Measurement and Control of pH in Wastewater Effluent

An Online Continuing Education Course for Engineers

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Measurement and Control of pH in Wastewater Effluent

In many areas of the country pH limits have been established for the acceptance /of treated wastewater effluent into public water systems. This course covers pH characteristics, measurement, control applications and various treatment processes as they apply to industrial wastewater.

This course does not address other characteristics of wastewater, such as suspended solids, the presence of heavy metals, or the biological makeup of the wastewater. For purposes of this course it is assumed that those conditions have been addressed prior to the wastewater's neutralization.

What is pH?

The term *pH*, which refers to the *potential of hydrogen*, is generally defined as a measurement of the relative *acidity* or *alkalinity* of the wastewater. Technically speaking, it is a number that represents the number of free hydrogen ions (H^+) and hydroxyl ions (OH^-) that are present in the water.

pH	H+	OH-
0	1	1E-15
1	0.1	1E-14
2	0.01	1E-13
3	0.001	1E-12
4	0.0001	1E-11
5	0.00001	1E-10
6	0.000001	0.000000001
7	0.00000001	0.00000001
8	0.000000001	0.000001
9	1E-10	0.00001
10	1E-11	0.0001
11	1E-12	0.001
12	1E-13	0.01
13	1E-14	0.1
14	1E-15	1

Table No. 1 – pH and Representative Hydrogen and Hydroxyl Ions

Ions are defined in Webster's Dictionary as being "an atom or a group of atoms that has acquired a net electric charge by gaining or losing one or more electrons". pH is the negative logarithm of the hydronium ion concentration in moles per liter (mol/l):

$$pH = -\log_{10}[H_3O^+]$$

Danish biochemist Soren Sorensen is credited with having developed the pH scale in 1909. His scale, which is still in use today, has a numerical range from 0 to 14. Pure water, having a pH of 7, is considered to be *neutral*. Progressively lower measured pH levels (i.e. levels that have more free hydrogen ions (H^+) than hydroxyl ions (OH^-)) indicate increasing acidity; while pH levels measured to be higher than 7 (having more hydroxyl ions (OH^-) than free hydrogen ions (H^+)) indicate progressively more basic solutions.

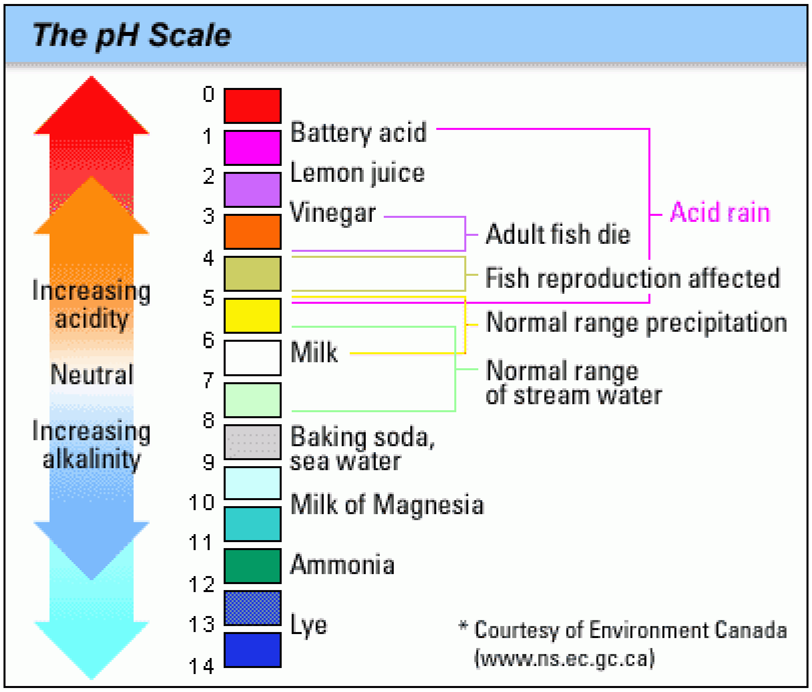

Figure No. 1 – Relative pH Levels for Various Substances

As illustrated in Figure No.1, battery (sulfuric) acid is an example of a very acidic (low pH) substance; while lye is an example of a very alkaline (high pH) substance. A substance such as milk or distilled water, which is not acidic or caustic, is considered to be "neutral".

A relatively high or low pH level in wastewater effluent can be a concern, as it may impact the treatment of public water systems, public health, and/or the safety of our natural environment. Effluent having a low or high pH can be corrosive to sewer facility components such as pipes, filters and pumps. Accurate pH measurements are important for determining the state of the raw effluent, for controlling the dosage of chemicals used in neutralization of the effluent prior to discharge and other necessary chemical treatment steps, as well as for monitoring the quality of the final discharge. Ideally, wastewater is neutralized before ever becoming effluent.

