

pH/ORP measurement

Amine scrubbers in foundries



Measurement made easy

Foundries
amine scrubbers

Introduction

The correct use of pH instrumentation to measure pH in foundry amine scrubbers is generally misunderstood. Environmental managers of iron and steel foundries must measure and record their amine scrubber pH values to ensure the scrubbers' compliance with national standards for hazardous air pollutants (NESHAP).

To ensure that maximum achievable control technology (MACT) is attained by an amine foundry scrubber, it is very important to understand the difficulties of measuring pH in strong acid solutions and what accuracy may reasonably be expected. In addition, foundries that want to recycle spent-acid solutions rely on accurate pH readings to meet the physical properties imposed by the recyclers.

The process

Most foundries run their scrubbers ‘batch wise’, starting with a batch of sulfuric acid of a known concentration. The acid is circulated until it is consumed or ‘spent’. The spent solution is then pumped out and replaced with a fresh batch of acid. The amine scrubber liquor starts out as a 22 to 25 % by weight sulfuric-acid solution (this is approximately a 5N solution and is around –0.5 on the pH scale). Over time the acid is consumed and very slowly the pH begins increasing. When the solution reaches 1N (approximately equal to 5 % by weight) the pH is 0; equating to a five-fold change in concentration for a change of approximately 0.5 pH. As more acid is consumed the concentration and hence the pH, continues to drop further – see Table 1.

Normality	Concentration	pH
5.0	~22 %	– 0.50
1.0	~5.0 %	+ 0.05
0.1	~0.5 %	1.03
0.01	~0.05 %	2.00
0.001	~0.005 %	3.00
0.0001	~0.0005 %	4.00

Table 1 Concentration/pH relationship in sulfuric acid

Table 1 shows that the pH changes very slowly as the first 80 % of the acid concentration is consumed. As the scrubber consumes the last 20 % of the acid the pH rate of change increases and when only 2 % of the original acid charge remains (the acid concentration drops below 0.1 %), the pH changes very quickly. For this reason, it is more important that pH is monitored accurately toward the end of the batch cycle than at its beginning or middle.

A pH sensor has difficulty measuring pH in strong acids. The sensor is non-linear below 1.5 pH. It can lose about 10 mV at 1.0 pH (6 mV is equal to ~0.1 pH with a perfect sensor), 20 to 30 mV at 0 pH and over 50 mV at –0.5 pH. Considering that 59.15 mV is one pH unit, acid error can be a serious one and the error affects the efficiency or slope of the sensor.

Since the acid error is non-linear (and somewhat unpredictable), calibration is very difficult. As an example, calibrating in conventional 4.01 and 6.86 (or 7.0) pH buffer solutions followed by a 1.0 pH solution causes the sensor to under-react and read 1.25 pH. Substituting the 1.0 pH solution for a 0 pH solution increases this effect, resulting in a reading of only 0.5 pH. This is because the 4.01 and 6.86 (or 7.0) pH buffer solution calibration determined a slope of 59 mV/pH change but, placing the sensor in the acid solution, produces a change that is considerably less than 59 mV/pH.

Conversely, calibrating in 0 and 2.0 pH buffer solutions followed by a 5.0 pH solution causes the sensor to over-react and read 4.6 pH. This is because the sensor is first being calibrated in its non-linear area where the slope may average only 48 mV/pH; the final 5.0 pH solution calibration produces the standard 59 mV/pH. Figure 1, page 3 shows the acid error of a general-purpose glass electrode (though it exaggerates the actual error to illustrate the point.)

So, if the sensor is calibrated conventionally, it never reads the low pH correctly and if the sensor is calibrated in acids, it never reads the more neutral solutions (>2.0 pH) correctly. What can be done?

For amine scrubber applications, calibrate the sensor using color-coded standard buffer solutions of 1.68 (colorless) and 4.01 (red) pH. Color-coded buffers prevent the user from accidentally using the wrong buffer during calibration.

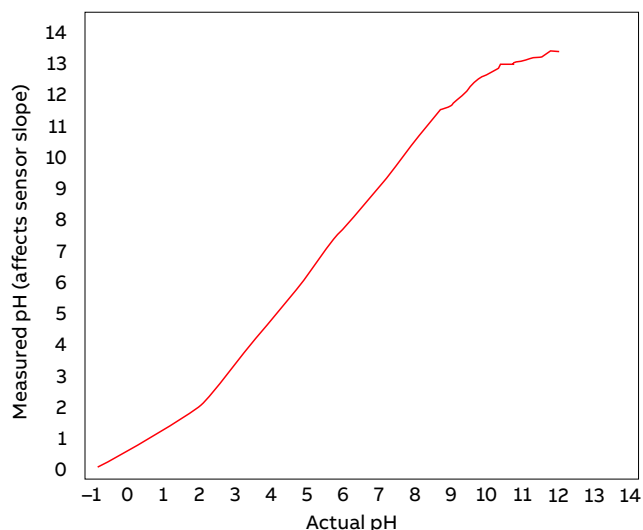


Figure 1 Acid error of a general purpose glass electrode

As described, once the pH value of the scrubber solution falls below 2.0, the readings from the sensor become inaccurate because of its non-linearity. This is not so important in amine scrubber applications. It is more important that the readings are accurate above 2.0 pH therefore set a setpoint value higher than 2.0 pH to indicate that once the setpoint is reached, it is time to drain the scrubber and start with a fresh batch of acid.

Also, any sensor that goes into a very low pH solution comes out of it with 'acid memory'. That is, if the sensor is placed in a 0 pH solution for 5 to 10 minutes and then put in a 4.0 pH solution, it may take approximately 30 minutes to read the 4.0 pH solution correctly because both the glass and the reference in the sensor must re-acclimate themselves to the more neutral solution. A process sensor that has sat for months in a strong acid solution that has become slowly less concentrated could take hours to recover fully if it is taken out of the strong acid and placed in a buffer. So, what to do then?

Unless starting with a brand new sensor, ensure the sensor has plenty of time to acclimatize to the higher pH values of the buffers. This may mean letting the sensor sit in the higher buffer for a couple of hours and then swapping the contaminated buffer solution for a fresh one, because acids coming out of the sensor's reference junction contaminate the buffer solution that the sensor originally sat in.

Finally, at pH values above 2.0 it is unrealistic to expect the sensor to agree with a grab or lab sample measurement closer than 0.25 pH (error on the lab/portable sensor is part of the reason.)

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