

Ultrafine Grinding and Atmospheric Oxidation for Refractory Gold Ores

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Abstract

The present study demonstrates the feasibility of the ultrafine grinding and atmospheric leaching process applied to refractory gold concentrates from Salave Project located in northern Spain. At bench scale, it was found acceptable sulfide oxidation was about 84-85% and CIL gold recoveries between 95-96% applying specific energy consumption between 30 and 60 kWh/t during ultrafine grinding. The atmospheric oxidation of the sulfide concentrate was controlled between pH 4.4 and 4.8 with a mixture 90/10 of CaCO₃/NaCO₃ with residence time of 48 hours for the atmospheric oxidation and 30 hours residence time for the CIL process.

Keywords: Refractory gold, ultrafine grinding, atmospheric oxidation

1 Introduction

Gold is a noble element under normal conditions and is highly valued due to its scarcity and its electrical properties and malleability for use in jewelry, as well as being a financial reserve for many countries. That is why gold extraction is a very important metal for the development of human activities and its demand is growing (Marsden, 2006). Unfortunately, gold extraction by conventional methods is becoming scarce and only ores containing gold associated or trapped in pyrite or arsenopyrite, gold tellurides, gold associated with carbon that generate pre-robbing and gold trapped in silica remain among the most important gold sources. These refractory gold ores need previous pre-treatment methods to release the fine gold contained or associated with these low-value compounds.

In the case of gold locked in sulfides such as pyrite/arsenopyrite, it is necessary to carry out a pre-oxidation treatment of the pyrite/arsenopyrite using processes such as pressure oxidation, biological oxidation, or ultrafine grinding-atmospheric leaching, among the most important. Comparative advantages regarding the high cost of installing autoclaves to oxidize under high pressure and the long residence times and potential bactericides in biological oxidation, the atmospheric oxidation is presented as an alternative method to unlock gold from pyrite/arsenopyrite ores.

The combination of ultrafine grinding and atmospheric oxidation overcomes the passivation layer of polysulfides that is produced when applied ferric media leaching. The atmospheric oxidation product of the pyrite and/or arsenopyrite locking gold is safe for disposal and liberates the gold for later conventional CIL process. The product of the ultrafine ground ore and atmospheric leaching of pyrite results in goethite which later is inert to cyanide solutions facilitating the CIL process without a CCD washing facility. When treating arsenopyrite locking gold the product of the atmospheric leaching is ferric arsenate. This product as well is inert to cyanide solutions; hence, no need for CCD wash prior to CIL and is safe for final disposal of the stabilized arsenic. Commercial application was achieved successfully at Envirogold-Las Lagunas in the Dominican Republic and Geopromin in Armenia.

2 Literature Review

Gold is inert in air or water at room temperature; so that, its occurrence is native gold and frequently alloyed to silver. Less gold occurrence is alloyed with tellurium, selenium, bismuth, mercury, copper, iron, rhodium and platinum. There are no natural occurrences of oxides, silicates, carbonates, sulfates or gold sulfides (Marsden, 2006).

2.1 Gold Mineralogy

The importance of knowing mineralogy is to be able to predict and solve processing problems (Zhou, 2012)

It allows us to predict:

- The response of gold to different processes
- Free or refractory gold
- Mineral factor affecting gold processing

It allows us to solve processing problems:

- Lost Gold Behavior
- Causes of Gold Loss and Other Valuable Losses
- How to improve recovery

As part of the prediction, for instance, mineralogy will allow us to know whether the material is free or refractory in extreme cases. Figure 2.1 shows that one possible path to treat free gold would be by gravity, flotation and/or cyanidation. If sub-microscopic gold is

observed, non-conventional extraction methods may be required pre-oxidation prior to cyanidation step.

