Electrochemical And Weight-Loss Study Of Carbon Steel Corrosion

V.J. Thomas and R.P. Olive
Supervisor: Dr. Derek Lister
University of New Brunswick, Canada

Abstract

The Point Lepreau Generating Station (PLGS) will undergo an 18 month refurbishment project beginning in April, 2008. During this time, most of the carbon steel piping in the primary loop will be drained of water and dried. However, some water will remain during the shutdown due to the lack of drains in some lower points in the piping system. As a result, it is necessary to examine the effect of corrosion during the refurbishment.

This study examined the effect of several variables on the corrosion rate of clean carbon steel. Specifically, the effect of oxygen in the system and the presence of chloride ions were evaluated. Corrosion rates were determined using both a weight-loss technique and electrochemical methods. The experiment was conducted at room temperature. The corrosion products from the experiment were analyzed using a Raman microscope.

The results of the weight-loss measurements show that the corrosion rate of polished carbon steel is independent of both the presence of oxygen and chloride ions. The electrochemical method failed to yield meaningful results due to the lack of clearly interpretable data and the inherent subjectivity in the analysis. Lepidocricite was found to be the main corrosion product using the Raman microscope.

1. Introduction

The PLGS employs a CANDU-6 nuclear reactor. CANDU-6 reactors make use of natural uranium fuel and use heavy water as moderator and coolant. The PLGS will begin refurbishment of their reactor in just under one year. This refurbishment is scheduled to last 18 months during which the station will be under outage conditions. This is required in order to extend the service life of the station to approximately 2032.

During the 18 month refurbishment several parts of the reactor will be replaced. This includes: the pressure tubes, the calandria tubes, the end fittings, and the feeders. Thus, to successfully replace these parts, draining of the majority of the piping will be required. Some water will inevitably be trapped in the primary heat transport system; as a result, the effect of corrosion on these pipes must be evaluated. Should corrosion be a concern, the station can then take preventative measures to avoid major problems like build-up of corrosion product in the pipes and leaks.

Piping in this system is mostly made of SA106 grade B carbon steel with some stainless steel sections. Different variables can affect the rate of corrosion such as the presence of chlorides as well as exposure to oxygen from the atmosphere. The variation of pH in the water trapped in the piping can be an indication of the rate of corrosion. One of the worse types of corrosion for piping, pitting corrosion, must be considered. As it is a localised type of corrosion, it can be dangerous and cause damage to the piping or, in severe cases, leaks.

2. Weight-loss analysis of carbon steel

2.1 Experimental Set-up

The operating conditions of the PLGS were approximated in this study. The pH is kept at approximately 10.2; however, this is for heavy water. For simplicity, de-ionized light water was used in the experiment. The pH was thus taken as 9.8 to account for the difference in fluid. This was achieved using lithium hydroxide. The difference in radiation level between the station and the Head Hall laboratory was disregarded as it was insignificant to this experiment. The temperature in the laboratory was assumed to be similar to that of the station and thus not considered in the analysis of the results.

SA106 grade B carbon steel and SA312 304L stainless steel samples were obtained from NB Power. The samples were machined into small coupons measuring approximately 1 cm by 1 cm with a 1 mm thickness. For the electrochemical experiment, the samples were placed into Mason jars using protected stainless steel wire, in which the station conditions were simulated. For the weight-loss experiments, the coupons were hung on small hooks inside the jars.

Over the 18-month outage, residual water will likely evaporate completely; nonetheless, the experiment considered cases where the water was allowed to evaporate completely as well as cases where water remains in the piping. In order to account for evaporation of the water, two coupons were placed towards the top of each jar and two very close to the bottom. This is because two of the coupons were tested for weight-loss on a weekly basis, whereas the other two were only tested at the end of the experiment. The arrangement can be observed in Figure 1, section 2.3. To account for the ‘worse case scenario’, a concentration of 0.1ppm lithium chloride was used in half of the jars. The oxygen was also purged out of half of the jars using hydrogen. Thus, four jars were required to represent four important cases. Their set-up is shown in Table 1.

