SEALING OF NON-INTRUSIVE HYDROGEN PROBE AT TEMPERATURES UP TO $500^{O}C$

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ABSTRACT

A non-intrusive hydrogen pressure probe that can maintain a leak-tight seal at temperatures up to 500 ^{o}C has been successfully designed. Industrial installations of this hydrogen probe have confirmed that the integrity of the seal can be maintained indefinitely throughout continuous high temperature operation as well as temperature transients. The present paper discusses the unique design of this probe, with a particular emphasis on the patented sealing technology. Also included are results from several industrial installations which confirm the robustness and reliability of the seal.

Keywords: corrosion monitoring, hydrogen probe, non-intrusive, leak-tight seal.

INTRODUCTION

There are four types of hydrogen pressure probes used to detect and monitor corrosion. NACE Publication 1C184 discusses three of these in extensive detail[1]. One style of probe discussed in this paper operates on the basis of pressure. Hydrogen pressure probes collect hydrogen which enters a vessel wall at its wetted surface, migrates through the vessel wall and emerges on the dry surface. By collecting the hydrogen in a known volume, the rate of hydrogen pressure increase can be correlated to the corrosion rate.

Pressure probes can be classified as either insertion style or clamp-on style probes. Clamp-on style hydrogen pressure probes are non-intrusive and thus offer an advantage in that they can be installed without penetrating a pressure boundary. If desired, they can be safely installed while a system is operating. NACE[1] identifies the main problem associated with clamp-on style pressure probes as leakage of the seal between the probe and vessel wall. Typically the seal of these hydrogen pressure probes to a vessel wall involves the use of epoxies or o-rings. In some cases the probes may be welded to the vessel wall.

Although NACE[1] identifies a poor probe to vessel seal as the main problem associated with the reliability of hydrogen pressure probes, the effectiveness of the leak-tight seal of a clamp-on style hydrogen pressure probe can be considered the sum of four distinct contributions related to the monitoring system as a whole.

1. Effectiveness of the seal between the probe body and the material being monitored (a vessel wall - typically a pipe or tube): In the case of a hydrogen pressure probe which operates above atmospheric pressure, a leaking seal will result in the loss of hydrogen to the atmosphere. In the case of a probe operating under vacuum, a poor probe to vessel seal will result in air ingress to the system. Air ingress will result in erroneously high corrosion rate measurements whereas hydrogen loss will manifest itself as erroneously low corrosion rates.

2. Leak-tightness of the fittings and valve: The valve used must have a low and known leak rate to ensure hydrogen does not escape (for probes operated above atmospheric pressure) or that air is not suctioned into the system (for probes operating under vacuum). This is also true for fittings. Hydrogen loss out of the system or air ingress into the system via the valve or fittings will result in inaccurate measurements of corrosion rate.

3. Loss of hydrogen through heated system surfaces: At high temperatures (> 100 ^{o}C) molecular hydrogen that has been collected within the volume of the hydrogen probe can dissociate and escape through the metal. To allow for quantitative measurements of corrosion rate the system must be designed so that hydrogen remains trapped within the system. If not, corrosion rates may be under-estimated.

4. Absorption of hydrogen into system surfaces at low temperature: Even at low temperatures molecular hydrogen can dissociate and be absorbed into the materials of

which the hydrogen probe was constructed. The greater the surface area the greater the percentage of hydrogen that will be absorbed. Absorption of hydrogen by system surfaces will manifest as a loss of hydrogen (i.e. lower hydrogen pressure will be observed).

A well designed hydrogen pressure probe should consider all leak paths (for both air and hydrogen) and must strive to minimize or eliminate leakage to ensure long-term reliable operation of the probe.

