APPLICATION NOTE

pH ANALYSIS CALCULATION WITH DIFFERENTIAL CONDUCTIVITY MEASUREMENT

Benefits

- The measurement is not susceptible to the contaminations typically associated with pH systems.
- On pH systems where loss of electrolyte causes system failings, this type of indirect measurement provides an efficient solution.
- Under normal water chemistry conditions, the algorithm gives reliable results.
- High sensitivity and conductivity give a linear response to ammonia content, where pH electrodes give a logarithmic response

How pH is Calculated

Introduction

The calculated pH requires five steps:

1. Total (specific) conductivity is measured (Cond 1)
2. The sample then flows through a cationic resin
3. The conductivity is again measured with a second conductivity probe (Cond 2)
4. By calculation, the contribution of NaCl in Cond 1 is taken away leaving the unknown Cond NH_3
5. A formula is then applied that links the ammonia (NH_3) conductivity, concentration and finally the pH calculation

VGB

VGB (Vereinigung der Großkraftwerksbetreiber e.V.) is the Germany-based International Association of Power Plant Operators. In determining pH by differential conductivity, a specific model consisting of an alkalizing agent and a specific impurity is used; the alkalizing agent being sodium hydroxide (NaOH), and the impurity sodium chloride (NaCl). The VGB first presented this model a number of years ago.

pH Calculation

The pH is a result of the sodium hydroxide (CNaOH) concentration. In addition, chemistry states that the conductivity of the acid (e.g., HCl) is three times higher than the conductivity of the corresponding salt (e.g. NaCl) due to the very high conductivity of the hydrogen ion (H^+). In the model used, the conductivity of hydrochloric acid (HCl) is three times higher than the conductivity of the sodium chloride (NaCl). Thus, the conductivity k_{acid} after the cation exchanger corresponds to three times the value before the cation exchanger.

Be Right™

The conductivity k_{spec} , before the cation exchanger, is composed of the contribution from the sodium hydroxide (NaOH) and from the sodium chloride (NaCl) that is 1/3 k_{acid}.

Thus, the concentration of sodium hydroxide is proportional to the direct measured conductivity minus one third of the post-cation exchanger conductivity.

With respect to the molecular conductivity of the sodium hydroxide (243 S/cm per mmol/L), it yields the concentration of the sodium hydroxide as:

$$NaOH = (k_{spec} - (k_{acid} /3))/243 \text{ mmol/L}$$

And the pH value will be:

$$pH = 14 + \log NaOH \quad \text{measured in mol/L}$$
$$pH = 11 + \log NaOH \quad \text{measured in mmol/L}$$
$$pH = 11 + \log ((k_{spec} - (k_{acid} /3))/243)$$
$$pH = 11 - \log 243 + \log (k_{spec} - (k_{acid} /3))$$
$$\underline{pH = 8.60 + \log (k_{direct} - (k_{acid} /3))}$$

Validity conditions

In order to give accurate results, some specific conditions related to the water chemistry parameters are applied:

- The conditioning of the boiler feed water should be alkaline-based, with sodium hydroxide (NaOH) or NH_4OH.
- Impurities that are present should consist predominantly of sodium chloride (NaCl).
- Low phosphates should be present in the water for water softening. As a recommendation, phosphates should be less than 0.5 mg/L.
- If the pH exceeds 8, the concentration of impurities must be small in comparison to the alkalizing agent.

Conclusion

The Hach 9523sc Cationic Conductivity Analyzer provides long-term, reliable and maintenance-free pH systems under normal water chemistry conditions in power plants.

This does not replace typical pH systems, but instead gives a complimentary parameter to the plant chemist for strengthening process understanding and control.

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