Table 1 Test matrix for weight-loss experiment

Jar #	Chloride	Sealed/Unsealed	Experiment
1	Yes	Unsealed	Weight-loss
2	Yes	Sealed	Weight-loss
3	No	Unsealed	Weight-loss
4	No	Sealed	Weight-loss

The sealed jars refer to the jars purged of oxygen, which were sealed after purging, and the unsealed jars were open to the atmosphere.

2.2 Descaling procedure and weight-loss analysis

The descaling procedure used was the ASTM standard procedure for cleaning corrosion test specimens [1]. Prior to the start of the experiment, the samples were weighed to determine their initial weights. Once a week, two samples from jars 1, 2, 3 and 4 were removed and tested: one sample from the top of the jar and one sample from the bottom. The weekly analysis was performed on the same eight coupons. The remaining 8 coupons were left undisturbed for 8 weeks.

The samples were removed from the jars using tweezers, dried with compressed air, and weighed. The samples were then descaled by being dipped for 25 minutes in agitated Clarke's solution, composed of 20g of antimony trioxide, 50g of tin chloride and one litre of high concentration HCl solution, as recommended by the ASTM Standards [1]. All samples were then rinsed under running de-ionized water, air-dried and weighed again before being returned to their respective positions in the Mason jars. This procedure was followed for 56 days for the eight samples that were analysed weekly. After the 56 days, the coupons were returned to their jars and left undisturbed until a final descaling was performed 13 weeks from the start of the experiment. The remaining 8 coupons were left undisturbed from the start of the experiment for 8 weeks and then descaled and weighed using the procedure described above. .

2.3 Results and discussion

The experiment ran for 56 days under weekly testing conditions for eight of the samples, and then for an additional 35 days during which none of the samples were displaced, giving a total of 91 days. During that time, the samples corroded significantly. An example of a Mason jar containing carbon steel coupons, after 56 days, is shown in Figure 1. From this figure, the oxide can be clearly observed on the coupons, as well as at the bottom of the jar. This photograph only illustrates one example; nonetheless, after 91 days, all 8 of the jars had a similar appearance. The oxide formation was actually quite significant as early as 10 days after beginning the experiment.

Also unclear in the photograph is the distinction between the samples that were descaled weekly and the undisturbed samples; however, measured corrosion rates demonstrate the effects of weekly descaling as opposed to allowing corrosion product build-up to form on the coupons.

Figure 2 illustrates a carbon steel coupon after undergoing descaling procedure. After descaling, the coupons returned to a state similar in appearance to their initial conditions. Although it is not very clear from this photograph, after descaling the coupons it was evident that visible pitting did not occur in the carbon steel samples. This can be explained by the high corrosion rates obtained.