CNER(1), in partnership with RPC(2), has designed a clamp-on style hydrogen pressure probe which operates under vacuum. The probe is commonly referred to as the Hydrogen Effusion Probe (HEP) and has been integrated into a fully automated, patented, corrosion monitoring system called the HEPro(1). This system has undergone significant laboratory testing and numerous field trials. It has been proven to maintain a leak-tight seal through temperature transients and during operation at temperatures as high as 500°C.

DISCUSSION

Design of the HEP

As mentioned, the HEP is a clamp-on style (i.e. non-intrusive) hydrogen pressure probe which operates under vacuum. The HEP system consists of a cup inserted into a clamp (refer to Figure 1). The cup is connected via tubing to a pressure transducer, valve and vacuum pump. When the cup is sealed to the vessel wall a vacuum tight seal is achieved. The pump is used to create a vacuum within the cup, tubing and transducer. The valve, when closed, maintains the vacuum. Hydrogen effusing through the vessel wall is collected within the system, resulting in an increase in absolute pressure. A pressure transducer measures the hydrogen pressure. The system is re-evacuated once a predetermined pressure set-point is reached. The data from the pressure transducer is used to calculate corrosion rate[2]. Multiple thermocouples provide data to allow for temperature compensation of the calculated corrosion rate. A data acquisition and control system is used to control the vacuum pump and valve operation and to record readings from the pressure transducer and thermocouples.

Seal Between Probe Body and Vessel Wall

To date, laboratory and field testing of the HEP has been conducted on pipes and tubes. The maximum pipe diameter that has been tested is 14” while the smallest tube size has been 2.5”. There are two HEP designs. One is for installation on a pipe where the clamp can encircle the entire cross section (Figure 1) and the second is for installations on an industrial boiler wall tube (Figure 2). In both designs the sealing mechanism is the same. Only the clamp design differs.

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The seal occurs between the cup and vessel (i.e. tube or pipe). The cup is manufactured from silver and is machined with a precisely engineered edge which deforms when the cup is clamped to the vessel wall. No o-rings, welding, or epoxies are required to create the seal. The HEP clamp is constructed from the same material as the vessel wall to allow for similar thermal expansion characteristics of the vessel and clamp. Compensating washers, positioned under the cap screws, were designed to provide dynamic loading capable of ensuring consistent force by the clamp to the tube during temperature fluctuations. Since the clamp and cup portions of the HEP are constructed from metal, the HEP can be installed on vessels with surface temperatures as high as 500 ^{o}C with no degradation of the seal.

Figure 3 shows the results from laboratory testing of an HEP installed on a boiler tube mock-up. The system temperature was controlled using heaters situated within the boiler tubes. The tubes were dry and there were no corrosion reactions occurring or gaseous hydrogen present. Thus, any measured pressure increase was either due to system off-gassing or air leakage into the HEP. Throughout the testing period the vacuum pump was operated for one hour each day. After the system was initially evacuated following installation (this involved a 12 hour pump-down) a system pressure increase of approximately 100 Pa/day was observed at room temperature. After a one hour pump-down this rate of pressure rise decreased significantly to less than 10 Pa/day. Once the system temperature was increased to 300 ^{o}C another peak in system pressure was observed. A similar but smaller peak was observed when the system temperature was increased to 380 ^{o}C. This behaviour (i.e. pressure peaks just after installation) has been observed routinely both in the field and in the laboratory and has been attributed to off-gassing of the system components(3). After approximately 200 hours the measured leak rate was essentially negligible and below the precision of the instrumentation. There are several more peaks once the temperature increased to 500 ^{o}C but for the remainder of the testing, which includes two 500 ^{o}C to room temperatures transients, the leak rate remained essentially negligible.

