NRR
— Part 21 Report

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Director, Office of Inspection & Enforcement
United States Nuclear Regulatory Commission
Washington, DC 20555

Subject: Final Report
Component Defect Evaluation
Hydrogen Sensor - Containment Atmosphere Monitoring System

Nature of the Deviation:

During normal operational surveillance testing of hydrogen analyzers at the Northern States Power, Prairie Island NPS, hydrogen sensors exhibited a loss of sensitivity at a rate beyond normal design specifications. The automatic calibration features in the analyzer systems continued to compensate for these sensitivity changes so system performance integrity was maintained.

All of the sensors at NSP that exhibited this characteristic were found to be from the same manufacturing lot. Serial numbers for that lot of sensors is C-2147 through C-2158.

The sensors within this serial number lot were manufactured in the 4Q91, and delivered in late 1991 and early 1992. Seven of the sensors have been returned to the factory and examined. Four units have been refurbished and returned to NSP. Three others are being rebuilt for return to service, the balance of five units have been recalled for rework.

Cause of the Deviation:

Each of the seven sensors examined and reworked were found to be extremely low in electrolyte. The electrolyte is not a consumable element in the sensor, it performs as the ionic current path between the electrodes and is therefore critical to operation. Refilling of the sensor with electrolyte in accord with the normal manufacturing process instructions restored each sensor to nominal performance. Volume of electrolyte added was nominally 1.3 to 1.7 cc, about 50% of the normally required amount.

There were signs of electrolyte leakage in only one of the sensors examined. Access to the area where acid was identified requires partial disassembly. In view of the fact that this was the only sensor showing leakage, and that the electrolyte had not dried out, it is likely that leakage occurred during the examination process and is therefore not being considered a failure mode for this group of sensors.

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In the normal range of environmental operating parameters for these units, evaporation processes should not be a factor. With leakage and evaporation either empirically of analytically discounted as the primary cause of low electrolyte, the focus falls on an inadequate charge of electrolyte during initial assembly. A review of process documentation indicated that these sensors were assembled by two different operators, one experienced, one as a trainee.

The major questions addressed were resolved into the following;

1. What are the paths for electrolyte loss?

   Electrolyte loss from the sensor can be caused by leaky seals or evaporation through the sensing electrode membrane.

   Leakage of electrolyte (25% solution of sulfuric acid) will leave a conductive path across the seal. This path is easily detected by voltage drop measurements between electrode leads and the outside surface. A leak will show up as a millivolt signal, while no leakage will be indicated on the meter as an open circuit. except as indicated above, leakage was not identified as a failure mode in any of the sensors.

   Evaporation of electrolyte (or water from the electrolyte) is considered to be a contributing factor in these failures, compounded by the originally low electrolyte volume. Water loss through evaporation in typically "dry" environments has been studied (during the design development phase, and periodically since then) and found to be within acceptable limits for the application. For a marginally filled sensor however, the exchange of water vapor across the membrane for relatively low RH, could conceivably accelerate the performance degradation.

   Sensors with 5-6 years of in-plant operating life have been examined and found to perform within specification, so the issue is not one of design.

2. How could the sensors not be fully charged with electrolyte?

   The filling procedure requires that electrolyte be added during a series of vacuum exposures to facilitate removal of entrapped air, and subsequent replacement with electrolyte. The procedure defines the vacuum level to be achieved, and a dwell time at that level. Repeat cycles are to be performed as needed. No specific minimum volume of electrolyte was defined.

   Without definition of quantitative requirements, i.e., how much electrolyte is enough, the volume of electrolyte added is left up to the discretion of the operator on the basis of their judgement as to whether all of the air has been removed. Observations through the vacuum bell jar are difficult and an inexperienced operator may not fully recognize electrolyte movement during vacuum cycling.

Discussions with the area supervisor defining the problems and changes to the procedure (with specific definition of minimum electrolyte volumes) have been put in place to eliminate these problems.

3. Since all sensors passed the standard acceptance test sequence, what causes the eventual loss of signal with time?

   The filling procedure involves a series of vacuum cycles to facilitate wetting of the electrodes with electrolyte. If this process was not rigidly followed, incomplete wetting of electrode materials will result. The test cycle follows the fill cycle closely in time and the tests are performed with the sensing electrode facing down. These factors would act to provide the maximum electrolyte contact with active electrode surfaces thereby masking the impact of low electrolyte volume.

   The installed orientation for the sensors is on the side, with the sensing electrode face vertical to the gravity vector. In this position, a partially filled sensor would seek a liquid level that could eventually soak into the counter electrode powder (platinum oxide) and uncover the sensing electrode causing a restriction to ion flow between the two electrodes, and/or uncovering a portion of the sensing electrode whereby the contact between electrode, electrolyte, and hydrogen is not possible. The result is a lower signal with hydrogen concentration.

Impact On Equipment Delivered:

1. All of the sensors in the lot identified have been recalled for rework. Utilities affected are the following;

   Northern States Power, Prairie Island, 8 sensors,
   Carolina Power & Light, Robinson 2 sensors,
   Southern California Edison, San Onofre, 2 sensors

2. A status review of other sensors installed indicated that those still in the field from other lots are performing satisfactorily. Detailed reviews of all returns and problem reports will continue to be monitored for trends.

Corrective Action:

1. Assembly procedures have been modified to specify a minimum electrolyte volume to be added.

2. Electrolyte volumes are required to be recorded.

3. Counter electrode packed density (platinum oxide) is being more closely controlled to facilitate addition of larger electrolyte volumes and electrode wetting.

4. The assembly procedures have been reviewed by the area supervisor and specific precautions discussed. The area supervisor is an experienced operator in the sensor production procedures.

Conclusions:

Sensors installed in systems would have continued to provide acceptable performance since the auto-calibration/adjustment process would have continued to maintain system accuracy.

The cause of premature changes in sensitivity to hydrogen is the result of low electrolyte volume.

Changes to the assembly procedures and training procedures will eliminate the potential for recurrence of completing a sensor fabrication with low electrolyte volume.

Modifying the internal material configuration (i.e., decreasing the density of the platinum oxide powder pack), thereby increasing the volume of electrolyte space will improve the filling process by facilitating air/liquid exchange and make room for more electrolyte.

Sincerely,

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