



Liquid Analysis in Mineral Processing

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Introduction

This paper describes the process applications that take place after mining and prior to refining as they relate to pH / ORP, dissolved oxygen and conductivity.

The implementation of the proper analytical sensors in the common metal extraction processes used today in the minerals industry go far beyond mere indication of status or process upset, but can give us an extremely accurate and meaningful measurement of the process condition. The new generation of analytical sensors can allow us to monitor and control applications never attempted before such as in-situ measurement of the leaching process or the control of chemical addition.

Base and precious metal processing operations frequently involve solids / liquid, liquid / liquid and liquid / gas applications in which there are ongoing chemical reactions and/or mass transfer. The meaningful association of measurements with known standards, custom calibration, measured ionic background and temperature will provide reliable results.

There are numerous applications that may use a continuous liquid analysis measurement in mineral processing /metal extraction. However, there are a number of processes in which proper control and application are critical for effective operation. The nature of the process stream causes measuring difficulties for liquid analyzers both from abrasion-related wear and chemical attack. The selection of an appropriate liquid analysis system, and an installation plan is essential for efficiency and longevity, which relates to economic value.

Flotation

Flotation is a process used to separate a desired mineral (i.e., copper, nickel, zinc) from an undesired material commonly known as gangue. Flotation is used extensively throughout minerals processing including after the ore has been reduced to a very small particle size by crushing and milling, the cleaning of hydrometallurgical liquors and the preparation of final con.

After milling, the finely ground ore which has the consistency of sand, is then transported in the form of a slurry with a relatively high percentage of solids (30 to 60% by wt.). As part of this process the use of a specific chemical called a collector is introduced, which enables a specific mineral to attach to a bubble and rise to or near to the surface. This process takes place in **flotation cells** designed for maximum particle bubble contact and resultant separation of the desired minerals from unwanted particulate. The bubbles are caused by either injecting air or inducing the entrainment of air through slurry flow into the flotation cell. The float material is then overflowed or skimmed off while the bottom material is sent to another separation process or to



waste (tailings). Flotation can be used to separate the desired mineral from the waste (gangue) or from another mineral.

Each mineral has certain conditions, which affect its ability to float. One of the important variables of these conditions is pH. pH as a variable in flotation affects: 1) the form of many ionic species present, 2) the charge state of the mineral surfaces, and 3) the form of many collectors.

Example: In copper processing it is important to maintain a high pH to maximize flotation. Most copper ore slurries are inherently acidic, as a result, an adjustment is necessary to make the slurry more alkaline in order create a condition for effective flotation and separation. The pH of the slurry is adjusted by the addition of **lime** to the mill circuit or flotation circuit. The pH may need to be adjusted at several points of the flotation process (Fig. 1).