Leak Tightness of Fittings and Valve

The valve used in the HEP system is a low volume, low leak valve. The valve has a specified leak rate of less than 10^{-5} Pa·L·day. The HEP system has been designed so the number of fittings is minimized. All connections in this apparatus are either silver soldered or use vacuum fittings. Figure 4 shows that after almost a year of industrial operation, an HEP installed on a 2.5” carbon steel pipe showed no air ingress or hydrogen leakage for a period of nearly 10 days at room temperature. In this case the pipe on which the HEP was installed was cooled for a maintenance outage at which time the corrosion rate was negligible (note: oxygen was also present which eliminated the production of through-wall hydrogen[2]). This observation

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(3) Procedures have now been developed to minimize off-gassing in industrial installations.

confirms that the fittings and valve are leak tight and that the probe to vessel seal remains intact after a year of operation at temperatures of approximately 300 °C.

Loss of Hydrogen Through Heated System Surfaces

Hydrogen can readily permeate most metals at high temperatures. For the HEP to obtain representative pressure measurements it is necessary to contain the hydrogen which has been collected. Silver is one of the most impermeable metals to hydrogen. In fact, the hydrogen permeability of silver at 350 °C is similar to stainless steel (SS) at approximately 100 °C[3,4]. Using a hydrogen probe as an example: If a 5 cm^2 stainless steel section of a hydrogen probe with a wall thickness of 0.2 cm was heated to 300 °C and the pressure inside the probe was allowed to increase to 50 kPa (i.e. one half of an atmosphere) then almost 35% of the hydrogen collected would be lost. Alternatively, if this same section was constructed from silver, the loss of hydrogen to atmosphere would be less than 0.05%.

The HEP corrosion monitoring system is unique in that all heated components are constructed from silver. Because the heated cup and tubing are constructed from silver the escape of hydrogen is minimized, thereby increasing the accuracy of the instrument.

Hydrogen Absorption onto Metal Surfaces

Dissociation of hydrogen molecules at metal surfaces is known to occur[5]. Once the hydrogen molecule has dissociated, the hydrogen atoms can be absorbed by the metal[6]. This phenomenon is certainly faster at high temperatures (as discussed in the previous section of this paper) but does occur even at low temperatures, particularly within vacuum environments exposed only to pure hydrogen. Under these conditions, oxide films are not present to interfere with the absorption process. This process is reversible in that hydrogen that has been absorbed can then be desorbed from the same surface. The absorption and/or desorption of hydrogen from the metal can affect the measured rate of hydrogen accumulation within a closed system.

Since the internal surfaces of the HEP are exposed only to pure hydrogen under vacuum, the resistance (in the form of an oxide layer) which would typically impede the absorption of hydrogen is not present. To reduce the extent of low temperature hydrogen absorption, SS was chosen for the low temperature components of the system since SS has a much lower hydrogen solubility at low temperatures than iron (on the order of 10^3 mol $H_2 \cdot m^{-3} \cdot Pa^{-1/2}$ lower [4,7,8]). The surface area of the SS is minimized by using small diameter tubing and making field runs as short as possible. The inaccuracy caused by desorption is minimized by operating the vacuum pump for a sufficient length of time such that absorbed hydrogen is released from the metal surface before the next cycle begins. Tests performed at CNER suggest that with the current HEP design, hydrogen absorption/desorption has a negligible impact on the measured hydrogen pressure increase.

CONCLUSION

Challenges associated with sealing a clamp-on style hydrogen pressure probe to a vessel wall have been identified. Creating and maintaining a seal by welding or using epoxies or o-rings has historically been considered problematic. A new patented sealing technology has demonstrated long term robustness in industrial environments. The non-intrusive hydrogen pressure probe discussed in the present paper has been designed to not only maintain a leak tight seal between the probe and vessel wall but also to minimize leakage via other routes including fittings and valve as well as loss of hydrogen by absorption and permeation.