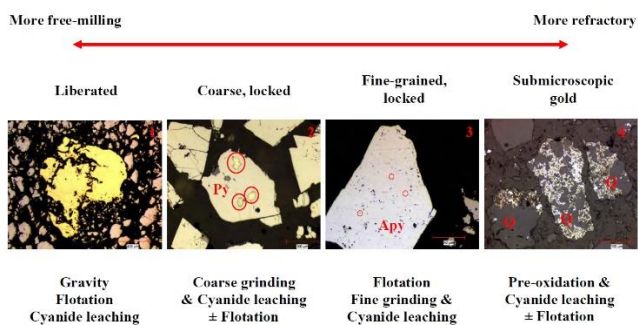


Figure 2.1 Gold locked in pyrite and its morphology (Zhou, 2012)

According to Zhou (2012), the nature of gold and its carriers are divided into microscopic gold which is visible, sub-microscopic or invisible gold and surface-bound gold which is absorbed into the structure of other minerals. Figure 2.2 shows this division criteria where it can be seen that sub-microscopic gold and surface-bound gold are difficult to extract by conventional methods (grinding and CIL/Merrill-Crowe). Within visible gold, gold tellurides are considered refractory as they are also difficult to extract by conventional methods.

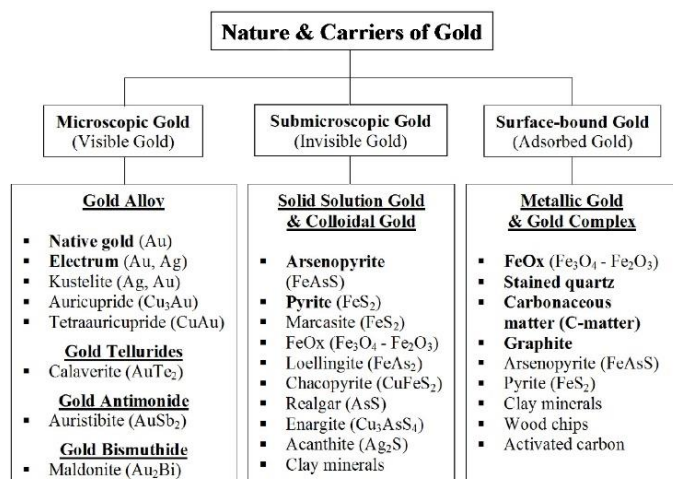


Figure 2.2 Gold ores and gold carriers (Zhou, 2012)

2.2 Refractory Gold Ores Extraction Methods

Gold ores responding with low recoveries below 80% to conventional cyanidation of milled ores between 75 and 150 microns are considered refractory (Yannopoulos, 1990).

The refractoriness of gold ores is either physical or chemical in nature although chemical refractoriness is rare and confined to only three conditions:

- Insoluble gold tellurides
- Minerals that break down and react with cyanide (cyanicides)
- Ore containing minerals that consume oxygen

The greater refractoriness of gold ores is physical as can be seen in Figure 2.3 which can normally be verified by microscopic or sub-microscopic mineralogical methods. Associated or encapsulated gold is generally fine in the host rock, then alloys with antimony and/or bismuth and/or lead. Gold could also be physically coated with iron oxides, silver chlorides, antimony, manganese, or lead compounds. Finally, the gold ore could be associated with carbonaceous materials and/or clays that absorb gold from the pregnant solution during cyanidation.

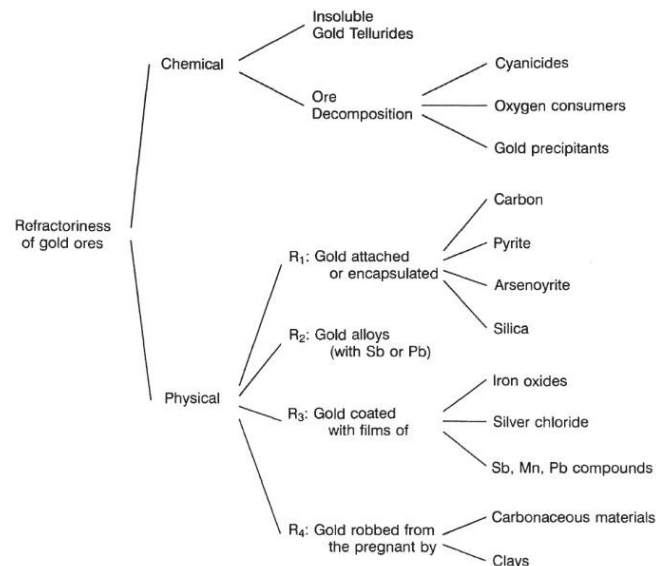


Figure 2.3 Refractory gold ores classification (Yannopoulos, 1990)

Figure 2.4 shows the classification of refractory gold ores. Among the different processes to treat refractory gold ores, we generally have a gravimetric pre-concentration and/or flotation, one of the most common problems of refractoriness is fine gold attached or encapsulated in pyrite, arsenopyrite or other sulfides. When gold is associated with sulfides, the concentration by flotation of sulfides is often considered. When there is a mixture of free and coarse gold with refractory, gravimetric concentration is considered in the underflow of the hydro cyclone to remove the coarse gold.

