Measuring pH in Cyanide Leaching

Background
Precious metals such as gold and silver are processed using cyanide compounds. Cyanide dissolves the precious metal by forming a chemical complex with it, thus separating the precious metal from the other constituents of the ore, which do not dissolve. The leaching process can be accomplished inexpensively by placing the ore on a simple liner (heap leaching) or more efficiently in a stirred tank (agitated leaching). More concentrated or richer ores make the more expensive techniques cost effective.

Process
Many mines will process both low-grade and high-grade ores. The low-grade ore will be slowly leached over 60 to 90 days with a 0.1 % sodium cyanide solution.

The heap leaching solution continuously flows over the ore and may be collected and stored in a pond. The gold cyanide is typically separated from the pregnant liquor using carbon adsorption beds. The activated carbon adsorbs the gold cyanide complex on the surface of the carbon particles. Later, the carbon is washed with hot caustic to remove the gold and then rinsed with acid to regenerate the carbon particles for reuse. In heap leaching, the carbon is usually held in a fixed column and the solution is passed over the columns repeatedly. When the pregnant liquor contains large amounts of silver, zinc precipitation may be used instead of carbon adsorption. Zinc precipitation liberates the gold metal by adding zinc metal to the solution, which rapidly displaces the gold in the Au(CN)$_2$.

Once the solution has been depleted of the gold cyanide, it is called barren solution and is returned to the heap to continue the leaching process. Long term use of the solution will cause the pH of the solution to change, so makeup caustic and / or lime may be added periodically to the barren solution. This process occurs so slowly that online instrumentation is rarely required.

\[
\text{Sodium cyanide (NaCN) releases free cyanide as long as the pH is above 10 (otherwise substantial HCN is formed). The cyanide chemically bonds to the gold metal in the reaction:}
\]
\[
4\text{Au} + 8\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4\text{Au(CN)}_2^- + 4\text{OH}^- 
\]

Richer ores make mechanical grinding and agitation cost effective, so rich ores are ground down to about 80 % -200 mesh and mixed with the same cyanide solution and lime as the heap leach. The process is similar to heap leaching, but the agitated leach is much faster and more efficient because the smaller particles have more surface area. The leaching process is conducted in leach tanks that have a total residence time of about 24 hours. The gold cyanide in the pregnant solution is adsorbed on granular activated carbon inside the carbon in pulp (CIP) tanks. The coarse laden carbon particles are screened out of the last tank, washed with caustic to remove the gold cyanide, and the gold metal is produced using a process called electrowinning. Due to the rapid reactions taking place in an agitated leach process, automatic pH control is strongly recommended.

pH Measurement
pH is controlled between 11 and 12 during the leaching process. pH values below 11 favor the formation of HCN, hydrogen cyanide that interferes with reaction (1). Hydrogen cyanide is a colorless and poisonous gas that, if released due to lower pH values, can quickly become deadly. Cyanide is also a relatively expensive chemical, so small losses in heap leaching can amount to large makeup costs over time. Gas leaks into the environment are a risk to the mine personnel and a future liability to the mining corporation that can be avoided using pH measurement.

Measuring pH with an inline sensor is complicated by the nature of the leaching solution here. The solution has finely ground abrasive ore, which can abrade glass measurement electrodes and generally coat the sensor. Lime (CaO) is frequently used for pH control, however it has low solubility and can form a hard coating on the pH sensor, effectively taking the sensor out of service. In addition, the high concentration of cyanide can, over time, penetrate the pH sensor and contaminate the reference, also causing large errors. The recommended pH sensor for this application must be rugged enough to withstand abrasion, resistant to attack by cyanide, and also resistant to coating. The TUpH™ design is an excellent choice for this environment.
Instrumentation

The TUpH™ sensor is especially designed with a high area reference to combat the effects of coating. The reference junction is composed of ultra-porous glass filled polypropylene that continues to function in processes with high solids. Inside the reference junction is a long helical pathway that protects the reference from attack by poisoning ions such as cyanide.

TUpH model 396P has forward and reverse facing threads for mounting versatility. The model 396P with flat glass (option -71) can be used in flow through installations to provide self-cleaning action as the process flows across the sensor. For measurements inside tanks, the standard hemi bulb is recommended with the shrouded tip. For extra resistance to coating, a jet spray cleaner accessory is available as PN 12707-00.

Figure 1 - Gold Ore Processing Using Cyanide

The 56 pH / ORP analyzer is ideal for monitoring and controlling the pH of the leaching area. In addition to standard features such as 4–20 mA outputs, four process alarm relays, and pH sensor diagnostics, the 56 pH is available with HART communication and PID control. A timer relay is included for periodic activation of a cleaning cycle.