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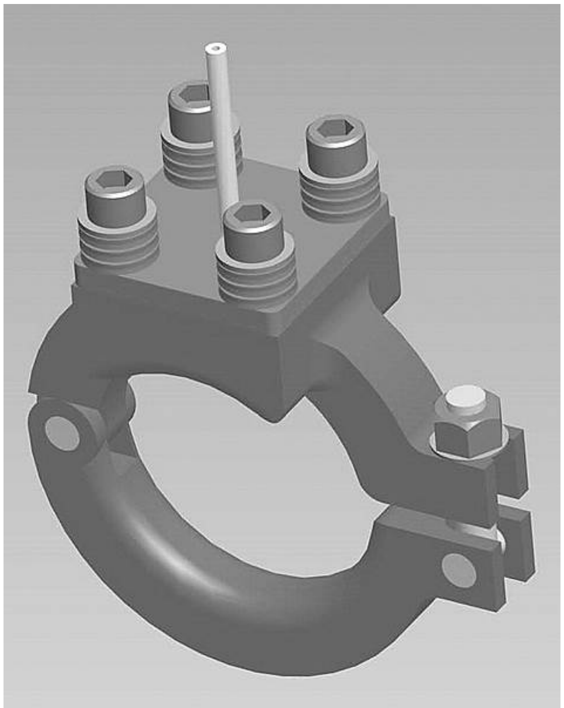

