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Online Corrosion Monitoring of Atmosphere Distillation Unit and Operation Parameter Correlation

Written by Shota Maeda from idemitsu Hokkaido Refinery and Zhou Huajun from Emerson Automation Solutions

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1. Introduction

Idemitsu Hokkaido Refinery is an oil refinery operated by Idemitsu Kosan. The refinery began operations in 1973.

Atmospheric distillation is one of the critical process in the refinery. It takes place in a distilling column at or near atmospheric pressure. The crude oil is heated to 350 – 400 ˚C and the vapor and liquid are piped into the distilling column. The dense liquid falls to the bottom and the vapor rise, passing through a series of perforated trays. Heavier hydrocarbons condense more quickly and settle on lower trays and lighter hydrocarbons remain as a vapor longer and condense on higher trays.

When managing corrosion in a refinery plant, the pipeline needs to be evaluated throughly, including operating conditions such as temperature and pressure, corrosion probes to measure corrosive substances in wastewater and oil, and periodic wall thickness measurement of each equipment. In the past, corrosion probes were installed to know the change in medium corrosivity. The pipeline thickness is measured to understand the corrosion rate and ensure pipeline reliability.

2. Customer Pain - Corrosion at Top of Distillation Unit

The corrosive environment of the atmospheric distillation unit is easily affected by the crude oil and changes significantly with different crude oil source. In recent years, Idemitsu Hokkaido has been using crude oil with high salinity and total acid number (TAN) that causes rapid corrosion at the distillation unit. Although it is possible to monitor the changes of corrosivity corrosion probes, it does not provide the required information on pipe wall thickness. To measure the estimated lifespan of the pipe, it is actually costly and labor intensive to measure on a daily basis.

Significant corrosion such as hydrochloric acid corrosion often occurs at the overhead system of the atmospheric distillation unit, so it is crucial to know corrosion is happening at an early stage.

As the corrosion rate changes drastically in an atmospheric distillation unit, corrosion probes alone are not sufficient to monitor the corrosion and reliability of the pipeline, hence thickness measurement is a crucial part of corrosion monitoring.

Idemitsu Hokkaido installed a Rosemount Wireless Permasense wireless online monitoring system, which enables daily wall thickness measurement at the overhead system of the atmospheric distillation unit to further improve the reliability of the pipeline. Together with key process variables, it enables the user to correlate the corrosion with operation conditions, better manage the corrosion impact and take necessary actions.

2.1 Corrosion Factors

There are various factors causing corrosion to happen in the atmospheric distillation unit, the main factors are shown in figure 1.

Erosion corrosion	Change in flow rate Disturbance in flow Increase of corrosion substances
Corrosion	Increase of chloride compound Hydration of NH_4Cl Increase of acid compound Low pH Condense water due to low ambient temperature Higher dew point
Erosion	Increase in flow rate Disturbance in flow Flush of neutralizer

Figure 1 Corrosion factors of overhead system of atmospheric distillation.

2.2 Common Monitoring Parameters and Challenges

2.2.1 Dew Point

Moisture is brought into the atmospheric distillation column by the raw materials and stripping steam and moves to the top of the column as water vapor. Due to changes in temperature and pressure, a slight amount of condensed water may be generated. Chloride ions are easily dissolved in condensed water, resulting in low pH and significant corrosion. As such, it is important to monitor the dew point that causes corrosion to take place.

2.2.2 Neutralizer Injection

The pH of the drain water discharged from the atmospheric pressure distillation column's overhead separation tank is generally controlled at 6.0±0.5 range by a neutralizer. One of the reasons for using or for fixing this pH range is that it can promote the formation of FeS_2 film that is a protective film.

Pourbaix diagram is the most common tool to study metal stable phases in an electrochemical corrosion system. Figure 2 is the Pourbaix diagram for Iron Sulfur corrosion system[2], the real environment is much more complicated because of other elements like carbon and chlorine, but it gives the user a guideline on what pH value should be maintained so that iron is protected in this environment.

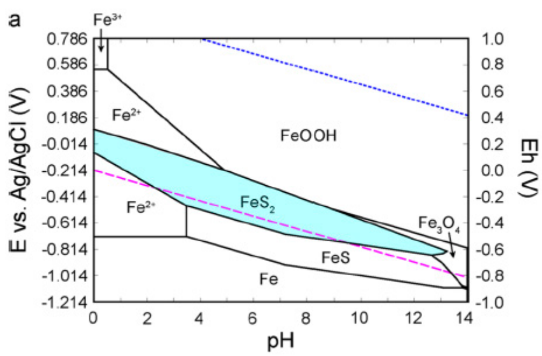

Figure 2 Pourbaix diagram of Iron Sulphur system.

