A NOVEL ELECTRICAL POTENTIAL DROP METHOD FOR THE DETECTION OF NAPHTHENIC ACID CORROSION IN OIL REFINING PROCESSING

T. Batzinger, A May, C. Lester, K. Kutty and P. Allison. General Electric, Niskayuna, New York

Abstract: Since the beginning of oil refining, the petrochemical industry has been plagued with corrosion due to acid within the crude oil. As oil fields age and refining processes require greater production, the industry is looking to produce petroleum products from crude oils containing greater concentration of acid leading to industry concerns about corrosion of the refining infrastructure. General Electric (GE) has developed a novel system capable of providing continuous monitoring of piping or vessel components during plant operation providing a measure of material removed due to corrosion. The operation of this system is based on the measurement of changes to electrical potential drop caused by the removal of material due to corrosion. The system developed has been shown to be capable of acquiring accurate corrosion data during plant operations. Measurement process data acquired from plant operation and laboratory experiments will be discussed.

Introduction: The demand for products manufactured from crude oil has increased steadily forcing petroleum refineries to increase production rates. With the increasing demands on crude oil refining facilities, the effects of corrosion to the infrastructure of crude oil refining have become a critical part of the issues facing the industry. To reduce the cost of refining crude oil, many refineries have turned to lower cost crude oil sources. These discounted crude oils tend to have higher concentrations of acid, or higher Total Acid Number (TAN)[1], and other constituents that can lead to the high corrosion rates within the refinery. One such family of acids commonly found in these discounted oils are the naphthenic acids [1]. Naphthenic acid induced corrosion occurs in the regions of the refinery where the temperature exceeds 400 degrees F. Figure 1 shows a schematic diagram of the crude unit region of the refinery process where naphthenic acid corrosion typically occurs.

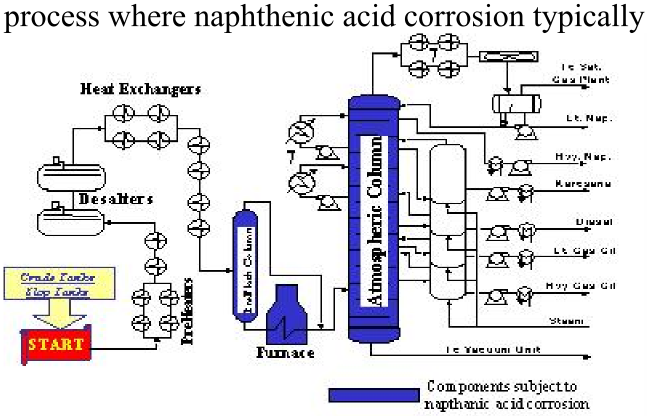

Figure 1: Crude oil refinery "Crude Unit".
Blue indicates components subject to naphthenic acid corrosion. [2]

Vessels and the piping connecting these components are operated at temperatures ranging from 400 degrees F to 900 degrees F. At this temperature range and the typical operating pressure within these vessels, naphthenic acid has the potential to condense on the inside walls of these vessels and pipes. At these temperatures, the majority of the crude oil travelling through these vessels is in the vapour state. The flow of the vapour is not sufficient to remove the condensed naphthenic acid therefore leading to regions of corrosion. Naphthenic acid corrosion typically removes a region of material from the wall of the vessel rather than single pits. Naphthenic acid corrosion appears like a series of pits that have coalesced into an area of relatively uniform material removed. Figure 2 shows the picture of a component exhibiting typical naphthenic acid corrosion.