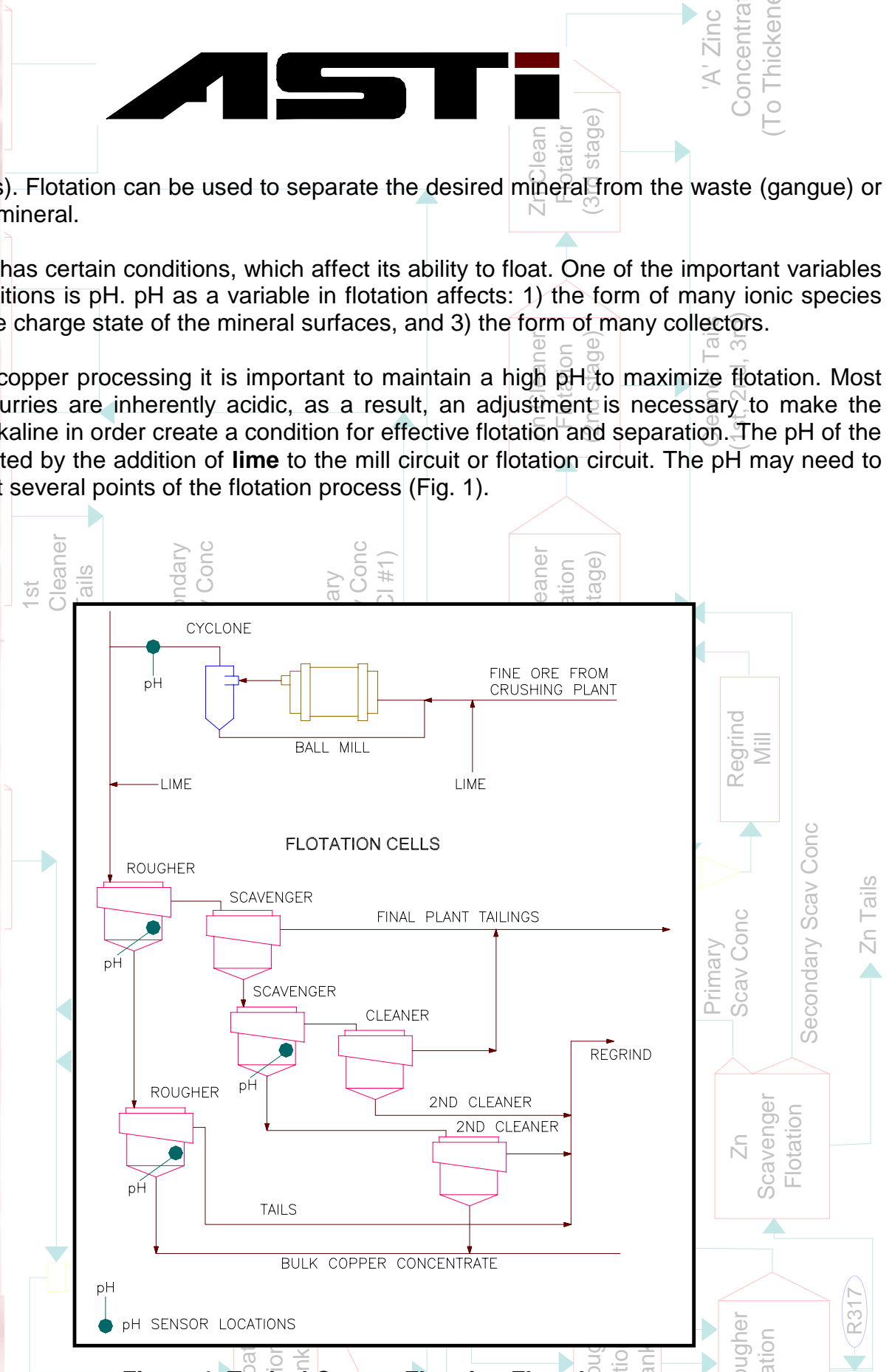


Figure 1. Typical Copper Flotation Flowsheet



Although the heavy addition of lime to the flotation circuit is essential for the correction / adjustment of pH, it can also result in problems such as the build up of dry CaCO_3 or abrasion. The accuracy, stability, reproducibility are vital and affected by the mounting, location and porosity of the pH sensor. Problems in this area can be compensated for through the selection of sensors engineered for the application, which includes body material, glass selection, the liquid junction, the use of a non-porous solid state reference and the adhesives used in the construction of the measurement element. The performance of each installation can also be better served by the implementation of salt cleaning apparatus the manufacturers designed cleaning procedure.

Some copper processing plants also have a molybdenum circuit where molybdenum and copper are separated by flotation. Reagents are added to promote Moly flotation and depress copper flotation. During this process it is usually necessary to lower the slurry pH by adding an acid. Monitoring pH will insure that optimum Moly flotation is taking place. ORP (oxidation reduction potential) measurements have also been used in the Moly circuit but it is much harder to correlate the reading to effective reagent addition. The difficulties of this measurement have since been overcome through joint efforts with ASTI to develop calibration procedures using flat ORP and polishing ORP sensors.

Other types of mineral processing in which pH affects flotation include zinc, nickel, silver, Copper/gold or just gold.

Application Concerns & Recommendations

The fluid in a flotation circuit or flotation feed will always have a high percentage of solids. This creates problems for any measurement device, especially pH sensors, since solids cause the fluid to be very abrasive, eventually damaging the glass measuring electrode, if the particle size is large enough, it can even break the glass. This requires a pH sensor, which is rugged and stands up to the inevitable abrasion that will take place. Flat glass measuring electrodes are suggested in this application. The lack of a protruding bulb also reduces breakage incidents and erosion effects.

The addition of lime to the slurry can create a scaling problem on all surface of the sensor. This can be complicated by the build-up of other solids present in the slurry. Typical pH sensors have small liquid junctions in order to retain their liquid or gel electrolyte. Sensors with gelatinous electrolytes have a life span limitations, because once the process fluid has compromised the liquid junction, the sensor will deteriorate. A liquid junction is a porous plastic interface between the electrolyte reservoir in the sensor and the process fluid. The very small particle size in mineral slurries can tend to plug or blind the liquid junction quickly if there is a small surface area of porous material. This can cause junction potentials and subsequently reference drift. Also, mineral processing slurries typically have a mixture of chemicals that can contaminate the reference of a pH or ORP sensor. The contamination of the probe actually begins as ions of the process solution diffuse into the junction causing drift and a need for re-calibration. Improvements have since been made through the use of non-porous polymer reference junctions, which also is a poor conductor of heat making the sensor better suited for higher temperature applications.