Figure 1 Carbon steel coupons in Mason jar after 91 days

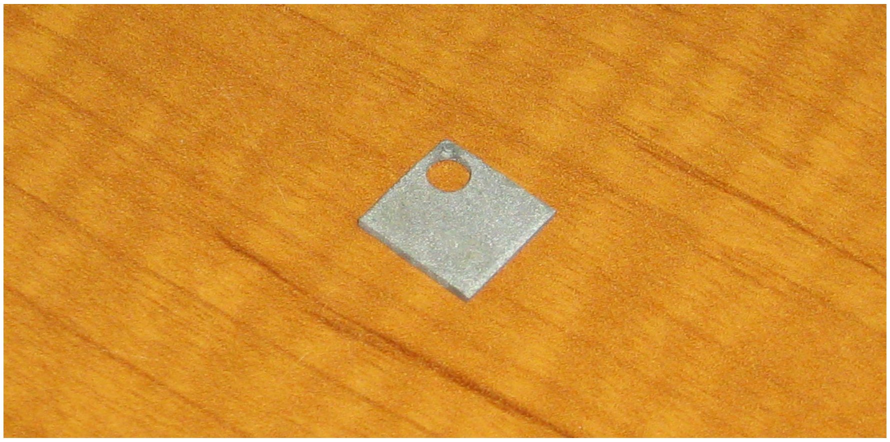

Figure 2 Carbon steel sample after descaling

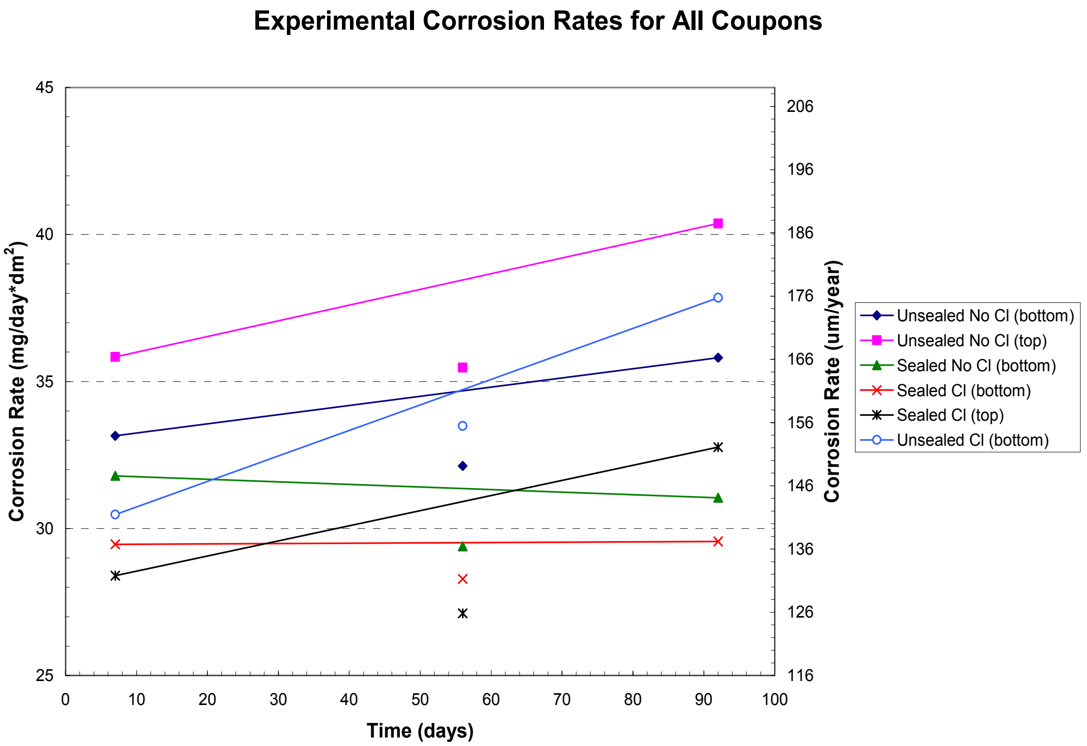

Figure 3   Corrosion rates of all carbon steel coupons

Figure 3 shows the experimental results from the weight-loss experiment. The weekly descaled coupons are represented by two connected data points; one at 7 days and the other at 91 days. Due to problems encountered with the Clarke's solution, these were the only two valid data points obtained in the experiment. The undisturbed coupons are plotted as points at 56 days.

Several important conclusions can be drawn from Figure 3. First, the coupons in jars that were unsealed exhibited higher rates of corrosion than did the ones in sealed jars. This was as expected as the presence of oxygen generally accelerates corrosion. Secondly, the presence of chloride had no effect on the corrosion rates. As observed in Figure 3, there is no specific trend among the samples in contact with chlorides. In addition, the weekly descaled coupons exhibited higher corrosion rates then their undisturbed counterparts. One reason for this may be the continual removal of oxide film each week.