Sulfide flotation from the hydro cyclone overflow is concentrated by flotation using pH regulating reagents such as soda ash (not hydrated lime since is a free gold depressant and inhibits pyrite flotation), collectors and frothers. In some cases, copper sulfate will be needed to accelerate the flotation of pyrite and arsenopyrite. Sodium sulfide addition is necessary in cases where there is partial oxidation of the pyrite surface but should be used with caution as it depresses free gold flotation. Roughing concentrate frequently requires regrinding prior to cleaning. In the flotation treatment of refractory gold ores, the objective is to achieve the

highest recoveries, even with low grades of gold in the concentrate if necessary.

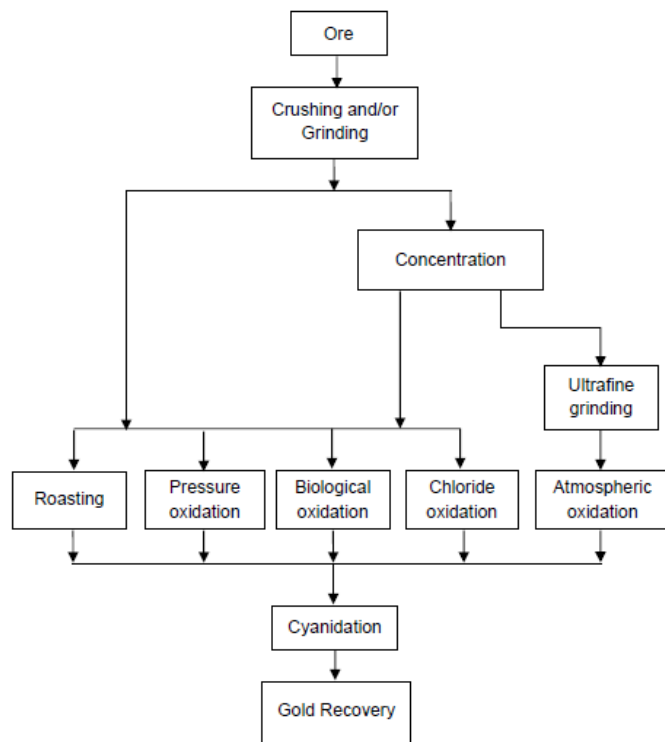


Figure 2.4 Potential treatment of refractory gold ores modified after Yannopoulos (1990)

The different routes to treat refractory gold ores after grinding or concentration can be roasting, pressure oxidation, biological oxidation, chloride oxidation and ultrafine grinding followed by atmospheric oxidation. This review focus on ultrafine grinding and atmospheric leaching, the other technologies to extract gold from refractory gold ores can be found elsewhere (i.e., Marsden and House, 2006; Niekerk, 1999).

2.3 Ultrafine Grinding and Atmospheric Leaching

The combination of ultrafine grinding and oxidative leaching at atmospheric pressure of sulfide concentrate containing precious metals or base metals liberates the locked gold from pyrite or arsenopyrite. Then these metals are recovered by conventional cyanidation methods (Hourn, 2012).

The first industrial application for refractory gold concentrates was Envirogold-Las Lagunas in the Dominican Republic, which began operations in 2012. Figure 2.5 presents an aerial view of Envirogold-Las Lagunas, with a yellow cooling tower on the left and behind the cooling tower the atmospheric oxidation tanks. On the right side this figure shows the CIL tanks.



Figure 2.5 Aerial view of the Envirogold-Las lagunas facility in the Dominican Republic.