Figure 2: Pump component showing naphthenic acid corrosion (Outlined in red)

In piping systems, this corrosion can lead to leakage of the vaporized crude oil, an extremely dangerous event. Many companies, such as GE Water and Process Technologies, have developed corrosion mitigating chemicals that are injected into the flow of the vaporized oil providing protection to naphthenic acid corrosion. Occasionally, regions of the crude unit are not suitably protected from these chemicals and it becomes necessary to be able to detect this type of corrosion so that refineries can process the high acid crude oil safely. Typically, the remaining wall material is measured occasionally using ultrasonic thickness inspection. These measurements can be made during plant outages. Thickness measurements taken using ultrasonic methods during plant operations require a great deal of planning in order to insure the safety of the inspector. For high temperature applications, it would be preferred to make use of an online inspection system. Online measurements allow the facility operators to understand the condition of the assets in the refinery and make decisions about how best to safely operate the facility. The temperatures of the components in the crude unit do not allow the use of traditional online inspection probes such as ultrasonic probes. This type of online measurement requires a probe to remain viable at temperatures reaching 900 degrees F and provide reliable measurements for a period of up to 20 years.

To accomplish this measurement, a resistance corrosion monitoring (RCM) system was developed by GE. This system makes use of the component, itself, as the probe. In the case of piping, the wall of the pipe is the probe and the system measures the electrical resistance within the wall of the pipe. As the wall thickness changes due to corrosion, the electrical resistance changes. This system uses high temperature wiring and attachments to connect the data acquisition system to the pipe. Electrical current, generated by a low voltage high amp hour rated battery, provides the means to determine the electrical resistance of the pipe or vessel wall of a specified region where electrical attachments provide for the measure of electrical potential. A plurality of electrical attachments, in the region of interest on the vessel or pipe, provides the signal path to the data acquisition system. The data acquisition system developed for this measurement provides for online monitoring of the measurements and can provide data to the facility operator indicating severe corrosion issues.

The remainder of the publication will be devoted to data collected from a prototype system and the means to evaluate the data to provide a reliable measure of the remaining wall thickness in the component displaying naphthenic acid corrosion.

Results: Use of the electrical resistance of the material has been used as a means to evaluate the condition of material [3]. This method of material evaluation makes use of current flowing through the material to be evaluated. Along the axis between the point of current supply and ground, a series of pairs of electrodes are used to measure the voltage or potential drop between the pair of electrodes. Figure 3 shows a schematic example of the potential drop measurement.

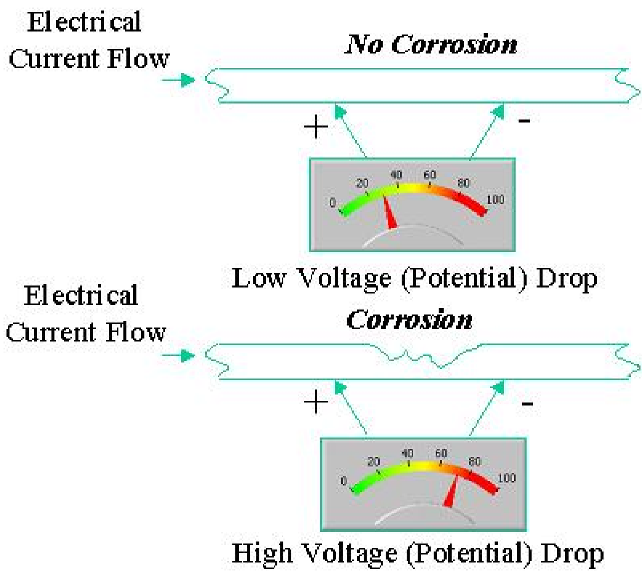

Figure 3: Schematic demonstration of the resistance corrosion measurement

The voltage measured in using this technique is typically in the microvolt range, depending on the current injected and the geometry of the component. Commercially available systems have been shown to be subject to measurement noise caused by a variety of sources. Noise sources can include thermocouple voltage, current fluctuations as well as electromagnetically induced noise from plant operation. These noise sources can produce voltages equal to and sometimes greater than the voltage indicating changes to the material thickness. With these noise sources in mind, the GE acquisition system was designed to acquire the data from the component with the sensitivity to the microvolt signal level while reducing the sensitivity to noise sources. The system can be configured to provide up to 1 square meter of material inspection coverage. Typically, two or more of the system channels available are used as reference channels. The reference data acquisition channels are connected to the reference sample that is attached to the component and is made from the same material as the component. The reference sample is at the same temperature as the component but is suspended to allow reference measurements prior to allowing the current to enter the test component. Figure 4 displays a picture of a typical setup as well as a schematic of the field test setup.