It should be noted that the pH of the jars was measured again at the end of the experiment. All of the jars had a pH of approximately 7.1. This explains the high rates of corrosion exhibited by the coupons. As well, the high corrosion rates may also explain why there was no observable pitting. Because pitting is a localized form of corrosion, the already high corrosion rates would not allow pits to develop [2].

3. Electrochemical analysis of carbon and stainless steel corrosion

3.1 Electrochemical corrosion experiments

For the electrochemical experiments, the arrangement of the coupons varied from the arrangement of the coupons subjected to the weight-loss analysis. In this case, only two carbon steel coupons per jar were used: one placed near the top of a Mason jar and one near the bottom. However, each coupon was paired with a stainless steel counter electrode. These were placed at the same height as and parallel to the carbon steel coupons, approximately half a centimetre away from them. These were connected to long wires to allow for connection of the testing equipment. Table 2 provides a summary of the specific conditions for each Mason jar.

Table 2 Test matrix for electrochemical experiments

Jar #	Chloride	Sealed/Unsealed	Experiment
5	Yes	Unsealed	Electrochemical
6	Yes	Sealed	Electrochemical
7	No	Unsealed	Electrochemical
8	No	Sealed	Electrochemical

Electrochemical analysis was performed on these samples using a PCI4 Family Potentiostat 300. This equipment enabled potentiodynamic scans on the carbon steel samples, using stainless steel as a counter electrode. These scans were meant to determine the corrosion potential. Pitting potential scans were also performed on the stainless steel samples only.

3.2 Results and Discussion

3.2.1 Potentiodynamic analysis of carbon steel

Potentiodynamic scans were run on each carbon steel sample weekly. The scans were then analysed using Gamry Echem Analysis Version 1.30 2003 software. The corrosion potential for each carbon steel sample was also determined each week. With this known, the anodic Tafel region was extrapolated back to the point of intersection. From this, the corrosion rate was determined.

However, the potentiodynamic scans proved unreliable for corrosion rate determination. Figure 4 illustrates the problem with this type of testing. From observation, there is no clear straight line anodic Tafel region. Thus, it is left to the judgement of the experimenter as to where the Tafel region actually is. Because of the inherent subjectivity of this technique, the potentiodynamic scans on the carbon steel samples failed to produce any meaningful results.

