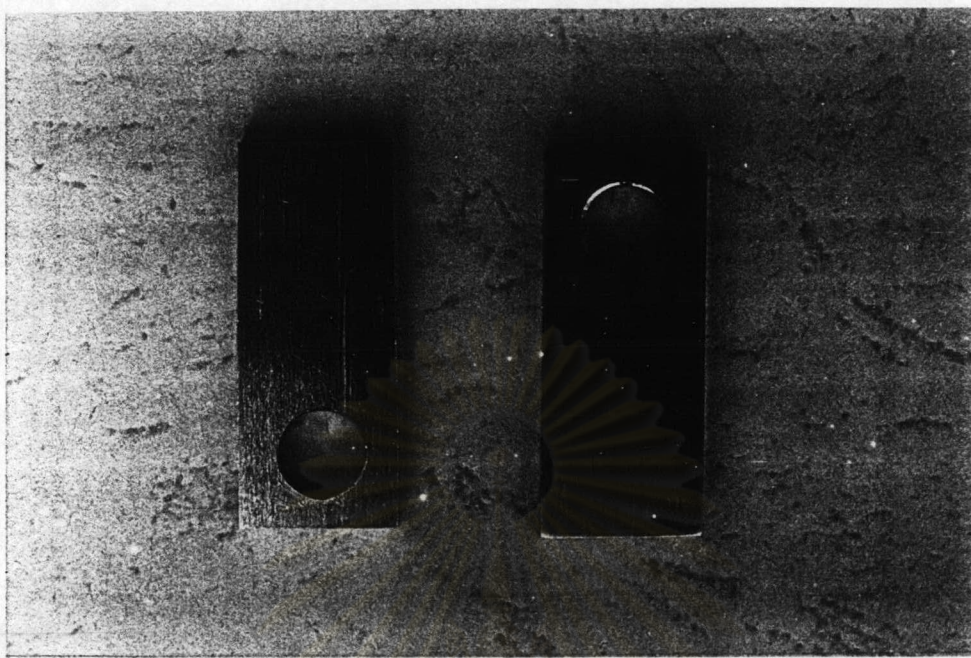


Figure 4.1 The finished surface of CS specimens



Figure 4.2 The finished surface of Al specimens



Figure 4.3 SEM photograph showing the finished surface of CS specimens



Figure 4.4 SEM photograph with magnification of 600 x showing the same surface as that in Figure 4.3



Figure 4.5 SEM photograph with magnification of 60 x showing surface of Al specimen

3. Surface structure of the CS and Al specimens after exposure test

For the same type of specimen, various corrosive solutions gave different corrosion results, meaning both the surface appearances and corrosive rates. On the other hand, if it was the same corrosive solution, the different corrosion results obtained were based upon various metals. Almost all corrosive solution systems provided more corrosion rates on Al specimens than on carbon steel. Among the corrosive solution systems, the $\text{CH}_3\text{OH}+\text{HCl}+\text{DMM}$ solution was the most interesting because it caused severe corrosive reaction, whereas the corresponding solutions of PE showed a little corrosion on the specimens.

3.1 Surface appearances of CS specimens after exposure test

Before reporting appearances of the CS specimen corroded by the DMM solution, the corrosion results obtained by other corrosive medias, such as H₂O, H₂O+HCl and Hg in cyclohexane needed to be discussed first to distinguish how important DMM was to the system. The table below organized photographs and photomicrographs showing the corrosive results corroded by these medias.

Table 4.3 Details of Figures 4.6-4.13 for carbon steel corrosion discussion

Corrosive solutions and conditions for exposure tests	visual observations	Photomicrographs from SEM
1. distilled water(H ₂ O), ambient temperature	Figure 4.6	Figure 4.7 (60x)
2. H ₂ O+HCl 150 ppm solution, ambient temperature.	Figure 4.8	Figure 4.9 (60x) Figure 4.10(600x)
3. Hg in cyclohexane, Temperature 50°C	Figure 4.11	Figure 4.12 (60x) Figure 4.13(600x)

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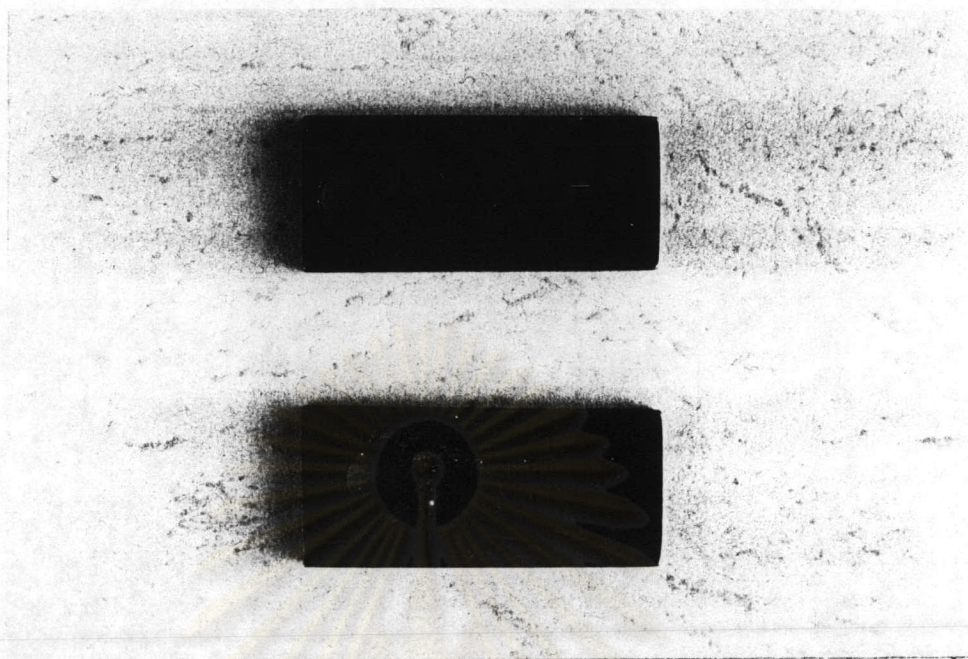


Figure 4.6 Photograph showing surface of CS specimens immersed in distilled H₂O for 662 h. at ambient temperature

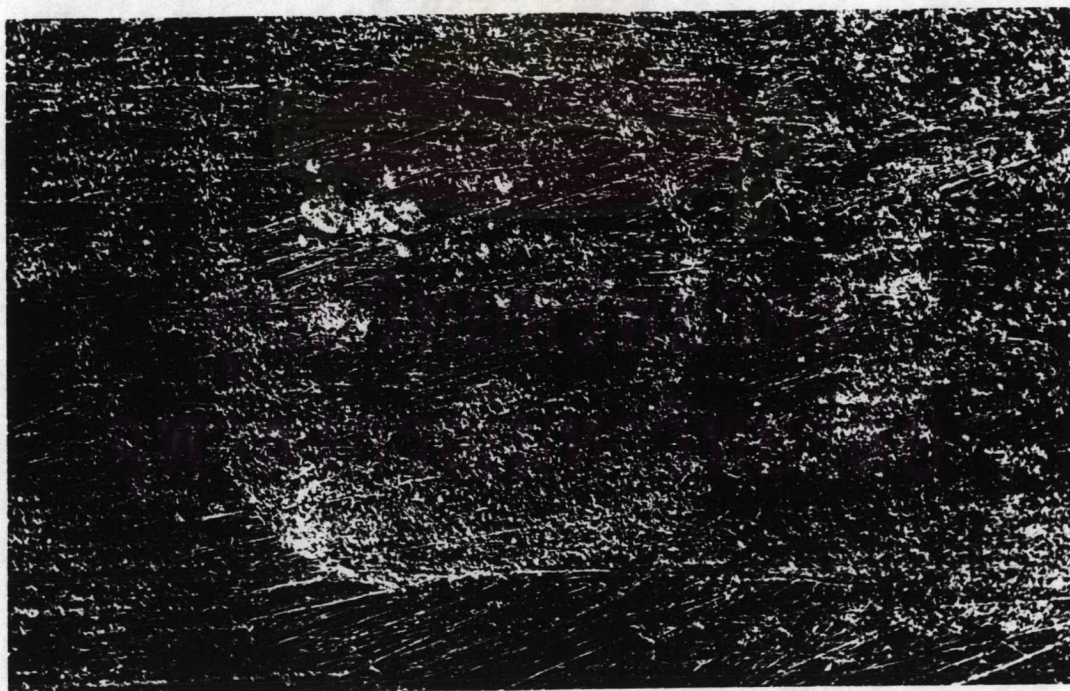


Figure 4.7 SEM photograph with magnification(60x) showing the same surface as that shown in Figure 4.6

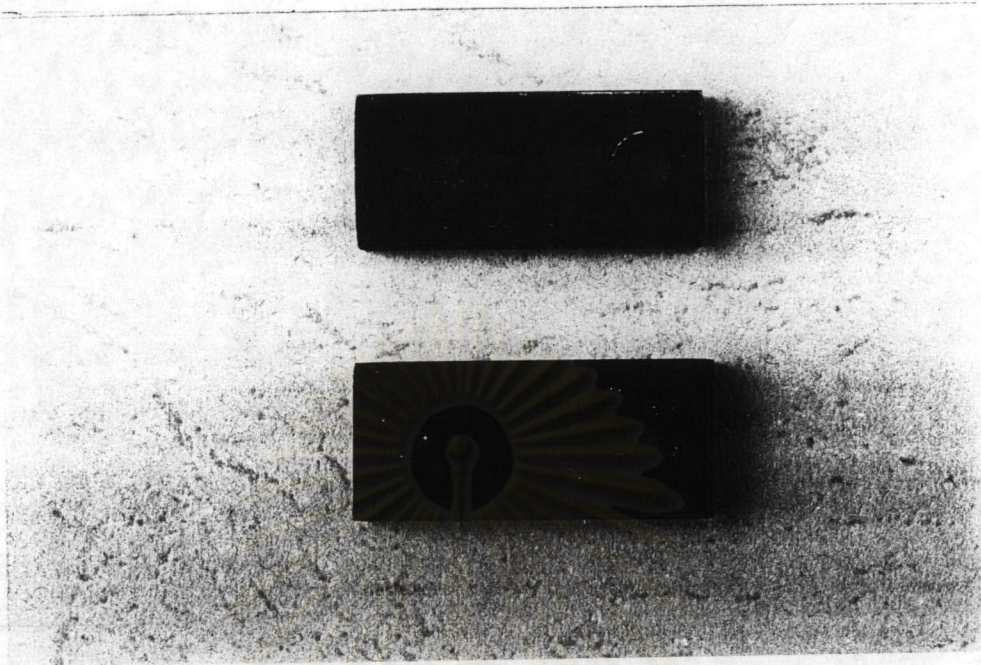


Figure 4.8 Photograph showing surface of the specimens immersed in the $\text{H}_2\text{O}+\text{HCl}$ 150 ppm solution for 662 h. at ambient temperature.

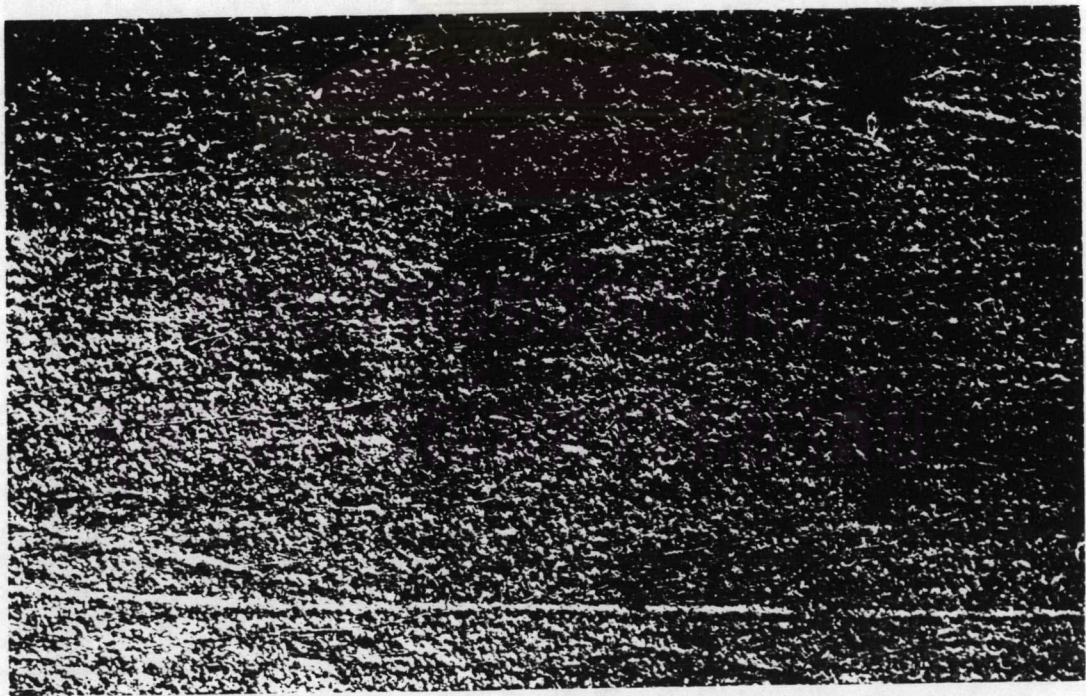


Figure 4.9 SEM photograph with magnification of x60 showing the detail of the corroded surface shown in Figure 4.8

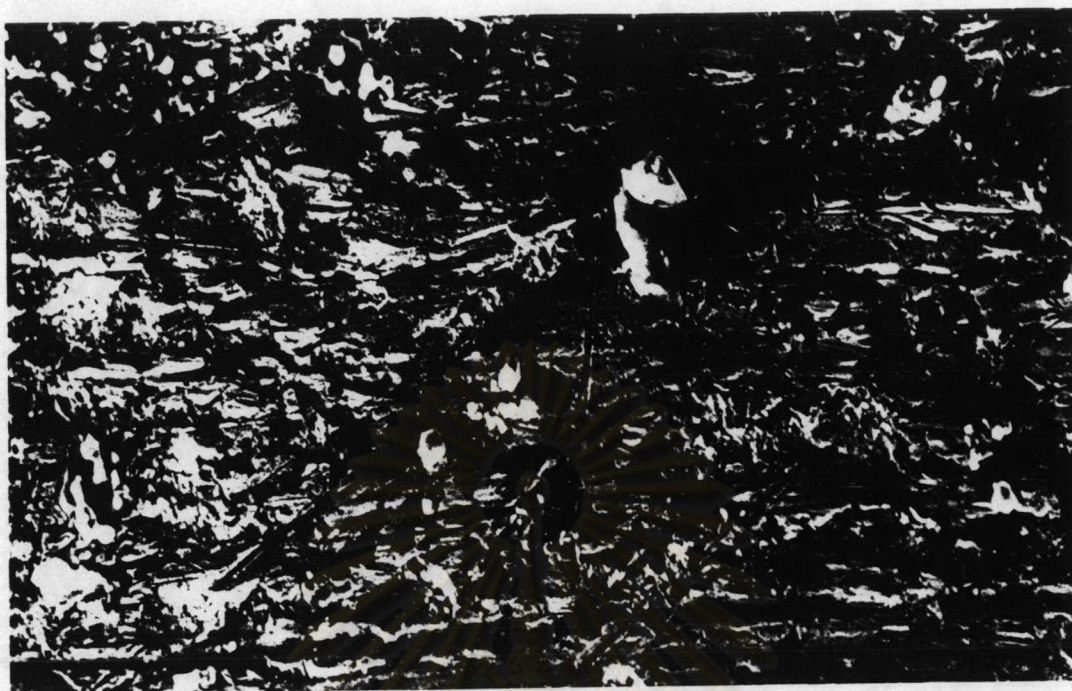


Figure 4.10 SEM photograph magnified x600, showing the appearance of the same corroded surface as that in Fig. 4.8-4.9



Figure 4.11 Photograph showing the corroded surface of CS specimen immersed in Hg-cyclohexane solution for 916.5 h. at 50°C



Figure 4.12 SEM photograph magnified x60, showing the characteristics of the same surface as that shown in Fig 4.11

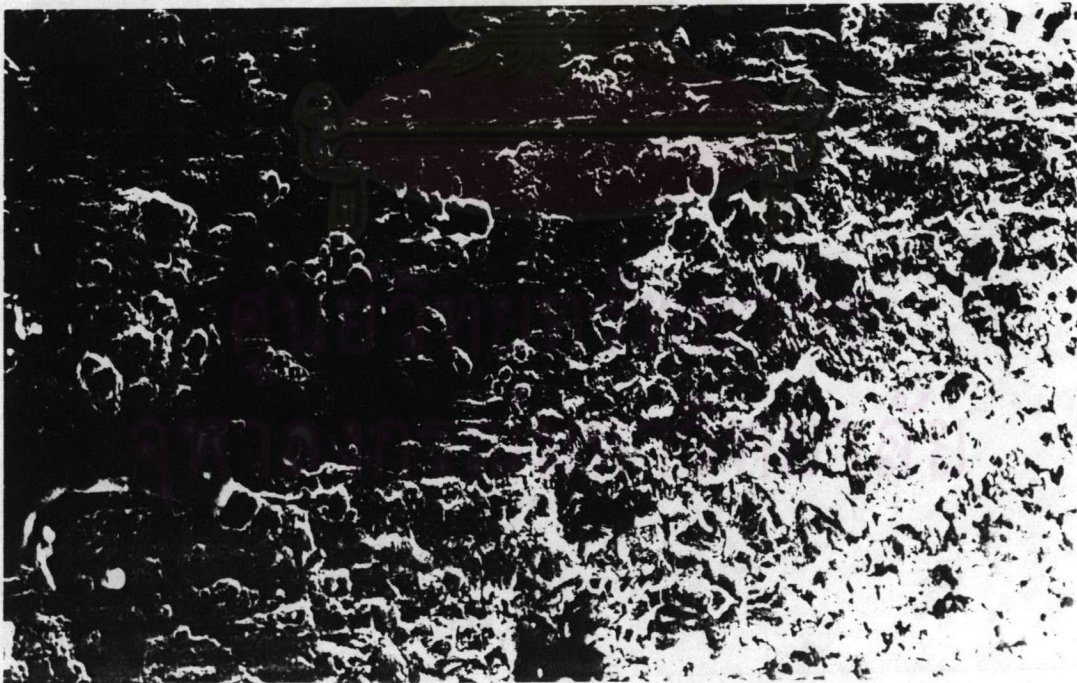


Figure 4.13 SEM photograph magnified x600, showing the porous surface of the same surface as those shown in Fig. 4.11-4.12

As can be considered the appearances on surface of the CS specimens corroded by distilled H₂O in Figure 4.6, it appeared a lot of smudges over the whole surface area, whereas its photomicrograph (60x) in Fig. 4.7 showed clearly that the appearances on the surface was uniform corrosion. Figure 4.8 showed the corroded surface exposed in the H₂O+HCl 150 ppm solution and Fig. 4.9-4.10 were its photomicrographs which scanned under magnification of x60 and x600 respectively. It was found that the appearance on the surface was also uniform corrosion but its penetration rate seemed to be very low. It was believed that because HCl concentration, 150 ppm, was too low to strongly attack, and the specimens themselves had high corrosive resistant due to chromium existed(see table 4.1)

From the Figure 4.11-4.13, the specimen surface was obviously corroded over wide area, white basin in Fig. 4.12. The characteristics of corrosion was also uniform corrosion.

As mentioned early, DMM was the interested corrosive media in this research. Then, it was desired to investigate corrosion results affected by DMM. Absolute CH₃OH and PE were chosen to dilute DMM, because both of them could dissolve DMM very well[22]. Before the characteristics of corrosion resulted from the DMM solution were identified, it was necessary to know how both solvents corroded the specimens, which these were assigned as blank tests. Fig. 4.14-4.15 showed surface of CS specimens immersed in absolute CH₃OH for 977 h. at 70°C. It was found by observing, see Fig. 4.15, that it appeared a little corrosion on right hand side below, the remaining area was still usual. The reason was scratches caused by abrasive paper. Table in appendix I showed that its weight loss was about 2 mg only.

Table 4.4 Details of Figures 4.14-4.32 for carbon steel corrosion discussion

corrosive solutions and condition for the exposure tests	visual observations	Photomicrograph from SEM
1. Pure absolute CH ₃ OH, at 70°C	Figure 4.14	Figure 4.15 (x60)
2. Pure petroleum ether, at 70°C	Figure 4.16	Figure 4.17 (x60)
3. Solution of abs. CH ₃ OH+DMM 150 ppm, 50°C	Figure 4.18	Figure 4.19 (x600) Figure 4.20 (x1000)
4. Solution of PE+DMM 150 ppm, at 50°C	Figure 4.21	Figure 4.22 (x60) Figure 4.23 (x600)
5. Solution of CH ₃ OH+DMM 150 ppm, at 50°C	Figure 4.24	Figure 4.25 (x60) Figure 4.26 (x600)
6. Solution of abs. CH ₃ OH+HCl 150 ppm, at 70°C	Figure 4.27	Figure 4.28 (x60)
7. Solution of PE+DMM 150 ppm+HCl 150 ppm, at 70°C	Figure 4.29	Figure 4.30 (x600)
8. Solution of PE+HCl 150 ppm, at 70°C	Figure 4.31	Figure 4.32 (x60)

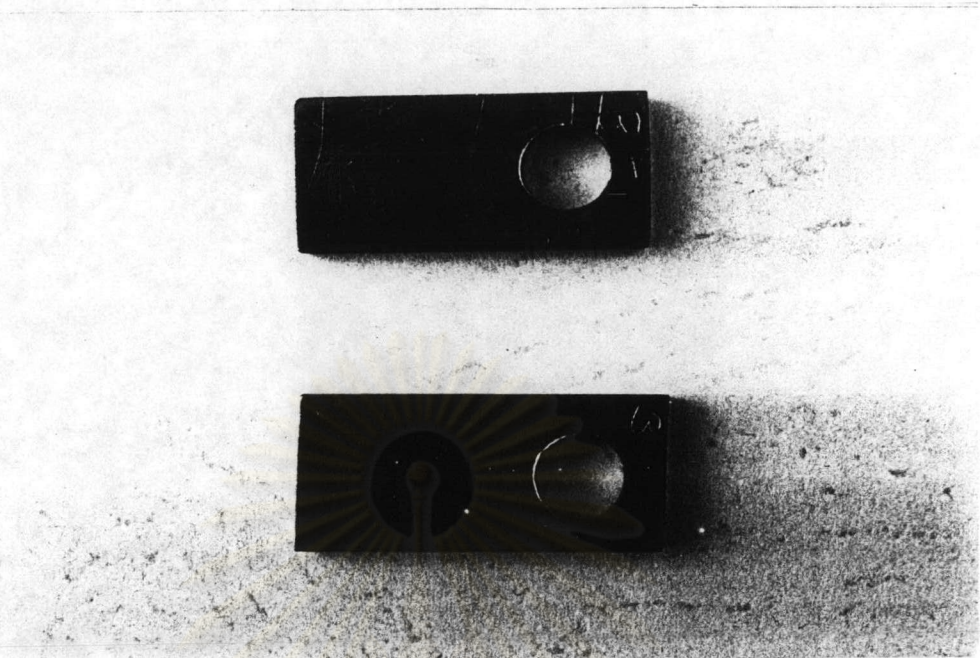


Figure 4.14 Photograph of the CS specimens immersed in pure absolute CH_3OH for 977 hr at 70°C .



Figure 4.15 SEM photograph magnified x60 showing the same surface as that in Figure 4.14

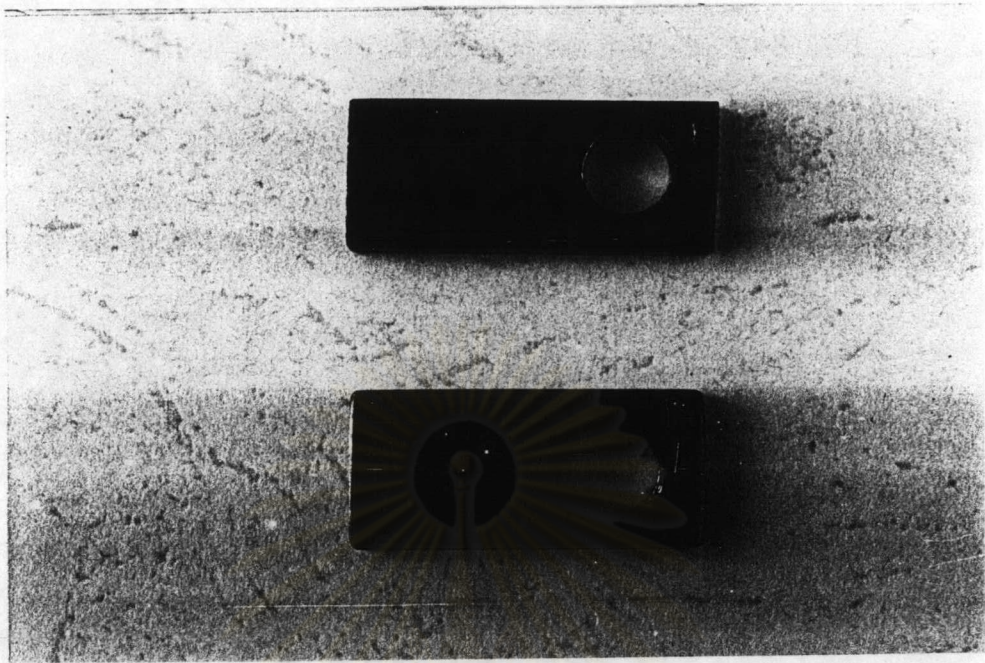


Figure 4.16 Photograph of the specimens exposed in pure PE for 977 h. at 70°C, as blank test.

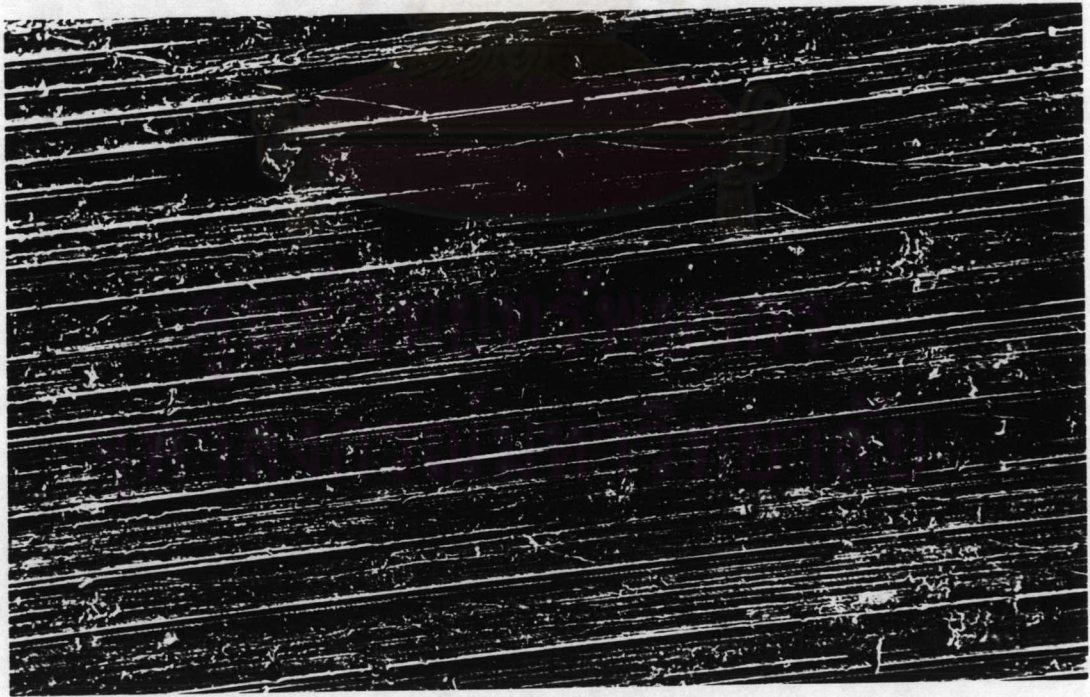


Figure 4.17 SEM photograph with magnification of 60 x showing the same surface as that in Fig 4.16

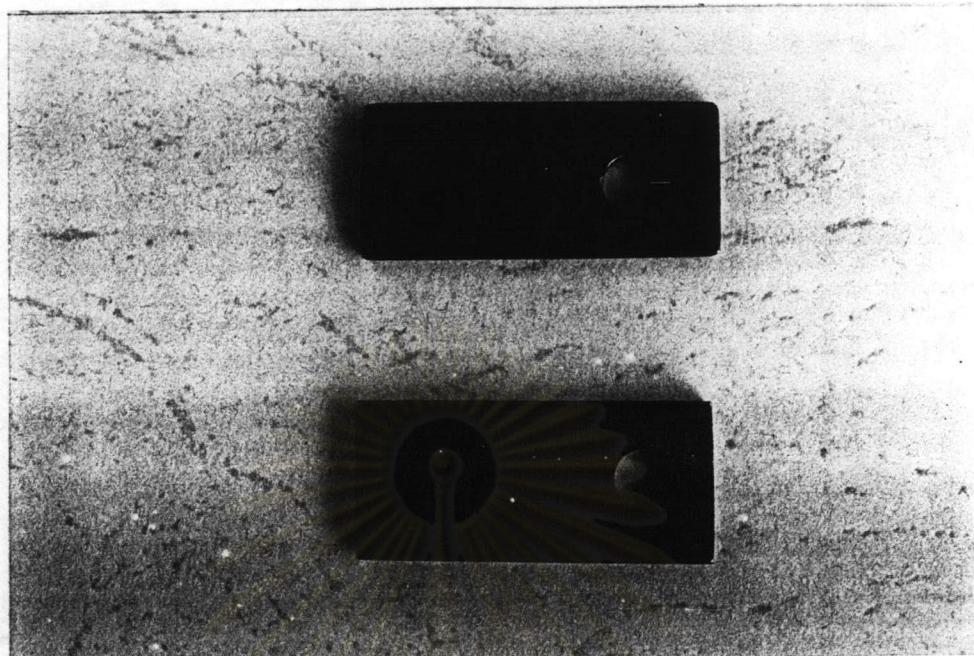


Figure 4.18 Photograph showing the corroded surface of the specimens immersed in the abs. CH_3OH +150 ppm DMM solution for 1024 h. at 50°C



Figure 4.19 SEM photograph with magnification of x600 showing the same corroded surface as that in Fig 4.18



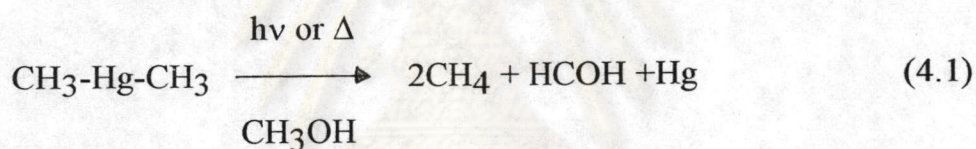
Figure 4.20 SEM photograph magnified x1000, showing the same corroded surface as those shown in Fig 4.18-4.19

Absolute CH_3OH could corrode the carbon steel specimens very slow, its corrosion rates in section 4.2 were low, mdd. It was believed that O_2 and H_2O existing less than 0.003 % in absolute CH_3OH resulted in corrosion on the CS specimen. If CH_3OH was an corrosive agent, the corrosion result should be much higher because the amount of CH_3OH was much more than H_2O . The same CH_3OH results also appeared with the specimens exposed in pure PE for 977 h. at 70°C . This means that PE solution could corrode specimen less than CH_3OH solution. The reason was there was no H_2O , in PE. Fig 4.16-4.17 showed that no corroded appearance was found because its surface did not differ from that before testing. Thus, it was appropriate to use as the solvent.

