Application Note
Refractory Gold Pretreatment - pH

Mining: Gold Processing

Refractory gold ores are defined as containing minerals or carbon compounds that trap encapsulated gold and make leaching extraction difficult. These types of ores require pretreatment prior to cyanidation. Options for pretreatment include the following processes:

- Roasting
- Bacterial Oxidation
- Pressure Oxidation (Autoclaving)
- Ultrafine Grinding

In this paper we will look at analytical measurements required in each process and investigate how Barben products can improve accuracy and reduce downtime.

Roasting

Roasting of refractory ore has historically been the method to remove sulfur up until the 1980s. The roasting process oxidizes the sulfur by converting it to gaseous sulfur dioxide (SO_2). Ore is ground to 100 - 200µm mesh and heated between 450ºC - 700ºC in a fluidized bed. With proper retention time >90% of the suflur can be converted. An additional benefit of the roasting process is the burn off of organic carbon which increases access to the gold for leaching.

Roasting has largely fallen out of favor due to emissions concerns. Roasting facilities will use a desulfurization scrubber to clean the flue gas prior to vent to atmosphere. If the ore has high sulfide content then an on-site acid plant may be used to convert the SO_2 to sulfuric acid. pH measurement will be the main control parameter of the desulfurization scrubber. Lime (CaO), or Limestone ($CaCO_3$) are used to convert the SO2 to gypsum ($CaCO_4$).

The reaction is detailed below.

Lime: $CaO + 2H_2O + SO_2 \blacktriangleright CaSO_4 + 2H_2O$

Limestone: $CaCO_3 + 2H_2O + SO_2 \blacktriangleright CaSO_4 + 2H_2O + CO_2$

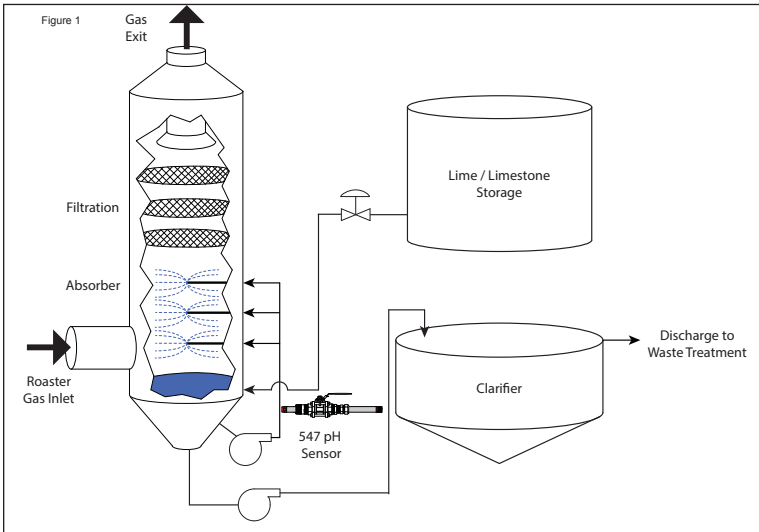
$CaSO_3 + H_2O + 1/2O_2 \blacktriangleright CaSO_4 + H_2O$

Measurement Challenges

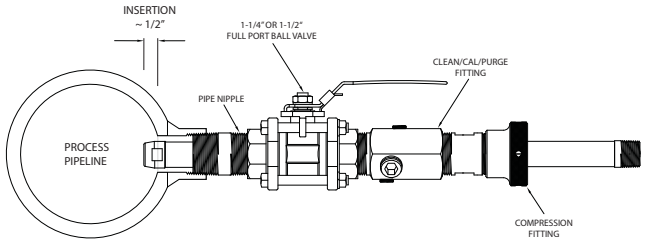
The pH measurements in the scrubber are typically used to control the process. The SO_2 will convert to sulfuric acid in the scrubber causing low pH and corrosion issues. A setpoint around 6.0 to 6.5pH will be used to control the lime addition. The application of the sensor is often difficult. The combination of solids from the roasting process and gypsum formation create a slurry. The high solids content of the slurry (up to 15% solids) can coat the pH sensor and plug the porous reference junction. Heavy metals and sulfide compounds will be present in the roaster gas. These contaminants are well known to poison the Ag/AgCl element used in pH sensors causing instability in the measurement.

Barben Analytical recommends using our Performance series pH sensors in scrubber applications. The Axial Ion Path® reference design of the Barben sensors is well suited to prevent poisoning of the sensor by chemical attack. The 547 retractable pH sensors is most commonly specified for scrubber applications. These sensors can easily be isolated from the process for cleaning, calibration and eventual replacement. Ideal mounting would be in a recirculation pipeline on the scrubber with 1/2 inch insertion depth (see figure 1 below). The flowrate in the pipeline will help prevent buildup from forming on the sensor thus reducing maintenance intervals.