In a common pipeline environment, there is a slightly negative potential, if pH value is kept at around 6, and a passive FeS_2 film will be formed, which acts as the protective layer to slow down further corrosion of the Iron inside. However, if the pH is lower than 5.5, the FeS will be formed which is a non-protective film[3]. Therefore, neutralizer injection must be monitored to control the pH value of the drain water.

2.2.3 Chloride Concentration

It is desirable to control the concentration of chloride in the drain water of the overhead separation layer of the atmospheric distillation column at low level, typically at 20 ppm or less. If this concentration exceeds this limit, the corrosion will generally deteriorate.

Chloride ions act as a catalyst in corrosion reactions and accelerate the process, referencing to half-cell reactions as follows[4]:

$$Fe + Cl^- + H_2O = [FeCl(OH)]^-_{ab} + H^+ + e$$
$$[FeCl(OH)]^-_{ab} \rightarrow FeClOH + e$$
$$FeClOH + H^+ = Fe^{2+} + Cl^- + H_2O$$

The corrosion rate of steel at different chloride concentrations was referenced in a table as shown below in table 1[4].

Table 1. Corrosion Rate of Steel Sample at Different Cl^- Concentrations.

	Corrosion Rate (mm/y)		
Cl^- concentration	20 ppm	40 ppm	120 ppm
	0.0041	0.0069	0.0092

Besides the catalyst effect, chloride is a common corrosive substance to promote localized corrosion like pitting. The pitting process starts with a pit in the passivation layer that protects the metal. A small area of the pit will act as anode and the large surface of the metal will act as cathode in electrochemical reactions. The large cathode to anode area ratio makes the corrosion in the pitting very fast, which produces more positive metal ions in the pit. To balance the positive charge, negative ions like chloride ions will flow from outside into the pit and form metal chloride (MCl) molecules. MCl will react with water and form H+, HCl and metal hydroxide. The solution in the pit will become even more acidic and accelerate the corrosion process. Therefore, if chloride concentration is high, pitting corrosion is more likely to happen.

With the dew point, neutralizer injection and chloride concentration monitoring, the refinery can understand the corrosive environment, but without the real-time pipe wall thickness measurement, the actual pipeline condition and its severity are unclear, or worse, remain unknown. Furthermore, the ability to correlate operation conditions with corrosion has not been developed prior to this. However, it is crucial to help the plant to achieve higher reliability while optimizing their processes.

3. Emerson Solution - Rosemount Wireless Permasense Online Monitoring System

3.1 Overview of Measurement Sensor

The Rosemount Wireless Permasense online monitoring system measures the wall thickness of the object using ultrasonic waves. The main configuration and function of the measurement sensor are as shown in figure 3.

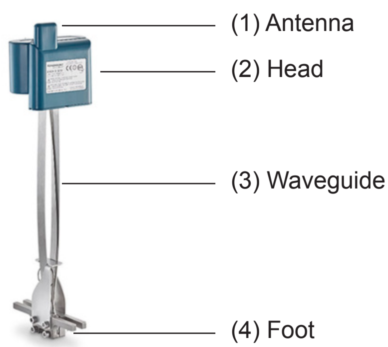

Figure 3 Schematic diagram of Permasense sensor.

3.2 Measurement Principle

The Permasense sensor works by measuring the time difference between the surface wave and the first reflection wave from the inner wall surface as shown in figure 4. It is the same ultrasonic thickness measurement principle used widely in the industry.

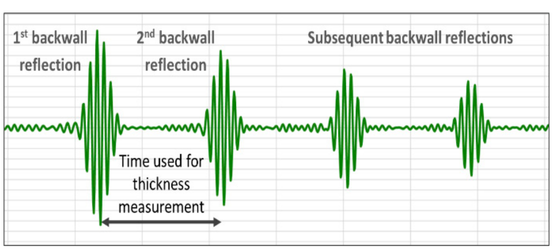

Figure 4 Permasense Measurement principle

3.3 Field Installation Overview

The Rosemount Wireless Permasense system is a non-intrusive wireless corrosion monitoring system that measures the thickness of the pipes; an illustration of devices installed and sensor network on site is shown in figure 5. The sensors communicate with each other wirelessly and build a network that automatically sends data to the receiver (*Wireless*HART® Gateway). The gateway will connect to the server using ethernet (LAN cable), the server will process the data and compute the thickness of the measurement point. Based on the thickness measured, the system will also be able to calculate the corrosion rate.