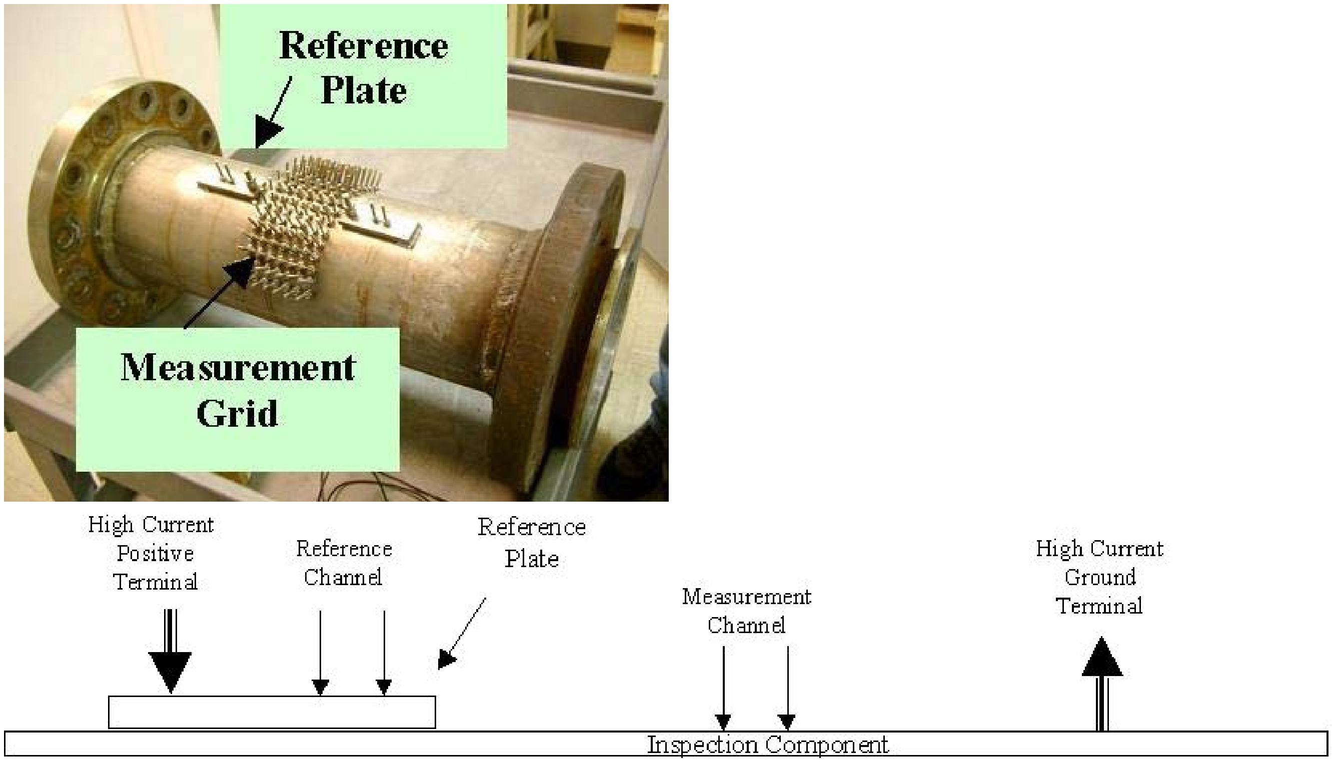

Figure 4: Typical field test setup

The acquisition system contains a microprocessor to control the acquisition, the high current switching, analog to digital conversion and data storage. The data is collected on a conventional USB memory stick for transport to an analysis computer. All system channels are sampled simultaneously rather than multiplexed. Although this makes for a larger system platform, it allows for all channels to detect signal from the component without concern for fluctuations in current flow in the component. It is well known that when batteries are used for high current applications, the voltage produced by the battery will “sag” or diminish in value. In multiplexed systems, it is typical that the battery is required to supply high current for the period of time required to switch through all channels completing the data acquisition cycle. By simultaneously acquiring all channels of data, the battery is required to produce high current for short period of time. The method of acquisition avoids battery voltage sag as well as preserves the battery charge for subsequent acquisition periods.

The reduction of sensitivity to thermocouple voltage and current flow is accomplished through use of reference signal acquisition. In any acquisition, 4 voltage measurements are taken. In order, the measurements acquired are 1) a measure of the voltage seen by each channel when the input to each channel is shorted (INT_ref_OFF), 2) a measure by each channel of an internal reference voltage (INT_ref_ON), 3) a measure by each channel of the voltage seen between adjacent electrodes located on the component to be inspected with no system current flowing (signal_OFF) and finally 4) a measure of the voltage between adjacent electrodes located on the component to be inspected with system high current flowing through the component (signal_ON). Measurements 1 and 2 are taken to develop an understanding of the variation of system channel gain. This data allows the analysis software to account for individual channel gain differences. Measurements 3 and 4 are collected to provide both the signal voltage and an indication of the thermocouple voltages between the electrodes and the component inspected. Equation 1 indicates how measurements 1 through 4 are used to calculate the potential drop from the component.

$$V_{corrected} = \frac{V_{signal\_ON} - V_{signal\_OFF}}{V_{INT\_ref\_ON} - V_{INT\_ref\_OFF}}$$

Equation 1: Determination of the voltage from the component corrected for systematic gain and thermocouple effects.

