Detecting real-time moisture leaks in acid plant process gas

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Sulfuric acid production requires a sulfur dioxide (SO_2) gas source, most commonly supplied by:

- Burning elemental sulfur.
- SO_2 off-gas from a primary process such as a copper smelter.
- Decomposition of H_2SO_2 in a spent acid regeneration process.

The SO_2 gas is passed over a catalyst in the presence of oxygen to oxidize it to sulfur trioxide (SO_3), which is then absorbed into 97–98 percent H_2SO_4 to form oleum ($H_2S_2O_7$), also known as fuming sulfuric acid. The oleum is then diluted with water to form concentrated sulfuric acid.

Acid dew point measurement

In sulfuric acid production, SO_2 is oxidized over a solid vanadium catalyst to generate SO_3. The SO_3 is then absorbed in water contained in 98 percent sulfuric acid to form new sulfuric acid. The gas laden with SO_3 in the process is kept moisture free and the only time moisture gets introduced in the gas is when there is a process upset. This is a highly undesirable condition and can be potentially hazardous.

Moisture in the flue gas combines with the SO_3, which condenses on the process equipment surfaces. This effect is generally indicative of one of the following conditions, among others:

- Drying tower malfunction
- Moisture in feed
- Waste heat boiler tube leaks
- Economizer tube leaks
- Cleaning system malfunctions

The presence of moisture and therefore weak acid vapor in the gas stream is detrimental to equipment health and can cause extreme corrosion.

A secondary impact of moisture in the flue gas can be the formation of hydrogen gas, which creates an explosion hazard [1]. The H_2 formed in the following equations can create an explosion in the presence of O_2 and an ignition source.

- $SO_3+H_2O \rightarrow H_2SO_4$
- $Fe+H_2SO_4 \rightarrow FeSO_4+H_2$

Moisture leak detection

As stated, there are several potential sources of moisture ingress into the process gas stream including the drying tower, feed stock, waste heat boiler tubes, and economizer tubes.

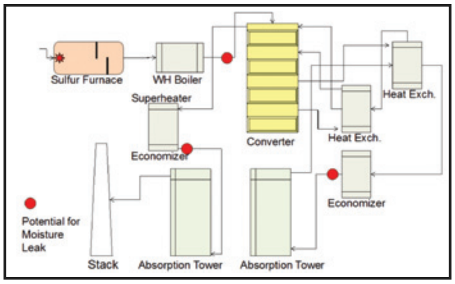

Fig. 1: Typical moisture ingress points in sulfuric acid manufacturing.

Monitoring each of these individual process points (Fig. 1) for malfunction and moisture ingress becomes expensive and manpower intensive. Traditionally, operators measured the acid dew point to indicate such moisture leaks. In theory this would provide a step change response should moisture enter the upstream process.

The commercial design for the Breen-SA Probe can be seen in Fig. 2. After successful factory testing, the probe was taken to a sulfuric acid manufacturing plant and installed at the exit of the economizer along the production train.

The economizer outlet location presents itself with a process gas temperature of approximately 400^{o}F and a process gas pressure between 6 and 10PSI. The process gas dew point was expected to be at approximately 250^{o}F.

Fig. 2: Breen-SA Probe Rev 2 for sulfuric acid plants.

After initial installation, the dew point probe provided sound dew point results as seen in Fig. 4.

"Above dew point" measurement

To keep the sensor free of process condensables for the long term and also provide moisture leak detection, it was decided to operate the system at an "above dew point cycle." The above dew point cycle would allow the probe to operate in the duct at a temperature higher than the process gas dew point, but low enough to detect an increase, or step change, in process gas dew point. There were two objectives that needed to be met during operation in this mode: detect moisture ingress and provide a method to verify measurement integrity.

Moisture leak detection—commercial design

In late September/early October 2018, Breen installed the commercial design into a sulfuric acid plant in California (Fig. 5).

The probe system was allowed to run at the above dew point mode, with a weekly "check cycle" cooling the sensor to the process gas dew point. The probe cycle and check cycles are shown in Fig. 6.