A solid state reference is a non-porous/non-permeable system in which only selective ionic communication with the secondary junction is permitted. The advantages of a solid state reference system over more conventional porous gel filled systems are: it experiences much less aging and deterioration, it is not easily dried out when exposed to air for prolonged periods, it does not absorb fluids or gases into the junction (thereby reducing premature aging) and it is significantly more impervious to solvents, harsh chemical attack and high temperature. This solid state reference system is housed in a matrix of either High-Density-Poly-Ethylene (HDPE) or Poly-Vinyl-Dene-Fluoride (PVDF).

The selection of the appropriate pH sensor especially suited for the application is vital. The sensor should have a flush surface, which reduces the adherence of particles, and a less susceptible to plugging. The use of a solid state reference design eliminates reference contamination resulting in a more stable and accurate measurement. In a typical copper operation there are many flotation cells, often with a pH sensor in each cell. Sensor life and maintenance quickly becomes an important economic factor.

The mounting location is also very important in these types of applications. The sensor should be located in an area that is representative of the stream, yet not subject to excess erosion or plugging. In-line installations are not recommended for this application. Most sensors are of a submersible design with a rigid mounting. Many applications call for the pH sensors to be installed at the flotation cell overflow. This will give the advantage of not having to totally submerge the back of the sensor, provided overflow depth remains constant. Care should be taken that the sensor is mounted deep enough to contact liquid rather than the froth on the top, which is a high percentage of air. Others may monitor pH further upstream of flotation in the mill circuit. A typical mill circuit installation point would be in the cyclone overflow. Exact sensor location and number of measuring points will vary from plant to plant and is largely dependent on solution chemistry. The usage of pH sensors for the monitoring of process chemistry can also impact the usage of chemicals and thus impact process economics. Moreover, the ore recovery and selective flotation is function of maintaining a certain advantageous pH. The pH measurement and control can then directly impart (promote) high(er) ore recovery.

Leaching

Leaching involves the dissolution of a mineral from a solid (ore). This is accomplished by contacting the ore with a solution containing reagents, which will dissolve the desired substance (and often some undesirable substances). Once the metal is in solution, various methods are used to concentrate it and/or remove it from its dissolved state. These include carbon adsorption, precipitation and solvent extraction.

Heap Leaching

In heap leaching, the ore is piled on a chemical resistant liner and then a solution is applied to the surface through a spray/shower system. This is often preceded by a crushing step to increase the surface area of the ore and permeability of the heap.



The solution permeates through the heap, dissolving the target mineral as it migrates in and out of the rock. The leachate (pregnant solution) is then collected at the bottom of the heap, through a series of ditches and ponds. A process plant will remove the metal from the pregnant solution and then return the barren solution to a pond to be recycled to the heap once again.

An agitated leach takes place in a tank or vessel with a much larger percentage of fluid. The ore is typically ground to a fine powder in a crushing and milling operation. The leaching solution is allowed a certain residence time to contact and dissolve the mineral aided by the violent action of the process agitator. This type of processing can be very efficient as it can be controlled in terms of residence time and solution to particle contact. It is much more expensive than heap leaching and is only done if the ore grade is high enough to justify the cost.

Acid Leach Circuit

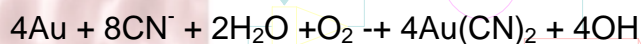
A number of minerals can be removed from an ore or concentrate by leaching with an acid. The acid is consumed as it dissolves the mineral. The optimum level of acidity is maintained by measuring the pH of the effluent and controlling acid addition. This would be done in an autoclave or tank where process variables can be more easily monitored, controlled and adjusted. Although this process is highly effective, it also is an inherently harsh environment for typical pH sensors.

In the liberation of some minerals such as gold and nickel can also result in the liberation of sulfides (HS^- , H_2S) by products. The process characteristics can include elevated temperatures and pressures, which limits the possible locations for on line continuous liquid analysis. For this reason a sensor used in continuous operations can be required to withstand temperatures $\approx 100^\circ C$ and 50 to 80 psi.

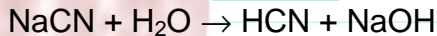
Acid leaching is also done on heaps and in-situ (sulfuric acid leaching of copper ores), however, a continuous pH measurement is not common.