The measurements taken from the component are further compared to the voltage detected from a reference sample as a means for a differential measure of the material thickness. The reference sample, mentioned above, is used for this differential measurement. The reference sample is positioned on the pipe such that no corrosion will occur on the reference but the reference will be at the same temperature of the component to be inspected. Normalization of the data relative to the reference sample and storage of the normalized data will be used to track the changes in measured voltage caused by component corrosion. Equation 2 is used to normalize the data collected from the reference and the component.

$$V_{normilized\_channeldata} = \frac{V_{corrected\_channelsignal}}{V_{corrected\_EXT\_refsignal}}$$

Equation 2: Normalization of component data with respect to the reference sample

Additionally, data is collected by the system over a period of time defined by the needs of the installation site. Typically, data is collected over a period of an hour. During this hour, several hundred acquisitions are produced. Each acquisition, containing the 4 measurements mentioned above, is analyzed using equations 1 and 2. The results are processed to reduce the sensitivity to electromagnetically coupled noise sources. Noise sources such as a pump motor, an electrically resistive heater or plant radio systems can produce signals detected by the RCM system. These noise sources typically produce short bursts of noise that can effect an individual measurement but are easily averaged out when data is collected for long periods of time.

The final step in the analysis process is to determine the amount of material removed from the original component wall due to corrosion. Equation 3 makes use of the normalized channel data and information concerning the original material thickness to determine the amount of material removed. The reader will notice that this system makes use of differential acquisition to determine the current potential drop but also a differential measurement with respect to the original data collected when the system was initially installed on the component. Once the system is installed, a baseline data is collected and stored and is used as the basis for differential analysis of subsequent data collected. Equation 3 indicates how the subsequent data is compared to the original data to determine the thickness (H) of the material removed by corrosion.

$$\Delta H \approx [\frac{(V_{current} - V_{original})}{V_{original}}] \times H_{original}$$

Equation 3: Determination of material removed by corrosion. [3]

ΔH in equation 3 has been determined to be equal to $[\frac{(V_{current} - V_{original})}{V_{original}}] \times H_{original}$ when the corrosion region is equal to or larger in dimension than the spacing between the acquisition channels. Additional factors need to be considered when the area of corrosion is smaller than the spacing between the data acquisition pin spacing. These additional factors are not discussed in this paper.

