Measurement of dissolved hydrogen as a determination of corrosion rate in power plants

Fast, accurate dissolved hydrogen measurement down to 0.03 ppb with process or portable configurations available for any application

Application description

For many years corrosion in boilers of a fossil power plant and in steam generators of PWR nuclear plants have been studied. In these environments, the metal surfaces react with water at high temperatures to form magnetite.

The basic reaction can be represented as:

3 Fe + 4 $H_2O \rightarrow$ Fe₃O₄ + 4 H_2

Under appropriate water chemistry conditions, this dense magnetite layer forms a protective coating on the metal surfaces. However, experience has shown that some flaking and reformation of the magnetite is likely. A water chemistry program to reduce metal loss (corrosion) is critical in the prevention of costly accidents and downtime.

As the reaction above indicates, magnetite and hydrogen formation are related. Therefore, in theory, the measurement of changes of hydrogen concentration correlates to the corrosion rate of the metal. It is important to note that the hydrogen generated by the formation of magnetite is not the only source of hydrogen in this application. The hydrogen concentration actually due to corrosion ($H_{2 \text{ corr}}$) is equal to the total hydrogen ($H_{2 \text{ tot}}$) less the contributions due to background ($H_{2 \text{ bkgnd}}$) and decomposition ($H_{2 \text{ decom}}$).

$$H_{2 \text{ corr}} = H_{2 \text{ tot}} - \{H_{2 \text{ bkgnd}} + H_{2 \text{ decom}}\}$$

Background hydrogen levels vary from plant to plant and can be measured on samples after the feed water pumps. Slightly higher levels can be expected in the secondary side of a PWR due to diffusion of hydrogen from the primary side. Another source of hydrogen in a steam cycle is due to the decomposition of hydrazine and neutralizing amines.

Factors that cause hydrogen levels to be different from plant to plant include the size of the plant, water chemistry, operating load, and corrosion rate. With this type of variability, a careful study of each factor must be undertaken to correctly deduce corrosion rates.

The background level of hydrogen can be determined from a sample after the feed water pumps, and before any pre-heaters or the economizer. The effect on the level of hydrogen due to decomposition can be shown by varying the chemical feed. In addition, the amount of hydrogen varies with load, and therefore results of background or decomposition hydrogen should first be collected at constant load.



To have a more complete picture it is recommended that data be evaluated at a minimum of two different loads. The lowest levels of dissolved hydrogen (>0.2 ppb) are usually found in samples just after the feed water pumps. The highest levels of dissolved hydrogen (>2.0 ppb) should be found in the main steam sample. The range of 0.2 to 2.0 ppb DH₂ in the steam cycle is only a rough guideline. If DH₂ levels are greater, a high likelihood of a corrosion problem exists. However, if levels are within this range, there still might be a corrosion concern.

To locate a specific corrosion problem, measurements of DH_2 before and after individual sections of the steam cycle are recommended. It also has been shown that as corrosion thins the walls of metal, the corrosion rate increases. Therefore, with continuous measurement of DH_2 , a known baseline hydrogen level can be established, and any increase can alarm of possible corrosion failure.

An accurate measurement of dissolved hydrogen can yield enlightening results!

Installation recommendations

Orbisphere hydrogen analyzers can be configured for portable or process use. Installation and operation are fairly simple, since these analyzers use the same flowing liquid samples, reduced in temperature and pressure, commonly used at power stations for all water chemistry analysis.

The sample of interest is connected via ¼" or 6-mm stainless steel tubing to a model 32001 flow chamber, with a flow rate of between 200 to 400 ml/minute. Calibration and/or verification of the analyzer are also easily accomplished by simply flowing a 1% hydrogen gas (balance nitrogen) through the flow chamber.

Recommended system components

Model	Description
510/B00/WIC00000	Single channel H ₂ analyzer, wall mounting enclosure (panel mount or table top are also available)
31230.01	H ₂ sensor, parts in contact with simple in stainless steel
32001.001	Flow chamber, stainless steel, with ¼" fittings (6-mm available)

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