Cyanide Leach Circuit

Cyanide leaching (Fig. 2) is most common in gold and silver ore processing. Cyanide will dissolve gold or silver from its host rock provided that the ore exists as an oxide and is not closely bound in the host rock. In low-grade ore, gold will exist in the form of microscopic particles. This is usually processed by heap leaching. If the gold exists in a larger, more concentrated state, the ore will be finely ground and leached in a tank. A gold cyanide complex is formed as gold is dissolved from the rock or pulp (finely ground ore). The reaction for this process is as follows:



The control of pH in a cyanide leach solution is important both from a safety and cost viewpoint. Cyanide is usually added to solution in the form of sodium cyanide ($NaCN$). As pH is lowered, the following reaction takes place.



The reaction causes the formation of hydrogen cyanide gas, which is lethal in high concentrations. A more significant concern is the high consumption of cyanide as it is slowly released into the atmosphere and permanently lost. Sodium cyanide is a costly reagent. To control costs and maintain worker safety, most operations will try to keep their pH in the 11 to 12 pH range which insures the cyanide remains in an ionic form.

Although caustic soda has been used, lime is the most common reagent for pH control. In a heap leach operation, lime is usually added to the crushed ore or into the barren solution pond. Continuous pH control is neither common nor necessary for heap leach operations. Adjustments are usually made on a batch basis at the barren pond.

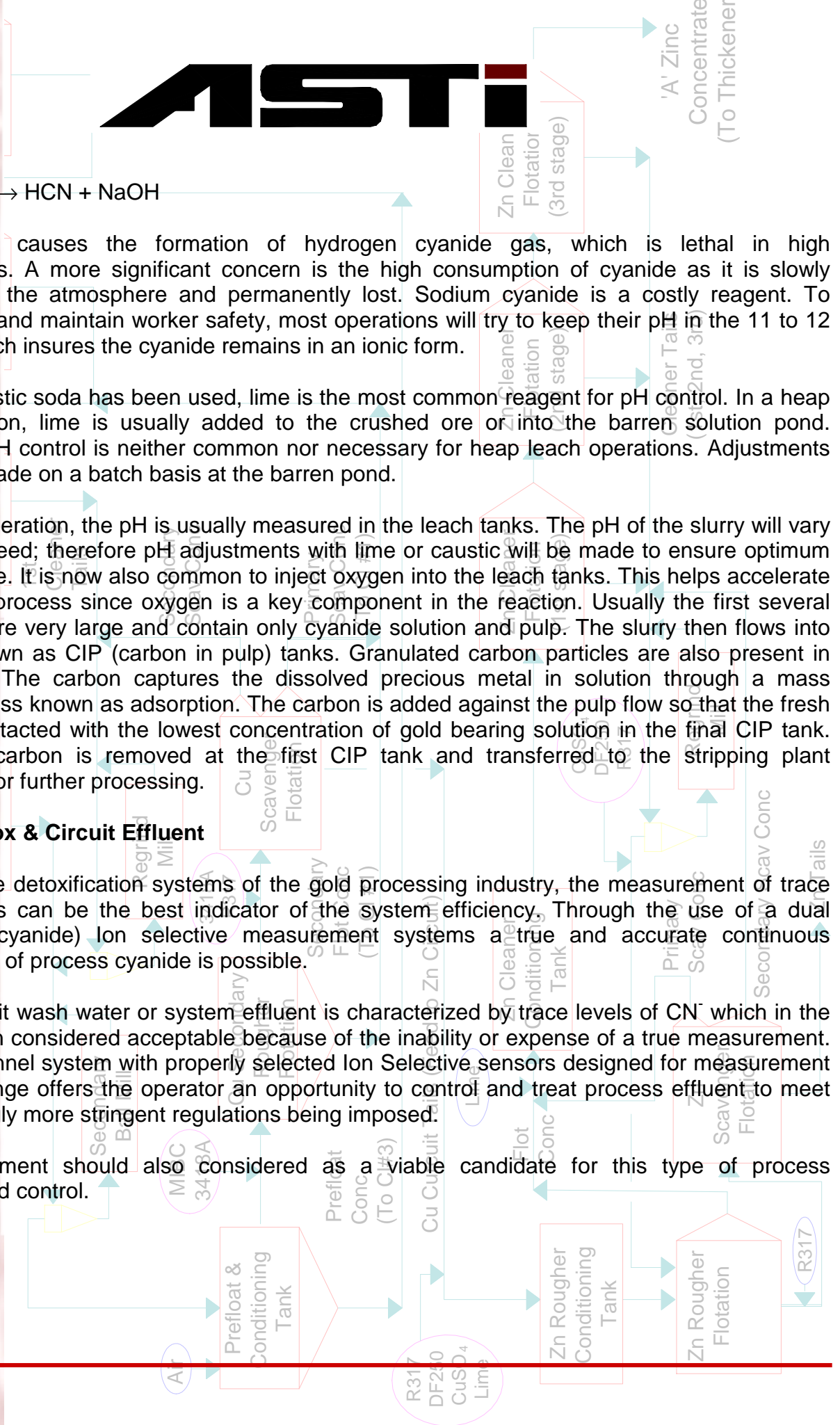
In a milling operation, the pH is usually measured in the leach tanks. The pH of the slurry will vary with the mill feed; therefore pH adjustments with lime or caustic will be made to ensure optimum use of cyanide. It is now also common to inject oxygen into the leach tanks. This helps accelerate the leaching process since oxygen is a key component in the reaction. Usually the first several leach tanks are very large and contain only cyanide solution and pulp. The slurry then flows into what are known as CIP (carbon in pulp) tanks. Granulated carbon particles are also present in these tanks. The carbon captures the dissolved precious metal in solution through a mass transfer process known as adsorption. The carbon is added against the pulp flow so that the fresh carbon is contacted with the lowest concentration of gold bearing solution in the final CIP tank. The loaded carbon is removed at the first CIP tank and transferred to the stripping plant (desorption) for further processing.