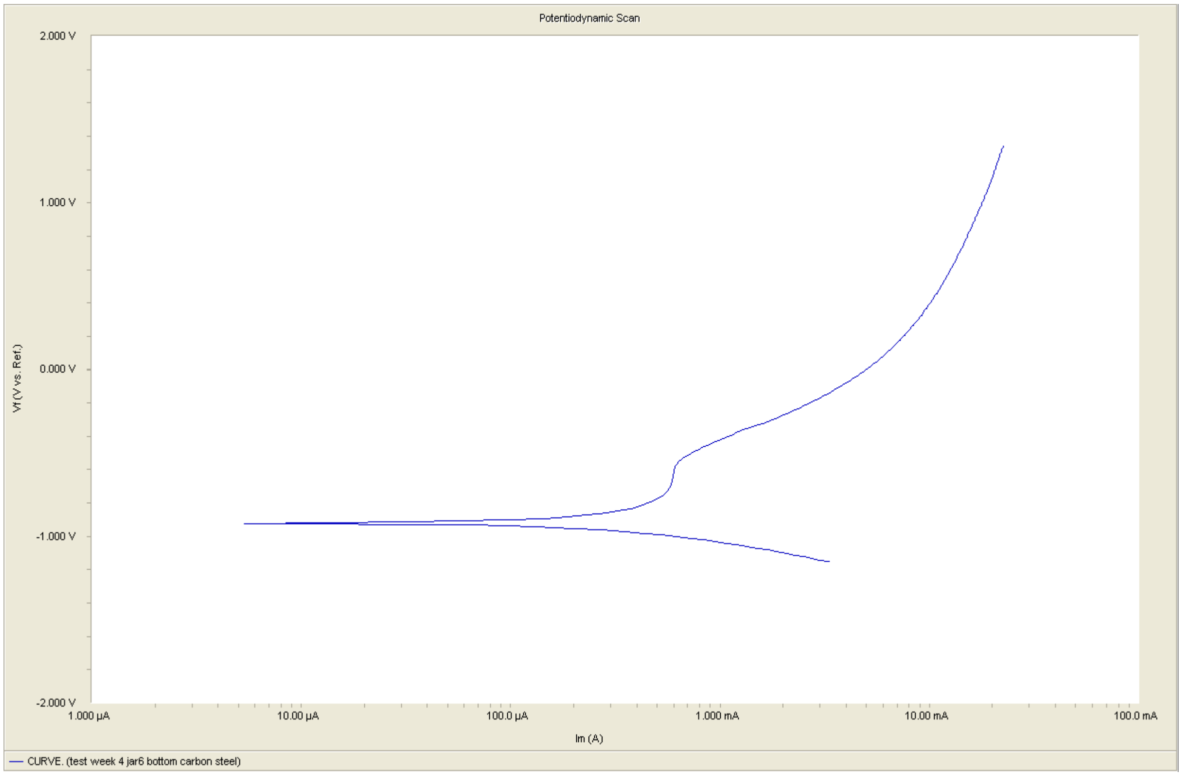

Figure 4 Potentiodynamic scan for unsealed carbon steel coupon, no chloride, located at the bottom of the jar, November 14, 2006.

3.2.2 Pitting potential of stainless steel

In addition to the potentiodynamic scans on the carbon steel samples, cyclic polarization scans were run on the stainless steel samples in order to determine pitting potentials. These scans were started 5 weeks into the experiment and were performed weekly for the next 3 weeks. Pitting potentials were determined using the method outlined by Roberge [3].

Figure 5 shows the cyclic polarization scan of the top stainless steel sample in the sealed with chloride Mason jar. From the scan, the pitting potential can be determined to be 560 mV. Figure 6 shows the same sample on week later. From this scan, the pitting potential cannot be readily determined. As a result, like the potentiodynamic scans on their carbon steel counterparts, the scans on the stainless steel samples also failed to yield any meaningful results.