The terms *effluent* and *wastewater* are used interchangeably, as both refer to water that is mixed with waste.

Variable Characteristics of pH in Wastewater

Direct measurement of the pH level of wastewater effluent can vary dramatically due to variations in water temperature or variations in the chemical makeup of the substances that are present in the water. Therefore, an accurate measurement of wastewater's pH value also requires the measurement of the water's temperature. Any required temperature compensation is then factored into the measurement in order to correct for measurement errors due to temperature fluctuations.

Also affecting the measurement of pH is variations in the effluent flow rate. Flow rate of wastewater effluent is typically a function of the rate of production occurring at an industrial facility, and the regulation of the plant's outflow by those operators or automated processes controlling its rate. The rate of effluent may also be affected by the rate of flow of the water stream outside of the plant that it will be blending with, whether it is a direct discharge into a lake or stream, or into a sanitary or storm pipeline.

In general, because the variability of such things as temperature, flow rate, chemical makeup and concentrations of compounds within the effluent will impact the measurement of pH, the accurate and reliable measurement of pH can be challenging and will be discussed further later in this course.

Measurement of pH

In 1906, Maxwell Cremer, during his studies of liquid interfaces (interactions between liquids and solids), discovered that an electrical potential would develop across a glass membrane that was proportional to the pH difference across the membrane. He did so by blowing a thin bubble of glass and then placing one liquid inside of it and another outside of it. Doing so produced a measurable electric potential (voltage) that varied proportionally with the difference in pH between the two liquids. By using a neutral substance, such as distilled water, as the "reference", the relative acidity or alkalinity of other sampled substance could be measured and displayed electrically.

Most pH electrodes are constructed from a special composition glass that readily reacts with the hydrogen ion concentration of the sampled wastewater. Such glass is typically composed of alkali metal ions. The alkali metal ions of the glass and the hydrogen ions in solution undergo an *ion exchange reaction*, generating a potential difference (voltage).

Electrical resistance of glass, such as that used in the construction of a pH probe, is very high; typically somewhere in the range of 10 to 100 megohms. Improvements have been made in the chemistry and quality of the glass such that pollution by halogen ions can now be avoided.

Internal components of a pH probe generally include:

- a *pH electrode*, which is an electrode whose output voltage changes as the hydrogen ion concentration of the measured wastewater changes
- A *reference electrode*, which is an electrode whose voltage output remains constant
- Most modern pH meters are additionally equipped with a thermistor-type temperature probe that allows for automatic temperature correction during pH measurement. The temperature probe is often built into the pH probe in order to detect water temperature at the same location as pH is being detected. Temperature correction is performed electronically within the analyzer.
- A digital or analog display

Reference electrodes, which had traditionally used silver chloride ($AgCl$), have been replaced by a mercury chloride ($HgCl_2$) electrode that uses mercuric chloride ($HgCl$) in a potassium chloride (KCl) solution in the form of a gel. Electrodes have a finite life and therefore need to be replaced whenever they begin to drift at an unacceptable level.

In a *combination pH electrode,* the most widely used variety of pH probe on the market today, there are actually two electrodes housed in one body. One portion is referred to as the *measuring electrode*, and the other is referred to as the *reference electrode*. The potential (measured in millivolts dc) is produced at the junction of the measuring portion of the probe due to the free hydrogen ions that are present in solution.

Figure No. 2 – Typical pH Probe Assemblies

Caring for a pH sensor depends upon the type of electrode being used and upon the manufacturer's recommendations. In older style probes, it was better to keep the probe's electrode moist, since moisturizing a dry electrode took a long time and was accompanied by signal drift. More modern pH sensors are not impaired by the electrodes being dried out - provided that they are rinsed thoroughly in tap water or potassium chloride prior to their reuse.

A system's pH electrodes require periodic maintenance in order to clean and calibrate them. The length of time between their cleaning and calibration depends on process conditions and the user's accuracy and stability needs. Over time, electrical properties of the reference electrode will change.

Ph Transmitters

When a pH sensor must be located some distance from its controller, analyzer or display, a pH transmitter will be used in lieu of simply using a lo[...] The output signal of a pH transmitter is typically [...] milliamperes) over [...] over a [...] milliampere is [...]

Prior to [...] do so, the [...] such as pure [...] a known, stable pH [...] used to adjust the displayed [...] of a buffer solution. Calibration buffers typically [...] of 4.0, 7.0 and 10.0.

Handheld Portable pH Meters

Spot sampling of pH can be accomplished using a handheld or pocket pH meter that essentially has the probe and analyzer contained in a small, portable package. The accuracy of such units is generally not as precise as that of more expensive, stationary analyzers. They typically do not have the ability to record or trend the measured data; or