Temperature variation and its effects on pH

This important parameter is often overlooked in day-to-day operations

K. R. RAMAKUMAR, Indian Oil Corp. Ltd., Gujarat, India

The pH of service solution in any piece of equipment like a boiler or heat exchanger is an important parameter that should be maintained in a specified range. Equipment metallurgical properties must also be considered. Normally, pH measurements are made by online pH analyzers located downstream of coolers at a much lower temperature compared to actual operating condition. These readings are generally cross-checked by operating personnel with color indication from time to time.

But the crux of this issue is whether measuring the pH at a temperature lower than actual operating condition fulfills the actual purpose of maintaining pH. Experimental data accentuates the fact that pH tends to be on the acidic side at higher temperatures. The catastrophic effect of material deterioration or corrosion associated with such a phenomenon is also explained using vis-à-vis Pourbaix diagrams. The need to specify pH as a function of temperature is indelibly felt in this regard.

Temperature. Ever wondered what a change in pH with temperature could do to the equipment material of construction? The shift in pH associated with temperature fluctuation can lead to rapid equipment deterioration, especially with boilers and heat exchangers.

Basically, pH can be defined as the negative logarithm of the hydronium ion (H_3O^+) concentration, where:

$$pH = -\log [H_3O^+]$$

It is measured on a scale ranging from 0 to 14. If the H_3O^+ concentration is more than the hydroxide ion (OH^-) concentration, the material is acidic, that is, its pH is less than 7.

pH measurement. A rough indication of pH can be obtained using pH papers or indicators, that change color as the pH level varies. These indicators have accuracy limitations and can be difficult to interpret correctly in colored or murky samples.

More accurate pH measurements are obtained with a pH meter. A pH measurement system has three parts:

1. pH measuring electrode
2. Reference electrode
3. High-input impedance meter.

The pH electrode can be thought of as a battery, with a voltage that varies with the solutions being measured. The pH measuring electrode is a hydrogen ion (H^+)-sensitive glass bulb, with a millivolt (MV) output that varies with the changes in the relative H^+ concentration inside and outside of the bulb. The reference electrode output does not vary with H^+ activity. The pH electrode has very high internal resistance, making the voltage change with pH difficult to measure. The input impedance of the pH meter and leakage resistances are therefore important factors.

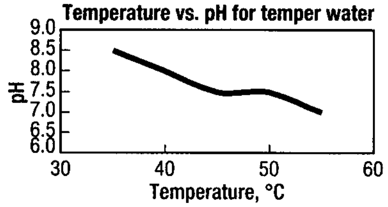

FIG. 1 Variation of pH with temperature.

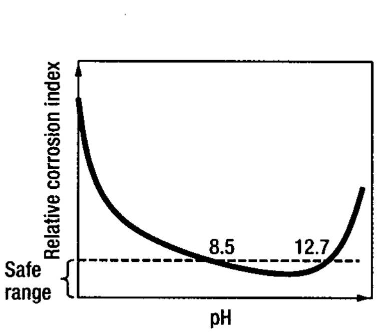

FIG. 2 The safe pH range for MS/CS.

The pH meter is basically a high impedance amplifier that accurately measures the minute electrode voltages and displays the results directly in pH units on either an analog or digital display. In some cases, voltages can also be read for special applications or for use with ion-selective or oxidation-reduction potential electrodes.

Temperature compensation. The pH electrode is temperature dependent and may be compensated for in the meter circuitry. This utilizes the Nernst equation, which is a general mathematical description of electrode behavior. The equation in terms of pH is:

$$E = E_o - 1.98\, RT\, pH$$

where:

E_o = Constant depending upon reference electrode
R = Constant
T = Absolute temperature (Kelvin).

Changes in solution temperature will vary the MV output of the glass pH electrode in accordance with the Nernst equation. Its variation in the electrode sensitivity versus temperature is a linear function, and most pH meters have circuitry designed to compensate for this.

The actual sample pH can change with temperature due to a change in the H^+ activity in the solution, because ionization of compounds and H^+ activity in the solution may be temperature dependent. Temperature compensation does not correct for this. It only corrects for the change in the electrode output, not for the change in the actual solution pH. Temperature will also affect the glass membrane's impedance.

Experiment. Temper water that is used for cooling the rundown products of a distillation was used as a sample for investigation. The specified pH at standard ambient conditions is 8.5 to 9.5.

The sample was collected downstream of the product cooler when the temperature was 90°C. The pH was measured when the sample was collected with a pH meter. The reading was cross-checked using color indication. The sample was allowed to cool and pH measurements were made at fixed intervals (Fig. 1).