On January 23, 2019, the plant performed

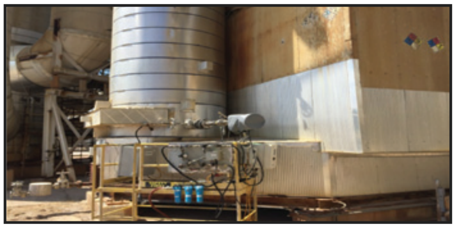

Fig. 3: Breen-SA Probe Rev 2 installation.

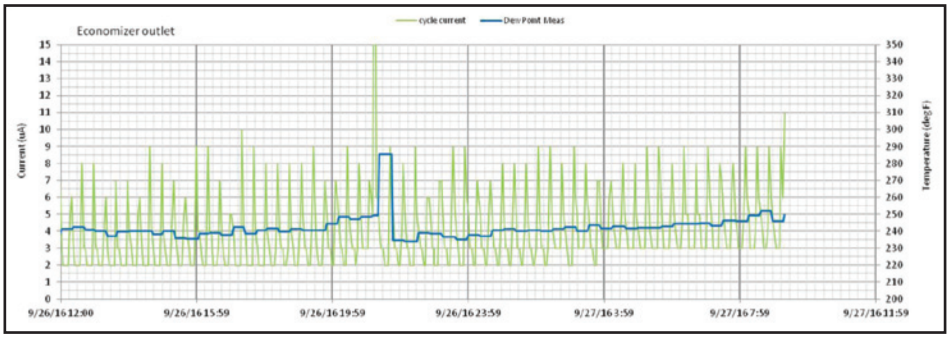

Fig. 4: Preliminary dew point measurements.

Fig. 5: Breen SA Probe installation at J.R. Simplot's Lathrop plant.

a test to verify that the system would indeed detect a moisture leak. At approximately 10:45 (Fig. 7) we can see a probe response when a pressure point line was cleared out with instrument air. A compressor was then hooked up to the line to pump ambient air into the duct; no response was seen, and it was assumed that the air pressure was not powerful enough to push sufficient air into the duct.

Subsequently, the process engineer put water into the pressure point line and used instrument air to push that water into the duct. The amount of water added was approximately a gallon. At 13:15 we can see the probe immediately responded to the event. It was concluded, with fairly strong certainty, that the probe is very responsive to even small amounts of moisture.

There were also other minor responses in the previous weeks, which were believed to have been caused when other pressure point lines were cleaned out.

In July 2019, a second system was installed in another acid plant in the Western United States. During start-up operations, this plant experienced a small leak. As shown in Fig. 8, the Breen-SA Probe detected the leak at about 5:00 on June 27th when the leak was still very small. The first plant DCS indication that there was an issue was about 13:30 on the 27th when the dilution water flow starts to drop, indicating the leak is large enough that less water is needed to maintain the acid concentration balance in the plant.

Clearly, the probe provided almost eight hours of advance notice compared to the traditional method of leak detection at the plant.

Additional features of the latest design include detection for sensor breakage and protection from back flow of the process gases though the probe. Periodically we have seen the probe sensor damaged when inserting the probe into the process, so shielding has been put in place to protect the sensor from breakage during installation.

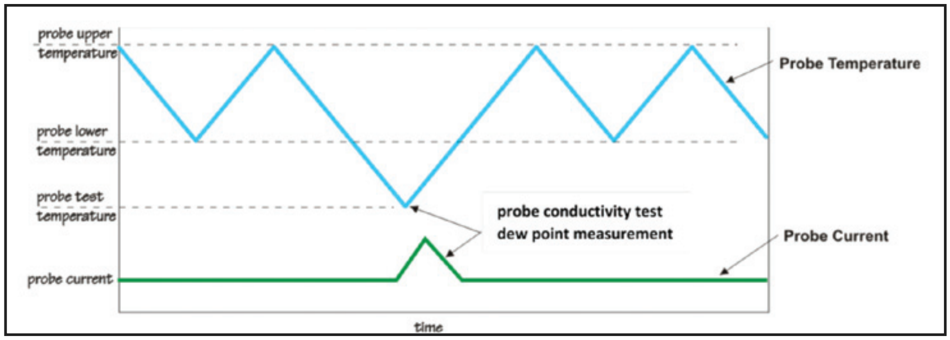

Fig. 6: Breen-SA Probe normal cycle and check cycle.