Table 2.1 shows plants using atmospheric leaching for base metals and two of them applied to precious metals: Panterra Gold in the Dominican Republic and GeoProMining in Armenia.

In general, process plants using the atmospheric leaching for precious metals begin their operations with conventional grinding after mining/dredging, then the sulfides containing the precious metal are concentrated by flotation, next the concentrates obtained are further reduced in size by ultrafine grinding mills, these ultrafine fine particles are subjected to atmospheric oxidative leaching, and then once oxidized, the released precious metal is subjected to a conventional cyanidation process preferentially CIL-desorption-electrowinning-smelting.

Table 2.1 Atmospheric leaching plants

Company	Plant	Metal	Status	Year
New Boliden	Kokkola 1	Zinc	Operative	
New Boliden	Kokkola 2	Zinc	Operative	
New Boliden	Odda	Zinc	Operative	
Korea-Zinc	Onsan	Zinc	Operative	
Birla/Western Metals	Mt Gordon	Copper	Decommisioned	
First Quantum	Las Cruces	Copper	Operative	
Zhuzhou Smelter	Shandong	Zinc	Operative	
Glencore	San Juan de Neiva	Zinc	Operative	2010
Glencore	Nordenham	Zinc	Operative	2011
Panterra Gold	Las Lagunas	Gold	Operative	2012
Kores	Boleo	Cu-Co-Zn	Operative	2015
GeoProMining LLC	Ararat	Gold	Operative	2014

2.3.1 Grinding

The purpose of grinding is to release the pyrite (containing the precious metal) from gangue minerals

to obtain better conditions to recover pyrite in the flotation stage, additionally the grinding provides mechanical activation which would improve flotation by about 12% (Akhgar, 2015). Generally, the liberation degree of pyrite is between 75 and 150 microns.

2.3.2 Froth Flotation

The objective of froth flotation is to concentrate the sulfide ore containing the precious metal to achieve sulfur as sulfide no less than 14% to ensure autogenous heat generation during atmospheric leaching. The principle of flotation is to use the hydrophobic properties of sulfides to separate the sulfides from the gangue. This separation is accelerated through the use of previously conditioned collectors and frothers.

The conditioning agent commonly used to regulate pH to alkaline conditions (6.5-7.5) is soda ash, since hydrated lime inhibits pyrite flotation. Sometimes it is necessary to use copper sulfate to accelerate the flotation of pyrite and arsenopyrite. In cases where the ore is partially oxidized it is necessary to use sodium sulfide to sulfurize the oxidized surface and make it hydrophobic. If free gold exists, it will be used with caution, because sodium sulfide depresses free gold flotation (Yannopoulos, 1990).

Because each deposit is particular in terms of the application of collectors and the influence of the ore granulometry, the pyrite flotation of the Barry project in Quebec is described below (Yalcin, 2008). This ore resulted in higher metal recovery (92%) at finer particle size (P80 53 μm) using amyl or isopropyl xanthate at about 60 g/t, with 50 g/t Dowfroth 250 at pH 8.50 to 8.85. However, at a time greater than 7 minutes the mass recovery of flotation is independent of the particle size, as can be seen in Figure 2.6

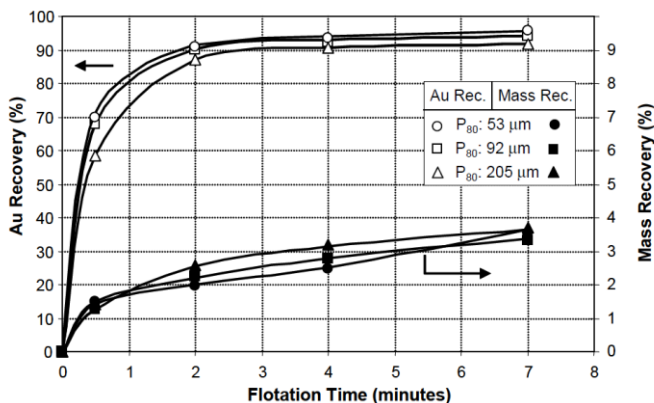


Figure 2.6 Flotation kinetics of the Barry gold ore deposit in Quebec (Yalcin, 2008)

In Figure 2.7, it is seen that a fine particle size contributes to a better recovery due to a higher release. Note also that there is a significant raise in

recovery when the size is reduced from 205 to 92 μm and becomes more asymptotic at 53 μm . That means, finer than 53 μm no longer significantly improves the metal recovery, as can be seen in this figure.