Discussion: Testing of the GE data acquisition system was accomplished in two stages. The first stage was to use the system to acquire data from a test sample in the laboratory where two methods of material removal were used. The second stage was to install the system at an operating GE Advanced Materials plastic manufacturing facility. These tests demonstrated that the system was capable of detecting the removal of material and was insensitive to the noise induced in piping systems operating in manufacturing facilities. Figure 5 displays the simulated corrosion used to test the acquisition system. The material removed on the left side of this image was accomplished using a mechanical grinder while that material removed on the right side of this image was accomplished using acid.

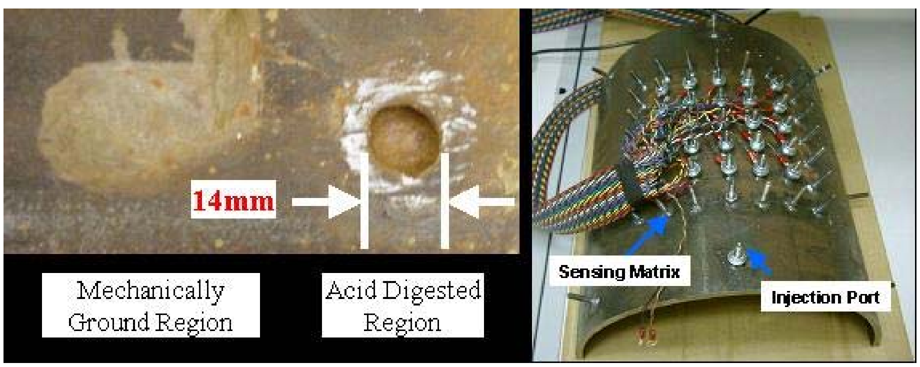

Figure 5: Test sample used for simulated corrosion tests

The sample used for these tests was a carbon steel sample with a wall thickness measuring 8.0mm. The mechanical grinding removed 15% of the wall thickness. Figure 6 contains images of data acquired by the RCM system during the grinding process. The image on the left side of figure 6 is the baseline data collected at the start of the test. The data on the right side of figure 6 is data collected after the grinding process was completed. The change in signal amplitude correlated very well with the amount of material removed from grinding.

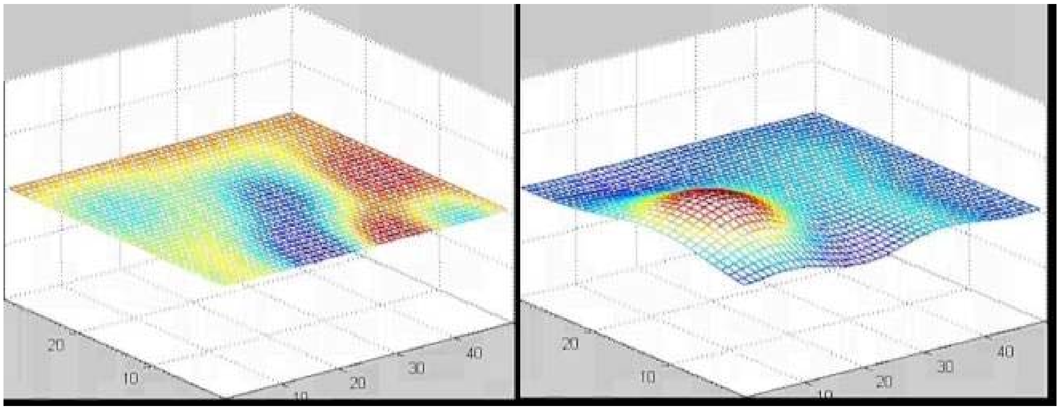

Figure 6: Resistance corrosion system data collected from mechanical grind test

The acid digestion test made use of a combination of hydrochloric and nitric acid to rapidly remove material from the test sample. Figure 7 displays data collected during the acid digestion test. The image on the left side of figure 7 indicates changes to the original baseline data when after the acid had digested material to same depth as the mechanical grinding or 15% of the original wall thickness. The image on the right side of figure 7 displays the data at the completion of the acid digestion test. Approximately 80% of the wall thickness had been removed. The data clear shows that the system is sensitive to the removal of material from either grinding or acid digestion.