Cyanide Detox & Circuit Effluent

In the cyanide detoxification systems of the gold processing industry, the measurement of trace cyanide levels can be the best indicator of the system efficiency. Through the use of a dual channel pH/(cyanide) ion selective measurement systems a true and accurate continuous measurement of process cyanide is possible.

Cyanide circuit wash water or system effluent is characterized by trace levels of CN^- which in the past has been considered acceptable because of the inability or expense of a true measurement. The dual channel system with properly selected Ion Selective sensors designed for measurement in the ppb range offers the operator an opportunity to control and treat process effluent to meet the increasingly more stringent regulations being imposed.

Tailings treatment should also be considered as a viable candidate for this type of process monitoring and control.



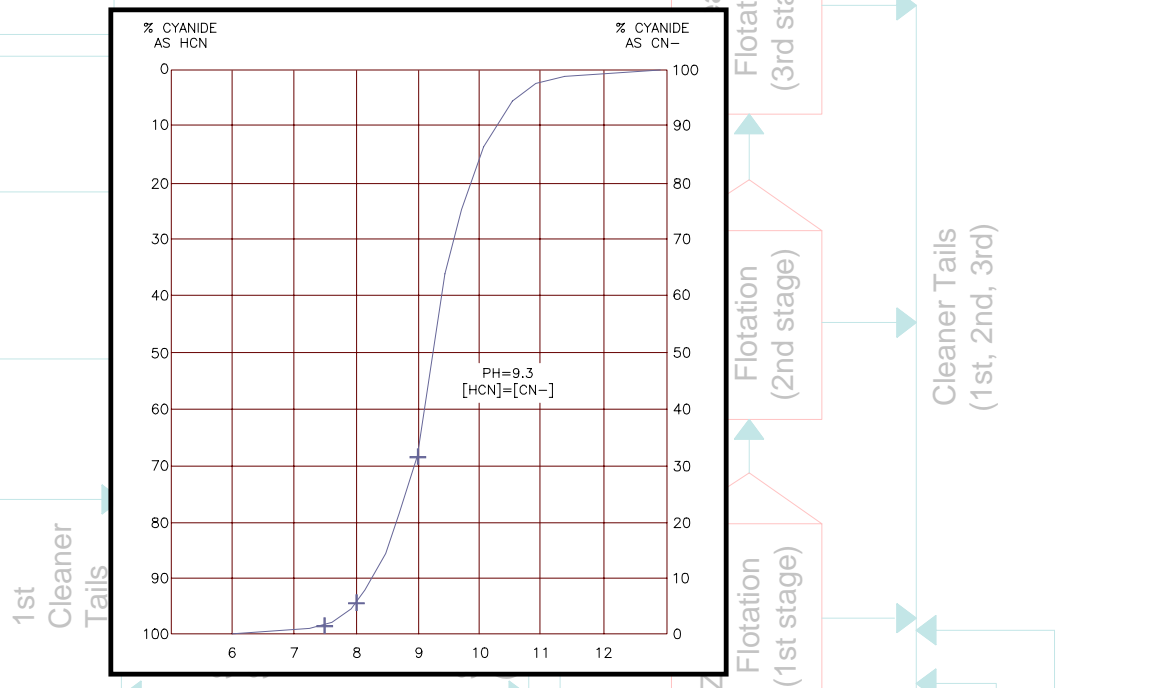


Figure 2. Aqueous NaCN Solution vs pH Independent of Concentration

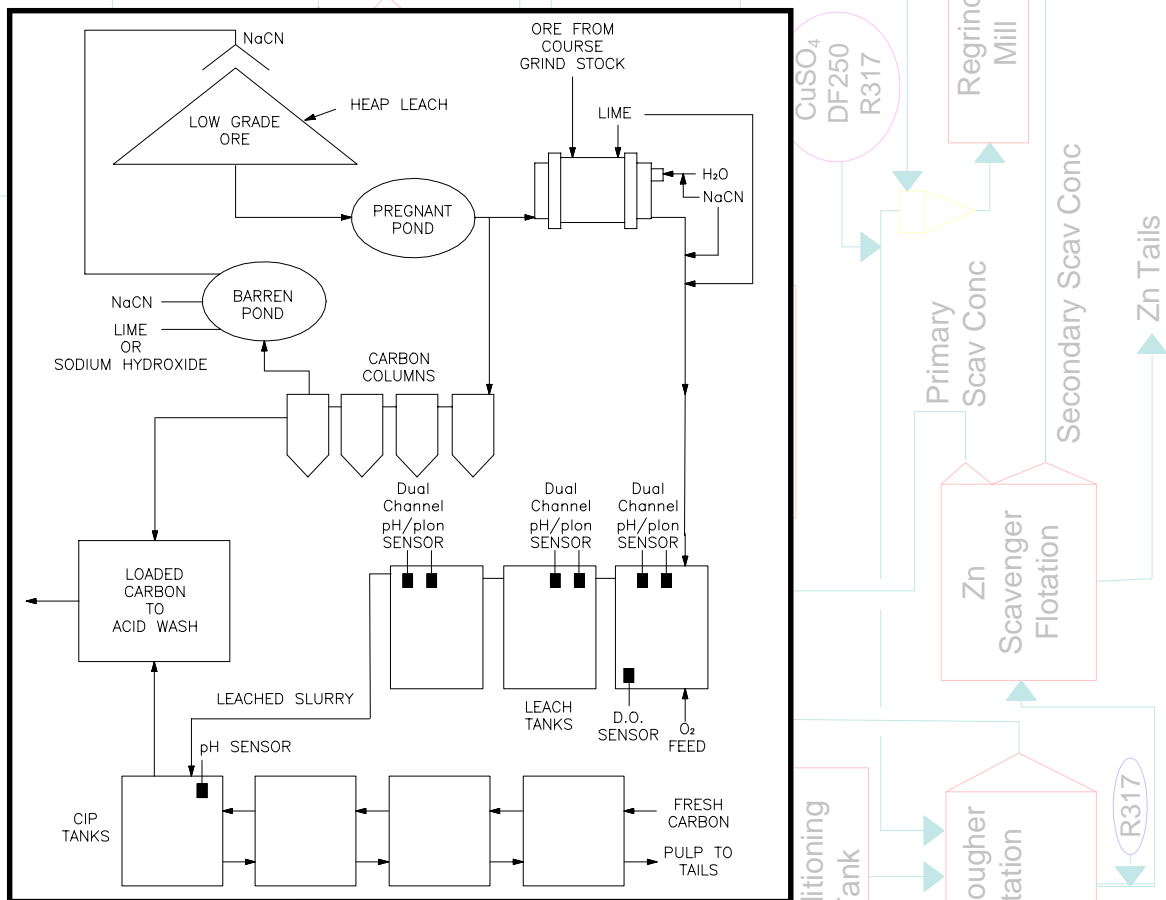


Figure 3. Typical Gold Process Flowsheet



A typical point for lime addition is at the fine ore feed to the mill. Control may be difficult if ore pH varies. To maintain tighter control, sensors may be located in the millstream or further lime addition can take place at a point closer to the leach tanks.

Application Concerns & Recommendations

Gold recovery through a cyanide complexation process has long been a staple of the gold ore mining industry. There are many serious hazards associated with this process, many of which can be reduced by an accurate aqueous process control. The result is an improved product yield which reduces the dangers not only to the plant workers, but also to the environment at large.

The Problem:

Below a pH of approximately 9.5, free cyanide begins to evolve hydrogen cyanide gas, which is a toxic compound. The control of pH is then critical to maintaining a safe extraction process. Depending upon the water quality used in the process it can be very expensive to raise the process pH higher than 10.5 due to the natural buffering action of hard water supplies. This leaves only a small margin for error on the pH process control. In addition, the leaching or extraction capability of a cyanide solution is determined by the total cyanide present, rather than just the free or ionized species. Thus a control system capable of determining the total HCN and pH is required. The first issue was that cyanide solutions quickly attack pH-glass and render them inoperable.