Figure 1



Roaster SO_2 Gas Scrubber



The 547 hot tap retractable sensor (shown above) can be mounted in the recirculation piping of the scrubber. The sensor is inserted into the process and held in place by the compression fitting. When cleaning, calibration, or eventual replacement of the pH sensor is required the sensor can be isolated from the process by the ball valve. An optional clean/cal/purge fitting can be installed for insitu access to the sensor.

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Bacterial Oxidation
Bacterial oxidation (Bio-oxidation) of refractory ores was first launched in the mid-1980's. Bio-oxidation uses bacteria of the Acidithiobacillus genus to metabolize sulfides, arsenic and iron into water soluable compounds. There are several patented bio-oxidation processes including BIOX and BACOX however the principle of using bacteria is the same. This type of pretreatment has been successfully applied in both heap leaching as well as in-tank applications. The byproduct of sulfide oxidation is sulfuric acid (H_2SO_4). The sulfuric acid will keep the pulp at <2pH. The most common reactions are listed below:

$4FeS_2 + 15O_2 + 2H_2O \blacktriangleright 2Fe_2(SO_4)_3 + 2H_2SO_4$
$2FeAsS + 7O_2 + H_2SO_4 + 2H_2O \blacktriangleright 2H_3AsO_4 + Fe_2(SO_4)_3$
$4FeS + 9O_2 + 2H_2SO_4 \blacktriangleright 2Fe_2(SO_4)_3 + 2H_2O$

The bacteria generates heat as it digest the sulfides. Reactors are maintained at 40 to 50ºC through the use of cooling water addition and agitation. Aeration will be used to promote bacteria growth. A heap leach process can require 100 to 300 days for effective oxidation while an in-tank application will require 3-5 days.

After digestion the pulp will go through solid-liquid separation. The gold-containing solids are diverted to a traditional cyanidation leach process while the low pH liquid is neutralized with lime or caustic and sent to tailings. pH control will be required in the bacteria reactors as well as the downstream neutralization stages.

Bacterial oxidation is very appealing since there are no emission concerns and no fuel costs. The type of bacteria used can also be customized depending on the mix of sulfide compounds present.

Measurement Challenges
Automated pH control is a requirement for any bio-oxidation pretreatment process. Reactors are typically maintained at 1.2 to 2pH through the use of lime addition. If the pH drops below this range then bacterial growth slows. At elevated pH the oxidation reaction is less effective thus gold recovery is reduced. The pulp is typically 20% solids. The combination of low pH and abrasion from solids both contribute to shortened sensor life. The presence of various sulfide compounds can poison the Ag/AgCl element used in the pH sensor reference half-cell. Downstream, in the neutralization processes, lime addition will create calcium carbonate and arsenic percipitates. These solids can coat the pH sensor and plug the porous reference junction. A two stage neutralization may be required to bring the effluent to 7pH for disposal. Gold laden pulp being sent to cyanidation will require an even further adjustment to >11pH. This pH adjustment is crucial to avoid the formation of hazardous hydrogen cyanide (HCN) gas.

Cyanidation (>11ph) Reaction
$4Au + 8CN^- + 2H_2O + O_2 \blacktriangleright 4Au(CN)_2 + 4OH$
Hydrogen Cyanide (<11pH) Formation
$NaCN + H_2O \blacktriangleright HCN + NaOH$

Barben 546 submersible pH sensors are most commonly used in these applications. The Axial Ion Path® reference design requires less cleaning and calibration then traditional double junction pH sensors. The sensor should