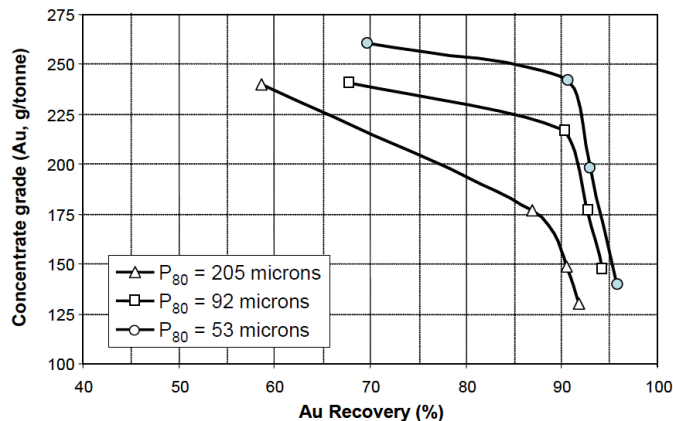


Figure 2.7 Grade recovery associated to P₈₀ from the Barry deposit in Quebec (Yalcin, 2008)

Envirogold-Las Lagunas uses flotation after grinding where the pyrite undergoes mechanical activation and potassium amyl xanthate (PAX), diethyl dithiophosphate (DTP) and MIBC (methyl isobutyl carbinol). The total addition to the PAX is about 120g/t and 40 g/t of DTP.

Additionally, aeration and management of froth bed are other important parameters to achieve sulfide grade requirements for the autogenous heat generation during atmospheric leaching, which requires 14% sulfur as sulfide. Aeration remains high in the first cells and decreases in the last cells. Froth beds are important to regulate mass pull or concentrate grade. In this way, when a higher grade of concentrate is required, the froth bed must be larger, since it allows a better selectivity of the hydrophobic sulfide.

2.3.3 Ultrafine Grinding

The objective of the ultrafine grinding is to reduce the degree of tension in the crystalline structure of the mineral in order to generate defects in the crystallographic structure of the mineral. Additionally, it reduces the activation energy for the oxidation of sulfides allowing leaching in atmospheric conditions. Considering also that ultrafine grinding increases the surface area; hence, increases the reaction kinetics.

Ultrafine grinding also prevents passivation of sulfide leaching. In coarse grain sizes (>75 μm), passivation is due to the formation of polysulfides on the surface of the particle, which prevent complete sulfide dissolution (Hackl, 1995). As this passivating layer prevents the access of chemical reagents to the surface of the particle, it is impossible to continue leaching; thus, resulting in partial oxidation. This normally occurs when the thickness of the passivating layer is about 2-3

μm . Ultra-fine grinding achieves a passivation P_{80} of 10-12 μm , which prevents passivation, since the ore that is being leached disintegrates before the sulfosalt precipitate layer is sufficiently dense (Hourn, 2012).

A series of mills have been developed for efficient use of energy to achieve ultrafine particles: Vertimill or Tower Mill, Stirred Media Detritor (SMD), Netzch or Isamill (Lichter and Davey, 2006) and finally HIGMill (High Intensity Grinding mill) among the commercial ones.