For the appearances on photomicrograph in Fig 4.19 in comparison to that in Fig 4.15, it was clear from these figures that DMM dissolved in absolute CH_3OH could corrode the CS specimen. The

appearances of corrosion in Fig 4.20 included a lot of small pores distributed uniformly over the whole surface area of the specimen. The appearances were more similar to that obtained by elemental Hg solution. It could be concluded that DMM must be a corrosive agent for this solution certainly.

For organomercury, such as DMM, dissolved in alcohols, which are high polar solvents, its C-Hg bond is weak to break. The activated energy for bond cleavage of DMM is only about 58 kcal/mol [18] and this bond can be broken either by photolysis or by thermal dissociation [17]. In the case of bond cleavage by pyrolysing of DMM in the presence of a hydrogen donor, such as CH₃OH [15]. The reaction is as follow



The elemental Hg occurred can continue reacting with the specimen, that is the starting point of corrosion

The appearances of the corroded surface in Figure 4.22-4.23 seemed to be uniform corrosion and the characteristics of the appearance were similar to that of specimens corroded by elemental Hg. In this study, the thermal reaction must be occurred very little because temperature was low (70°C), and the thermal dissociation temperature should be about 200°C[17]. In the next section, corrosion rates in mdd and mpy were reported to support this answer.

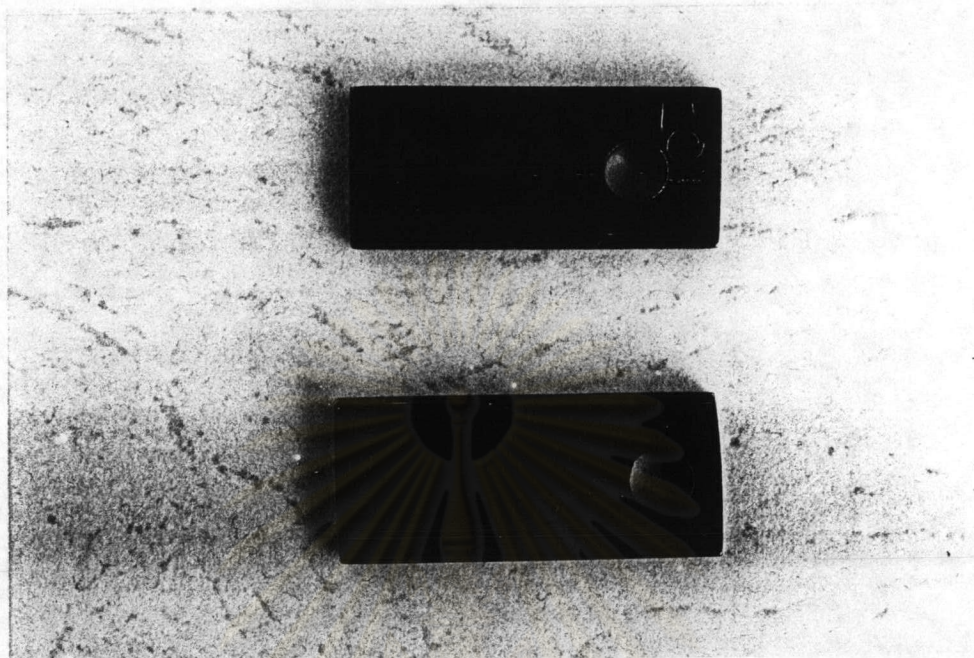


Figure 4.21 Photograph showing the corroded surface of specimens exposed in the PE+150 ppm DMM solution for 1024 h. at 50°C



Figure 4.22 SEM photograph magnified x60 of the same surface as that in Fig 4.21



Figure 4.23 SEM photograph magnified x600 showing same surface of specimen as those shown in Figures 4.21-4.22



Figure 4.24 Photograph showing the specimen surface immersed in the $\text{CH}_3\text{OH}+150$ ppm DMM +150 ppm HCl solution for 1024 h. at 50°C



Figure 4.25 SEM photograph magnified x60 showing the appearance on the same surface as that in Fig 4.24

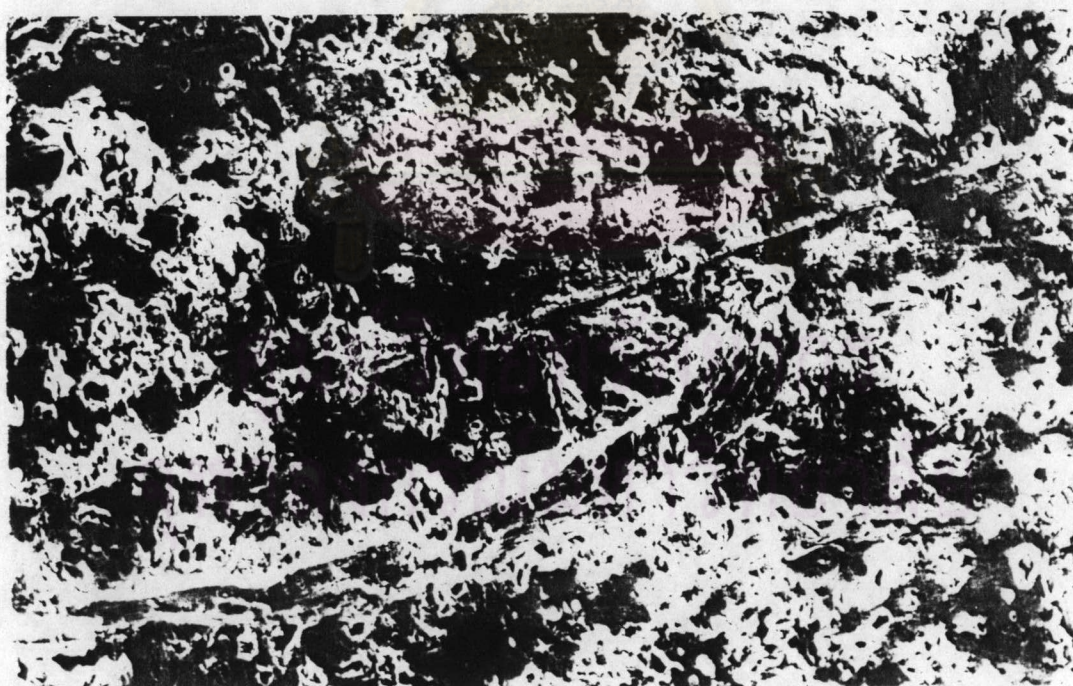


Figure 4.26 SEM photograph with mag. x600 showing the appearance on the same surface as those shown in Figures 4.24-4.25

Figures 4.24-4.26 showed corrosion results of the CS specimens that exposed in the absolute $\text{CH}_3\text{OH}+150$ ppm DMM+150 ppm HCl solution. It was appeared that the corrosion reaction was taken place by this corrosive solution system more severely than every previous systems. The results of corrosion-rate calculation (listed in the appendix III) showed that the result of adding 150 ppm HCl into the $\text{CH}_3\text{OH}+150$ ppm DDM solution increased its corrosion rate about 10 times. The appearance on the specimen surface composed of a lot of small pits distributed uniformly on the whole surface area. The corrosion of small pits tended to be expanded more by width than by depth, it was then expected that they would developed to the form of uniform corrosion finally. This corrosion appearance was similar to that of specimen in Fig 4.20 which was corroded by DMM.

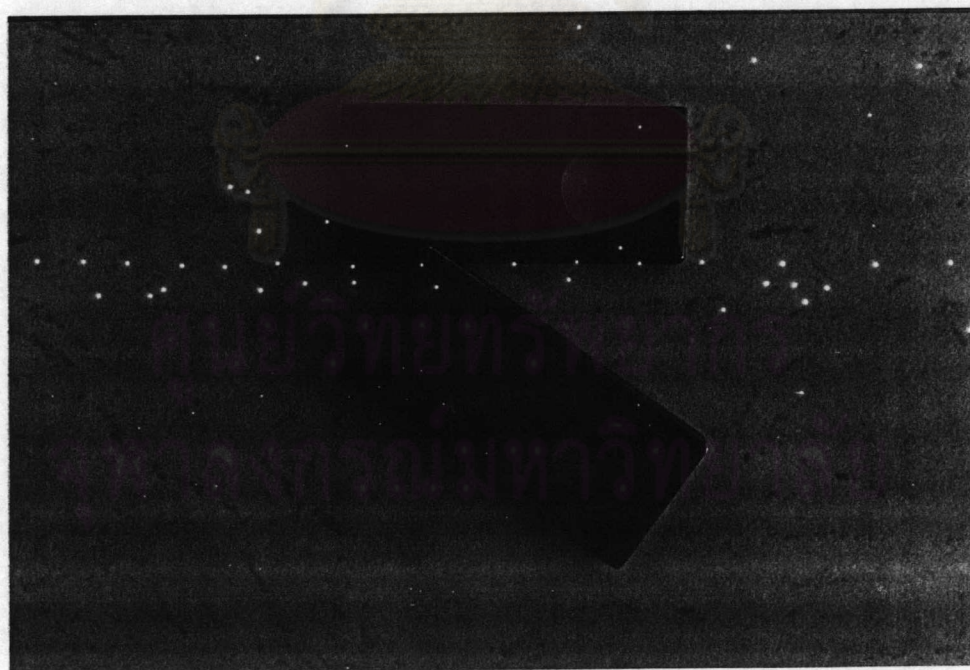


Figure 4.27 Photograph of the carbon steel specimen immersed in the absolute $\text{CH}_3\text{OH}+150$ ppm HCl solution for 978 h. at 70°C

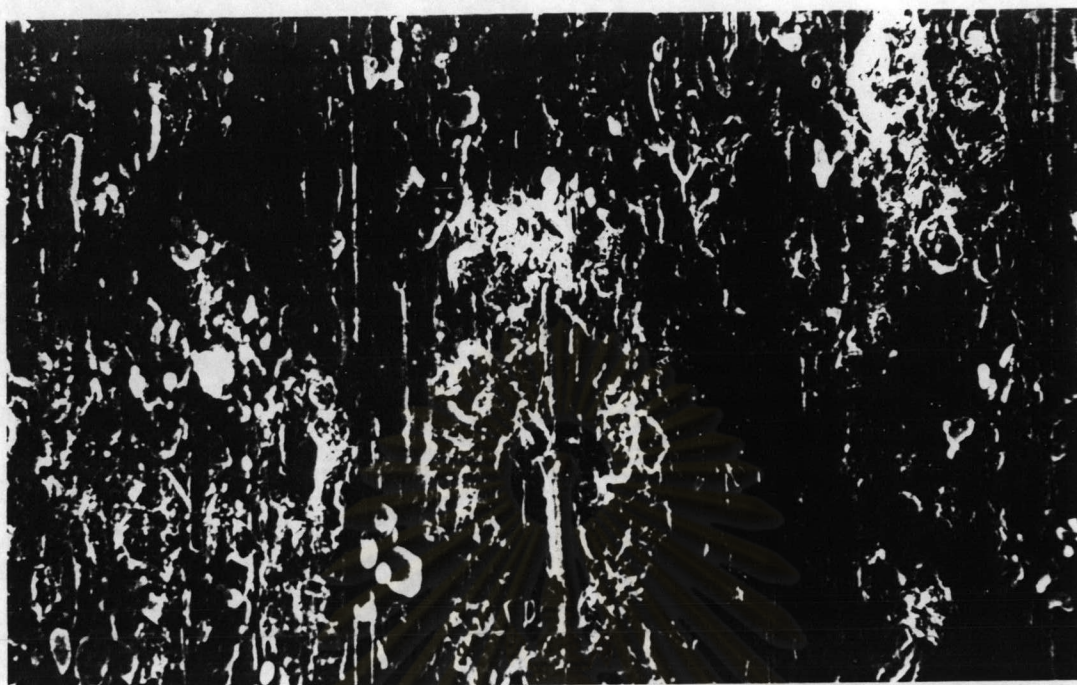
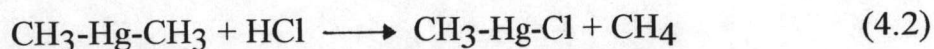


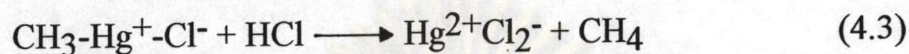
Figure 4.28 SEM photograph with mag. x60 showing the same corroded surface as that shown in Fig 4.27

The appearance on the corroded surface of specimen in Fig 4.27-4.28 were identified to be in the form of uniform corrosion because the surfaces were corroded over the whole surface area and it seemed to be a lot of small pores distributed uniformly on the surface, without large pores developed at any position. The corrosion rate of CS specimen corroded by the $\text{CH}_3\text{OH}+150$ ppm HCl solution was low with relative to that corroded by $\text{CH}_3\text{OH}+150$ ppm DMM+150 ppm HCl solution. For example, the corrosion rate of the former system was about 8.39 mdd at 70°C , but the latter was about 12.04 mdd at the same temperature, which it was clear that the $\text{CH}_3\text{OH}+\text{DMM}+\text{HCl}$ solution could corrode the CS specimen about 1.5 times higher than the $\text{CH}_3\text{OH}+\text{DMM}$ solution

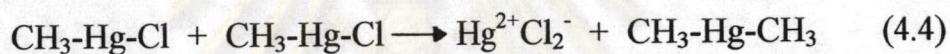
In addition to photolysis and thermal dissociation, the C-Hg bond cleavage of DMM in any solvents might be accomplished by reacting with acid. Coincidentally the experimental results of Dessey and Kim [19] showed that HCl underwent to do that according to the following reactions



If a vigorous condition, higher acid concentration, was existed, the following reaction could also be accomplished;



The condition with both heat (70°C) and acid may be even stronger to drive the above reaction to occur[15]. Another route of reaction for producing $\text{Hg}^{2+}\text{Cl}_2^-$ is the following reversible reaction[15]:



Both reactions (4.3) and (4.4) provide $\text{Hg}^{2+}\text{Cl}_2^-$, which is also the severe corrosive agent [22] and well soluble in both H_2O and CH_3OH . That is, HgCl_2 was considered to be a cause of corrosion in this test

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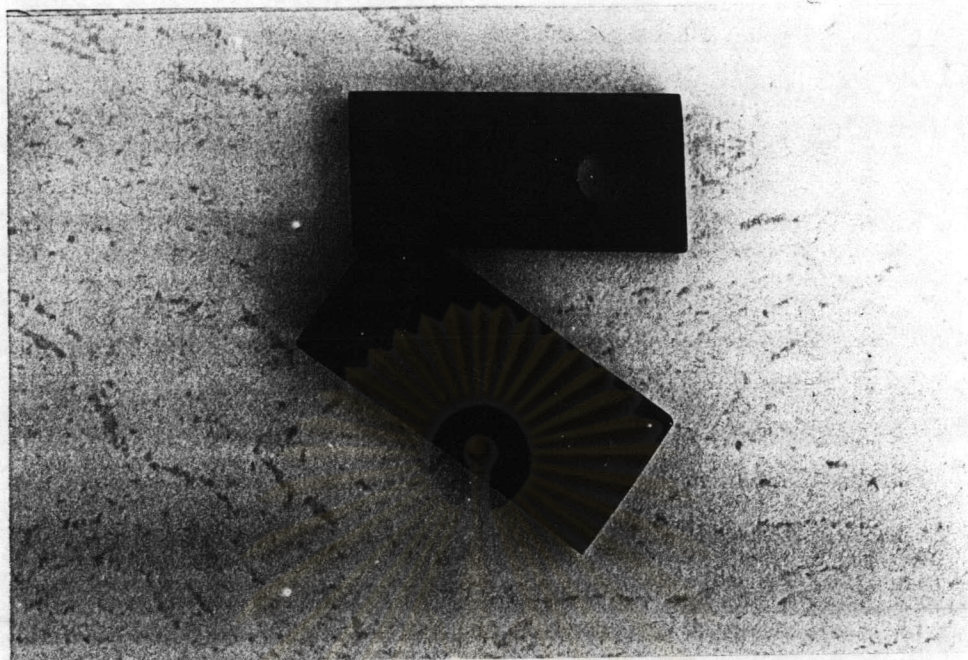


Figure 4.29 Photograph showing the corroded surface immersed in the PE+150 ppm DDM+150 ppm HCl solution for 978 h. at 70°C.

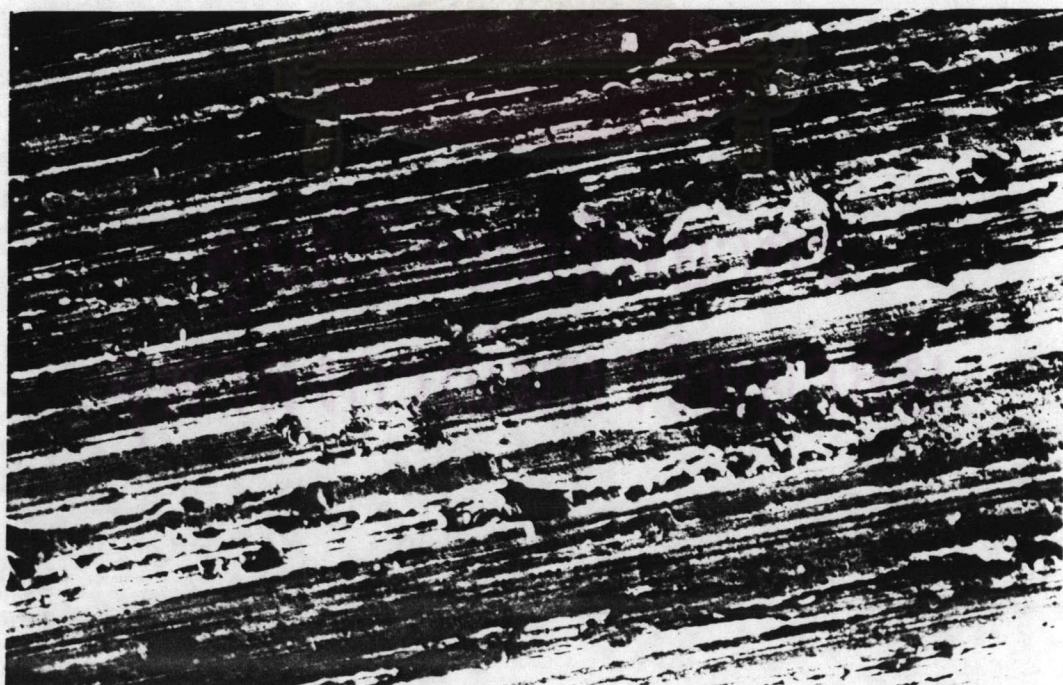


Figure 4.30 SEM photograph with mag.x600 showing the appearance on the same surface as that in Fig 4.29



Figure 4.31 Photograph showing surface of the corroded specimens immersed in the solution of PE+150 ppm HCl as a blank solution, for 978 h. at 70°C



Figure 4.32 SEM photograph with magnification of x60 showing the appearance on the same surface as that in Fig 4.31

It was found that, see fig 4.30, the corrosion of CS specimen immersed in the PE+150 ppm DMM+150 ppm HCl solution was very low which its C.R. value was about 3.45 mdd at 70°C after exposure for 978 h., and that the appearance was difficult to identify the form of corrosion. However, it should not be pitting because the corrosion did not grow at any point. Furthermore, if this corrosion result was compared to that corroded by the PE+150 ppm HCl solution at the same temperature, it was found that the latter system showed higher value of C.R. The C.R. of the PE+DMM+HCl system calculated and put in the appendix was about 4.42 mdd at 70°C. It indicated that adding HCl into the PE+DMM solution system was not significant.

It was also observed during the experiment that acid HCl could dissolve in PE very poorly. The small yellow droplet of HCl was seen on the bottom of volumetric flask. The little solubility of HCl in PE made its reaction with DMM difficult. As a result, HgCl_2 generated was too low to corrode the specimen, which was the reason why the corrosion by the PE solution was so small

3.2 Surface Appearance of Aluminium Specimens after Test

The corrosive solution systems were divided into 3 groups as follow;

- 1) Reference corrosive solutions such as H_2O , $\text{H}_2\text{O}+150$ ppm HCl, and Hg in cyclohexane
- 2) Interested corrosive solutions prepared by dissolving DMM into absolute CH_3OH and PE
- 3) Advanced corrosive solution which were solutions in group no.2 added HCl.

Another reason to choose PE as solvent was that, PE is hydrocarbon like natural gas, which organomercury can be dissolved in

metal which had somewhat lower corrosion resistance than the others. Table 4.5 Figure list for CS corrosion discussion

Group 1 was carried out as indicated in table 3.5. The corrosion appearance of Al specimen immersed in H₂O, H₂O+HCl, and elemental Hg in cyclohexane were shown in Figures 4.33-4.38.

Table 4.5 Details of Figures 4.33-4.38 for Al corrosion discussion

Corrosive solutions and conditions for the test	visual observations	Photomicrogras from SEM
1. Distilled water, at 50°C, for 890 hr	Figure 4.33	Figure 4.34 (X60)
2. H ₂ O+HCl 150 ppm acid solution, at 50°C, for 890 hr	Figure 4.35	Figure 4.36 (x60)
3. Saturated Hg-in-cyclohexane solution, at 50°C, for 891 hr	Figure 4.37	Figure 4.38 (x60)

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Figure 4.33 Photograph showing the corroded Al specimen immersed in the distilled H₂O at 50°C for 890 h.

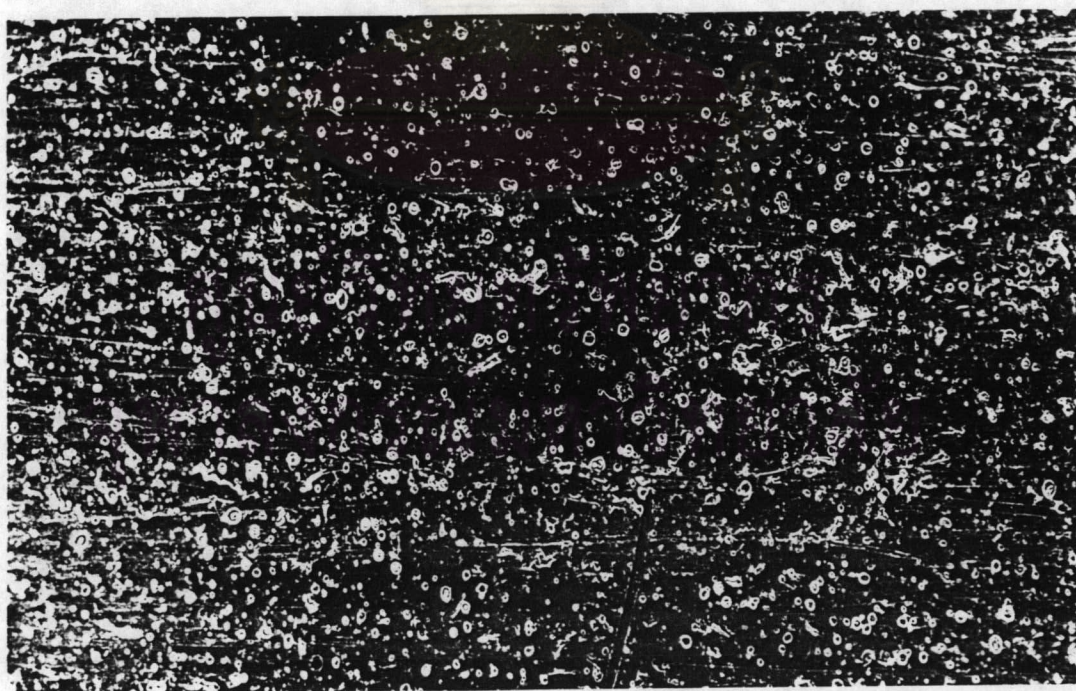
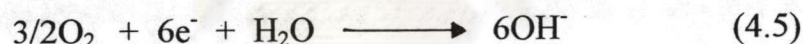
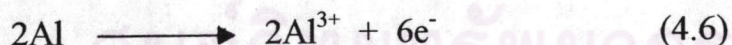


Figure 4.34 SEM photograph showing the appearance on the same corroded surface of Al as that in Fig 4.33.

Figure 4.34 shows a lot of small pits appeared on surface of the corroded specimen over the whole surface area. Its C.R. calculated in section 4.2 was about 0.5 mdd at 50°C. Both the appearance and C.R. confirmed that the Al specimen was also corroded by distilled H₂O used. Unless H₂O is not pure, Al metal will not be corroded [25]. This is indicated that distilled water used in the test, was insufficiently clean, It might contain H⁺, CO₃²⁻, etc. which could also corrode aluminium specimens. Furthermore, table 4.2 specified that the Al specimen itself composed of several components, such as Si, Cu, Sn, etc, which these were noble metal, they might result in self-stimulation to aluminium corrosion in form of galvanic attack. In the H₂O-aluminium system, it was believed that trace amount of H₂CO₃ absorbed by water could activate O₂-reduction at any O₂ -enrich area on specimen surface as shown in the following equation ;



and Al would activate oxidation reaction at the adjacent area on the same surface, according to the follow reaction,



This implied that positions of pits were the area covered by low concentration of O₂ at the initial time of the test. The C.R. was then very low.

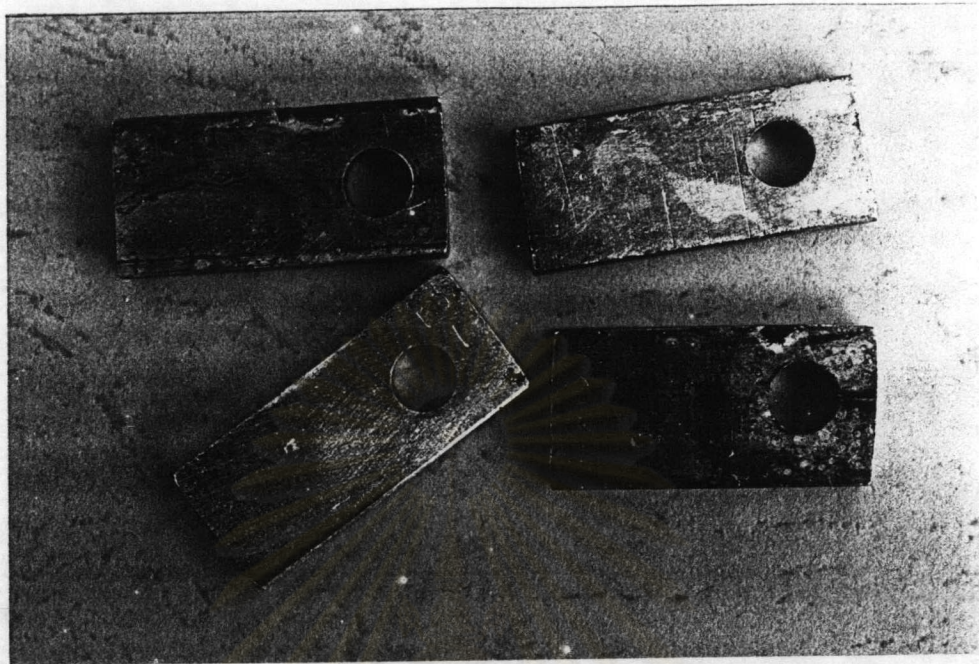


Figure 4.35 Photograph showing surface of the corroded specimen immersed in the $\text{H}_2\text{O}+150\text{ppm HCl}$ solution for 890 h at 50°C .