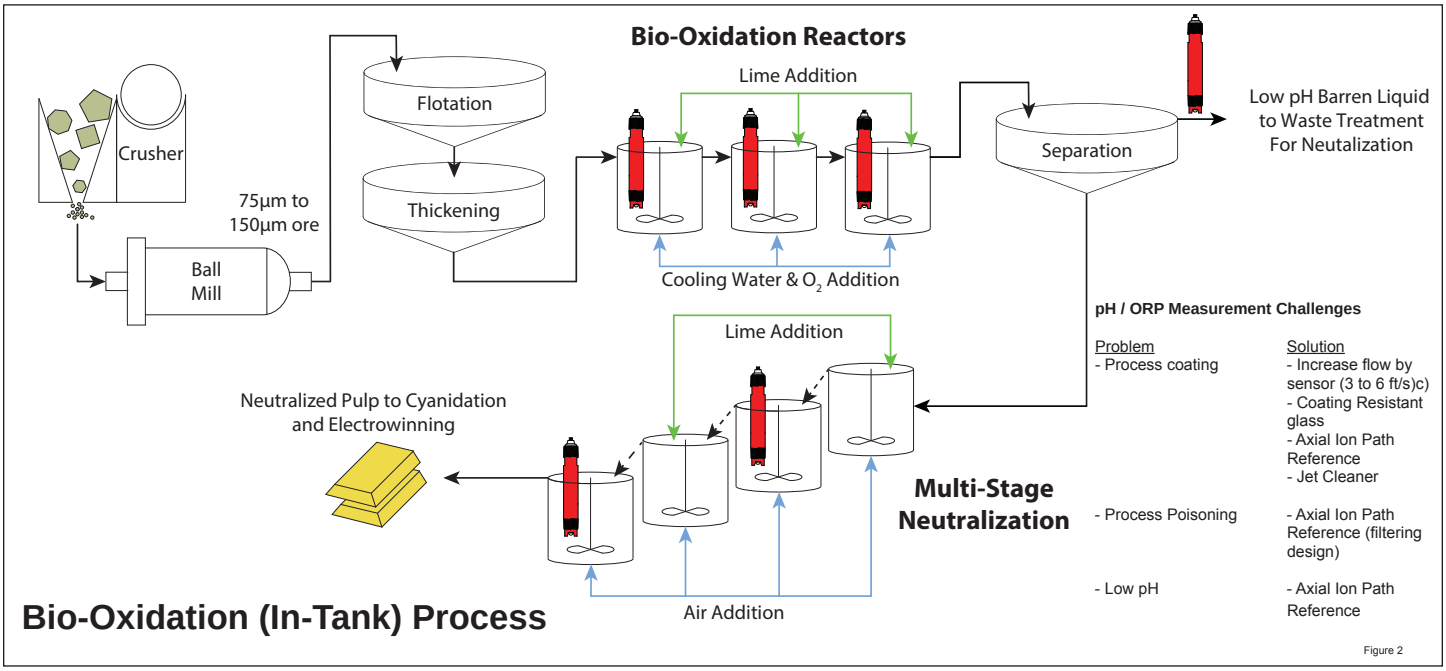
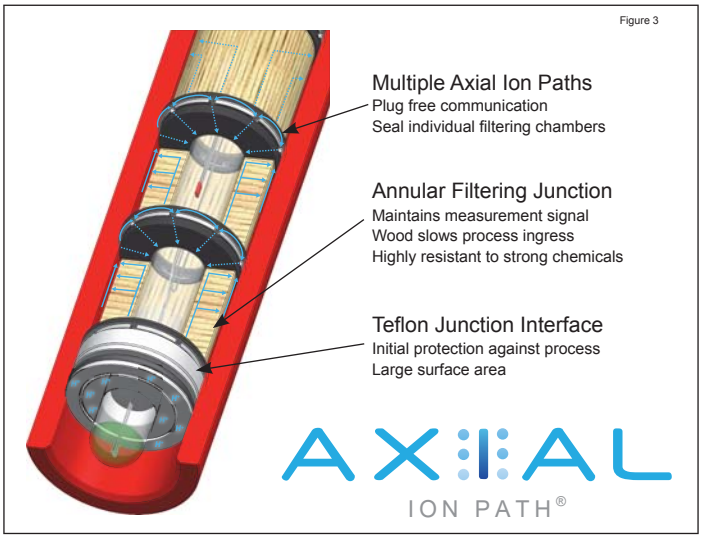


Figure 2



be specified with a notched tip to prevent breakage and reduce abrasion. Reduced maintenance is the main priority in these processes thus a flat glass electrode may be desired if solids content causes severe abrasion.