Since the solution was comprised of a thick slurry ore and was constantly stirred, a build-up of this ore upon the pH and reference element is another cause of short sensor lifetime. The small amount of liberated gas attacked the reference and ion sensing elements.

The Solution:

A dual channel analyzer which capable of computing and outputting a 4-20 mA signal for the total HCN content and pH value. The use a thick walled 1" Twist Lock body housing mounted via a 1" MNPT standpipe will reduce breakage of the body. The ASTI pH sensor specially designed for use in a cyanide solution consisting of a cyanide resistant pH element, and is reference sealed against both ionic and gaseous attack. The slurry/viscous resistant pH glass also reduces down time and maintenance costs associated with breakage. The polycrystalline cyanide ion selective sensor is designed specifically for a gold leaching application. This specially designed ion selective sensor is not susceptible to the membrane erosion and dissolving from which most common cyanide sensors suffer. The immunity from erosion also reduces the required calibration and cleaning of the membrane.

Dual Channel installations have indicated that the process was able to run safer and more efficiently than previously, saving money and reducing employee time involved with the cyanide



process control system. The use of custom formulated calibrations solution will improve accuracy and solve the problem of incongruities between laboratory titrations and process measurements. Once the accuracy of the system and consistency between process and laboratory measurement is established, remote one-point calibrations are employed based upon titration results after the an initial determination of the sensor span (two-point calibration indicating the slope or efficiency of a given sensor). The use of the remote one-point calibration will further reduce costs by avoiding dangerous and time-consuming sensor cleaning and calibration on-site.

Much the same as flotation there inherent problems with the general pH measurements in gold processing mills. The measurement is in an abrasive slurry, which can result in damage to the glass electrode. Again, the use of lime can cause scaling problems. Another problem is the very nature of the fluid. Cyanide is a strong oxidizer, which makes this a very reactive solution. The reference electrolyte and reference element are subject to chemical contamination and lose stability much more rapidly than in a more neutral solution.

The sensor in any mineral processing slurry should be mounted so that there is sufficient velocity past the sensor to minimize lime scale and material buildup. However, a compromise should be attempted so that abrasion to the sensor glass and body are reduced. A good mounting location would be an overflow weir or a transfer point in the leach or CIP tanks. Typically it is high rather than low flows which can be an issue.

The dissolved oxygen measurement can also be difficult due to the abrasive effect on the membrane. A double layer of membranes helps to combat this effect and extend sensor life. It is important to note that the measurement of D.O. in any slurry application is difficult even under the best of circumstances.

Bacterial Oxidation

Bacterial oxidation is used to recover metals from sulfidic ore deposits. The bacteria catalyzes the oxidation of some elements allowing for the mineral to break down. One of the principal applications of bacterial oxidation is for the liberation of refractory gold where the gold is encapsulated in pyrite. By working on the pyrite crystal, the bacteria gradually causes it to break down and open up, liberating the gold. The gold-bearing ore is then processed through a conventional cyanidation process. Biological oxidation is becoming more prevalent as surface oxide reserves are depleted. Increasing use will be made of biological help in processing deeper refractory sulfidic gold ores and ores of other metals, such as copper, and nickel.

There are several different methods for carrying out bacterial oxidation on a commercial scale. The most common are agitated tank reactors, and heap leaching. There are typical bacterium, which thrive in the pH range 1.0 to 6.0 with optimum pH for growth being between 2.0 and 2.5. It survives in the temperature range of two to 40 degrees centigrade, doing best at 28 to 35 degrees centigrade. Survival also depends on an adequate supply of oxygen. As expected, major control variables are pH, temperature, and dissolved oxygen.

In an agitated reactor, pH and dissolved oxygen are monitored and carefully controlled. Sulfuric acid or milk of lime are added to maintain the slurry pH at optimum levels. This measurement would be very similar to that in a leach tank so the same recommendations for sensor selection and care should be followed. The success of any analytical measurement in the Bio-Oxidation process can be directly attributed to the stability of the calibration through regular maintenance.

Solvent Extraction

The most common solvent extraction for metals is for the recovery of copper, however it is becoming more prevalent in the recover of laterite nickel as well as uranium. This process is preceded by a leaching step and followed by electrowinning. Copper leaching is typically done with sulfuric acid or sometimes with ammonia. The solvent-extraction electrowinning (SX/EW) process typically consists of three closed stages (Fig. 4). In the first stage, copper-bearing pregnant leach solution is contacted with a synthetic organic solution. This solution consists of an organic extractant and kerosene. The organic solution chemistry is designed to selectively extract copper. The barren leach solution (raffinate) is pumped to the raffinate pond to be used to leach more copper, while the loaded organic solution flows to the stripping stage. In the stripping stage, highly-acidic spent electrolyte solution from electrowinning strips the copper from the organic. This flows to electrowinning while the stripped organic returns to the extraction section. The rich electrolyte (copper rich solution) flows to electrowinning where high purity cathode copper is deposited by electrolysis. The spent electrolyte is returned back to the SX stripping section.