FIGURE 1 - Clamp-On Style HEP for Use on Pipes

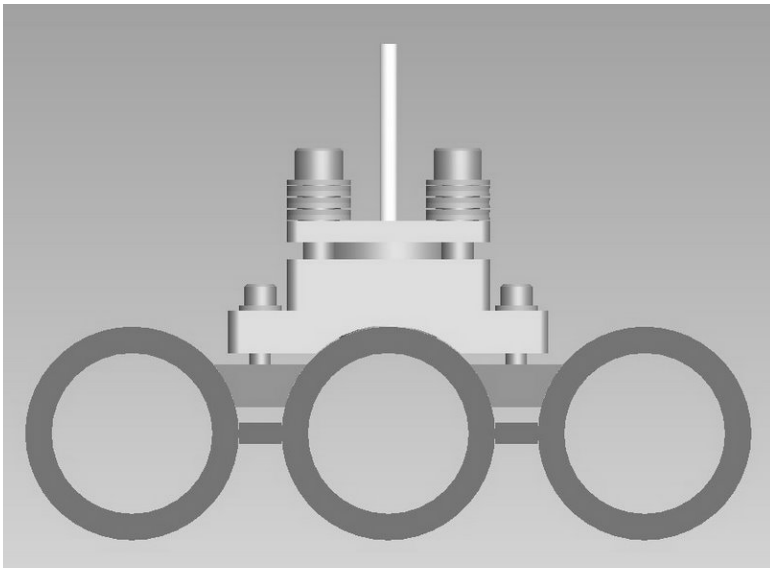

FIGURE 2 - Clamp-On Style HEP for Use on Boiler Wall Tubes

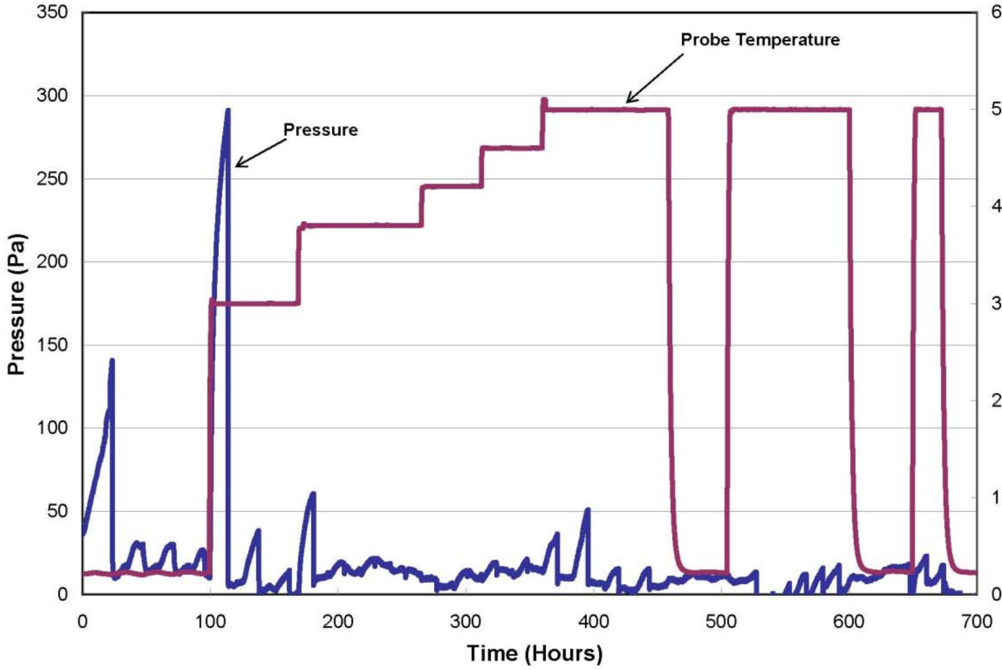

FIGURE 3 - Leak-Tightness Confirmation in Laboratory Testing up to 500 °C

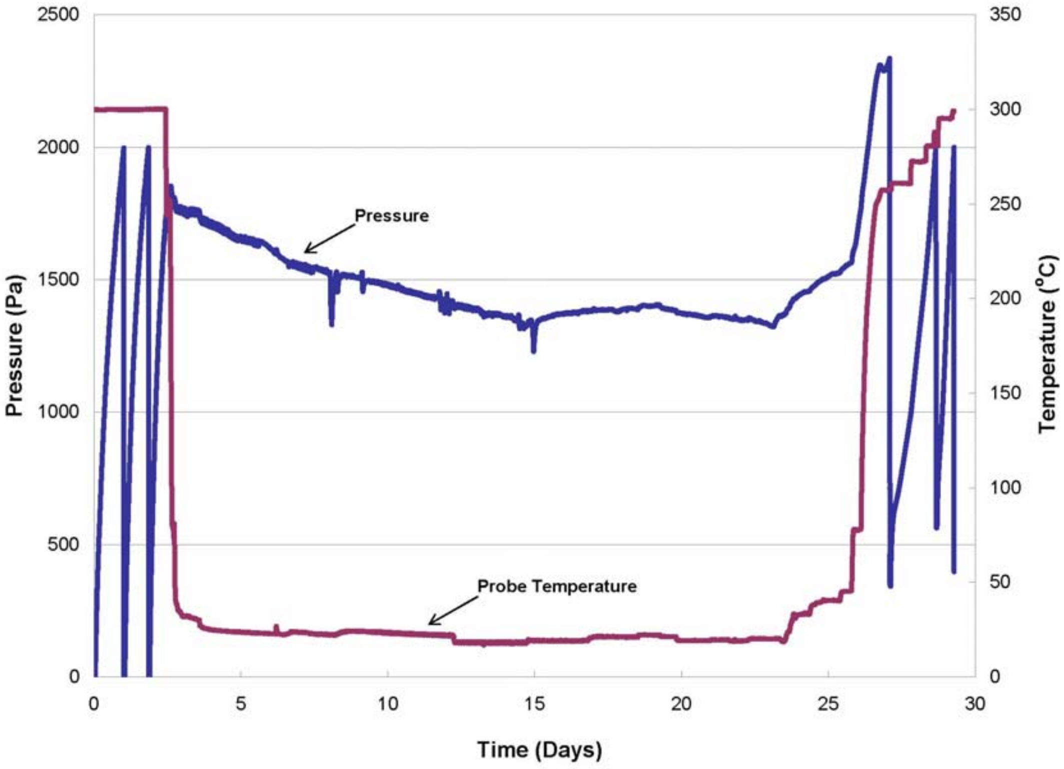

FIGURE 4 - Leak Tightness Confirmation During Field Installation