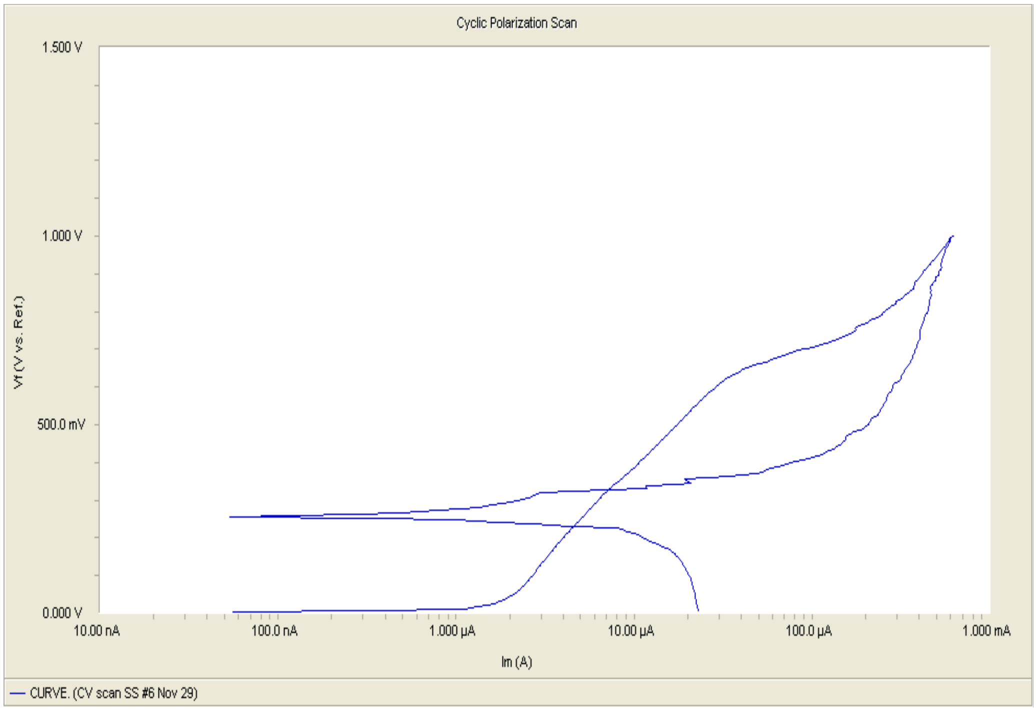

Figure 5 Pitting potential for stainless steel coupon with chloride, located at the top of a sealed jar, November 29, 2006. Pitting potential is 630mV.

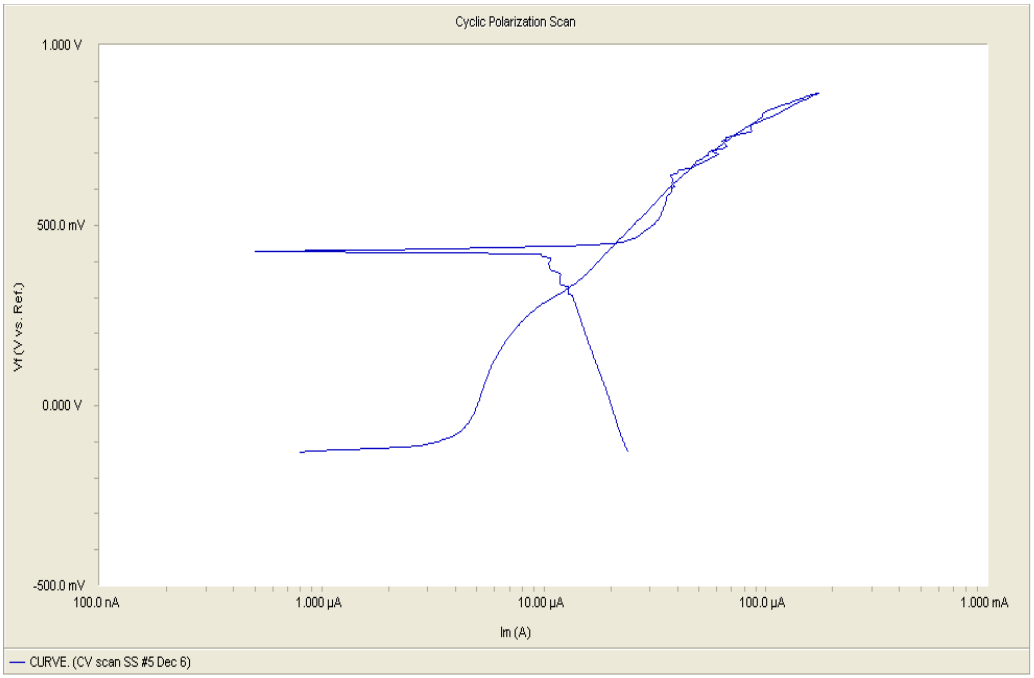

Figure 6 Pitting potential for stainless steel coupon with chloride, located at the top of a sealed jar, December 5, 2006. Pitting potential is ambiguous.

4. Surface analysis

4.1 Results

After completion of the experiment, the contents of the Mason jars were analysed. The Laser Raman microscope was used to determine the substance formed in the jars. The results are shown in Figure 7.