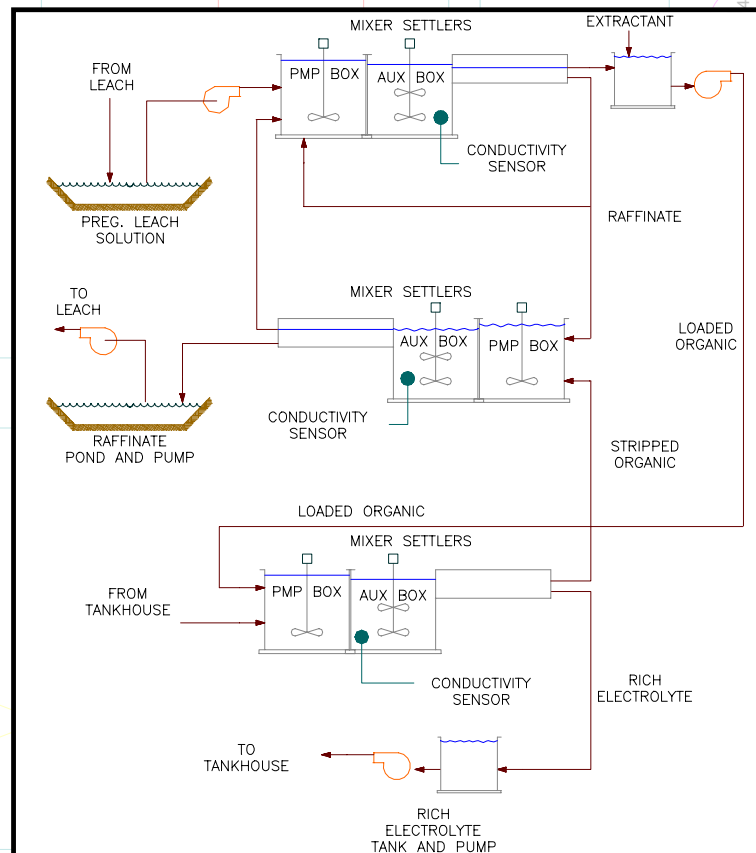


Figure 4. Typical Copper Solvent Extraction Flowsheet



The contacting of the organic and aqueous solutions takes place in what is called a mixer settler system. The organic and aqueous solutions are introduced into the pump box used to optimize droplet formation, The liquor then over flows to the auxiliary mix box(es) where maximum phase contact takes place. Various surfactants are used to reduce the surface tension between the phases and allow for better inter mixing of the aqueous and organic phases. The use of such chemicals, while highly effective for emulsification, can present entrainment problems in the disengagement zone. The two phases are allowed to separate in the settling section, which is usually a long rectangular basin. It is crucial to balance the flows of these two fluids so that optimum extraction can take place. Some installations monitor phase conditions by a conductivity measurement. The conductivity of solution in the aqueous phase will be different than the organic phase. However, this is not a specific measurement as different mixes, concentrations etc. can affect the conductivity reading. It is simply an aid to the operators that indicates when a change has taken place. During the commissioning of a SX/EW system, it can be difficult to set the continuous phase (aqueous continuous / organic continuous) operators will set an alarm at a certain level to let them know when upset conditions are present. However this alarm point is seldom constant and usually has to be adjusted. Although many SX/EW plants operate without this measurement, it is becoming more popular as higher efficiencies are desired.

The conductivity measurement is made in the mix box. It is important to place the sensor where optimum mixing is taking place to avoid false alarms caused by slugs of a single phase liquid. The conductivity will read in the millisiemen range. Mounting should be such that the sensor is fully submersed and rigidly mounted. Conductivity readings are noted at different flow conditions and used to balance and optimize the flow. This is a relative measurement, which will change as solution chemistry changes.

The liquid analysis of the solvent extraction system has been characterized primarily by the use of conductivity where pH measurements have been problematic. The use of organic resistant pH sensors have proven effective in monitoring the quality of the barren leach solution. The use of pH/(Copper) Ion Selective Sensors in the pregnant leach feed system can provide the operator better control options for the organic/aqueous ratios of the mixer settlers. This success of this type of system will be reflected in reduced chemical costs and entrainment values.

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