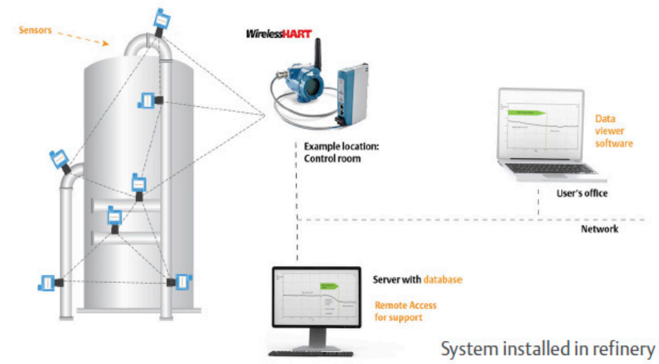

Figure 5 Schematic diagram of online monitoring installation.

3.4 Features of Permasense Sensors

(1) The sensors can measure up to 600 °C pipe surface temperature, it can be applied to a wide range of industry applications such as upstream and refining.

(2) The thickness of the pipe can be measured more than once a day.

(3) The Permasense sensors are wireless. It is easy to maintain the sensors and relocate as wiring is not required.

(4) Sensors are maintenance free, manual inspection frequency is lowered, and potential incidents and costs can be significantly reduced.

4. Idemitsu Site Installation and Results

4.1 Online Monitoring Installation Location

At the overhead system of the atmospheric distillation column, corrosion of the pipe due to chloride has been progressing over the past years. Since corrosion is likely to occur at the initial condensation point and when the flow rate changes, the Rosemount Wireless Permasense system was installed at those sections of the overhead piping. The detailed sensor installation positions are shown in figure 6, 16 sensors were installed, and a site picture of the installation is shown in figure 7.

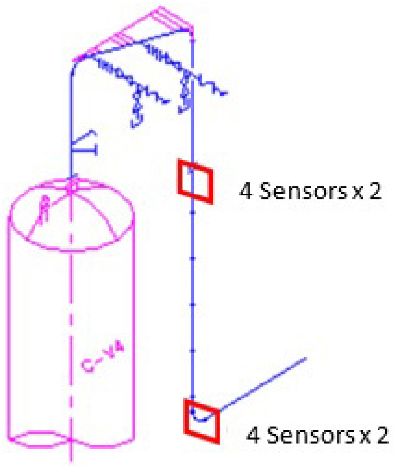

Figure 6 Schematic diagram on sensor installation locations.

Figure 7 Idemitsu site installation picture.

4.2 Monitoring Results

4.2.1 Example of Measurement Sensor Results

The Permasense sensor measured the surface temperature and wall thickness of the pipe, and results for 2016 and 2017 are shown in figure 8. While maintaining this position, the measurement was carried out twice a day.

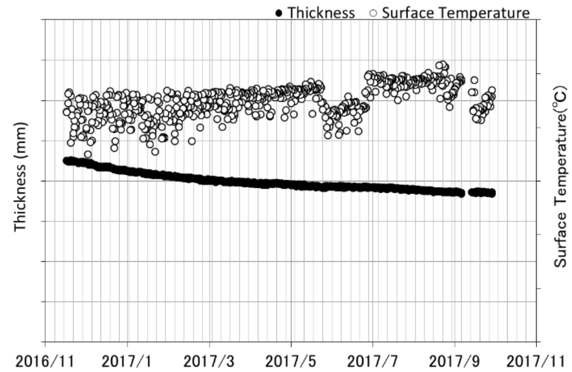

Figure 8 Example of measurement sensor results (surface temperature, wall thickness).

4.2.2 Unique Advantage - Correlation of Thickness Data with Operating Condition

The thickness data measured is utilized by Idemitsu to correlate the operation conditions and further understand the corrosion mechanism and behavior. Corrosion is complicated and may be caused by more than one variable, hence in order to understand the importance and reason for corrosion to happen, the thickness trend is compared with dew point and chloride concentration. The comparison results are shown in figure 9 and 10.

Figure 9 compares the dew point and wall thickness. Generally, a lower dew point will result in a higher corrosion rate because water is easier to condense as mentioned in section 2 above. The monitored result shows the dew point was changing cyclically and did not match with measured corrosion rate trend, this implies the dew point change may not be the main cause for corrosion to happen inside the distillation unit in Idemitsu. However, they decided to monitor this correlation continuously to understand how the dew point will affect corrosion rate in the plant environment, as it is deemed as one of the important process variables in the long term.