Pressure Oxidation

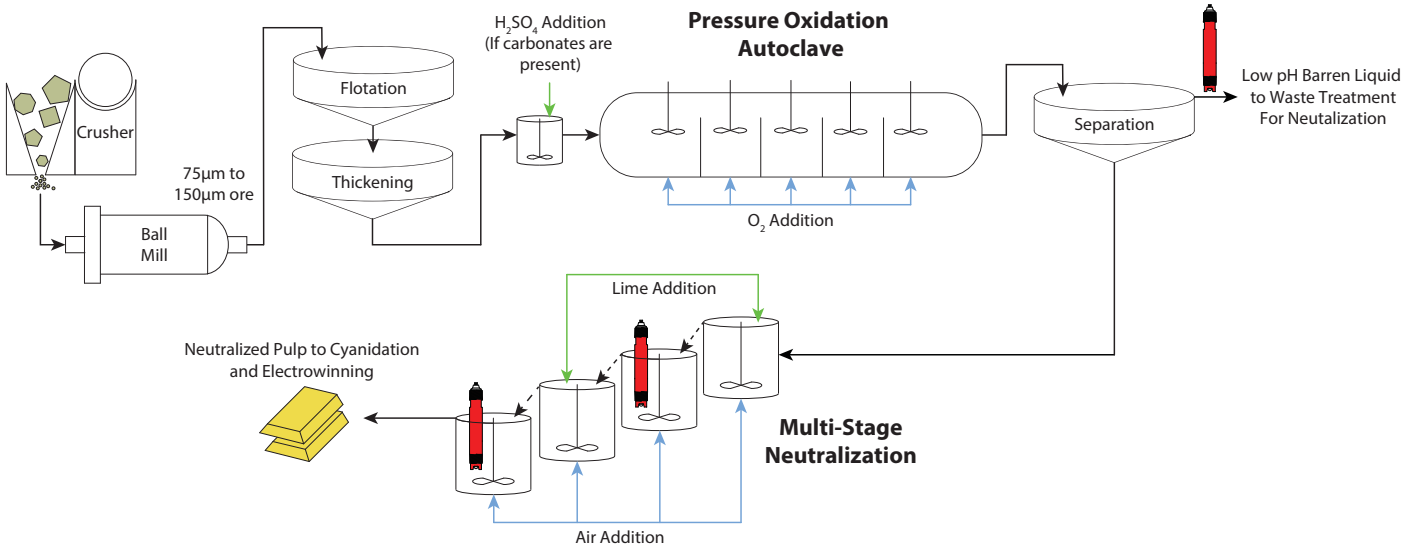
Our third method for refractory ore pre-treatment involves oxidation within an autoclave at elevated temperatures and pressures. This is referred to as pressure oxidation (POX). Gold laden ore is pulverized to a similar consistency as found with bio-oxidation processes (~75µm). The slurry is pumped through thickeners to remove water prior to entering the autoclave. If carbonate compounds are present then sulfuric acid will be added to the slurry to improve autoclave performance. The pulp is pumped into the autoclave where it is exposed to 180 - 225ºC at pressures up to 3000kPa (435 PSI). During the autoclave process pure oxygen is injected directly into the autoclave to oxidize the sulfide compounds to aqueous sulfuric acid. Due to the temperatures, pressures, and corrosive nature of the process material selection of the autoclave, agitators, and related pipeworks is crucial. Exotic alloys such as titanium and ferrilium are required. Total residence time in the autoclave will be 45 - 200 minute based on sulfide levels. The treated slurry leaving the autoclave will be <1.5pH due to the increased sulfuric acid concentration. Similar to the bio-oxidation process, the pH of the slurry must neutralized prior to the cyanidation process due to safety concerns over dangerous HCN gas.

Measurement Challenges

pH measurements in the pressure oxidation process are found in the neutralization circuit after the autoclave. If acid addition is done on the front end of the autoclave the pH is so low and the solids content so high that measurement is all but impractical. All of the difficulties of pH measurement discussed in the bio-oxidation neutralization process are present here. The pH must be elevated to >11pH for the downstream cyanidation process. Issues with abrasion, poisoning of the reference half cell and coating of the sensor will be present. The Barben 546 sensor mounted on a dip tube will be the most common choice for these applications.

Ultrafine Grinding

Our final refractory treatment involves ultrafine grinding of the ore. Typical ore processing reduces particle size down to 75 - 200µm. The goal with ultrafine grinding is to further reduce the ore to <10µm to expose trapped gold to



Pressure Oxidation Process

Figure 4

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cyanide. This type of process is purely mechanical and will be selected if the economics of the mining site deem in worthy. The main advantages of ultrafine grinding is that no pretreatment chemicals are required prior to cyanidation. No pH measurements are required prior to the gold leaching process.

Summary

Barben Performance Series pH sensors offer many advantages for gold processing facilities including the following:

- Less frequent cleaning and calibration intervals
- High pH / ORP measurement accuracy
- Increased pH / ORP sensor lifespan
- Simplified sensor specification

Maintenance expenses are decreased as spares inventory is reduced and fewer calibration hours are required to keep measurements accurate.

Contact Us

Barben Analytical is a leading supplier of analytical measurement technology targeting the industrial marketplace. It is a wholly owned subsidiary of Ametek.

Ametek has nearly 14,000 colleagues at over 120 manufacturing locations around the world. Supporting those operations are more than 80 sales and service locations across the United States and in more than 30 other countries around the world.

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