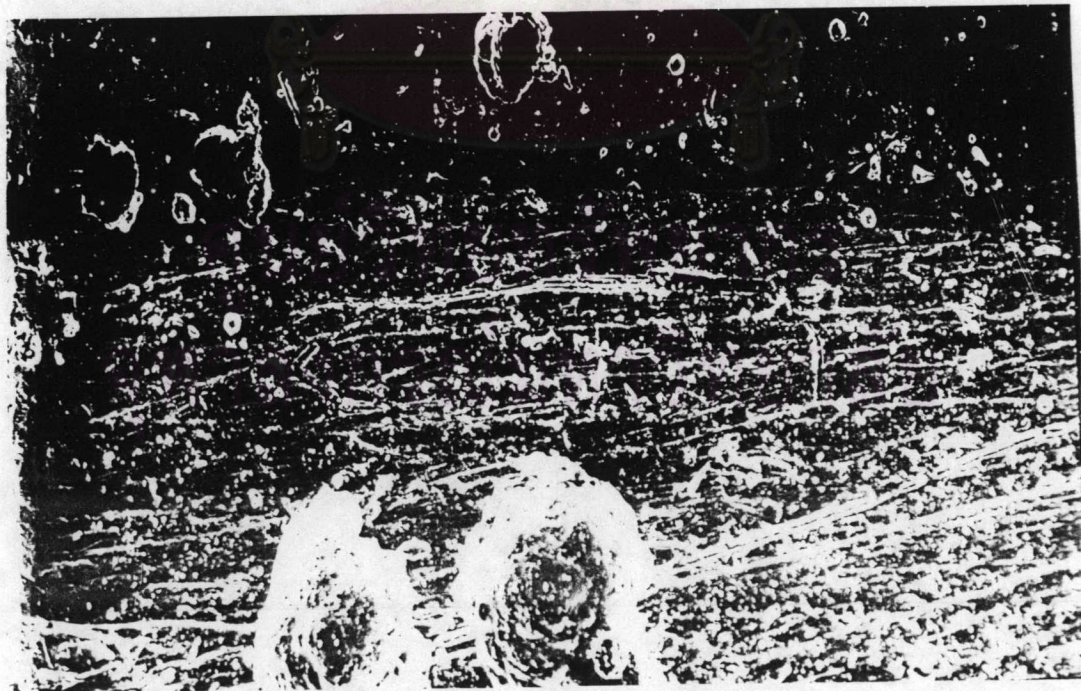


Figure 4.36 SEM photograph with magnification of x60 showing the same corroded surface as that shown in Fig.4.35

Figure 4.40 showed that the characteristics of the appearance on the corroded surface were in pitting form which tended to grow in depth more than in width. The location of pits at the initial time was the H⁺-enrich area which the H⁺-ion reduction occurred at the adjacent area to balance electron from the oxidation reaction (eq.4.6)

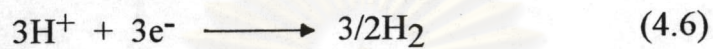


Figure 4.37 Photograph illustrating surface of the corroded specimen immersed in the saturated Hg-cyclohexane solution for 890 hr at 50°C.



Figure 4.38 SEM photograph with mag. x60 showing the same surface of the corroded specimen as that shown in Fig. 4.37

Figure 4.37 showed the appearances on surface of the Al specimen corroded by the Hg-in-cyclohexane solution. There was a big black hole appeared on the edge, this corrosion characteristics made it seem to be in the form of pitting. However, if the hole in Fig 4.38 were considered in it was found that corrosion in the hole also tended to grow in width because the hold is expanded to the right hand side. This was believed that the corrosion resulted from HgO left in the solution because elemental Hg dissolved in cyclohexane was old and not shine, meaning that Hg had formed oxide with O₂ in air.

The second group was to study how Al was corroded in the DMM solution system, as organized in table 4.6.

Table 4.6 Details of Figure 4.39-4.46 for Al corrosion discussion

Corrosive solution and condition for exposure of Al-test specimens	visual observation	Scanning image from SEM
Absolute methanol, for 890 h, at 50°C (blank test)	Figure 4.39	Figure 4.40 (X60)
Petroleum ether, at 50°C, for 890 h (blank test)	Figure 4.41	Figure 4.42 (x60)
The absolute CH ₃ OH+DMM 150 ppm solution, at 50°C, for 890 h	Figure 4.43	Figure 4.44 (x60)
The Petroleum ether+DMM 150 ppm solution, at 50°C, for 890 h	Figure 4.45	Figure 4.46 (x60)

ศูนย์วิทยทรัพยากร
จุฬาลงกรณ์มหาวิทยาลัย

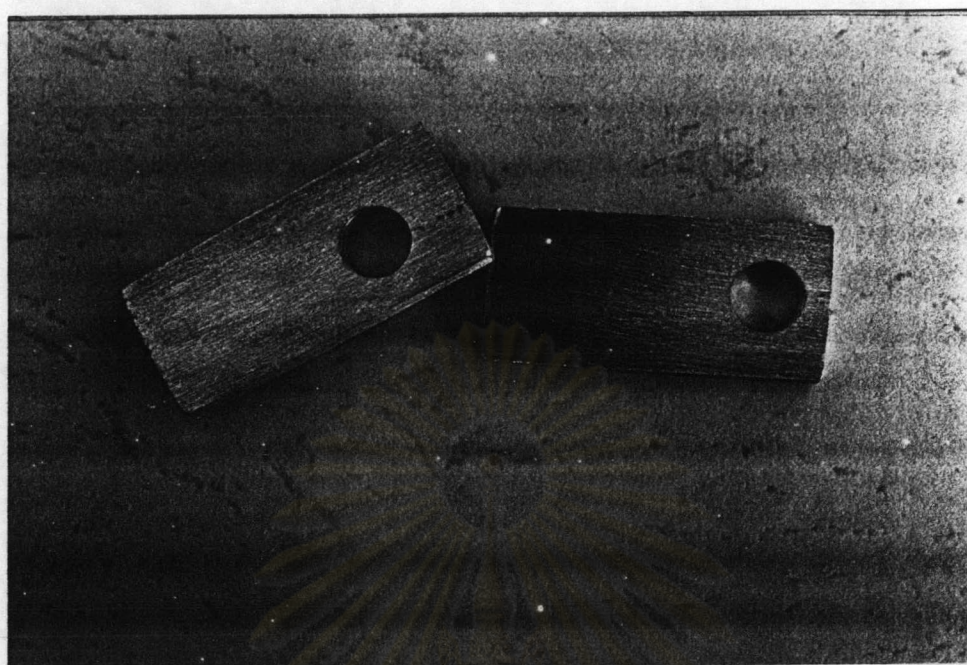


Figure 4.39 Photograph illustrating the surface of the corroded specimen immersed in absolute CH_3OH for 890 h at 50°C , as a blank test.

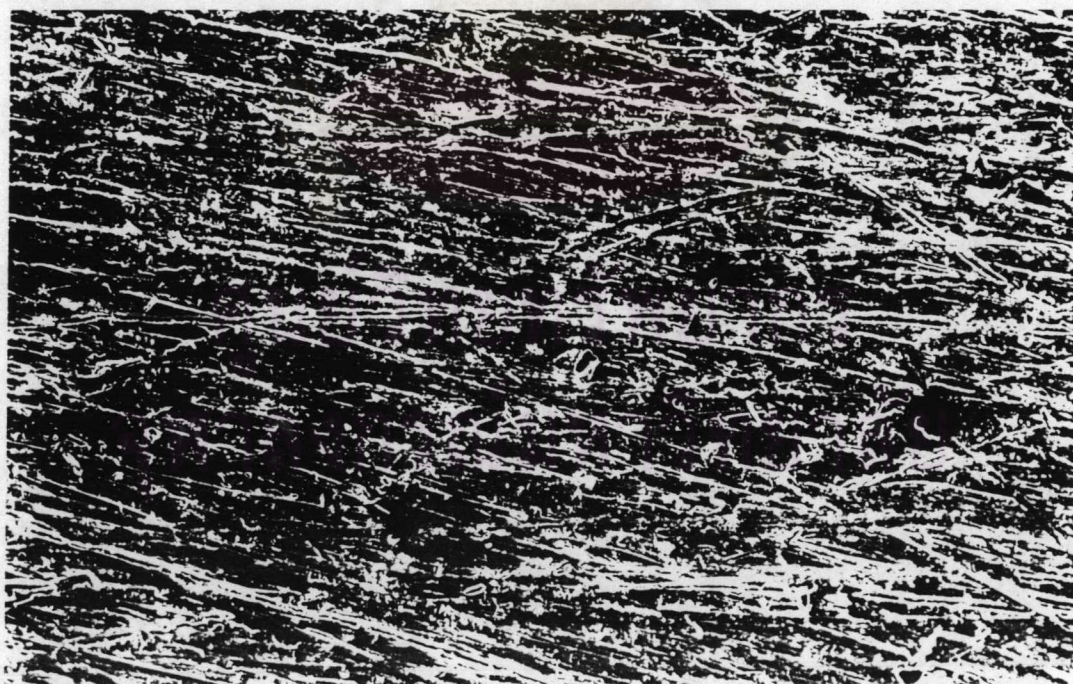


Figure 4.40 SEM photograph with mag. x60 showing the appearance on the same surface as shown in Fig 4.39

From Figure 4.39, the appearance was not found on the specimen surface and Figure 4.40 also supported that absolute methanol did not corrode the Al specimen, even though it was exposed for 890 h. All of scratches from abrasive paper were still appeared nicely on photomicrograph Its C.R. was about 0.43 mdd (at 50°C), which was very low with relative to the corrosion resulted from the CH₃OH+DMM solution to be described next

Figure 4.41 and 4.42 showed the surface of specimen that was immersed in pure PE for 890 h at 50°C, which was also another blank test. Corrosion was found a little, which its average weight loss was only 0.15 mg

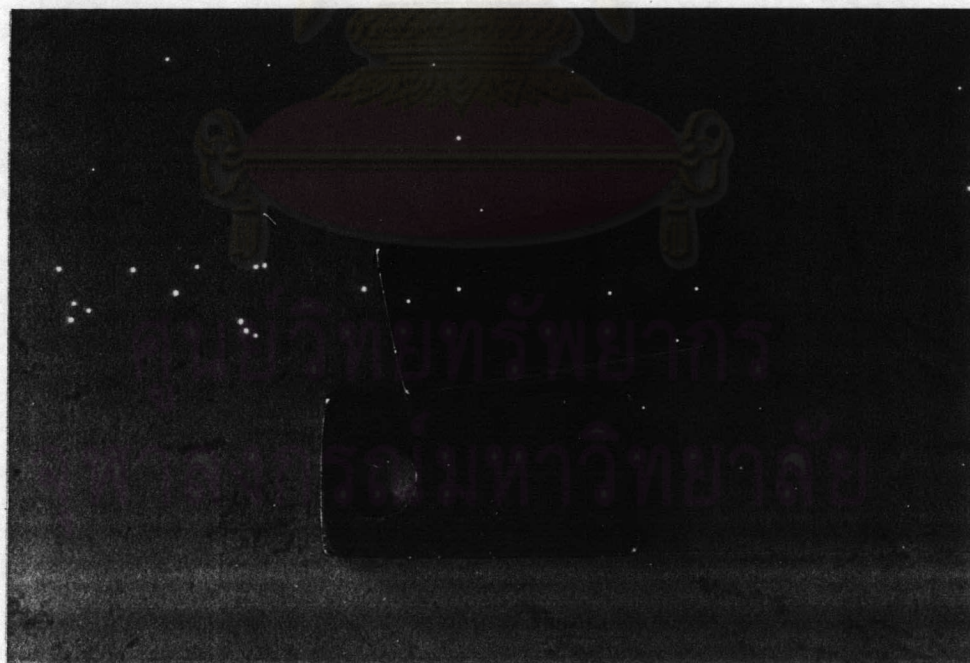


Figure 4.41 Photograph illustrating the corroded surface of Al specimen immersed in pure PE for 890 h at 50°C.

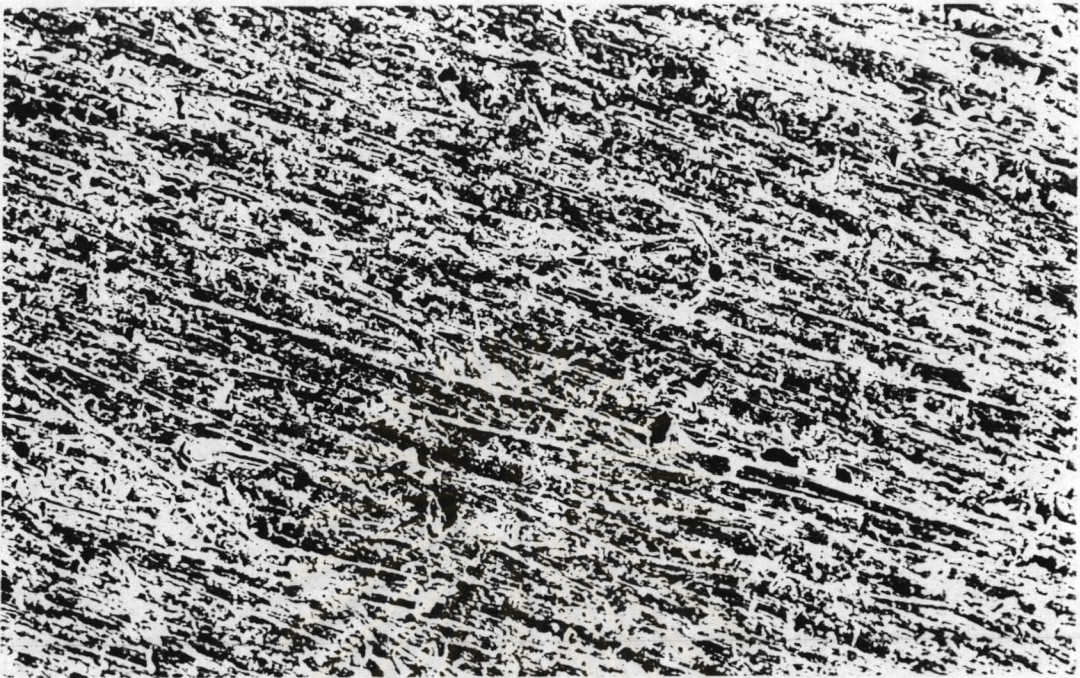


Figure 4.42 SEM photograph with mag.x60 showing the corrosion appearance on the same surface as that shown in Fig 4.41



Figure 4.43 Photograph illustrating the surface of the corroded specimen exposed in the absolute $\text{CH}_3\text{OH} + \text{DMM}$ 150 ppm solution for 890 h at 50°C



Figure 4.44 SEM photograph with mag.x60 showing the corrosion appearance of the specimen surface shown in Fig 4.43

Figures 4.43-4.44 showed the corrosion appearance on the specimen surface, immersed in the $\text{CH}_3\text{OH} + 150\text{ppm DMM}$ solution for 890 h at 50°C . Its characteristics was obviously in the form of pitting. Both characteristics, large holes and small pits, were distributed uniformly over the whole surface. When compared Fig 4.44 to fig 4.34, the specimen immersed in distilled H_2O , similar small pits were found on both figures, but no large hole was appeared in Fig 4.34. This result implied that small pits in this system might be corroded by H_2O containing in absolute CH_3OH (0.003%), whereas large holes were resulted from the decomposition of DMM into elemental mercury, described previously. Heat together with the presence of a hydrogen donor, such as CH_3OH , in the system could easily accomplish the reaction according to equation (4.1) and the elemental Hg generated could corrode the aluminium [11]. From table 4.2 showing various components of the aluminium specimen used in the test, Mg metal was the most component. This was interesting question

on whether those large holes may be caused by corrosion of Mg metal or not

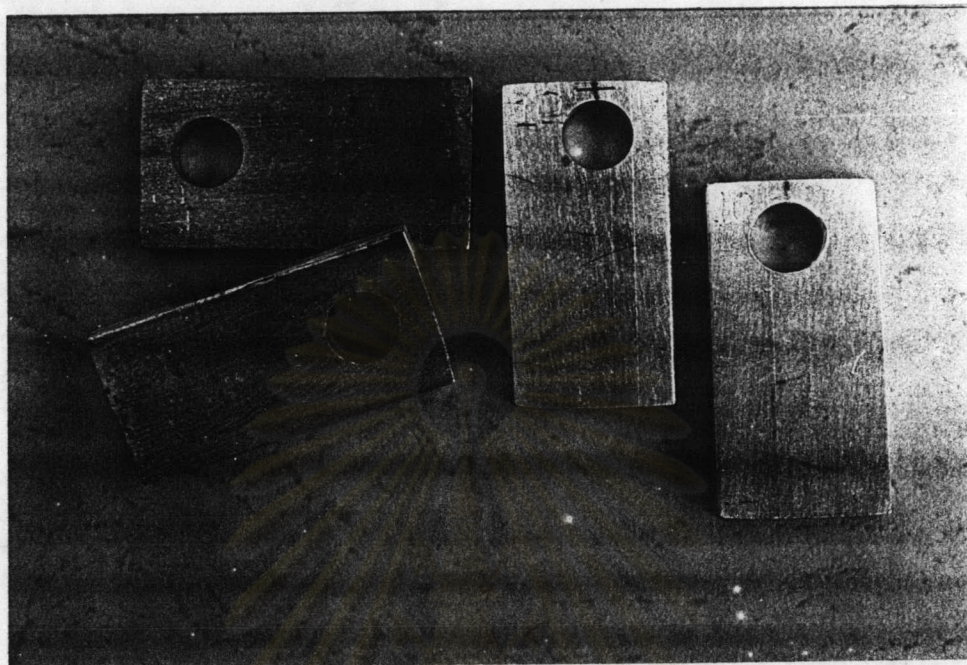


Figure 4.45 Photograph showing the surface of corroded specimen immersed in the PE+150ppm DMM solution for 890 h at 50°C

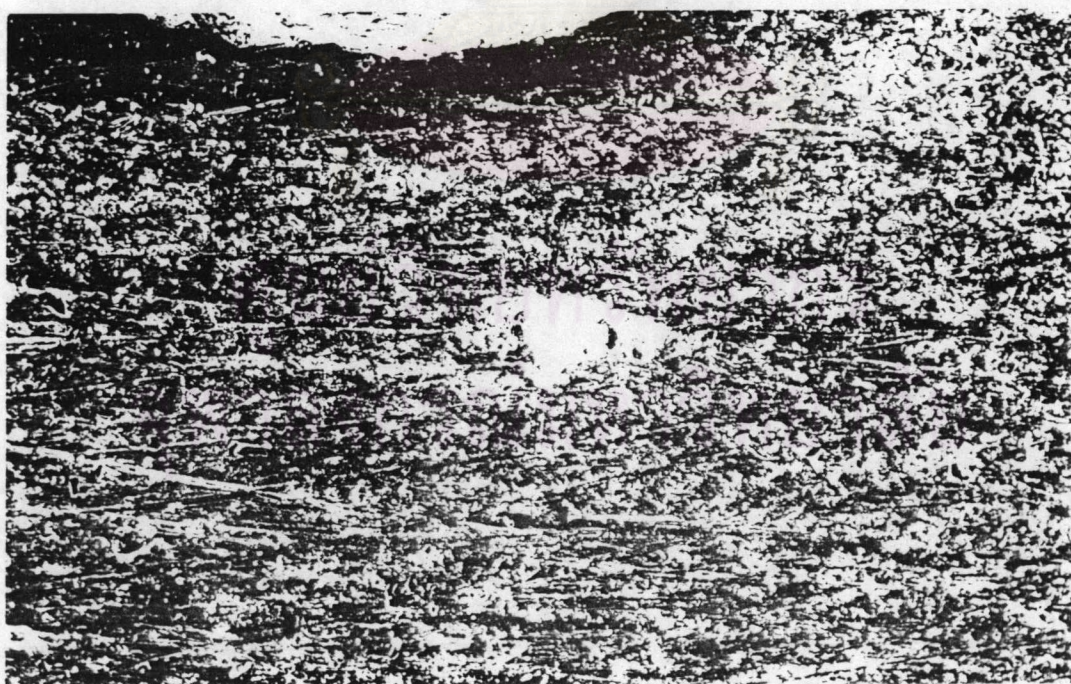


Figure 4.46 SEM photograph with magnification of x60 showing the corrosion appearance on surface shown in Fig 4.45

From visual check, it was found a few pits on the surface similar to the corrosion result obtained from the immersion of aluminium specimen in the $\text{CH}_3\text{OH}+150\text{ppm}$ DMM solution, see figures 4.45-4.46. Basically, PE heated together with DMM, it may act as hydrogen donor for the C-Hg bond cleavage reaction corresponding to equation (4.1) and the elemental Hg generated continued corroding. Its corrosion rate were about 0.086 mdd (at 50°C), which it is close to that corroded by the $\text{CH}_3\text{OH}+\text{DMM}$ solution at the same temperature (0.0689 mdd).

Table 4.7 Details of figures 4.47-4.62 for Al corrosion rate discussion

Corrosive solutions and conditions for the exposure test of Al specimen	visual observation	Micrograph from SEM
1. Exposure in PE+DMM 150 ppm+HCl 150 ppm solution, vary temp. between $10^\circ-30^\circ\text{C}$ for 763 h	Figure 4.47	Figure 4.48 (x60) Figure 4.49 (x600)
2. Exposure in PE+DMM 150 ppm+HCl 150 ppm solution, vary temp between $10^\circ-30^\circ\text{C}$ for 763 h	Figure 4.50	Figure 4.51 (x60) Figure 4.52 (x600)

Corrosive solutions and conditions for exposure of Al specimen	v i s u a l observation	Scanning image from SEM
3. Comparison between immersion in PE+HCl 150 ppm solution and in PE+DMM 150 ppm+HCl 150 ppm solution, for 763 hr at 30°C	Figure 4.53	-
4. Exposure in the PE+HCl 150 ppm+DMM solution, vary concentration of DMM between 100-250 ppm, for 763 hr at 30°C	Figure 4.54	-
5 Exposure in the PE+HCl+DMM solution with [HCl] : [DMM] = :], vary conc. of DMM (HCl) as 0.015, 0.15, 1.5, 15 and 150 ppm, for 679 hr at 30°C	Figure 4.55	Figure 4.56 (x60) Figure 4.57 (x600)
6. Exposure in the PE+DMM 150 ppm+HCl 150 ppm solution, vary RPM of agitated between 0-1200 rpm, at 30°C	Figure 4.58	Figure 4.59 (x600)
7. Exposure in the PE 100 ml+DMM 150 ppm+H ₂ O 50 ml+HCl 150 ppm solution, for 100 hr at 30°C (two phase)	Figure 4.60	Figure 4.61 (x20) Figure 4.62 (x60)

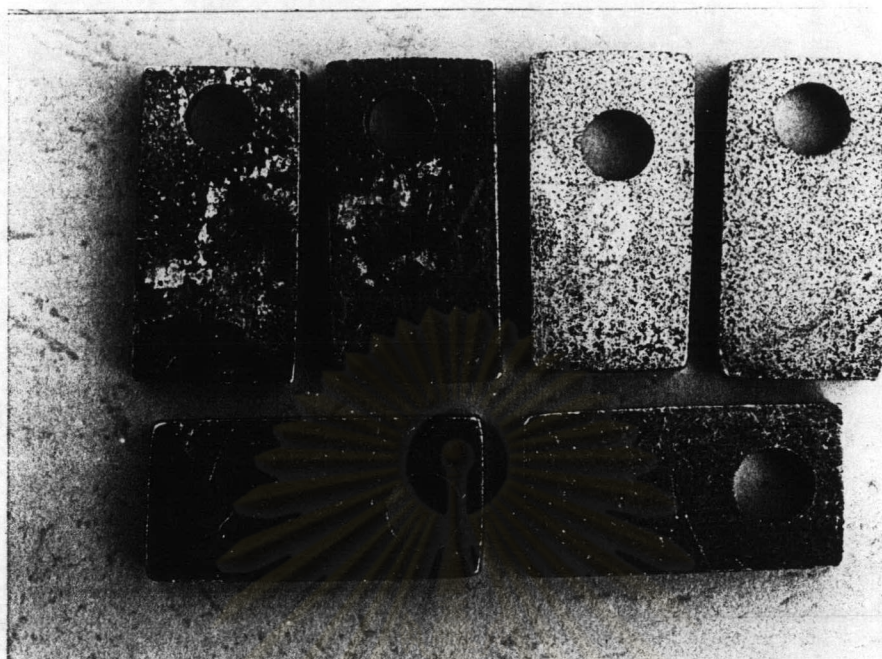


Figure 4.47 Photograph illustrating the surface of the corroded specimens immersed in the PE+150 ppm HCl solution for 763 h at varied temperature of test between 10°C-30°C

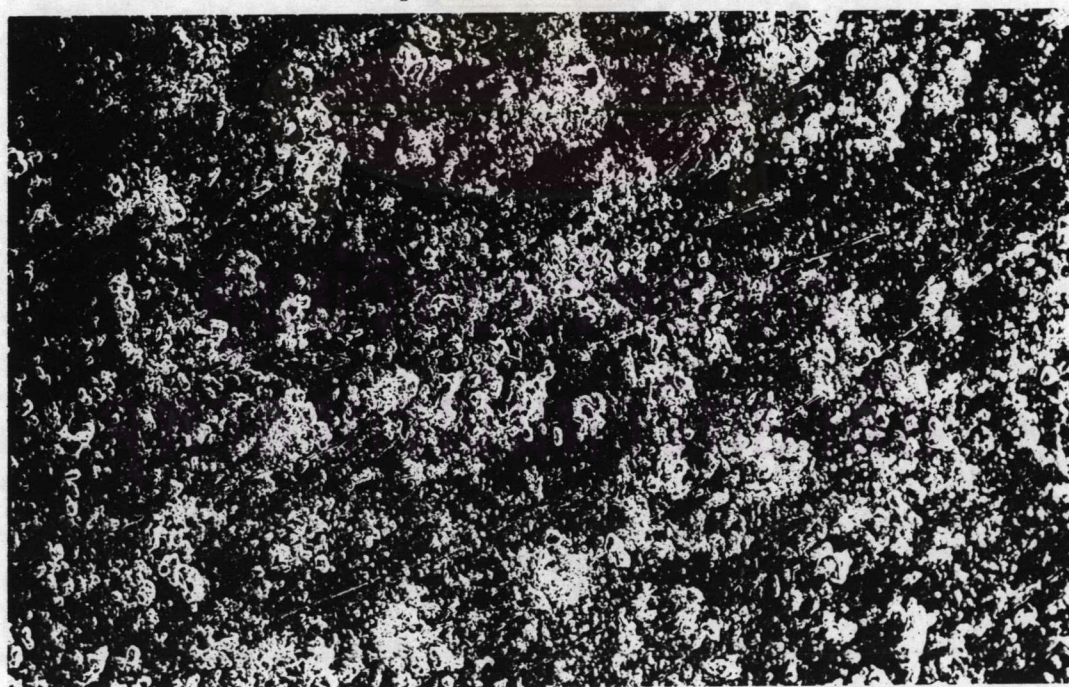


Figure 4.48 SEM photograph with mag.x60 showing the appearances on the surface shown in Figure 4.47 in detail

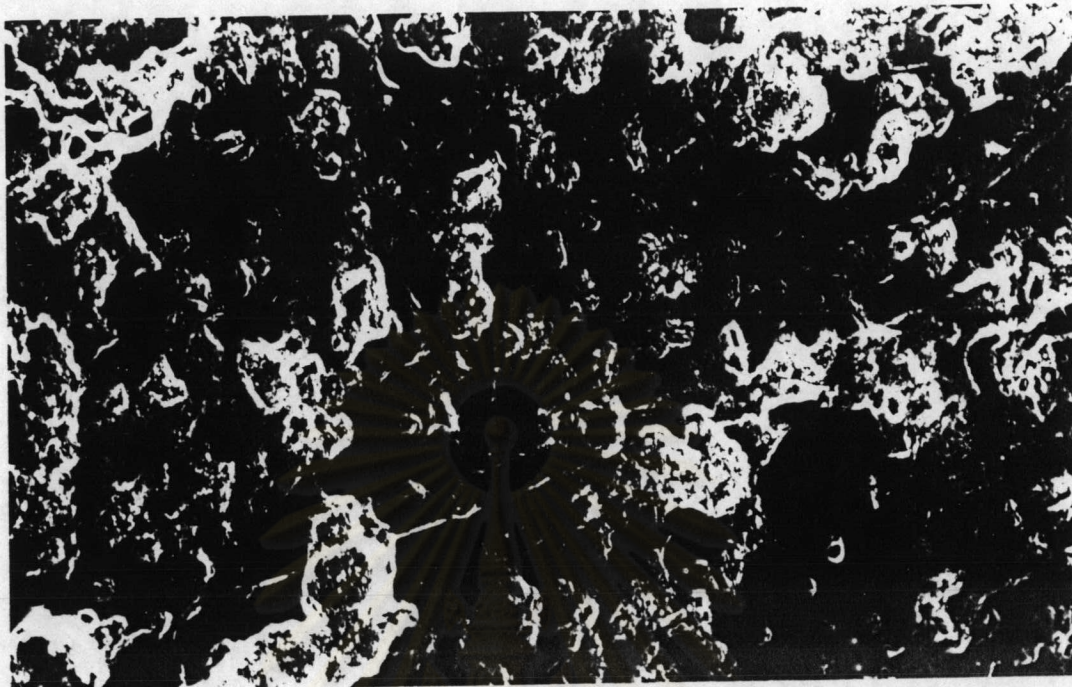


Figure 4.49 SEM photograph with mag.x600 showing the appearance on the surface shown in Fig 4.47-4.48.