Observations. The trend is for pH to be on the acidic side as temperature increases. The phenomenon can be explained in terms of an equilibrium constant (K_w).

For pure water, the ionization constant is:

$$K_w = [H_3O^+] [OH^-]$$

At standard temperature and pressure:

$$K_w = [H_3O^+] [OH^-] = 1.0 \times 10^{-14}$$

K_w is sensitive to both temperature and pressure fluctuations. Since K_w increases as temperature increases, hot water has a higher concentration of H_3O^+ than cold water and, hence, a lower pH.

$$pK_w = -\log 10\ K_w.$$

pK_w also varies with temperature. As temperature increases, pK_w decreases; and as temperature decreases, pK_w increases.

Phenomenon effects. For mild steel (MS) or carbon steel (CS) exposed to water, a protective scale of iron oxide (Fe_3O_4) is formed in the safe pH range (8.5 to 12.7) as in Fig. 2. The scale is magnetic oxide and is thin and protective. Beyond the safe range, unprotective ferric oxide (Fe_2O_3) is formed and this is detrimental to exposed metal. The type of scale formed also depends on the oxygen content in water, thus making it very important to scavenge oxygen from water.

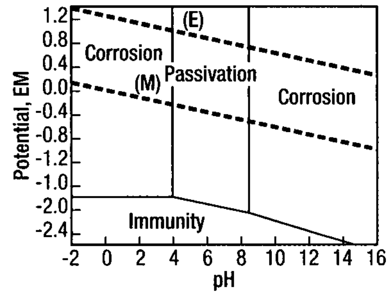

FIG. 3 Pourbaix diagram of aluminum.

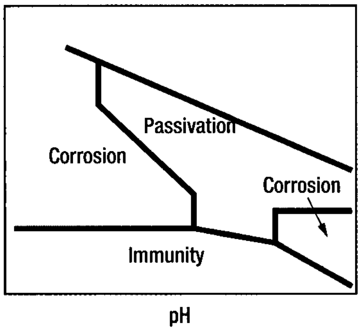

FIG. 4 Simplified Pourbaix diagram of iron.

At higher temperatures, there is a chance of pH going beyond the safe range and thereby deteriorating the exposed metal surface. This is just one example to accentuate the effect that temperature increases have on service solution and exposed metal. To more easily understand the phenomenon, a Pourbaix diagram that shows the relationship between potential and pH is shown in Fig. 3. The basic electrochemical equation for aluminum (Al) is:

$$Al = = Al_n^+ + ne$$

If the equation progresses from left to right due to existing conditions, the material is deteriorating.

Three distinct regions are shown: corrosion, passivation and immunity. In the regions where Al_n^+ species is stable, corrosion is dominant. Where aluminum oxide (AlO_2) is stable, passivation is dominant, and, in the area where Al is stable, immunity is dominant. The change in pH with temperature can bring the metal into the corrosion zone and can lead to its deterioration.

The safe range is:

$$E_{M/M^{n+}} = E_o + \frac{2.3RT \log K}{nF}$$

where:

E_M = Electrode half cell potential at the conditions
E_o = Redox potential
K = Constant rate for the particular reaction
n = The number of electrons involved
F = Universal gas constant.

The distinct zones of immunity, corrosion and passivation are shown in Fig. 4. In the immunity zone, Fe is stable since it does not undergo deterioration. In the corrosion zone, Fe^{n+} species is stable, and in the passivation zone, a protective Fe_2O_3 is stable which prevents further corrosion.

However, since the lines represent equations at 25°C, even Pourbaix diagrams at standard conditions do not sufficiently explain this phenomenon. Developing such diagrams at operating temperatures is therefore needed. Nevertheless, the zones vary depending on temperature, thus highlighting the deleterious effects that changing pH can have on exposed metals.

Inferences. Pourbaix diagrams serve as a reference to qualitatively indicate the effect of decreasing pH with increasing temperatures. With changing pH and potential, transition zones may occur and this phenomenon accentuates the need to specify pH as a function of temperature. The effect of changing pH with temperature needs to be carefully analyzed with service solution. **HP**

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K R Ramakumar is a production engineer at Indian Oil Corp. Ltd., Gujarat, India. He has a BS degree in chemical engineering from Sardar Vallabhbhai National Institute of Technology, Surat, Gujarat, where he was a bachelor of chemical engineering gold medalist. Mr. Ramakumar is interested in reaction engineering, aqueous and high temperature corrosion, and chemical thermodynamics.

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