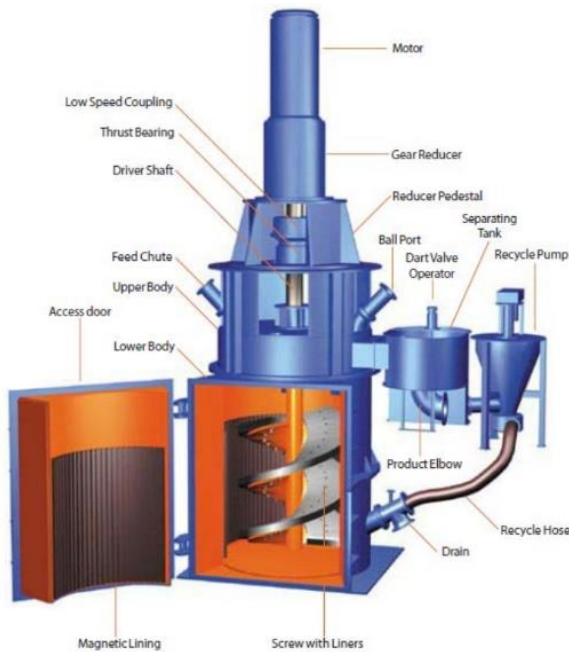


Figure 2.8 Vertimill or Tower mill

The Vertimill is an agitated mill that has a vertical cylinder in which a propeller rotates at low rotational speed (Figure 2.8). This mill is frequently used to regrind concentrates with a typical feed of 100-300 μm with a 100-15 μm product. Finer product sizes using Vertimill is possible if finer grinding media are used. This mill predominantly uses steel balls in the range of 6-40 mm and are capable of using cypebs which are more economical where less than 25 mm media is required. Commercial applications of the Vertimill have achieved a P_{80} of 25 μm at laboratory scale. Sizes below 5 μm have been achieved with energy consumption close to other agitated mills (Lichter and Davey, 2006).

The SMD (Stirred Media Detritor) mill uses a vertical axis stirrer with equally spaced horizontal pins on two parallel levels. The grinding media used by this mill is 1-3mm ceramic balls. The mixture of pulp and ceramic balls is fluidized by the rotation of the shaft at high speed, the discharge is carried out with meshes located in the upper overflow, in this way the ceramic balls are retained. The feeding of these mills is in the range from 100 μm to 15 μm The grinding product that this

equipment can achieve is up to a P_{80} of 2 μm . Figure 2.19 shows the SMD mill (Lichter and Davey, 2006).



Figure 2.9 Stirred Media Detritor (SMD) from Metso (Lichter and Davey 2006)

The Isamill mill is an energy efficient continuous grinding technology for metallurgical metal extraction applications. According to Glencore (formerly Xtrata), the number of installations using IsaMills exceeds 130 worldwide. The Isamill mill uses high intensity energy around 300 kW/m^3 inside the grinding chamber, so its size is compact and installation is simple. The grinding media for this equipment is in the range of 1.5-3.5 mm. The Isamill has 8 discs on its horizontal axis, each disc acting as a separate grinding element. The residence time in this type of mill is close to a perfect plug flow without short circuits, therefore it is possible to operate this mill in open circuit without the need for an external classification system. Figure 2.10 shows the Isamill equipment.

Particularly the Isamill of Envirogold-Las Lagunas, operates at 35 kWh/t using high alumina ceramic grinding media with a diameter of 2.0 mm. It operates both in a closed configuration with classification cyclones, as well as in an open configuration without the use of classification cyclones. This configuration depends on the type of material being treated and according to the temperatures required for the atmospheric oxidative leaching process when sulfide grade does not reach 14% for operational issues.

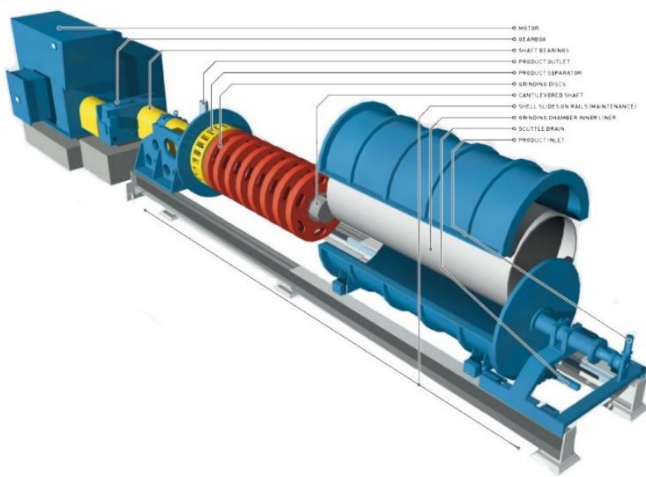


Figure 2.10 Isamill (Glencore)