The corrosion result in Fig 4.47-4.48 was higher than that shown in Figure 4.42, which was corroded by pure PE. Clearly, HCl is an agent to corrode. The corrosion appearance seemed to be more uniform than pitting because it is distributed over the whole surface area, not at local. When considering Fig 4.49 with magnification of x600, it was seen that the corroded area was covered by passive film and some of that film was falling off. The specimen then revealed a lot of small pits. If comparing corrosion results by PE+150 ppm HCl solution to that by CH₃OH+150 ppm HCl solution in Fig 4.67 showed that the former was corroded widely and covered all of the specimen surface, whereas the latter was somewhat grew in depth. Although HCl was less soluble in PE than in CH₃OH, PE showed wettability on metal surface better than CH₃OH. It was then it is believed that this effect enhanced corrosion of PE+HCl solution on Al specimens.

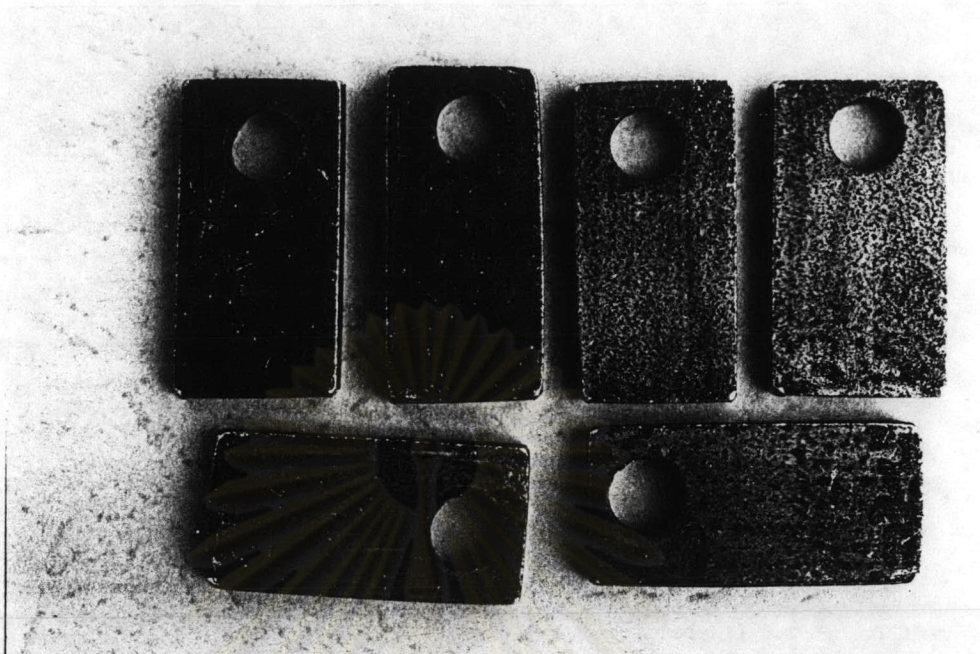


Figure 4.50 Photograph illustrating the surface of the corroded specimen immersed in the PE+150ppm DMM +150 ppm HCl solution for 762 h at 30°C.

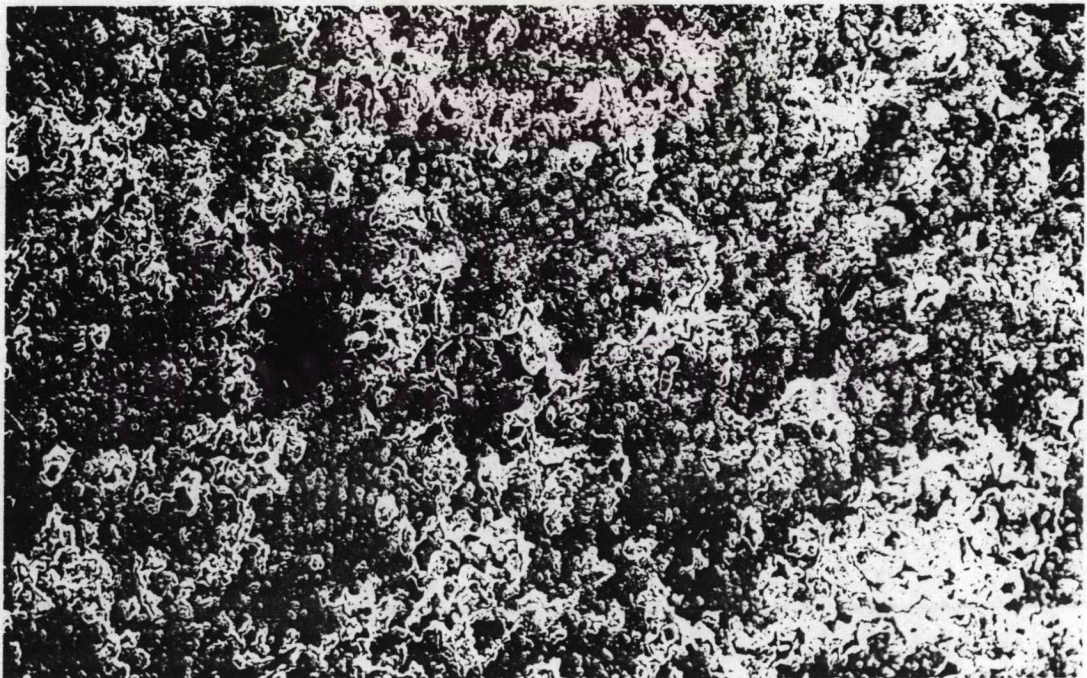


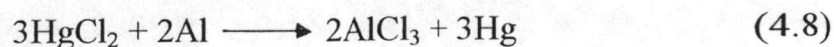
Figure 4.51 SEM photograph with mag.x60 showing the some appearance on surface as that shown in Fig 4.50



Figure 4.52 SEM photograph with mag.x600 showing the appearance of the corroded surface shown in Fig 4.51 in details

The corrosion appearance on Al specimen surface shown in fig 4.50-4.52 was rather similar to that corroded by the PE+150 ppm HCl solution (without DMM), but it was corroded broader and deeper. This appearance was rather in the form of uniform corrosion

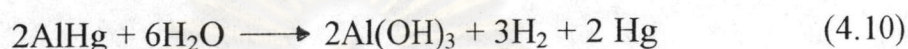
The HCl originally used to dissolve in PE composed of HCl 35.6% mass, therefore, there would be H₂O more than 250 ppm mixed together in the 150 ppm HCl in PE solution prepared. The amount of H₂O thus took part in the corrosion reaction. As mentioned in the corrosion results of CS specimens, DMM could react with HCl to form CH₃-Hg-Cl or HgCl₂, which continued reacting with aluminium metal to form elemental Hg (eq. 4.8)



and the elemental Hg generated then formed amalgam with aluminium metal, as illustrated in the following reaction ;



If water was existed, the amalgam would further react to give Hg's.



The elemental Hg generated would attack the specimen repeatedly. This corrosion process became more severe if it is not that because amount of water was not constraint to reaction. Corrosion rate of this corrosive system at 10°C was 10.4 mdd, which was more than that of the system without DMM at the same temperature (see the appendix C).

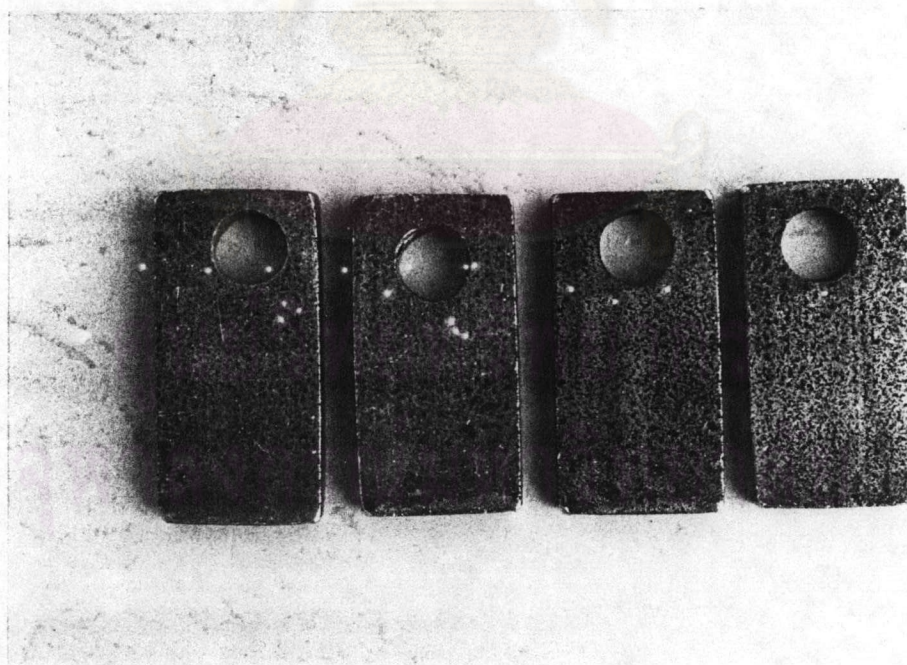


Figure 4.53 Photograph illustrating the corroded surface immersed in the PE+150 ppm HCl solution in comparison to that immersed in the PE+150 ppm HCl+150 ppm DMM solution for 762 h. at 30°C.

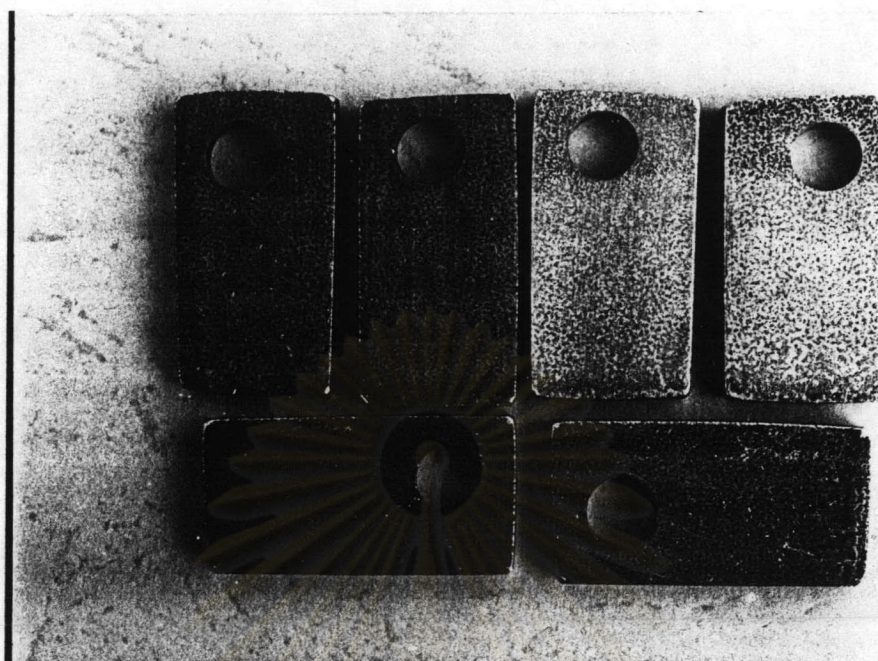


Figure 4.54 Photograph illustrating surface of several corroded specimens immersed in the PE+150 ppm HCl+DMM solution for 677 h at 30°C. by varying the DMM concentration between 50-250 ppm (50, 100, 150, 200, 250 ppm).

Figure 4.53 showed surface of the corroded Al specimens exposed in the PE+150 ppm HCl solution for 677 h at 30°C in comparison to that exposed in the PE+150 ppm HCl+150 ppm DMM solution for the same period of time and temperature. Two pieces on the left hand side were exposed in the PE+150 ppm HCl solution and two on the right hand side were exposed in the other corrosive solution. It was clear that the specimen pair exposed in the corrosive solution with DMM appeared much more small pits which were broader and deeper. Their corrosion rates shown in Fig 4.93 in the next section supported this conclusion because their corrosion rate were higher at various exposure temperatures.

Figure 4.54 showed the appearances on surfaces of several corroded specimens exposed in the PE+150 ppm HCl+DMM solution for 677 h at 30°C by varying concentration of DMM between 50-250 ppm. Such appearances were rather similar to that shown in Fig 4.51-4.52, that was uniform corrosion with lots of small pits. All of the specimens showed the similar appearance, thus it indicated that the variation of DMM concentration was not affected on corrosion, which the C.R calculated and shown in Fig 4.94 would supported results of these appearances.



Figure 4.55 Photograph showing the surface of the corroded specimens immersed in the PE+HCl+DMM solution with $[HCl] : [DMM] = 1:1$ for 679 h at 30°C



Figure 4.56 SEM photograph with magnification of x60 showing the appearances on surface of the corroded specimens immersed in the same corrosive solution as that in Fig 4.55 for 679 h at 30°C.



Figure 4.57 SEM photograph with mag.x600 showing the appearances on surface shown in Fig 4.55-4.56.

Figures 4.55-4.57 showed the appearance on surface of the corroded specimens exposed in the PE+DMM+HCl solution with [DMM]:[HCl] = 1:1 for 679 h at 30°C. The DMM concentration was varied as follow 0.015, 0.15, 1.5,15 and 150 ppm. The reasons for using [HCl]:[DMM] equal 1:1 were that the appropriate ratio of DMM to HCl affecting to break the C-Hg bond of DMM [19] was equal to 1:1. Another was according to the conclusion of Fig 4.54, which it was stated that the variation of DMM concentration did not have any effect on corrosion results. When considering Figure 4.57 in detail, small pits was found on the surface, which its passive film was falling off. This was little corroded and difficult to identify whether it is uniform corrosion or pitting. The corrosion rate of this corrosive system changed with concentration of DMM, which was described later in the next section



Figure 4.58 Photograph illustrating the surface of the corroded specimens immersed in the PE+200 ppm DMM +150 ppm HCl solution for 444 h at 30°C by varying RPM agitating the corrosive solution between 0-1200 rev/min

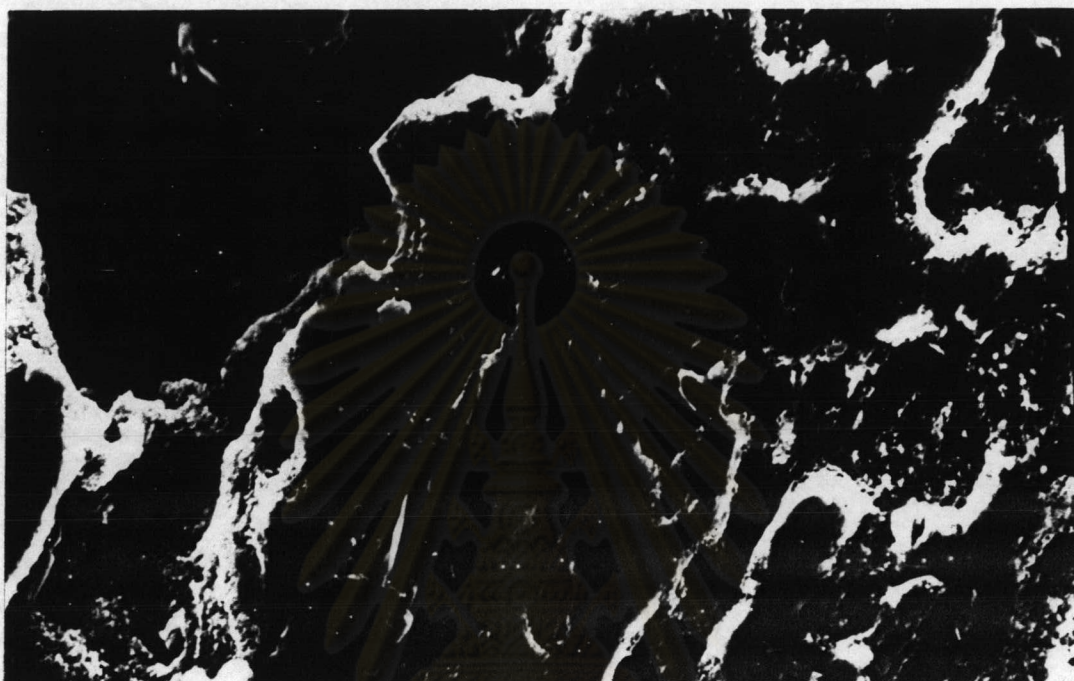


Figure 4.59 SEM photograph with magnification of x600 showing the appearance on surface of the corroded specimens exposed in the same corrosive system as that in Fig 4.58

Figures 4.58-4.59 showed that the appearances were somewhat similar to that obtained by the corrosive system without agitation shown in fig 4.50, but its small pits was broader because it was not only corroded by HCl+DMM but it was also reinforced by the effect of erosion corrosion due to agitation

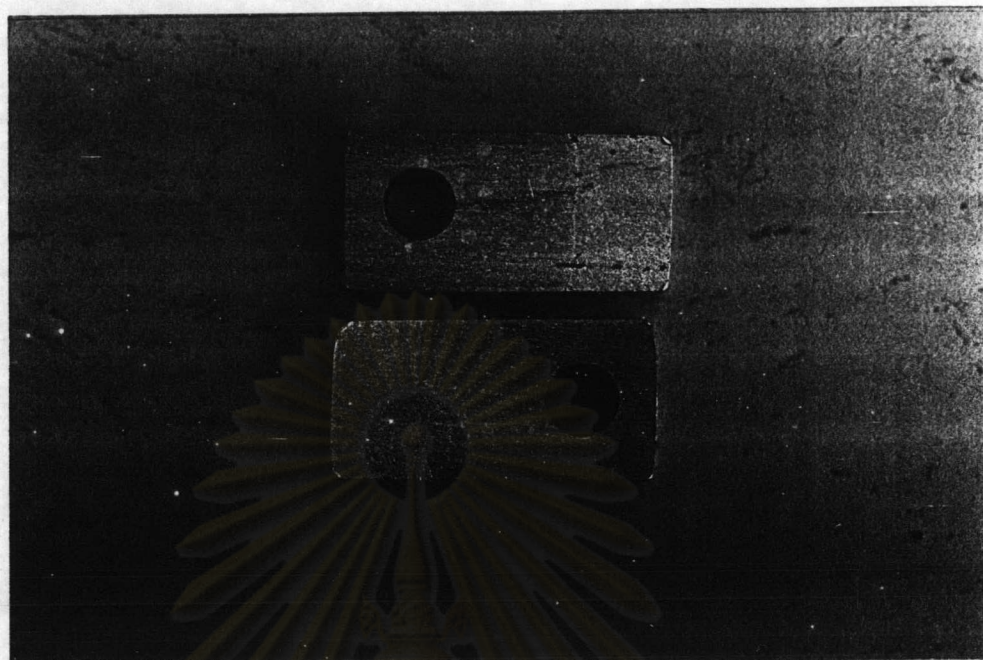


Figure 4.60 Photograph of the corroded surface immersed in the 150 ml corrosive solution composed of 100 ml PE+50 ml H₂O+200 ppm DDM+150 ppm HCl for 600 h at ambient temperature (30°C).



Figure 4.61 SEM photograph with mag.x60 of the same corroded surface as that shown in the Fig 4.60 for 600 h at ambient temperature.

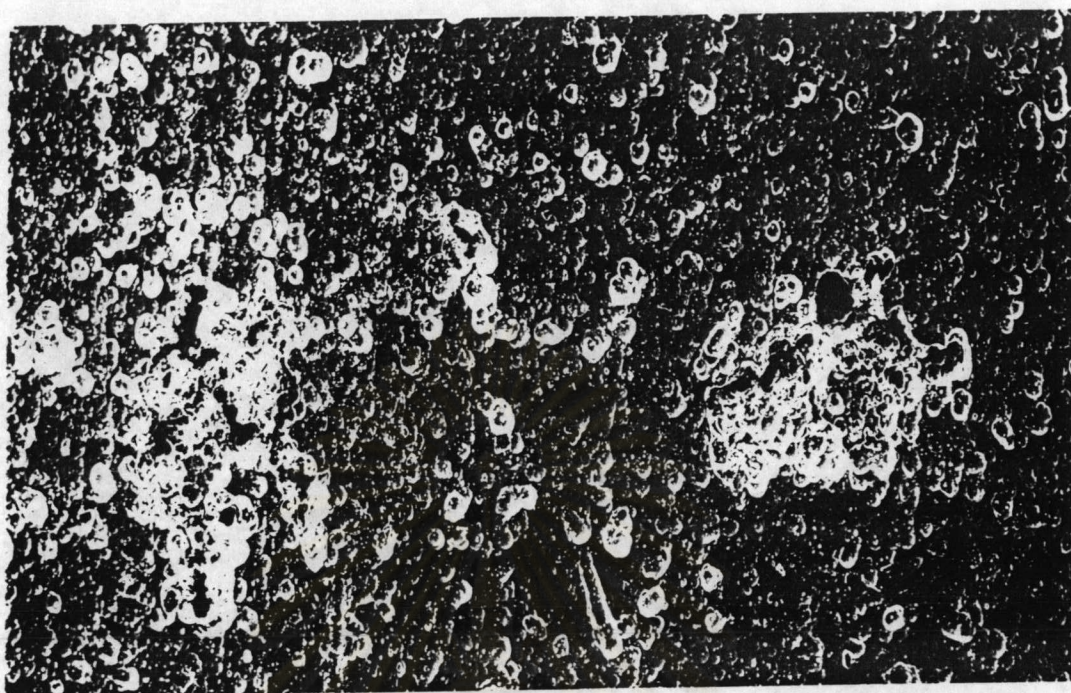


Figure 4.62 SEM photograph with magnification of x600 showing the appearance on the surface as those shown in Fig 4.60-4.61 in detail.

The 150 ml-corrosive solution used for the test was prepared by dissolving DMM in 100 ml of PE and HCl in 50 ml of H₂O, and mixing, both solutions together to obtain final solution according to the required DMM/HCl concentration. It was appeared that this corrosive solution was immiscible and separated into two phases, therefore the exposed specimens showed two appearances on surface as in Fig 4.60. Figures 4.61-4.62 indicated its appearances in detail. Two small basins were found on the surface at the interphase of H₂O-PE, which was corroded by mercury (see fig 4.50). The part of surface immersed in H₂O appears the appearance similar to that corroded by H₂O and HCl (see Fig 4.34, 4.36).

The following corrosion results were obtained by exposure of the aluminium specimens in corrosive solution using absolute CH₃OH as solvent. Their results, both the corrosion appearances and reaction rate, were very interesting. The analysis of heterogeneous reaction in this system showed that

absolute CH_3OH was not only the solvent but, it also reacted, with corrosion product which led to the loss of Al specimens enormously.

Table 4.8 Details of Figures 4.63-4.82 for aluminium corrosion discussion

Corrosive solutions and conditions for the exposure test	visual observation	photomicrograph form SEM
1. Exposure in the $\text{CH}_3\text{OH}+150$ ppm HCl solution, vary temperature between $10^\circ-60^\circ$ C	Figure 4.63	Figure 4.64 (x60) Figure 65 (x600)
2. Exposure in $\text{CH}_3\text{OH}+200$ ppm DMM+ 150 ppm HCl solution, vary temperature between $10^\circ - 60^\circ$ C	-	- - -
2.1 temperature $10^\circ\text{C}-20^\circ\text{C}$	Figure 4.66	Figure 4.67 (x60)
2.2 temperature $20^\circ\text{C}-60^\circ\text{C}$	-	Figure 4.68(x600) Figure 4.69 (x60)
3. Comparison of corrosion results of specimen exposed in 150 ppm CH_3OH solution with that exposed in solution, at 30° C	Figure 4.70	-

Corrosive solutions and conditions for the exposure test	v i s u a l observation	photomicrograph form SEM
4. Comparison of corrosion results of specimens exposed in the CH ₃ OH+ 150 ppm HCL+DMM <150 ppm solution with that exposed in the CH ₃ OH +150 ppm DMM+DMM> 150 ppm solution, at 30°C	Figure 4.71	-
5. Exposure of specimens in the CH ₃ OH +HCl 150 ppm + DMM 200 ppm solution, vary RPM agitated solution, at 30° C	Figure 4.72	Figure 4.73 (x40)
6. Exposure in the CH ₃ OH +HCl + DMM solution with [DMM]:[HCl] = 1:1, vary concentration of DMM (HCl) as 0.015 ppm, 1.5 ppm, and 150 ppm	Figure 4.74	-
7. Comparison of corrosion results of specimens exposed in the CH ₃ OH + H ₂ S saturated + 200 ppm DMM solution with that exposed in the CH ₃ OH + H ₂ S saturated solution	Figure 4.75	(No DMM) Figure 4.76 (x60) (with DMM) Figure 4.77 (x60) Figure4.78(x600)

Corrosive solutions and conditions for the exposure test	visual observation	photomicrograph form SEM
8. Comparison of corrosion reaction of specimens exposed in absolute $\text{CH}_3\text{OH} + \text{HgCl}_2$ solution with that exposed in the ether + HgCl_2 solution, at 30°C	Figure 4.79	-
9. Comparison of corrosion reaction of specimens exposed in the $\text{CH}_3\text{OH} + 150 \text{ ppm HCl} + 200 \text{ ppm DMM}$ solution with that exposed in the $\text{DMSO} + 200 \text{ ppm DMM} + \text{Dioxane} + 150 \text{ ppm HCl}$ solution, at 30°C	Figure 4.80	-
10. Comparison of corrosion results of specimens exposed in the $\text{CH}_3\text{OH} + \text{HCl} 150 \text{ ppm} + \text{DMM} 200 \text{ ppm}$ solution with those exposed in the $\text{CH}_3\text{OH} + \text{H}_2\text{S} 300 \text{ ppm} + \text{DMM} 200 \text{ ppm}$ solution	Figure 4.81	-
11. Compare the surface of specimens in the following corrosive solutions 1. $\text{CH}_3\text{OH} + 150 \text{ ppm HCl} + 200 \text{ ppm DMM}$ 2. $\text{CH}_3\text{OH} + 300 \text{ ppm H}_2\text{S} + 200 \text{ ppm DMM}$ with that before test	Figure 4.82	-

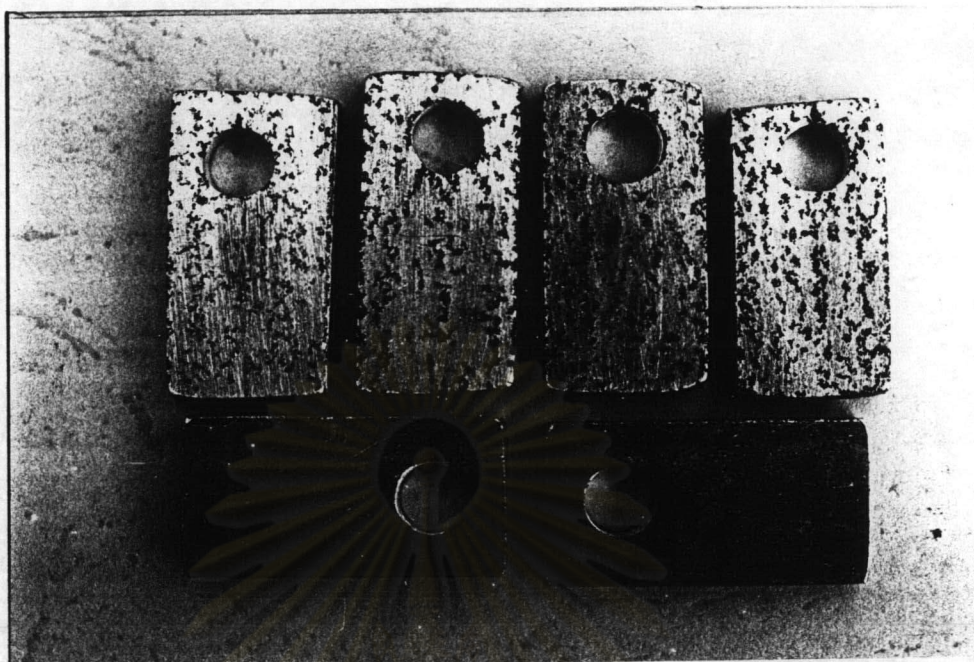


Figure 4.63 Photograph of the corroded surface of specimens immersed in the $\text{CH}_3\text{OH}+150$ ppm HCl solution at varied temperature between 10° - 60°C

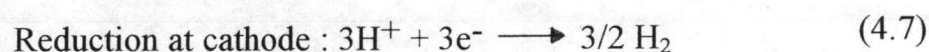
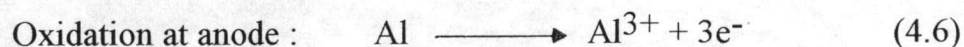


Figure 4.64 SEM photograph with mag. x60 showing the appearance on the same surface as that shown in Fig 4.63



Figure 4.65 SEM photograph with magnification of x600 showing the appearance on the same surface shown in Figure 4.63-4.64 in detail

Observation of HCl solubility in CH_3OH indicate that HCl dissolved in CH_3OH very well, then corrosion results shown in Fig 4.63-4.65 should be caused by HCl. The characteristics of the corrosion shown in Fig 4.64 was large pits which were certainly developed to the form of uniform corrosion because the corrosion was more expanded in width than in depth. The corrosion process of aluminium specimens caused by the dilute acid solution was accomplished by self-stimulation from oxidation-reduction of the system as the following:



or if O_2 was available in the solution, it would also undergo the reduction process :



Any point on the surface that was exactly attacked by H^+ ion became pits, that was the anode, and the adjacent area to the pits, which occurs reduction, was cathode.