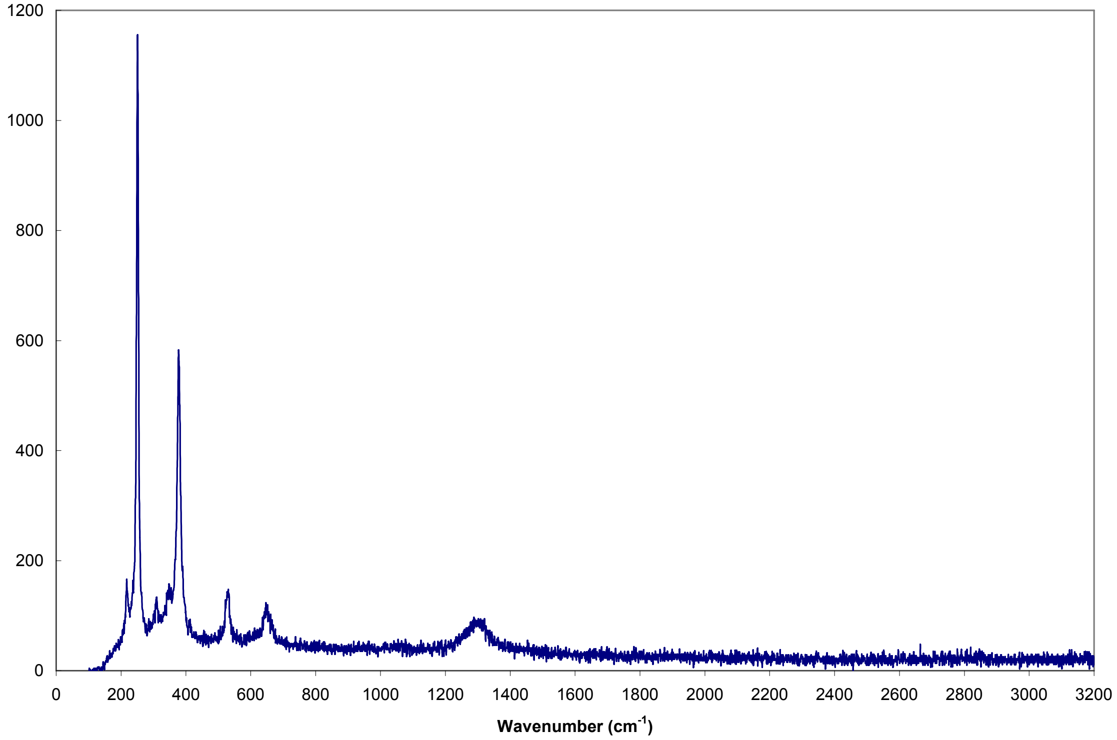

Figure 7 Raman spectrum of Mason jar corrosion product

From Figure 7, the corrosion product was determined to be Lepidocricite. The peaks at $250cm^{-1}$, $378cm^{-1}$, correspond to the reference spectrum of Lepidocricite [4].

5. Conclusion

The experiment showed that the presence of chlorides had no effect on the corrosion rates of the samples. As expected, the unsealed samples all exhibited higher rates of corrosion than those purged of oxygen. Also, pitting was determined not to be a concern for SA106 grade B carbon steel under the tested conditions due to high general corrosion rates and observations. The orange sludge corrosion product forming on the coupons was determined to be Lepidocricite using the Laser Raman microscope.

Finally, any electrochemical method should be carefully used. The majority of analysis of such data is very subjective to each individual researcher; as a result, these methods should always be supported or accompanied by other forms of analysis.

6. References

[1] Designation G1-90, "Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens", *Annual Book of ASTM Standards*, Vol. 03.02 (Wear and Erosion; Metal Corrosion), 2000, pp.15-21

[2] Fontana M.G., "Corrosion Engineering", Second Edition, McGraw-Hill, NY USA, 1978

[3] Roberge P.R., "Handbook of Corrosion Engineering", McGraw-Hill, NY, USA, 2000

[4] R.J. Thibeau, C.W. Brown, and R.H. HeidersbachRaman, "Spectra of Possible Corrosion Products of Iron Applied Spectroscopy", Volume 32, Number 6, 1978, pp. 532-535

7. Acknowledgements

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