Figure 10 compares the chloride concentration with wall thickness measured. In section 2, it is understood that higher chloride concentrations will result in higher corrosion rates. There is a clear decrease of chloride concentration after May 2017. The average corrosion rate before May 2017 was also significantly higher after July 2017. It shows that chloride is the primary element that expedite the pipe corrosion rate. This correlation has proven the cause and affect relationship between chloride concentration and corrosion rate in Idemitsu distillation unit. The information was further used to control inhibitor injection to obtain the right level of chloride concentration in the process.

The advantage of using Rosemount Wireless Permasense system is enabling the engineer to correlate daily wall thickness measurement with other monitored parameters such as chlorine concentration and dew point. This will greatly improve the efficiency in planning maintenance and taking necessary corrosion prevention actions, it also helps the plant to better plan their production and ultimately improve throughput.

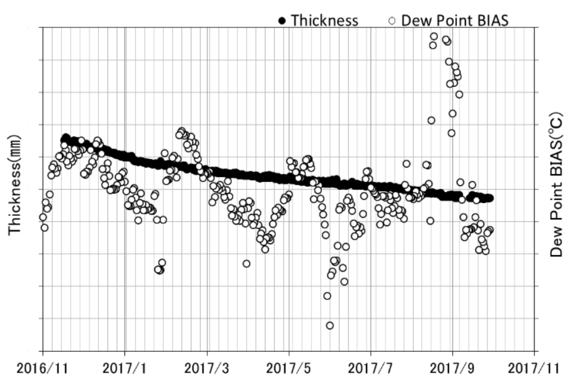

Figure 9 Graph comparing tower top dew point and wall thickness.

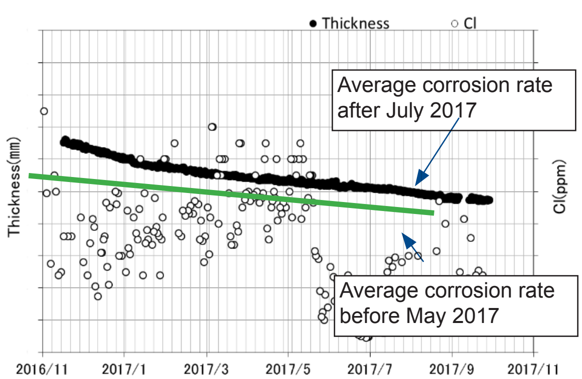

Figure 10 Graph comparing chlorine concentration and wall thickness.

5. Conclusion

The Rosemount Wireless Permasense Corrosion Monitoring System has delivered significant value to plant safety and integrity as it helps Idemitsu to know the timing of a corrosion occurrence by comparing the wall thickness data. Moreover, this wireless system eliminates the need for manual inspection and maintenance, it enables the engineers to view the process parameters that coincide with the operation parameters such as chloride concentration with corrosion behavior. In most cases, the corrosion in the distillation unit is caused by multiple factors, therefore long-term monitoring data will give an advantage in analysis and more in-depth insight.

References

1. Maeda, S., The Japan Petroleum Institute, *48th discussion for The Japan Petroleum Institute, 48th discussion for equipment study,* presentation 39, (2017)

2. Guan, X., Enalls, B. C., Clarke, D. R., Giicuis, P., Iron Sulfide Formation on Iron Substrates by Electrochemical Reaction in Anoxic Conditions, *Crystal Growth & Design,* 17 (12), 6332-6340 (2017)

3. Sun, W., Nesic, S., Kinetics of Iron Sulfide and Mixed Iron Sulfide/Carbonate Scale Precipitation in CO_2/H_2S Corrosion, *Corrosion 2006,* 06644, 1-20 (2006))

4. Zhao, X. H., Sheng, Y. X., Yin, C.X., Lin, G.F., Han, Y., Effects of Cl- concentration on corrosion behavior of carbon steel and super 13cr steel in simulated oilfield environments, *International Conference on Innovative Material Science and Technology,* 334 (2016)

Emerson Automation Solutions
6021 Innovation Blvd
Shakopee MN 55379
USA
+1 800 999 9307 or +1 952 906 8888
+1 952 204 8889
RFQ.RMD-RCC@Emerson.com

Linkedin.com/company/Emerson-Automation-Solutions
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