Figure 4.66 Photograph showing the surface of the corrode specimen immersed in the $\text{CH}_3\text{OH}+150 \text{ ppm HCl} +200 \text{ ppm DMM}$ solution, which the exposure temperature was varied from 10^0-60^0C ,



Figure 4.67 SEM photograph with mag. x60 showing the appearance on the same corroded surface immersed in the $\text{CH}_3\text{OH}+150$ ppm $\text{HCl}+150$ ppm DMM solution at temperature, lower than 20°C .

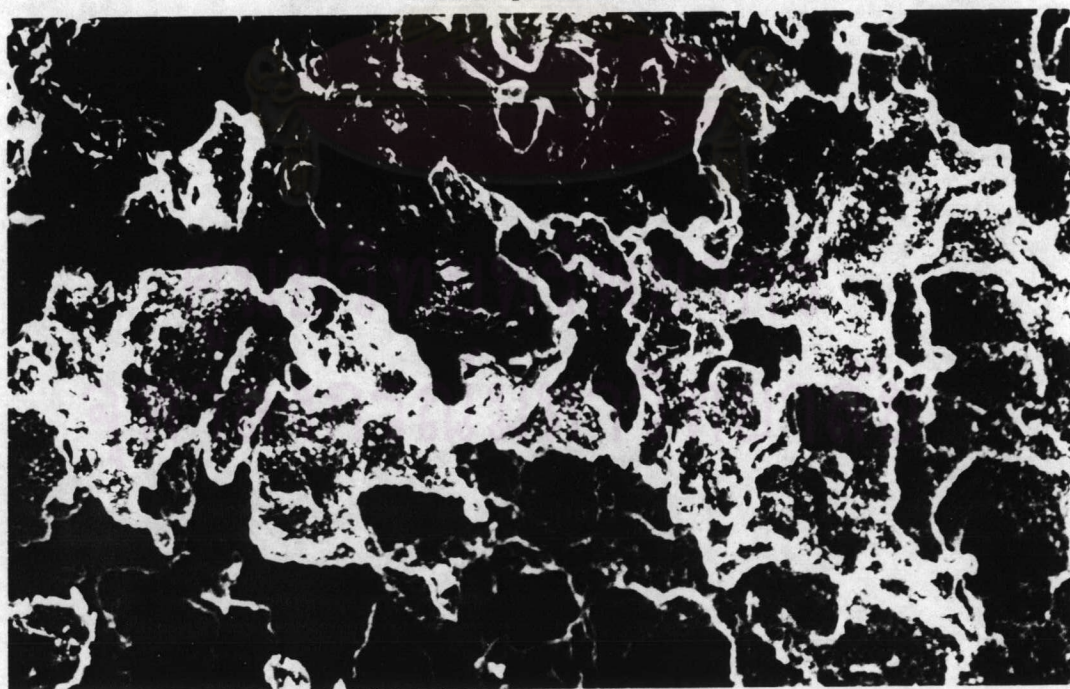


Figure 4.68 SEM photograph with mag.x600 showing the appearance on the same corroded surface as that shown in figure 4.67 in detail.

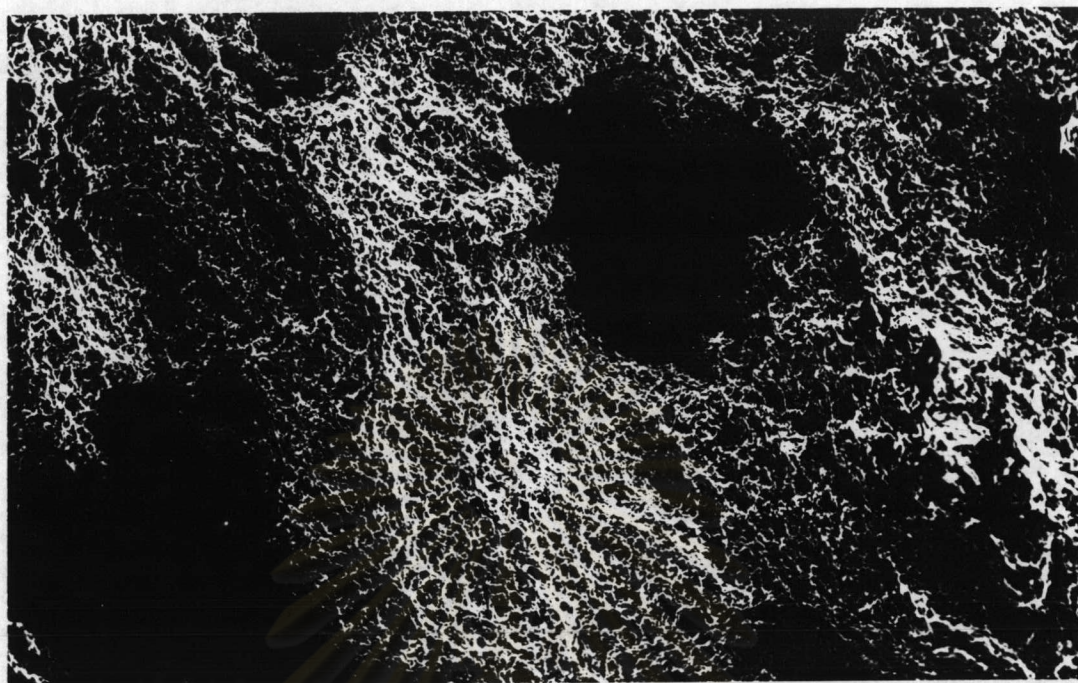
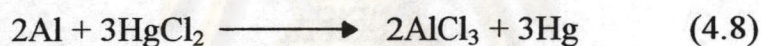


Figure 4.69 SEM photograph with mag.x60 showing the appearance on surface of the corroded specimens immersed in the $\text{CH}_3\text{OH}+150 \text{ ppm HCl}+200 \text{ ppm DMM}$ solution at the exposure temp. higher than 20°C

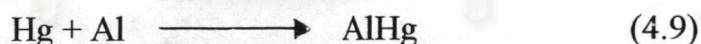
Figure 4.66 showed the surface of six corroded aluminium specimens exposed in the $\text{CH}_3\text{OH}+150 \text{ ppm HCl}+200 \text{ ppm DMM}$ solution by varying the exposure temperatures as 10° , 20° , 30° , 40° , 50° and 60°C . Their corrosion results, both the appearances and corrosion rates, were quite different (see fig 4.2-15 in section 4.2). A pair of specimens on the left hand side below, which were immersed in the solution at 10°C , just showed the corrosion appearance as small pits, whereas the others, which immersed at temperature higher than 20°C were too much lost in weight and corroded all over the whole surface. This implied that the corrosion reactions of both system may be different. Figures 4.67-4.68 showed the appearance of the small pits in detail, which was somewhat similar in shape to that corroded by the $\text{CH}_3\text{OH}+150 \text{ ppm HCl}$ without DMM, but these pits were broader. It was believed that if this corrosion took longer period of time than this, these pits would be greatly corroded until its appearance becomes uniform corrosion. Figure 4.69 showed

the appearance on surface of the corroded specimen exposed in the corrosive solution at the exposure temperature higher than 10°C. It was clear that its appearance was completely uniform corrosion. From the observation at the reaction flask during conducting the experiment, it was evident that corrosion reaction of the system (higher than 20°C) severely occurred, there was a large amount of gas evolved and corrosion product fell off from the specimen to the bottom of the reaction flask all time. When comparing with the system undergone at the temp. lower than 20°C, it was found that both of these were different completely because there was no change in the latter

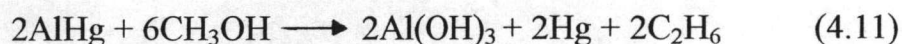
As described previously, DMM added together with HCl into a solution resulted in $\text{CH}_3\text{-Hg}^+\text{Cl}^-$ and HgCl_2 . The HgCl_2 generated attacked the specimen surface further according to the following reaction :



When the elemental mercury was generated, the amalgamation of aluminium should be follow [11] :



Aluminium amalgam was weaker than aluminium itself. It could be attacked by H_2O or CH_3OH , as shown in the following :



However, absolute methanol could reduce aluminium amalgam more severe than H_2O . It was found at the same temperature the reaction occurred severely, and elemental Hg generated would circulate to attack the aluminium again. Now, it was accepted that absolute CH_3OH not only was solvent, but it also became the reagent for corrosion reaction as well. However, at temperature

lower than 10°C , this corrosion occurred very slowly no matter how long. it took .This was indicated that reaction according to equation (4.1) could not accomplish at low temperature.



Figure 4.70 Photograph showing the differences of the corroded specimens surface immersed in the $\text{CH}_3\text{OH}+150$ ppm HCl solution from those immersed in the $\text{CH}_3\text{OH}+150$ ppm DMM+200 ppm DMM solution at 30°C

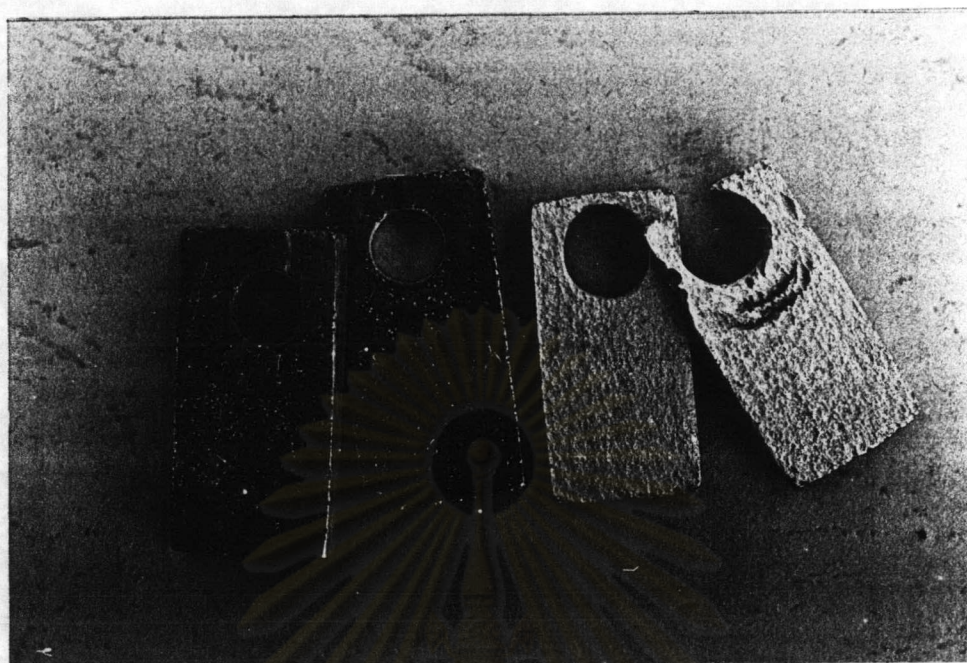
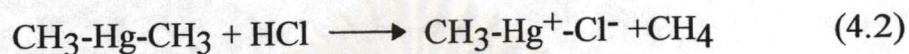


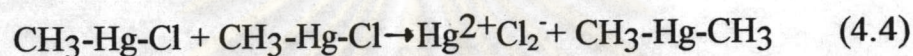
Figure 4.71 Photograph showing the differences of corrosion results of the specimen corroded by the $\text{CH}_3\text{OH}+150$ ppm HCl +lower-than 150 ppm DMM solution from those corroded by the $\text{CH}_3\text{OH}+150$ ppm HCl +higher-than-150-ppm DMM solution at 30°C

A pair of the corroded specimen on the right hand side in Fig 4.70 were immersed in the $\text{CH}_3\text{OH}+150$ ppm HCl solution (without DMM) for 142 h. It appeared lots of small pits distributed over the whole surface area, which this corrosion was resulted from the attack by HCl , whereas the other pair of specimens were immersed in the $\text{CH}_3\text{OH}+150$ ppm $\text{HCl}+\text{DMM}$ solution at the same exposure temperature. In such a corrosive system, the specimens were attacked by the corrosive media-DMM severely, which its weight was lost approximately 1.16 g (more than 50%) within 53 h only. Now it was accepted that DMM together with HCl could promote the corrosion on aluminium metal much more severely than HCl alone. In Figure 4.71, a pair of specimens on the right hand side were immersed in the $\text{CH}_3\text{OH}+150$ ppm $\text{HCl}+200$ ppm DMM (more than 150 ppm) solution and appeared the severe corrosion like the pair of specimens on the left hand side in Fig 4.70 (solution with DMM), whereas

the other pair was immersed in the solution with DMM 100 ppm (lower than 200 ppm) and appeared the corrosion as small pits only. This implied that the achievement of severe attack on the specimen by DMM together with HCl was depended on both exposure temperature and concentration of DMM. Usually, adding HCl into DMM forms the following result [19]



and the following reversible reaction can also be occurred [15]



The HgCl_2 will attack aluminium specimens as mentioned previously



Figure 4.72 Photograph showing surface of the corroded specimens immersed in the $\text{CH}_3\text{OH}+\text{HCl}$ 150 ppm+DMM 200 ppm solution with varying RPM agitation between 0-1200 rev/min at ambient temperature

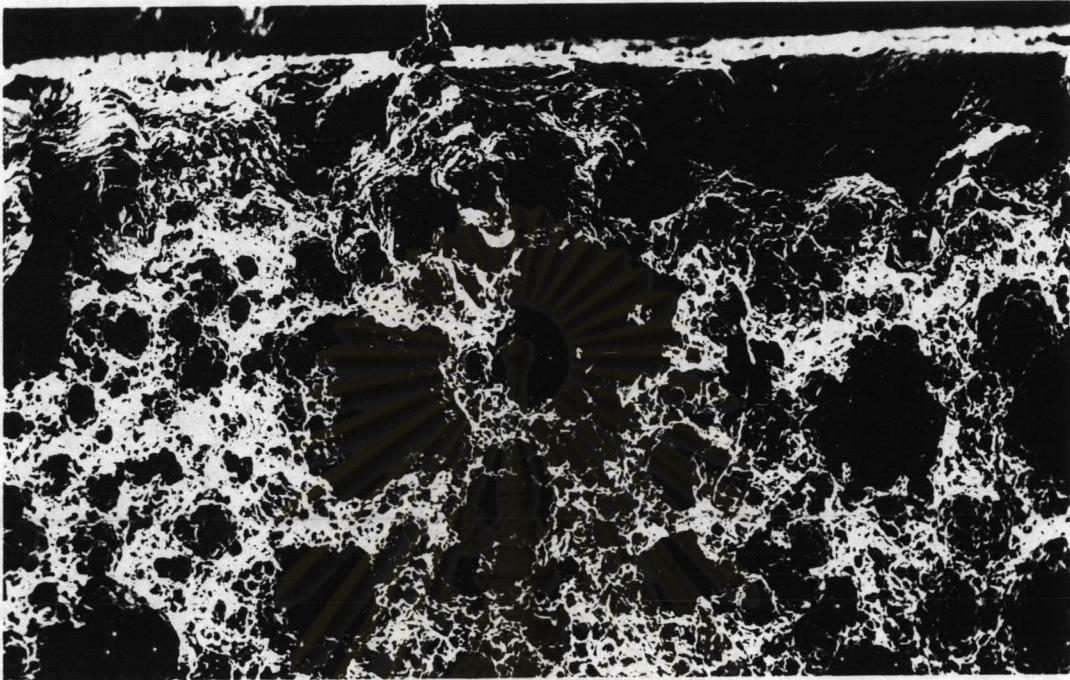


Figure 4.73 SEM photograph with magnification of x60 showing the cavitation on lower surface of the corroded specimen immersed in the $\text{CH}_3\text{OH}+150 \text{ ppm HCl}+200 \text{ ppm DMM}$ solution agitated 900 rpm for 127 h

Figure 4.72 showed surface of the corroded specimens exposed in the $\text{CH}_3\text{OH}+\text{HCl}+\text{DMM}$ solution with agitation between 0-1200 rev/min. A pair of specimens on the right hand side below were resulted from the corrosion of solution without agitation (0 rev/min). Its corrosion appearance was in the form of general corrosion which the surface was rough. The pairs of specimen on the left hand side below and upper were immersed in the solution with agitation 300-1200 rev/min. Its corroded surface was found from visual check that there were less roughness on the surface than a pair of that on the right hand side as mentioned above, and that these surface characteristics were large basin and cavitations on local area on which the solution flowing to impact, for example, on the lower surface (specimens were hung vertically).

Photomicrograph on Fig 4.73 showed the characteristics of cavitation very obviously. These cavitations were resulted from impact and breaking of the solution bubbles generated by agitation of magnetic stirrers. When the bubbles impact on some points on specimen surface, it was broken and destroyed the protective film at that point, which revealed new grain of aluminium to corrosive solution again. As a matter fact, cavitation was one form of erosion corrosion



Figure 4.79 Photograph showing surfaces of the corroded specimens immersed in the $\text{CH}_3\text{OH}+\text{HCl}+\text{DMM}$ solution with $[\text{HCl}]:[\text{DMM}]=1:1$ by varying conc. of DMM as 0.015 ppm, 0.15 ppm, 1.5 ppm, 15 ppm and 150 ppm

Figure 4.74 showed that the corrosion result was appeared to be some of pits with shape-like pits obtained by the $\text{CH}_3\text{OH}+150$ ppm $\text{HCl}+200$ ppm DMM solution (see Fig 4.66), but the numbers of them were much less. The less concentration of DMM, the less numbers of pits

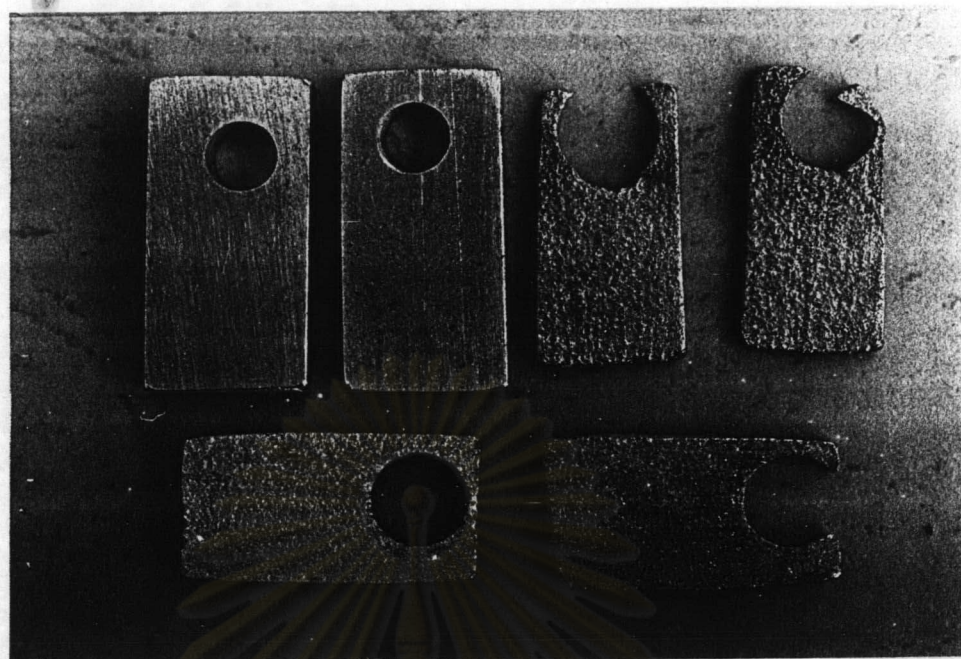


Figure 4.75 Photograph showing the surface of the corroded specimens immersed in the CH_3OH +saturated H_2S +200 ppm DMM solution in comparison with that immersed in the solution without DMM for 133 h at ambient temperature

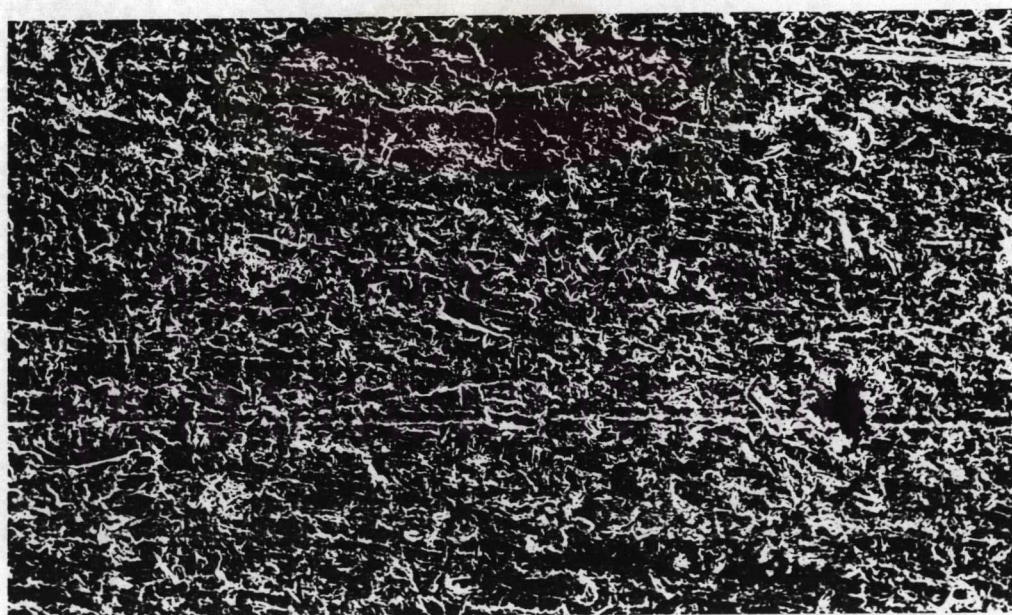


Figure 4.76 SEM photograph with mag.x60 showing the appearance on surface of the corroded specimen immersed in the absolute CH_3OH +saturated H_2S solution at ambient temperature for 183 h



Figure 4.77 SEM photograph with magnification of x60 showing the appearance on surface of the corroded specimens exposed in the CH_3OH +saturated H_2S +200 ppm DMM solution at ambient temperature for 133 h

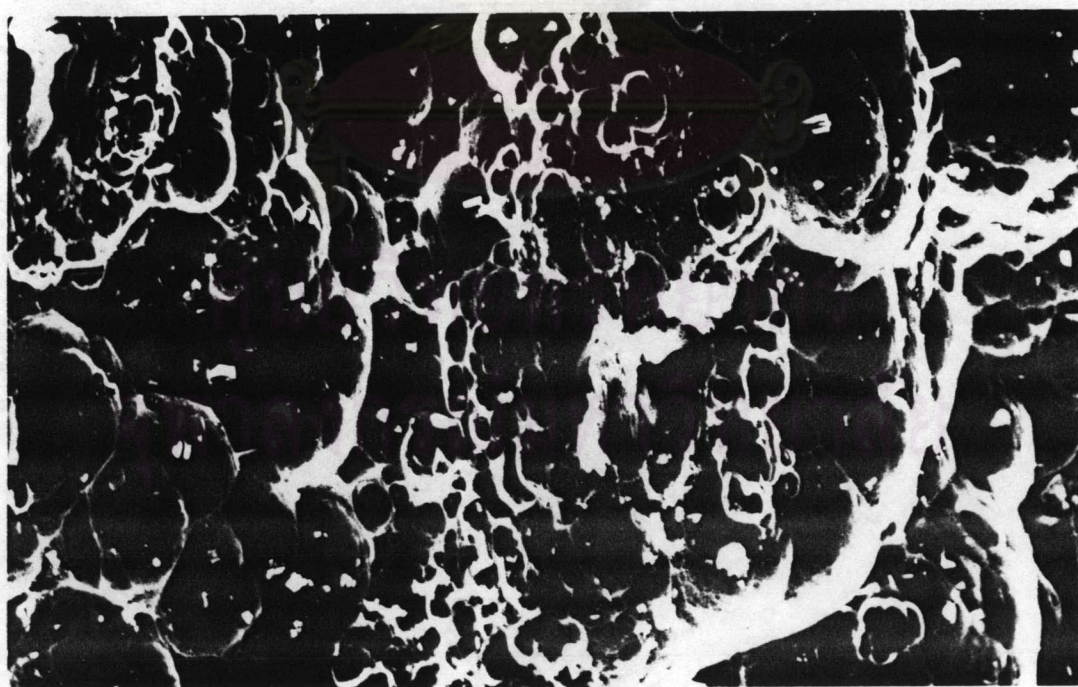
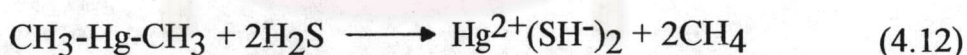


Figure 4.78 SEM photograph with mag.x600 showing the appearance on the same surface of the corroded specimens as that shown in Fig 4.77 in detail

The corrosive solutions used in the foregoing tests were solutions of DMM in absolute CH₃OH and added with 150 ppm HCl to break C-Hg bond in DMM to give elemental mercury which was active to the corrosion reaction of aluminium specimens. The corrosion occurred drastically, for example, at 30°C the CH₃OH+150 ppm HCl+200 ppm DMM solution corroded the aluminium specimens approximately 2675.9 milligrams/sq. decimetre/day (mdd), which was about 40 times more than that corroded by the solution without DMM (see these data in the appendix C). The corrosion test in Figure 4.75 used H₂S in stead of HCl in breaking C-Hg bond of DMM. It was appeared that it had the same potential to cause corrosion. A pair of specimens on the left hand side upper are corroded by the CH₃OH+saturated H₂S solution (without DMM), which it appeared a few small black pits on the surface. Photomicrograph magnified x60 in Fig 4.76 showed the appearance of these pits in detail. In the case of specimens immersed in the CH₃OH+saturated H₂S+200 ppm DMM solution, the corrosion results shown in Fig 4.77 were severe as well as that corrode by the solution with HCl and its corrosion rate was about 1800 mdd. H₂S added to break C-Hg bond in DMM may be undergone the reaction corresponding to the equation (4.2) and (4.3) :



Hg²⁺-(SH⁻)₂ generated in this equation may continue corroding aluminium specimens. From the visual observation in the reaction flasks, it was found that the reaction occurred severely. There was a large amount of gas evolved from the "Whisker", porous deposited to the specimen surface, and corrosion products, yellow and gray color, fell off to the bottom of the flask. This was believed that the corrosive solution added with H₂S occurred the circulation reaction of corrosion as that accomplished by HCl. Figure 4.78 with magnification of x600 showed the appearance on the corroded surface in detail, which it was obviously appeared in the form of uniform corrosion.

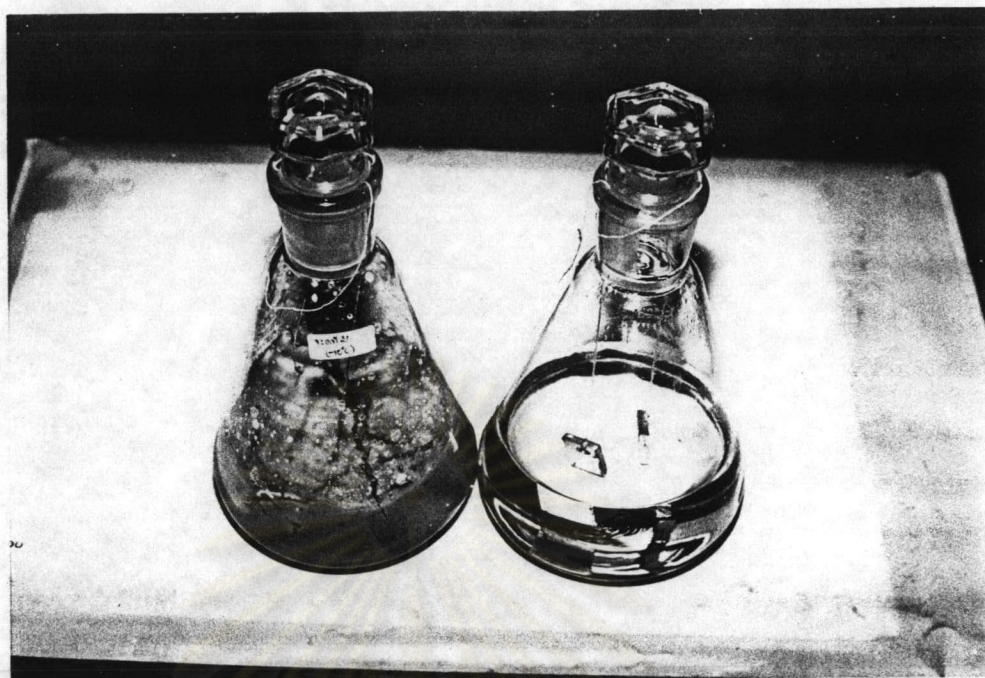


Figure 4.79 Comparison of the Al corrosion reaction undergone in $\text{CH}_3\text{OH}+150$ ppm $\text{HCl}+200$ ppm DMM solution with that undergone in the $\text{DMSO}+200$ ppm DMM+Dioxane+150 ppm HCl solution.