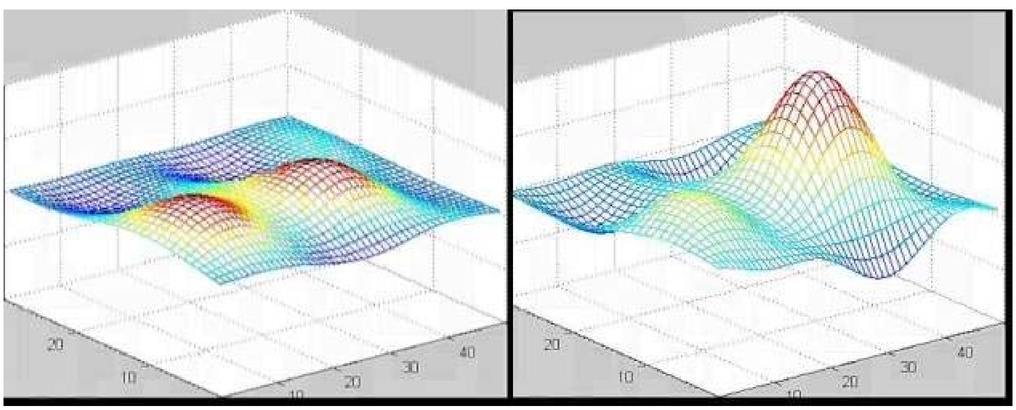

Figure 7: Resistance corrosion system data collected from acid digestion test

An interesting artifact appeared in the data displayed from the end of the acid digestion test. Adjacent to the peak amplitude are minimum values that are lower amplitude than the original baseline data. These minimum regions were predicted using modeling tools. The density of current flow around acute corrosion sites (or corrosion pits) will decrease as the flow diverts around the corrosion site. The diversion of current begins before the actual corrosion site and will decrease the current density in a region where no corrosion occurred. In this region where the material is still the original thickness, the current has been diverted, and a voltage lower that the original baseline voltage will be measured.

One of the largest sources of error in this measurement technique was determined to be due to non-uniformity of test sample temperature. During the mechanical grind test, it was noticed that the heat generated from the grinding process caused erroneous data. Once the localized grind region returned to the temperature of the remainder of the sample, the data was again reliable. The effects noticed during the grinding test reinforced the need to insure that the reference sample must be at the same temperature of the component for test. To insure that the reference and inspection region is thermally stable, the setup needs to be insulated from atmospheric conditions.

The second aspect of the system test, where the data acquisition system was installed in an operating facility, proved that the system was capable of maintaining sensitivity to microvolt level signals while reducing overall system sensitivity to plant noise. Data collected during system operation at the plastic manufacturing facility indicated individual acquisitions where the system input was saturated. These data were infrequent during the one hour long acquisition period and the effects on the data were easily reduced by averaging the data collected over the hour long acquisition period. Systems that collect only a limited number of acquisitions for analysis are subject to facility noise and typically are operated during periods when plant activity is minimized to reduce the effect of plant induced noise to the measurement.

Conclusions: The resistance corrosion monitoring system developed at GE has been proven to be an effective tool for the determination of remaining wall thickness of components subject to corrosive attack. This system has been shown to be sensitive to the changes in material thickness while insensitive to plant and facility noise. The design of the system allows for online measurement of material thickness at temperatures reaching as high as 900 degrees F and can be programmed to provide the data necessary for assisting the safe refining of high acid crude oil.

References:

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