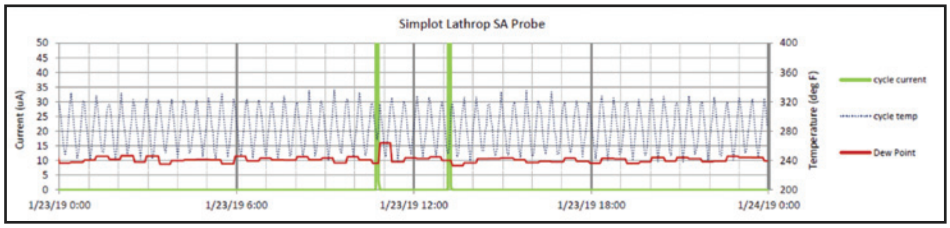

Fig. 7: Leak detection simulation.

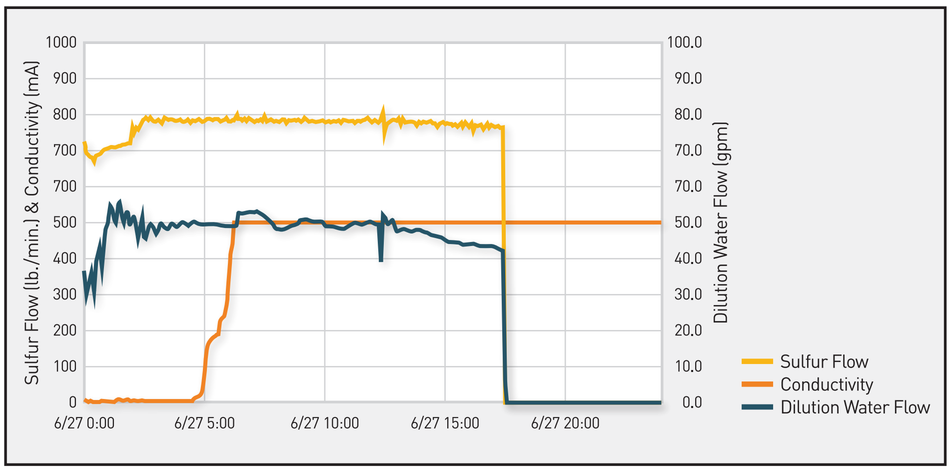

Fig. 8: Leak detection from Breen-SA Probe vs. dilution water flow.

Summary

It has been demonstrated that the dew point measurement system has the capability to measure continuous process gas dew point temperatures. Understanding that the industry desires long term, ultra-low maintenance, it appears that the "above dew point mode" measurement philosophy has been commercialized and proven effective to detect moisture leaks, while maintaining a clean and dry sensor in between moisture events. It has also been shown that the probe consistently responds to moisture ingress into the process in real time and demonstrably quicker than traditional methods.

This method also allows for the insitu verification of sensor function using a periodic system "check cycle" outputting a measured dew point on demand.

At the time of writing, the commercial system has been running for 18 months with no failures or maintenance. During a turnaround last September, the probe was pulled for inspection and re-installation. There were no signs or premature deterioration of the sensor or probe.

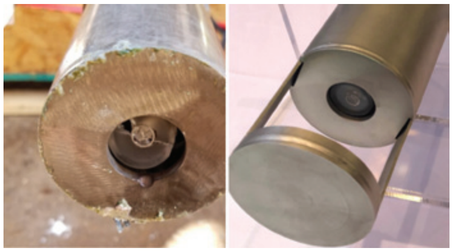

Fig. 9: During installation, SA Probe sensor, left, damaged from obstruction in port. At right, sensor protective shield.

For more information on Breen sensors or the full range of Breen products and services, visit www.breenes.com. ❑

Reference:

[1] Information developed and presented by the Hydrogen Safety Workgroup.