Figure 4.80 Comparison of the Al corrosion reactions undergone in the absolute $\text{CH}_3\text{OH}+150$ ppm HgCl_2 solution with that undergone in the Ether+150 ppm HgCl_2 solution.

Figure 4.79 showed the corrosion reaction on aluminium specimen by the $\text{CH}_3\text{OH}+150 \text{ ppm HCl}+200 \text{ ppm DMM}$ solution in comparison with that by the $\text{DMSO}+150 \text{ ppm DMM}+\text{Dioxane}+150 \text{ ppm HCl}$ solution. From the observe at both systems all time, it was found that the corrosion reaction occurred severely only in the former, which absolute methanol disappeared within about 60 h, whereas the conversion in the latter was slowly, which no corrosion product appeared and gas evolved in sight, until one week ago a few pits shape like pits shown in Fig 4.74 appeared. These implied that both corrosion systems could generate $\text{Hg}^{2+}\text{Cl}_2^-$ according to equation (4.2) and (4.4) successfully, but only the former system could accomplish the other contionous reactions according to the equation (4.11), whereas the latter can not do that because no absolute CH_3OH supports the reaction according to equation (4.11)

Figure 4.80 showed the corrosion reaction on the specimens corroded by the $\text{CH}_3\text{OH}+150 \text{ ppm HgCl}_2$ solution in comparison with that corroded by the ether+ HgCl_2 solution. It was found that the $\text{CH}_3\text{OH}+\text{HgCl}_2$ solution occurred the severe reaction on aluminium like the $\text{CH}_3\text{OH}+\text{HCl}+\text{DMM}$ solution, that was because $\text{HCl}+\text{DMM}$ can form $\text{Hg}^{2+}\text{Cl}_2^-$ in solution successfully. If the corrosion reaction occured by the $\text{CH}_3\text{OH}+\text{HgCl}_2$ solution is compared with that occured by the $\text{CH}_3\text{-O-CH}_3+\text{HgCl}_2$, it has appeared the difference completely because no reaction appeared in sight in the $\text{CH}_3\text{-O-CH}_3+\text{HgCl}_2$ solution,even a few small black pits. Ether can not provide OH^- group to the reaction according to equation (4.11), then the reaction occurred little and slow. The value of corrosion rate undergoned by the $\text{CH}_3\text{OH}+150 \text{ ppm HCl}+200 \text{ ppm DMM}$ solution was 2075.9 mdd, by the $\text{DMSO}+200 \text{ ppm DMM}+\text{Dioxane}+150 \text{ ppm HCl}$ solution was 14.95 mdd, by the $\text{CH}_3\text{OH}+\text{HgCl}_2$ solution was 1179.5 mdd and by the $\text{CH}_3\text{O-CH}_3+\text{HgCl}_2$ was 0.015 mdd. These value could support the foregoing discussion.

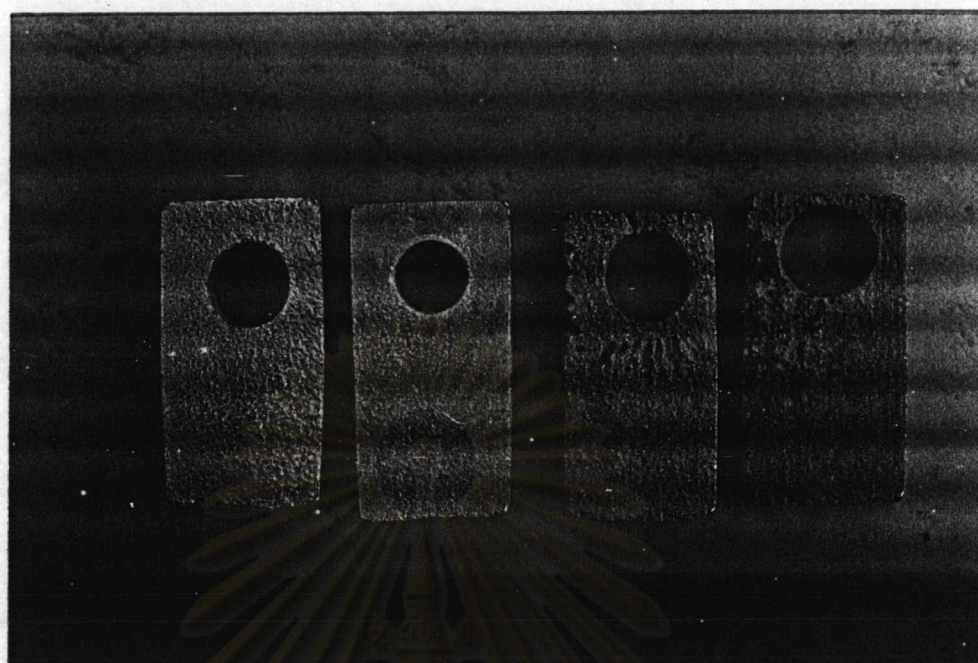


Figure 4.81 Photograph showing surface of the corroded specimens immersed in the $\text{CH}_3\text{OH}+150$ ppm $\text{HCl}+200$ ppm DMM solution in comparison with that immersed in the $\text{CH}_3\text{OH}+300$ ppm $\text{H}_2\text{S}+200$ ppm DMM solution.

Figures 4.81-4.82 showed that the form of corrosion of the specimens immersed in the $\text{CH}_3\text{OH}+150$ ppm $\text{HCl}+200$ ppm DMM solution was similar to that immersed in the $\text{CH}_3\text{OH}+300$ ppm $\text{H}_2\text{S}+200$ ppm DMM solution, which were uniform corrosion. The corrosion rate values of these systems, which were shown in the appendix C, were also very close each other ($\text{H}_2\text{S} = 2978.5, \text{mdd}$, $\text{HCl} 2675.95 \text{ mdd}$). A few furrows appeared near the hole for mounting was another form of corrosion, it is called intergranular corrosion. This corrosion form was caused by enrichment or depletion of one of the alloying elements in the grain boundary, which made grain boundaries and area adjacent to it weak for being attacked by the corrosive solution in comparison to grain matrix. From table 4.2, it was found that there were lots of alloying elements in aluminium specimen, those were little amount of compositions. One that was worth noting was magnesium. The reason for

appearing intergranular corrosion was that drilling holes for mounting on specimens was made without cooling simultaneously, which made specimens too hot. Thus its grain matrix and grain boundary may be deformed and makes residual stress left in the area near and around the hole, which made the area be attacked by corrosive solution easily. When specimen was heated during drilling, some compositions, such as Fe, Mg, would move to grain boundary and form oxide with O_2 . This makes quantity of Fe and Mg in grain boundary differed from in grain matrix, which consequently made grain boundary weak to be corroded by the solution.



Figure 4.82 Photograph showing the surface of the corroded specimens immersed in the $CH_3OH+150$ ppm $HCl+200$ ppm DMM solution, those immersed in the $CH_3OH+300$ ppm H_2S+200 ppm DMM solution and those before test

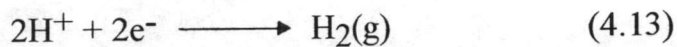
Environmental Effects on Corrosion Result of Test Specimen

1. Corrosion Rate of CS Test Specimen

1.1 Effects of Temperature on Corrosion Rate of CS Specimens

In order to report the CS corrosion rate corroded by DMM solution more obviously, the following corrosive systems, such as, CS-H₂O, CS-HCl in water, CH₃OH, and PE, were reported first in comparison to that corroded by DMM solution. All of corrosion rates obtained by various corrosive systems were collected in the appendix C. Three factors affected to corrosion rate, such as temperature, concentration, and velocity of corrosive solution, were also analysed and reported its effects on the rates.

For the corrosion rate of CS specimens exposed in various corrosive solutions in Figure 4.83, it was found that corrosion results by those were not the same. The corrosion rate resulted from the acid solution (150 ppm HCl in H₂O) provided the highest value, which its value were in an interval of 20.85-82.11 mdd. For the corrosion rate resulted from the other medias, those were descended in order, from H₂O, CH₃OH+HCl, PE+HCl, and the remaining solutions providing corrosion rate very low and close to each other. Besides, the depended temperature of corrosion rates corroded by various medias were not the same either. The effect of temperature on the corrosion rate of specimens corroded by the acid solution was the highest one, followed by that corroded by H₂O. Those corroded by the remaining solutions were not significant. It was clear from the Figure 4.83 that the corrosion rate resulted from the acid solution(H₂O+150 ppm HCl) increased exponentially with temperature. This was in agreement with the findings of Uhling [26]. Usually, the cathodic reductions on metal corrosion by aqueous acid solution occurred freely and was not necessary to depend on O₂ dissolved in H₂O, according the following reaction:



O_2 dissolved in H_2O could also support this cathodic reduction by the following reaction :

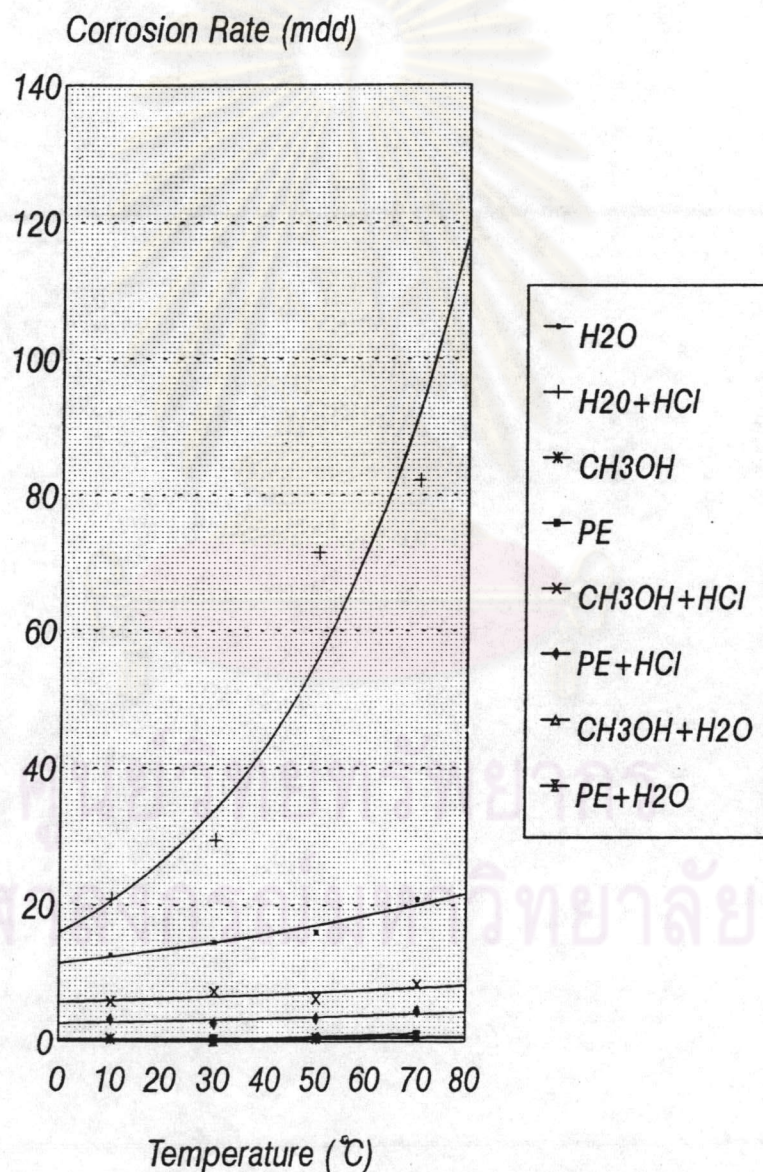
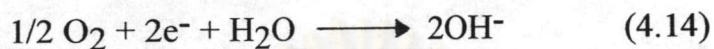


Figure 4.83 Effects of temperature on corrosion rate of carbon steel specimens immersed in various corrosive solutions.

Therefore, while the exposure temperature was increasing at any time, even O_2 could always escape from the flask, its corrosion rate still increased with temperature by equation (4.13). This causes corrosion rate of the metal- H_2O corrosion system slightly increased as the exposure temperature increases

In the case of corrosion by the $CH_3OH+150$ ppm HCl solution, in addition to the low corrosion rate, its dependence on temperature was also low because by nature, CH_3OH itself less dissolves and dissociates HCl and O_2 than water, either H^+ ion or O_2 reduction can thus occur less

The PE+150 ppm HCl solution corroded the CS specimens very little because HCl dissolved in PE very poorly in comparison to CH_3OH/H_2O . This reduced the opportunity of its molecules to contact with specimen surface, however, when temperature was elevated, the opportunity was slightly increased

Figure 4.84 showed the effect of temperature on corrosion rate of the corroded specimens immersed in the $CH_3OH+150$ ppm DMM solution in comparison to that corroded by the $CH_3OH+150$ ppm DMM+150 ppm HCl solution. First it should be considered the effects of solvents, absolute CH_3OH and PE, on corrosion. It was found that both of them corroded the CS specimens very low, for example, their corrosion rates were 0.41 and 0.51 mdd at $50^\circ C$, respectively. Although their corrosion rates increased with temperature, the effect of temperature on their corrosion was very low because pure CH_3OH occurred very low oxygen reduction (eq.4.14). Furthermore, H_2O

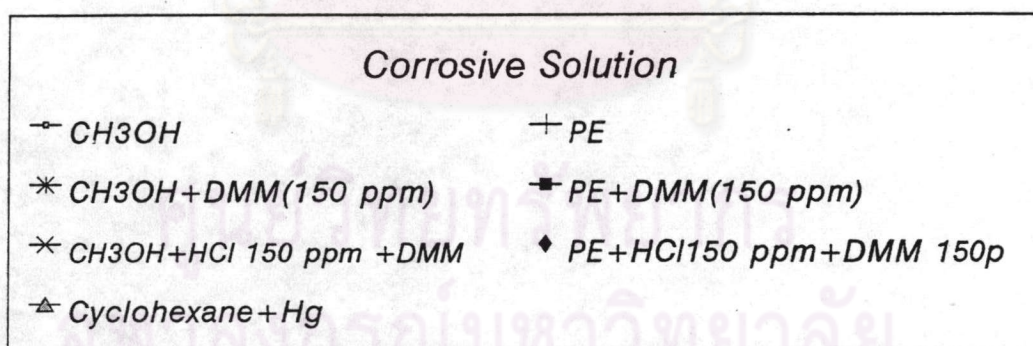
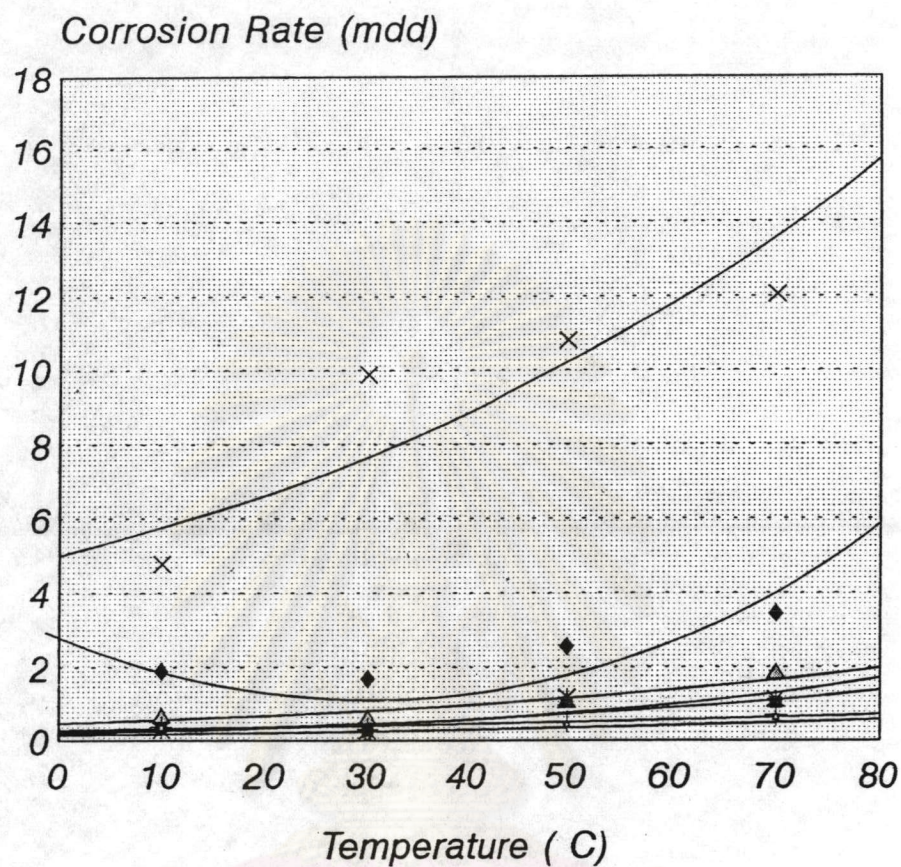
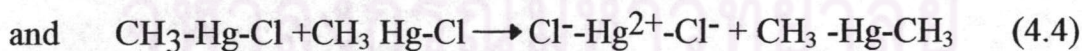
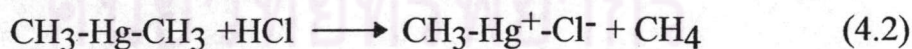


Figure 4.84 Effect of temperature on corrosion rate of carbon steel specimen corroded by the DMM solution (CH₃OH+DMM, PE+DMM) without HCl in comparison to that corroded by the solution with HCl

existed in absolute CH_3OH was too low to dissolve. When the corrosion rates caused by the $\text{CH}_3\text{OH}+150$ ppm DMM solution was compared to that obtained by absolute CH_3OH , it was found that the former was higher than that caused by CH_3OH very obviously and also increased with temperature. From the appearance on surface of the corroded CS specimen immersed in this solution in section 4.1 (in Fig 4.19-4.20), it could conclude that those CS specimens in the $\text{CH}_3\text{OH}+\text{DMM}$ solution were corroded by the elemental mercury dissociated from DMM by heat supplied to the system. As well-known, increasing temperature increased dissociation of DMM, then corrosion rate became higher. In the case of PE as solvent, corrosion rate obtained by the $\text{PE}+150$ ppm DMM solution was slightly increased with temperature because of the similar reasons claimed in discussion of corrosion by $\text{CH}_3\text{OH}+\text{DMM}$.

The $\text{CH}_3\text{OH}+150$ ppm $\text{HCl}+200$ ppm DMM solutions resulted in the highest corrosion rate of all solutions appeared in figure 4.89 and the corrosion rate was also obviously increased with the exposure temperatures. However, from section 4.1, it was evident that this solution corroded the carbon steel slightly in comparison with the aluminium. In section 4.1, two reactions for the acid cleavage of C-Hg bond of DMM were purposed according to equation (4.2) and (4.4) :



Both reactions (4.2) and (4.4) required the vigorous condition to overcome the barrier energy, which the exposure temperature elevated in the those experiments became the vigorous condition for promoting both reactions. In addition to increase the amounts of HgCl_2 according to equations (4.2) and (4.4), the elevating temperature would also promote the heterogeneous reaction on the surface of carbon steel. In the case of the $\text{PE}+150$ ppm

HCl+150 ppm DMM solution, in Fig. 4.84, it could be concluded that the corrosion rates of CS specimens were increased with the exposure temperature. It was believed that the corrosion result caused by this solution was low because of the low solubility of HCl in PE. Even though the exposure temperature was elevated, HCl was still not be able to dissolve and dissociate in PE more, which could not increase the amount of $HgCl_2$.

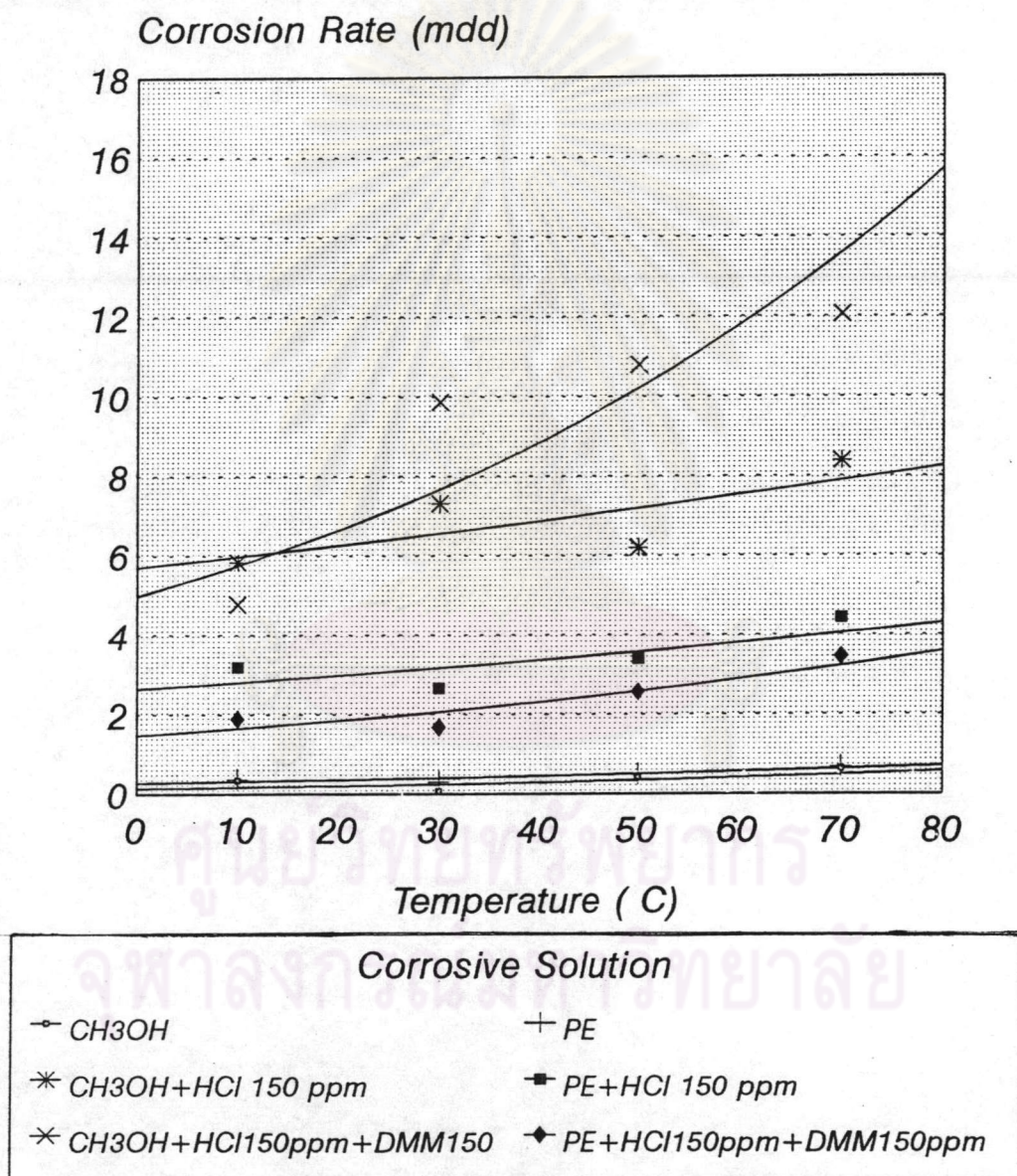


Figure 4.85 Effect of temperature on corrosion rate of CS specimens corroded by the acid solution without DMM(CH₃OH+HCl, PE+HCl) in comparison with that with DMM.

Figure 4.85 was proposed to compare corrosion results of CS specimens immersed in the $\text{CH}_3\text{OH}/\text{PE}+150$ ppm HCl solution with that in the $\text{CH}_3\text{OH}/\text{PE}+150$ ppm HCl solution. It was showed that the $\text{CH}_3\text{OH}+\text{HCl}$ 150 ppm+200 ppm DMM solution provided higher corrosion rate than the $\text{CH}_3\text{OH}+150$ ppm HCl solution (without DMM) and its corrosion rate was higher increased with the exposure temperatures than the other corrosive solution system, that is because of breaking C-Hg bond of DMM with HCl to generate HgCl_2 for starting corrosion reaction. Another interesting point in this figure was that the $\text{PE}+\text{DMM}+\text{HCl}$ solution provided less corrosion rate to carbon steel specimen than the $\text{PE}+150$ ppm HCl solution, while those corrosion rates caused by both of solutions still increased with the exposure temperature.

The appearance on the corroded surface caused by the $\text{PE}+\text{HCl}+\text{DMM}$ solution in section 4.1 was similar to that caused by the $\text{PE}+\text{HCl}$ solution, but different from that caused by Hg in cyclohexane. therefore it was believed that the important corrosive agent in this solution should be HCl rather than elemental mercury dissociated from DMM. Eventhough it was dissolved a little, HCl corroded carbon steel specimen about 4.1 mdd. In the $\text{PE}+\text{HCl}+\text{DMM}$ solution, DMM reacted with HCl to break C-Hg bond according to equation (4.2) and(4.4). These reactions reduced the potential of HCl to corrosion. Although there might be CH_3 -Hg-Cl or HgCl_2 occur, their potential to corrosion was much lower than HCl. This makes corrosion caused by the $\text{PE}+\text{DMM}+\text{HCl}$ solution was lower than that caused by the $\text{PE}+\text{HCl}$ solution.

1.2 Effect of Concentration of Corrosive Media on Corrosion Rate

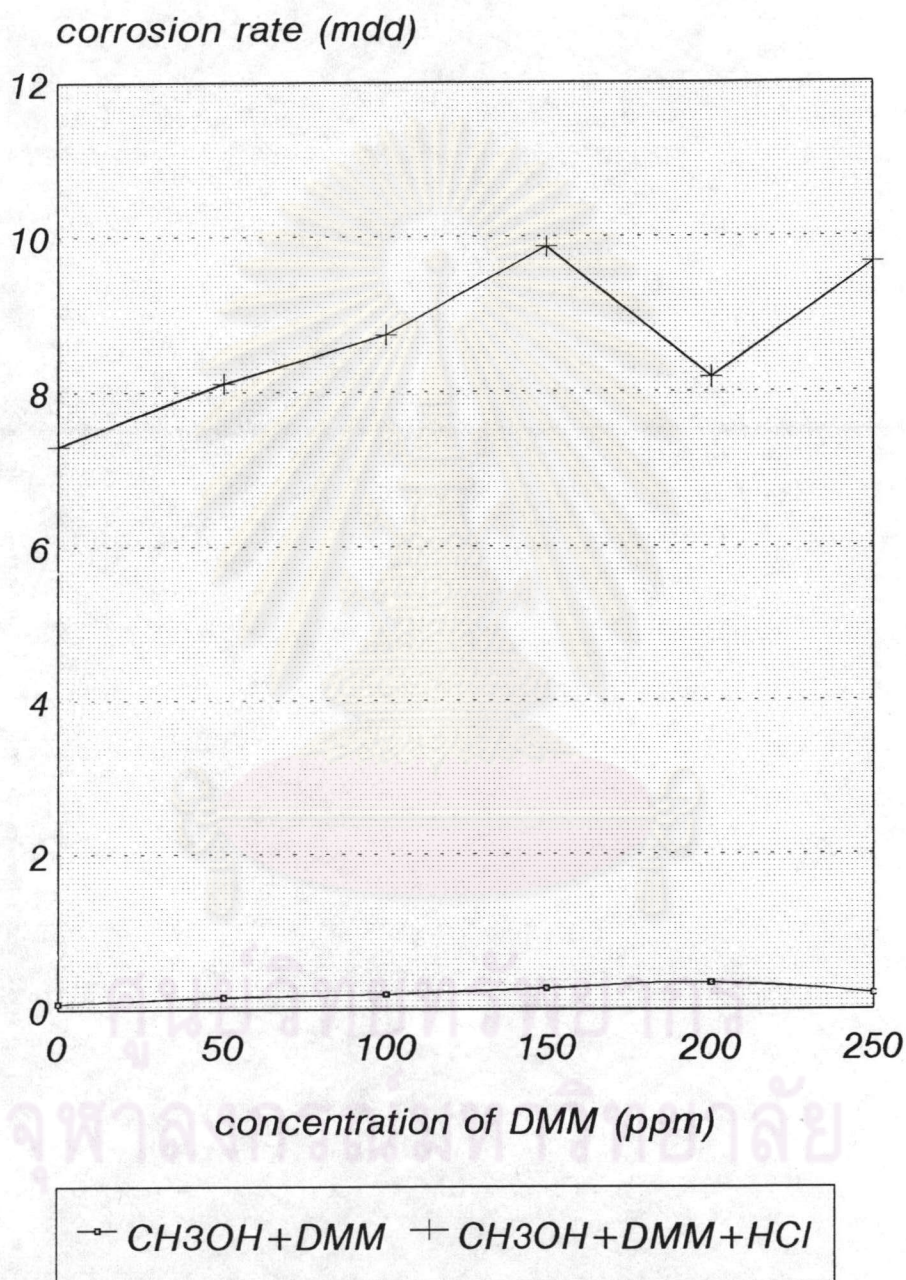


Figure 4.86 Effect of DMM concentration on corrosion rate of carbon steel specimens corroded by the $CH_3OH+150$ ppm $HCl+DMM$ solution in comparison to that corroded by the $CH_3OH+DMM$ solution at $30^\circ C$

It was appeared from Figure 4.86 that at 30°C the CH₃OH+150 ppm HCl+DMM solution provided corrosion rate of carbon steel specimens to increase slightly with the DMM concentration. The corrosion rate at the first point on the left hand side was obtained by corrosion of the CH₃OH+150 ppm HCl solution and after DMM was added (50 ppm), its corrosion rate became higher and the more DMM concentration, the higher corrosion rate higher up to 150 ppm, after that it tended to be steady. This might be due to the limited amount of HCl existing in solution. However, this corrosive system still provided higher dependent of corrosion rate on the DMM concentration than the CH₃OH+DMM solution system which its dependence on that seemed to be to increase slightly with DMM concentration. This might be due to constant temperature which limited the dissociation of DMM not to increase, although the DMM amount in those solutions was increased.

Figure 4.87 showed corrosion rates obtained by immersion in both the PE+DMM solution and the PE+DMM+150 ppm HCl solution which tended to be independent on DMM concentration. Especially, the corrosion rate of the latter was lower than that of the former. The reasons may be due to reducing of the HCl potential to metal-corrosion, which resulted from its reaction with DMM.

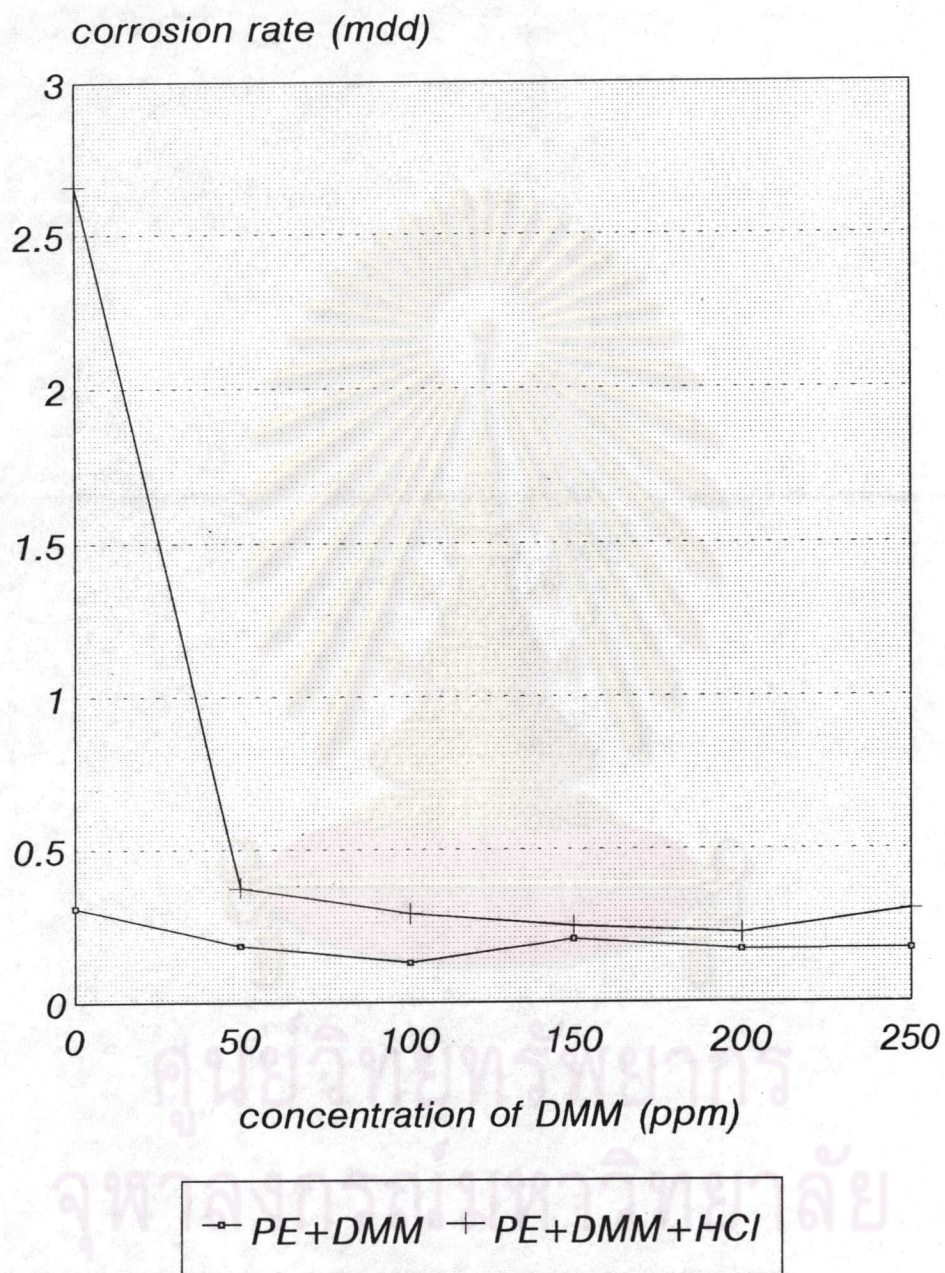


Figure 4.87 Effect of DMM concentration on corrosion rate of carbon steel specimens corroded by the PE+150 ppm HCl+DMM solution in comparison to those corroded by the PE+DMM solution (without HCl) at exposure temperature 30°C

Table 4.9 Corrosion rate (mdd) of CS and Al specimens immersed in various corrosive solutions, both with and without DMM at 10° and 30°C

corrosive solutions	Temp. (°C)	Corrosion Rate	
		Al specimen	CS specimen
CH ₃ OH+150 ppm HCl	30°C	16.54	7.30
CH ₃ OH+150 ppm HCl+150 ppm DMM	30°C	746.40	9.90
CH ₃ OH+150 ppm HCl	10°C	7.76	5.83
CH ₃ OH+150 ppm HCl+150 ppm DMM	10°C	6.15	4.77
PE+150 ppm HCl	30°C	3.87	2.66
PE+150 ppm HCl+150 ppm DMM	30°C	4.20	0.25
PE+150 ppm HCl	10°C	4.09	3.19
PE+150 ppm HCl+150 ppm DMM	10°C	6.25	1.89

It was clear from table 4.2 that every corrosive solutions at various temperature, either CH₃OH or PE as solvent, corroded the aluminium specimens much more than carbon steel. Especially, in the case of the CH₃OH+150 ppm HCl+150 ppm DMM solution, it corroded the aluminium specimens severely, but it did to carbon steel very little. This meant that carbon steel had higher resistance to corrosion resulted from organomereury together with acid. From table 4.1, there are 0.1% chromium contributed in the test specimen, which was about 10 times higher than that contributed in the standard steel test specimen, which it was mild steel but the test specimens were carbon steel. It is well known that chromium added into steel in order to improves its resistance to corrosion. This is the reason why the carbon steel test specimens were corroded a little

2. Corrosion Rate of Aluminium Test Specimen

The corrosion rate of the aluminium test specimen reported here was divided into 3 groups based on corrosive solution as criteria, as follow:

- 1) Reference corrosive : H_2O , aqueous acid solution (HCl)
- 2) Solvents : CH_3OH , PE, $CH_3OH+HCl$, $PE+HCl$, CH_3OH+H_2S
- 3) Interested corrosive solution : all of corrosive solutions with DMM, such as $CH_3OH+150$ ppm HCl+150 ppm DMM, $PE+150$ ppm HCl+150ppm DMM, etc.

2.1 Corrosion Rate by Various Corrosive Medias

Some other corrosive medias were chosen to run the tests, such as H_2O and H_2O+150 ppm HCl solution. Figure 4.88 showed the results corroded by both of these solutions, which it was found that corrosion rates on aluminium specimens by H_2O were very low. While the temperature was elevated, the corrosion rate became significant. Usually, pure water will not corrode the aluminium metal[25], but if there is only trace amount of ions contained in the water, such as H^+ , CO_3^- , Cl^- , it may corrode aluminium metal. The distilled water used in this test was produced by the simple equipment in laboratory, then it may absorb some species, such as H_2CO_3 in it.

Corrosions on test specimen corroded by HCl either dissolved in H_2O or in absolute CH_3OH or PE were much higher than that immersed in pure CH_3OH and PE and increased with increasing the exposure temperature. Those trends were found to be exponential. One interesting thing was that the $CH_3OH+150$ ppm HCl solution obtained increased the corrosion rate more than the aqueous acid solution. Figure 4.36 and 4.64 showed that the corrosion appearances obtained by both H_2O+150 ppm HCl solution and the $CH_3OH+150$ ppm HCl solution were rather different. The former appeared

pitting obviously but the latter was somewhat uniform corrosion. By nature, CH_3OH can dissolve fat and oil better than H_2O . Even, in cleaning specimen,

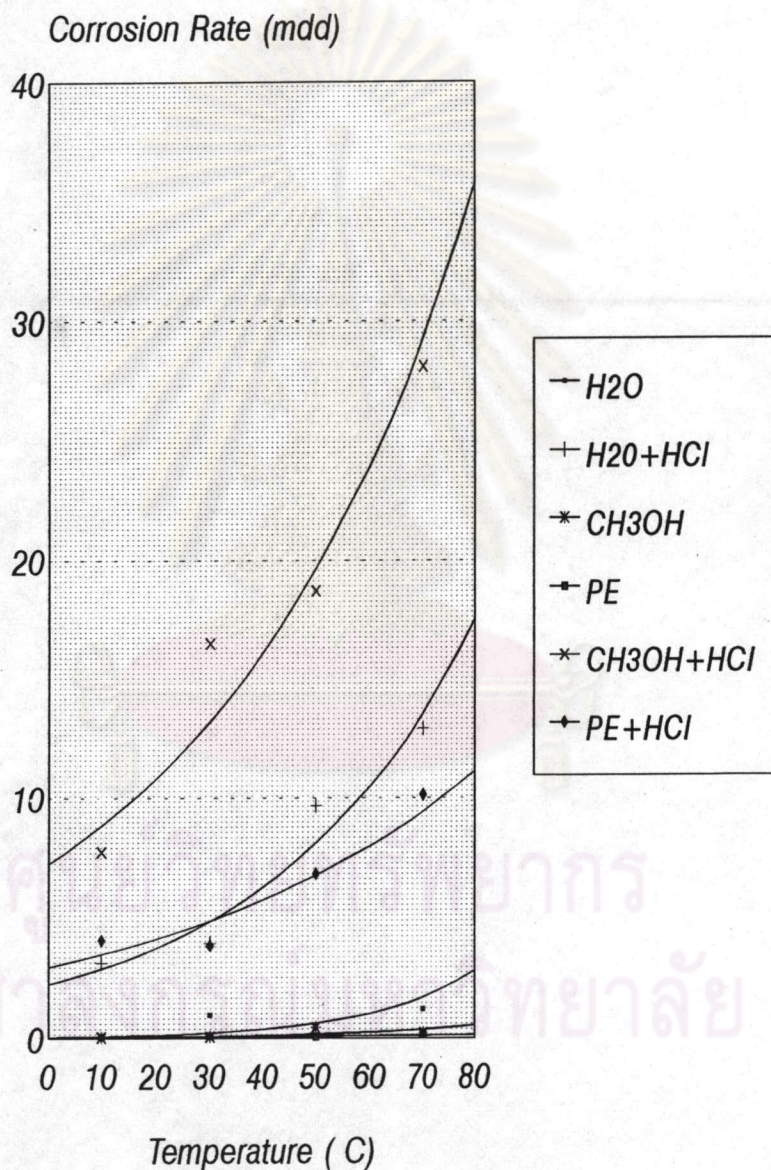


Figure 4.88 The relationship between corrosion rate (mdd) on the aluminium specimens immersed in various corrosive solutions and the exposure temperature

CH₃OH and ether was used to remove impurities from specimen surface after rubbing with abrasive paper. Therefore, it was believed that immersing specimen in CH₃OH made acid in solution be contacted to specimen surface more thoroughly than immersing that in water. The corrosion rate by the CH₃OH+150 ppm Hcl solution should be more and the appearance should be uniform corrosion.

If one specimen was not removed all of fat stain out of the surface, some fat was still cover the surface. When this specimen was immersed, then acid could not corrode the surface under the stain, conversely, immersing it in the CH₃OH+acid solution, after CH₃OH dissolved all of fat on that stain, can corrode surface more thoroughly.

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2.2 Corrosion Rate by DMM-Corrosive Solution with PE as Solvent

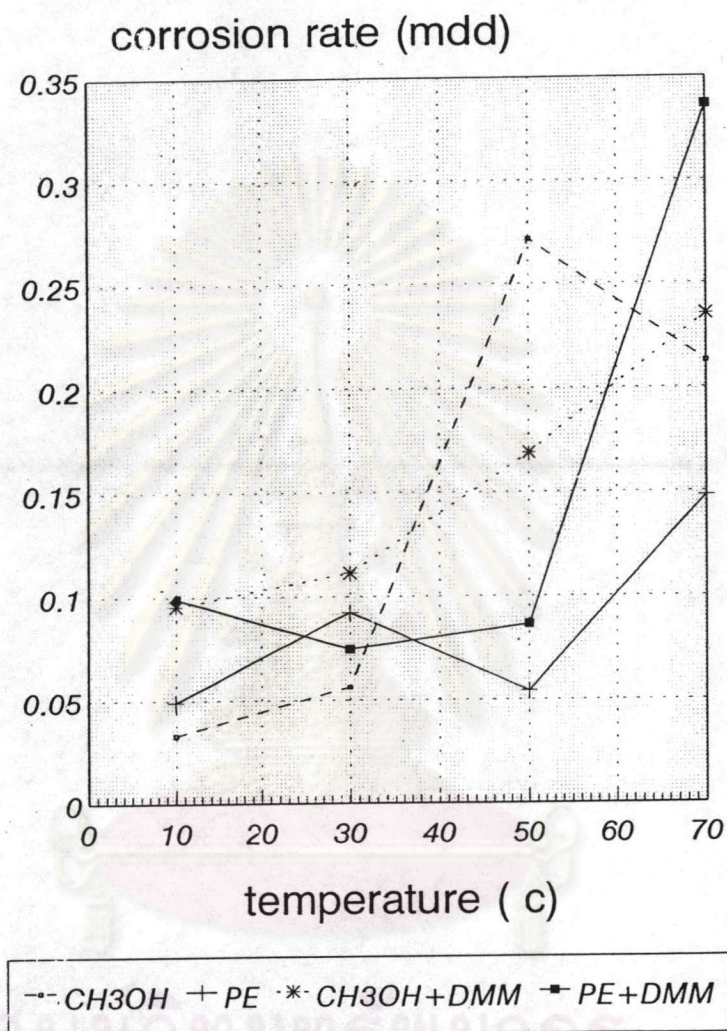


Figure 4.89 Relationship between corrosion results caused by the PE+150 ppm DMM solution and the exposure temperature

It was seen from the figure 4.89 that corrosion rates obtained by immersion in the PE+150 ppm DMM solution were closed to those corroded by pure PE. The differences were not much significant. The rates slightly increased with increasing the exposure temperature. This indicated that conversion of DMM dissociation in PE at temperature between 30°-70°C was

too low to produce large amount of elemental mercury for starting metal corrosion

1. Effect of Exposure Temperature

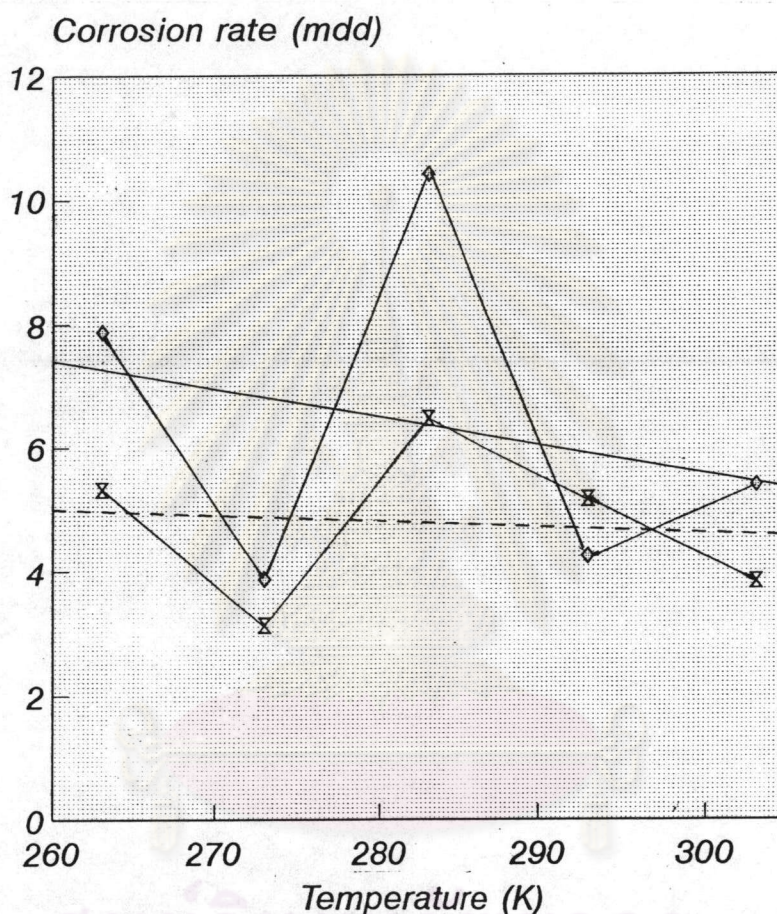


Figure 4.90 Relationship between corrosion rates and the exposure temperature (-10^o-30^oC) of corrosion system by the PE+150 ppm HCl solution in comparison to that by the PE+150 ppm HCl+150 ppm DMM solution

Figure 4.90 showed corrosion rates of the aluminium specimens immersed in the PE+150 ppm HCl solution (without DMM) in comparison to that immersed in the PE+150 ppm HCl solution at various temperature (-10^o-30^oC). It was indicated that corrosion rates of the DMM-corrosive solution were higher than those of the other and tended to slightly increase

with decreasing temperature over temperature interval of -10°C - 30°C , whereas the rates obtained by the PE+HCl solution seemed to be independent on temperature on that interval.

2. Effect of DMM Concentration

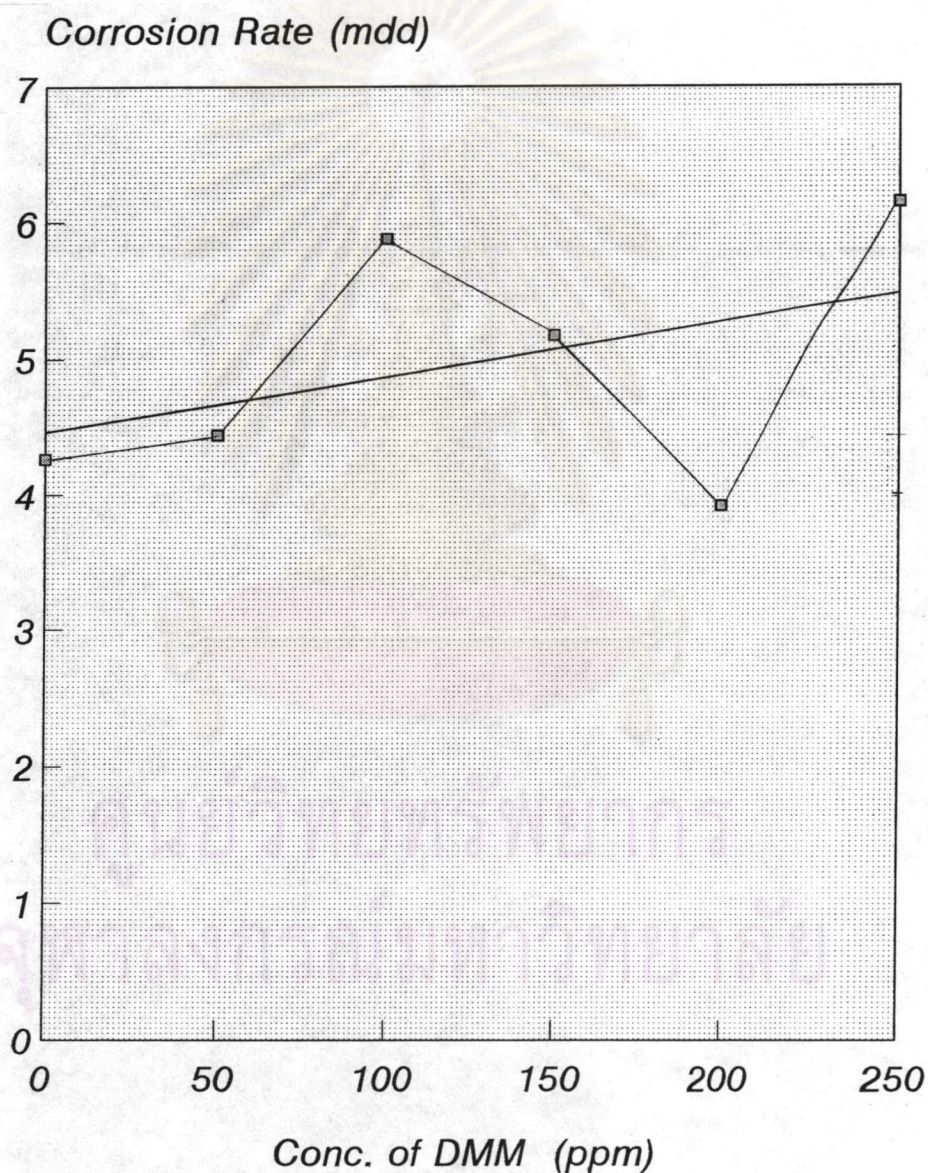
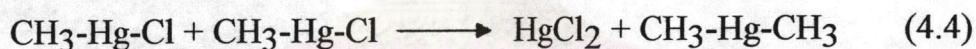


Figure 4.91 Relationship between corrosion rates obtained by immersion in the PE+150 ppm HCl+DMM solution and concentration of DMM at ambient temperature

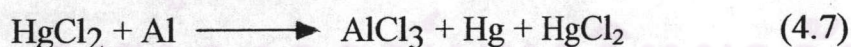
Figure 4.91 illustrated that corrosion rates obtained by the PE+150ppm HCl+DMM solution tended to slightly increase with concentration of DMM. Dessy had done the experiment to observe the breaking of C-Hg bond of DMM in DMSO-Dioxane solvents which the result were according to equation 4.2



and also reported that rates of this reaction are independent on concentration of DMM. On the other hand, increasing concentration of DMM beyond the ratio 1:1 would not make CH₃-Hg-Cl increase. Furthermore, this experiment used PE, which dissolved much less amount of HCl than DMSO+Dioxane, as solvent. Therefore it was believed that the amount of HgCl₂ obtained by the following equation :



would not be varied with the DMM concentration either. As a result, the following corrosion reaction must not be varied with DMM concentration either.



Therefore, variation of concentration ratio of DMM : HCl beyond 1:1 would not affect the on corrosion rate of the system.

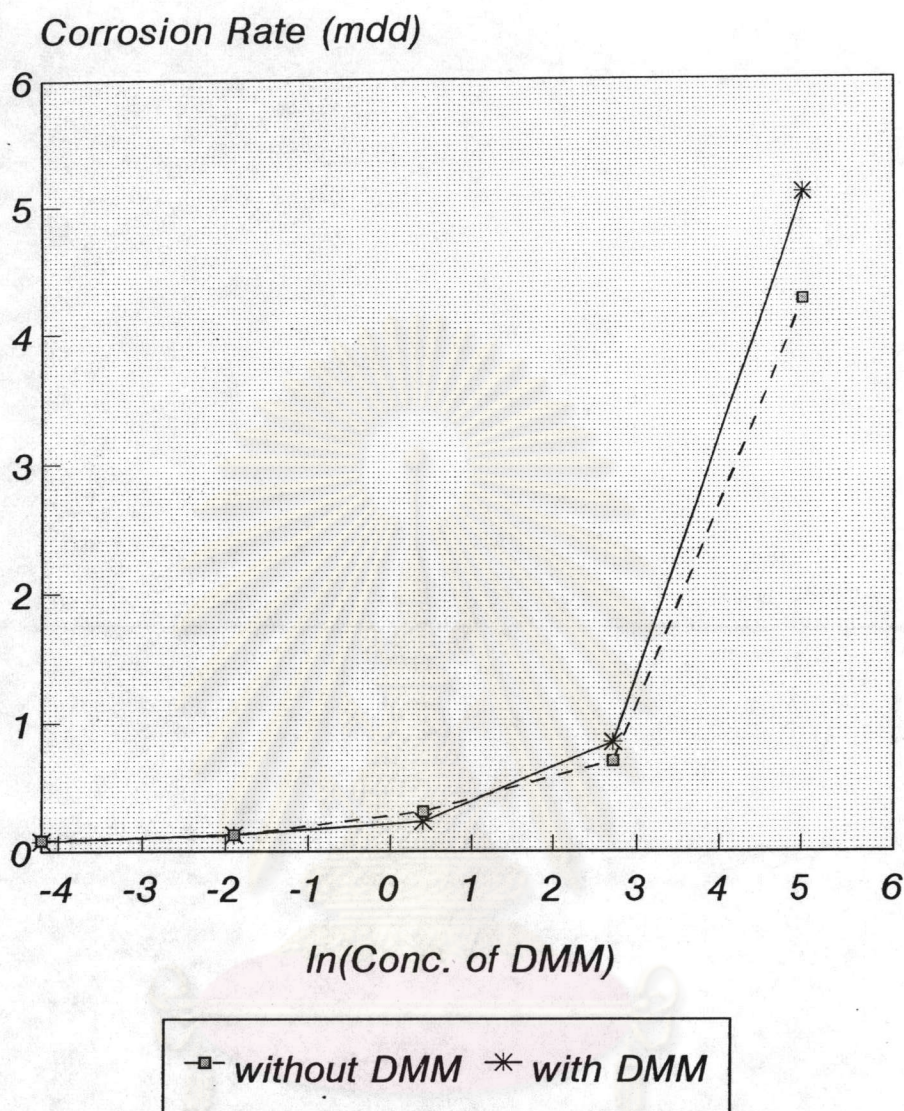


Figure 4.92 Relationship between natural logarithmic value of corrosion rates and concentration of DMM for corrosive system obtained by immersion in the PE+HCl+DMM solution with [HCl]:[DMM] = 1:1 and with [DMM] lower than 150 ppm at ambient temperature

The experiments in Fig 4.92 was carried out by varying concentration of DMM together with HCl as follow : 0.015, 0.15, 1.5, 15, and 150 ppm. It was found that these rates obtained by immersion in the PE+HCl+DMM solutions obviously increased with concentration of

DMM/HCl. Those rates were also higher than that obtained by the PE+HCl solution and maintained their higher values over entire ranks of the concentration. At the end, corrosion rates of both corrosive systems (15 ppm and 150 ppm) increased drastically.

3. Effect of Velocity

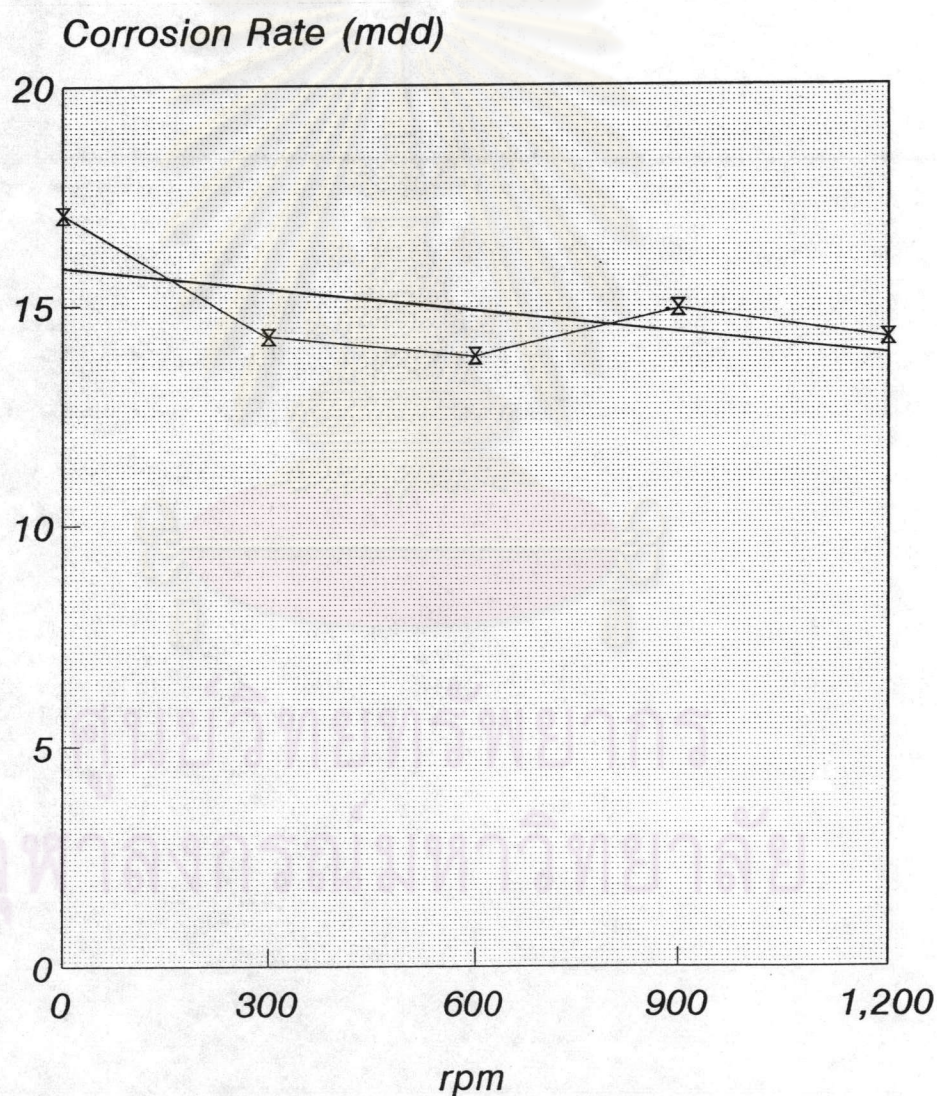


Figure 4.93 Relationship between corrosion rates of specimen immersed in the PE+150 ppm HCl+200 ppm DMM solutions and RPM agitated the solution

From Figure 4.93 it was evident that agitation and velocity of corrosive solution had no effect on corrosion rate of the aluminium specimens. Furthermore, the immersion of those specimens with agitation slightly lowered corrosion rates as compare to that without agitation. The corrosion rate of the first point on the left hand side of Fig 4.93 (no agitation) was 17.0754 mdd, whereas the other points obtained with agitation 100-1200 rpm provided corrosion rates between 13.8389-14.9338 mdd. Normally, in the PE+150 ppm HCl+200 ppm DMM solution used, HCl reacted with DMM to form corrosive agent HgCl_2 , which attacked specimen surface directly. Thus it was believed that corrosion process must not be diffusion controlled, but be activation controlled. Therefore, varying agitation and velocity of corrosive media were insignificant to increase corrosion rate. Furthermore solution agitation would destroy the "whisker" adhered on specimen surface (whisker is corrosion product absorbing corrosive intermediates together on specimen surface). Spreading whisker out reduced concentration of corrosive species near the surface, the corrosion rate was reduced.

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Table 4.10 Corrosion rates of Al specimens immersed in various corrosive solutions with PE as solvent and H₂S added in stead of HCl in some systems

Solvents & corrosive solutions	Corrosion Results	
	mdd	mpy
PE 150 ml+150 ppm HCl	3.83	1.87
PE 150 ml+150 ppm HCL+200 ppm DMM	5.40	2.63
PE 100 ml+200 ppm DMM+H ₂ O 50 ml+ 150 ppm HCl	21.95	10.70
PE 150 ml+200 ppm DMM+H ₂ O ml+saturated H ₂ S	0.82	0.40
PE 150 ml+200 ppm DMM+300 ppmH ₂ O+sat.H ₂ S	0.07	0.03
PE 140 ml+300 ppm H ₂ O+200 ppm DMM+ether 10 ml+H ₂ S	0.03	0.02
PE 150 ml+300 ppm H ₂ O+H ₂ S	0.05	0.02

Trace quantities of H₂S is appeared together with mercury in natural gas, then it was reasonably considered that whether it may enhance the corrosive activity of organomercury like HCl or not. Thus, H₂S was substituted HCl in the PE+HCl+DMM corrosive solution. Table 4.3 showed corrosion rate obtained by immersion specimen in the 150 mL PE+200 ppm DMM+100 ml H₂O+saturated H₂S solution. It was about 0.8172 mdd, which it was low with relative to that corroded by the PE+HCl+DMM solution. This corrosive solution was immiscible and separated into two phases, probability of reactivity between H₂S and DMM was then low because each one was dissolved in each phase. If these species mixed together in gas phase like natural gas, it is expected that their reactivity may be better and corrosion result may be higher.

2.3 Corrosion Rates by DMM-Corrosive Solution with CH₃OH as Solvent

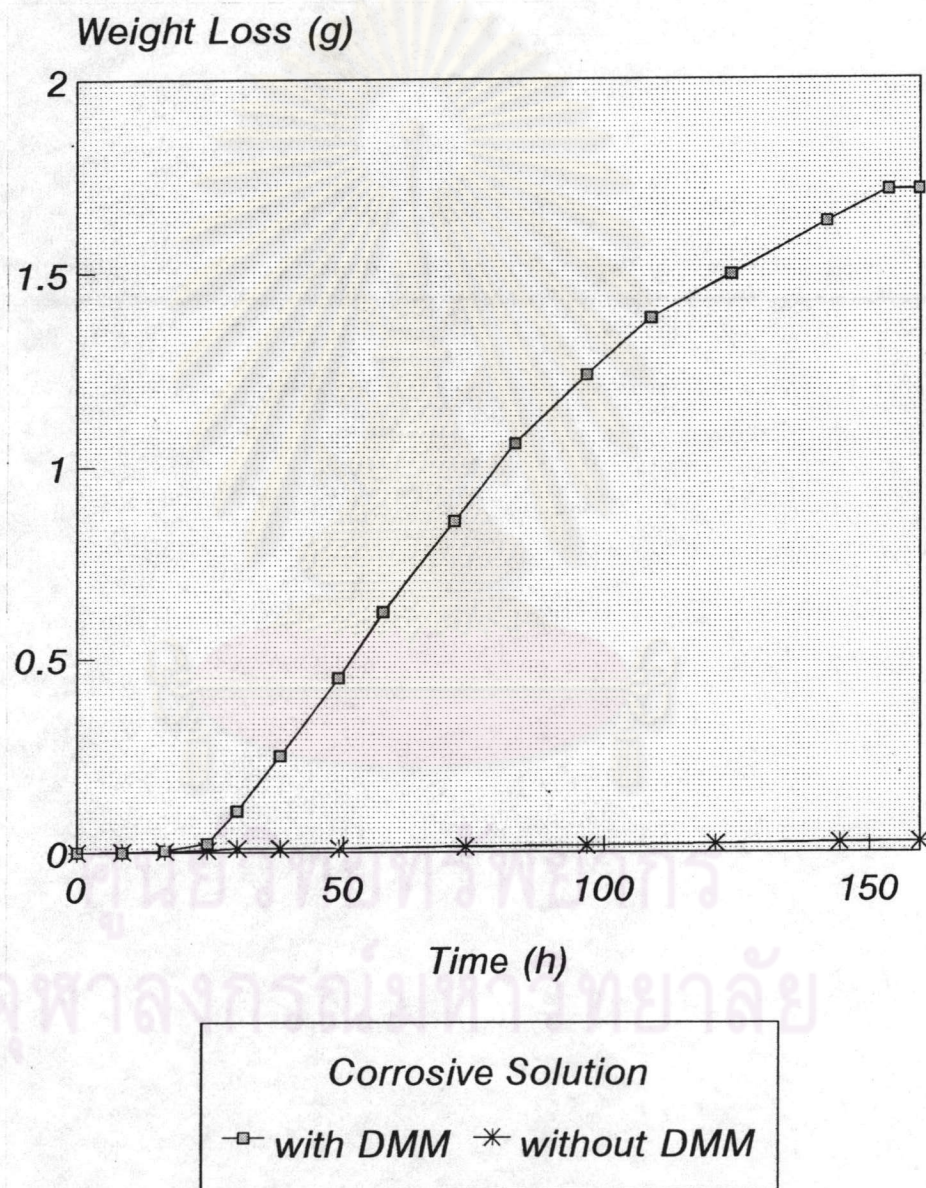
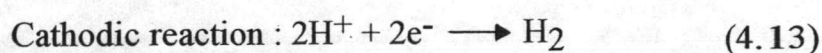
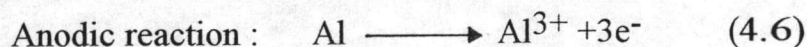


Figure 4.94 Relationship between weight loss of the aluminium specimens immersed in the CH₃OH+150 ppm HCl+200 ppm DMM solution and the exposure time.

The potential of absolute CH_3OH to enhance corrosion reaction of the aluminium by DMM was quite interesting, as mentioned in section 4.1. The weight loss of the specimens at the above figure showed damage by DMM together with CH_3OH . It was evident that weight loss of specimen was increased slowly within 25 h, after that it was rapidly increased with the exposure time until the specimen was finished at about 160 h. Comparison of weight loss obtained by the $\text{CH}_3\text{OH}+150 \text{ ppm HCl}+200 \text{ ppm DMM}$ solution with that obtained by the solution without DMM in Fig 4.94 showed completely different. The weight loss by the $\text{CH}_3\text{OH}+150 \text{ ppm HCl}$ solution was increased with increasing temperature gradually. From the observation at the reaction flask all time, it was found that there was little corrosion on specimen surface within 25 h. It appeared a few small black points and some small gas bubbles, which its size was equal to the end of needle, evolved from specimen surface. The gas bubble evolved lifted up to the solution surface. Then small half-moon porous material shape like whisker was intruded from the surface. A large amounts of gas evolved from these whiskers and the base of whiskers adhered to the specimen surface were expanded by corrosion processes rapidly. At this point, corrosion reaction became severe and was maintained its physical characteristics until either the specimen was finished or CH_3OH was finished. At the end of corrosion process, a large amounts of deposits was left in reaction flask. It was believed that corrosion reaction occurred slowly at earlier because of the attack of HCl on the surface according to the following reaction :



whereas the severe reaction which occurred later may be from new reaction concerning with CH_3OH closely.

2.Effect of Exposure Temperature

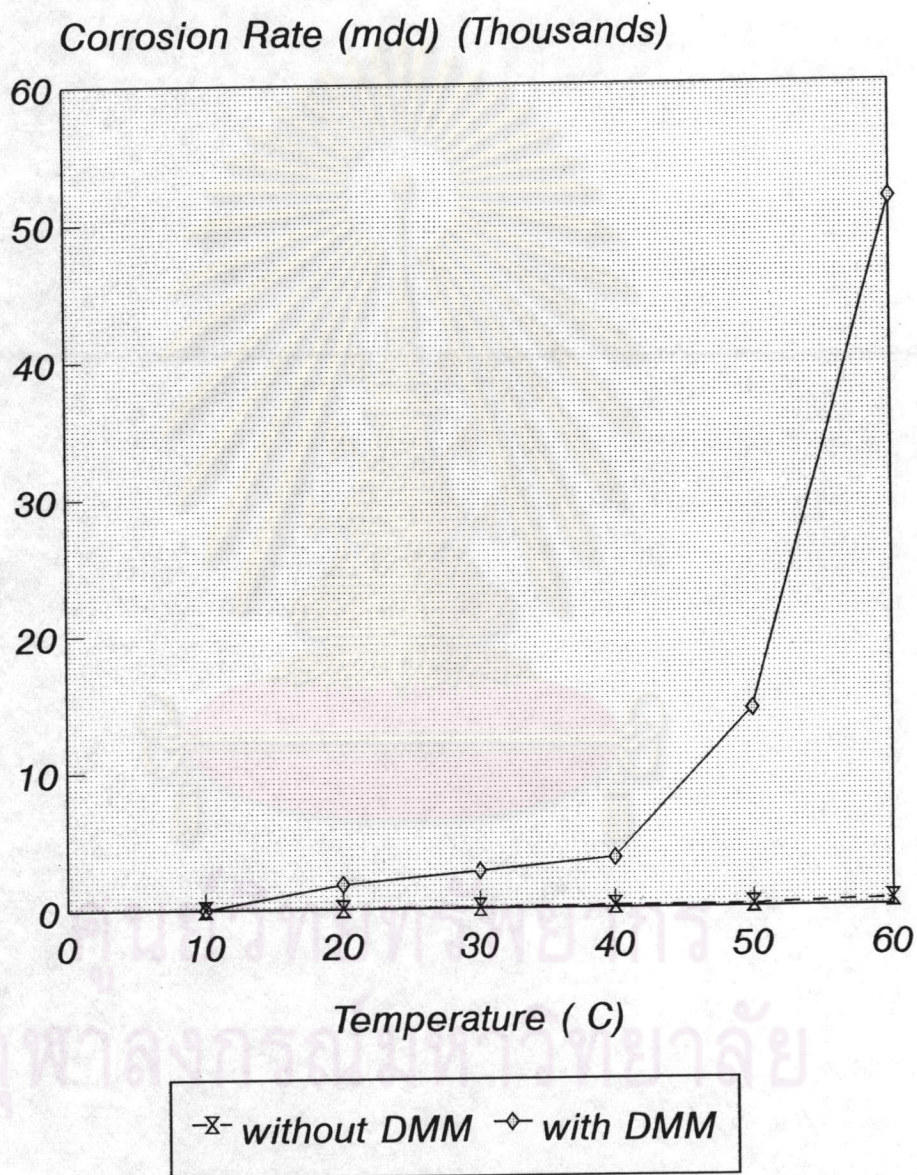


Figure 4.95 Relationship between corrosion rates of the aluminium specimens immersed in the $\text{CH}_3\text{OH}+150$ ppm $\text{HCl}+200$ ppm DMM solution and the exposure temperature

Figure 4.95 showed relationship between corrosion rates and the exposure temperature for the $\text{CH}_3\text{OH}+150 \text{ ppm HCl}+200 \text{ ppm DMM}$ corrosive system in comparison with that by the solution without DMM.

It was found that corrosion rate of the latter increased with increasing temperature gradually (see corresponding figures in the appendix C), whereas those obtained by the former increased with increasing temperature enormously and exponentially. The stage of corrosion process by the $\text{CH}_3\text{OH}+\text{HCl}$ solution was mentioned previously [see equation (4.2), (4.4), (4.7), (4.8) and (4.11)]. Corrosion rates obtained by the $\text{CH}_3\text{OH}+\text{HCl}+\text{DMM}$ system at 10°C were still close up to that corroded by the $\text{CH}_3\text{OH}+\text{HCl}$ system but their corrosion appearances on surface shown in section 4.1 were different. It was believed that the corrosion reaction at 10°C resulted in the attack on metal surface by mercury derivative, HgCl_2 .

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3.Effect of the DMM concentration

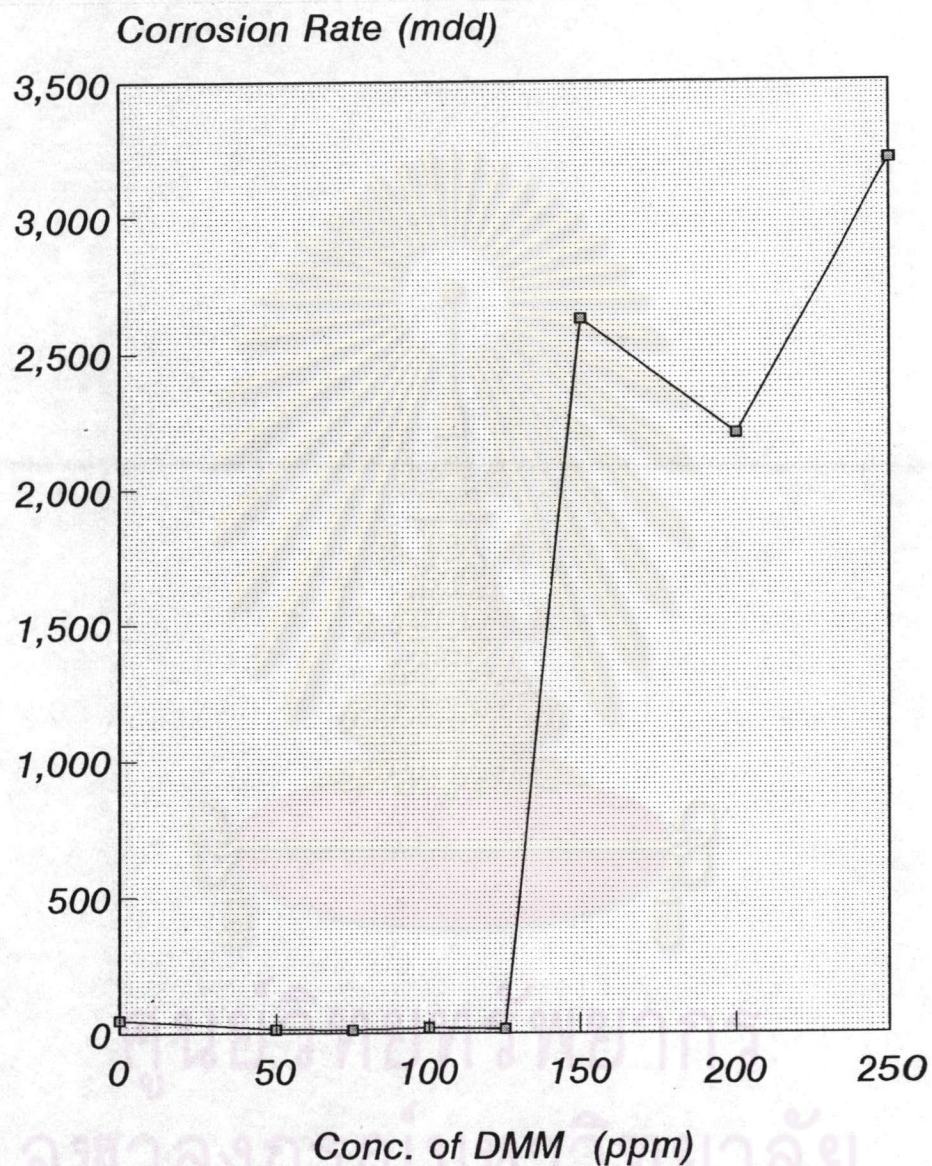


Figure 4.96 Relationship between corrosion rate of Al. specimen immersed in the $\text{CH}_3\text{OH}+150$ ppm $\text{HCl}+\text{DMM}$ solution and concentration of DMM at ambient temperature

It was that depending of corrosion rate on the DMM concentration could be divided into two parts at the concentration of DMM about 125 ppm.

Corrosion rate of the first part, starting from 0-125 ppm, was almost steady with concentration of DMM, whereas the other part slightly increased with increasing DMM concentration. This indicated that circulated corrosion process according to equation (4.8) and (4.11) could not be accomplished, if DMM concentration was lower than 125 ppm. When DMM concentration was equal to and above higher than 125 ppm, the same figure showed that corrosion rate was very high and seemed to be independent on DMM concentration.

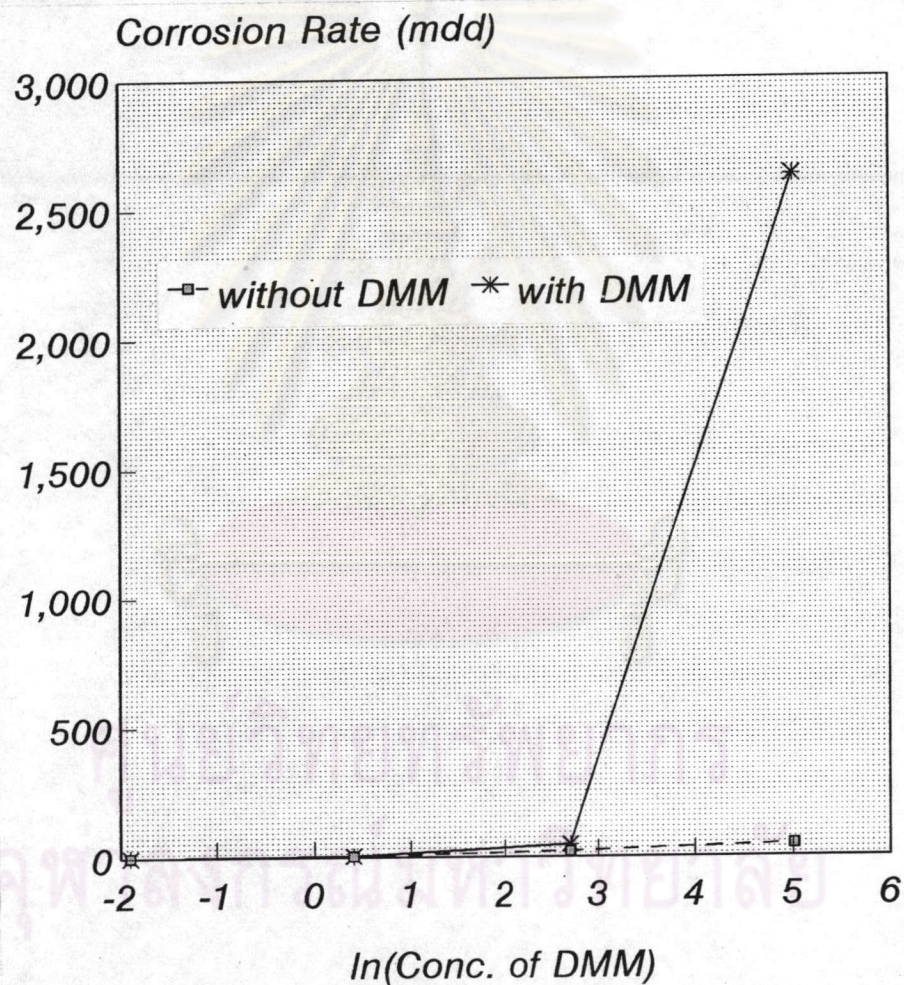


Figure 4.97 Relationship between corrosion rates of the Al. specimens immersed in the $\text{CH}_3\text{OH}+\text{HCl}+\text{DMM}$ solution and concentration of DMM/HCl lower than 150 ppm.

The ratio of [DMM] to [HCl] used in the test was fixed at 1:1 and the concentration was varied as 0.015, 0.15, 1.5, 15 and 150 ppm. By increasing DMM concentration, the corrosion rates obtained by the $\text{CH}_3\text{OH}+\text{HCl}+\text{DMM}$ solution was higher than that obtained by the $\text{CH}_3\text{OH}+\text{HCl}$ solution. The interval concentration of DMM/HCl used were too wide and difficult to plot graph. They are then changed to natural logarithmic values and plotted on horizontal axis. It was found from the Figure 4.97 that both corrosive systems, with and without DMM, provided corrosion rate that increased with increasing concentration of DMM/HCl. The rates obtained by the $\text{CH}_3\text{OH}+\text{HCl}+\text{DMM}$ solution were much higher than that obtained by the other.

4.Effect of Agitation/Velocity

Figure 4.98 indicated that corrosion rates of the specimen were independent on solution agitation and corrosion rates of agitated solution provided slightly lower corrosion rates than that without agitation. From figure 4.97, the point on vertical axis showed the rate of system without agitation at about 3000 mdd, whereas the other values obtained from the agitation system were about 2305 mdd-2500 mdd. From the observation during doing experiment, it was found that the "whisker" adhered to specimen surface would be a source to keep mercury contact to the surface and to evolve gas product. If agitation made the "whisker" fall off, the corrosion process would become more difficult.

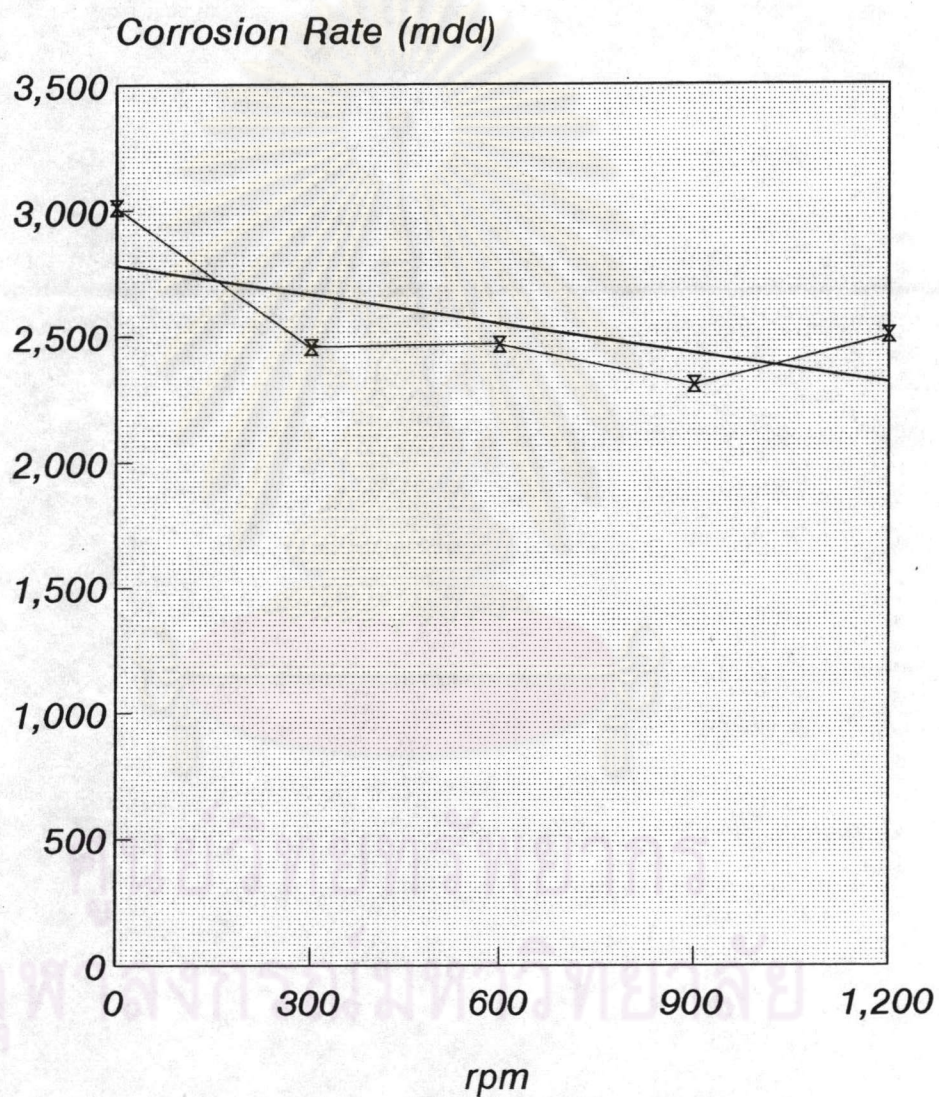


Figure 4.98 Relationship between corrosion rates of the specimens immersed in the $\text{CH}_3\text{OH}+150$ ppm $\text{HCl}+200$ ppm DMM solution and RPM agitating the solution

Table 4.11 Corrosion rates of the aluminium specimen immersed in the CH₃OH+acid+DMM solution systems using H₂S instead of HCl

Solvents & corrosive solutions	Corrosion	Role
	mdd	mpy
CH ₃ OH+saturated H ₂ S (200,000)	3.7	1.8
CH ₃ OH+saturated H ₂ S+200 ppm DMM(flask no.1)	3693.8	1799.9
CH ₃ OH+saturated H ₂ S+200 ppm DMM(flask no. 2)	3339.4	1627.2
CH ₃ OH+300 ppm H ₂ S+200 ppm DMM(flask no. 1)	2978.9	1451.4
CH ₃ OH+300 ppm H ₂ S+200 ppm DMM(flask no. 2)	2228.5	1115.2
CH ₃ OH+150 ppm HCl	70.8	34.5
CH ₃ OH+150 ppm HCl+200 ppm DMM	2675.9	1304.0

H₂S dissolved in absolute CH₃OH rather well, in which H₂S 1 gram dissolved in 943 ml absolute alcohol at 20°C [22]. H₂S is the impurity appeared together with elemental Hg and Hg derivative in natural gas. Thus, it was substituted HCl in the test in order to study its corrosive potential to corrode aluminium together with organomercury, DMM. Their corrosion results in table 4.4 showed that H₂S together with DMM corroded aluminium specimens severely similar to HCl. The average corrosion rate obtained by the CH₃OH+300 ppm H₂S+200 ppm DMM solution was 2633.523 mdd, which it was much close to that obtained by the CH₃OH+150 ppm HCl+200 ppm DMM solution, 2675.954 mdd. When this corrosion rate is compared to rate obtained by the CH₃OH+saturated H₂S solution, it was so much higher. This implied that there would be some of circulating corrosion reactions occurred in the CH₃OH+H₂S+DMM system, corresponding to those in the CH₃OH+HCl+DMM system as mentioned in section 4.1, for example, the reaction corresponding to equation 4.2 would be