HIGmill was launched on the market in April 2012 by Outotec, which has high energy efficiency due to its vertical rotor and counter-ring design, which enables high energy intensities even at low speed. It does not require an external size classification system. Having 15-20 stages of rings that this mill behaves as plug flow reactor. Figure 2.11, shows the HIGmil equipment. Usually, the volume of grinding ceramic media is 60-75% with sizes 1-6 mm. The operation of a HIGmill consists of feeding pulp into the lower part of the mill, this combination of pulp, ceramic media and rotating rotors, provide movement to remove the load against a series of stationary counter-rings. The grinding mechanism is mainly attrition. The vertical arrangement of the mill simultaneously allows the classification of particle sizes, since coarse particles remain longer to move upwards; so that, an external classification system is not necessary (Lehto, 2016).

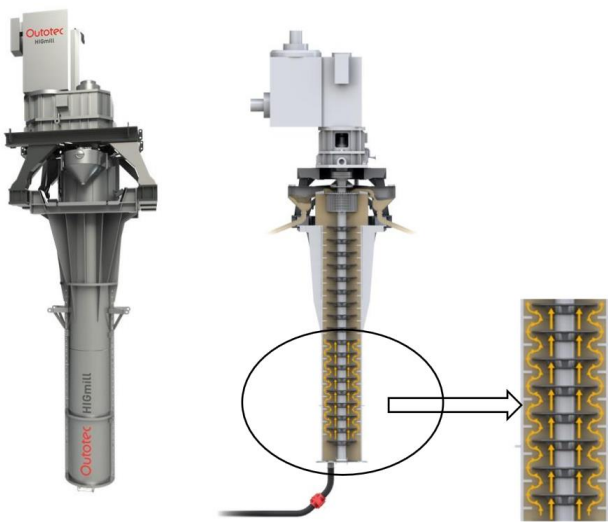


Figure 2.11 HIGmill, High Intensity Grinding mill (Lehto, 2016)

The characterization of ultrafine particles is carried out using laser diffraction, sedimentation, cyclone, and optical methods, among the main ones. Most

commercialized units are: Malvern Mastersizer, Microtrac, Cyclosizer, Coulter counter and Sedigraph. Each of the mentioned equipment has different characteristics and its reading can be affected by the shape, density and translucency of the particles. It is important to clarify that the reading of these machines is not always consistent and the finer the particles, the less repeatability is observed even using the same type of equipment. Even with standard procedures and trained personnel, the results may vary due to particle agglomeration, mainly due to the use of dispersants; thus, adding another source of potential error (Lichter and Davey, 2006).

The use of grinding media is an important factor when ultrafine grinding is required. The media parameters to be considered are: size, type and hardness.

Figure 2.12, shows that a Vertimill reflect significant reductions in energy use by reducing the size of the grinding media.

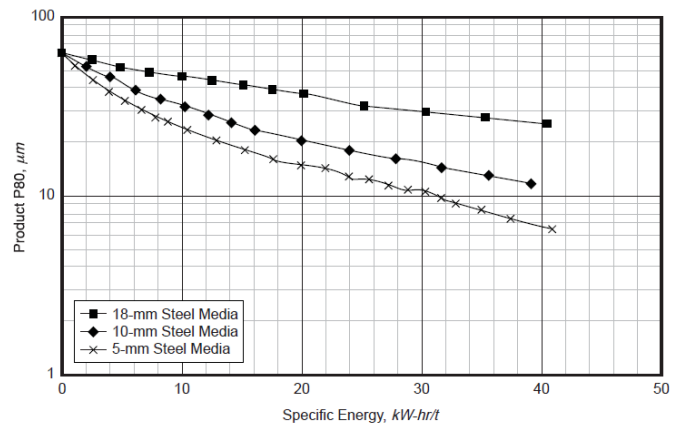


Figure 2.12 Grinding media size effect in the product efficiency of a Vertimill.

The type of grinding media used influences the hardness; therefore, the duration of the grinding media (Lichter and Davey, 2006). Table 2.2 shows the composition of several grinding media types used industrially. Figure 2.13 shows the dimensions of an aluminum-rich ceramic grinding media.

Ceramic Media	Chemical Composition	Apparent Density
Aluminum	Al ₂ O ₃ ≥ 85% - SiO ₂	2.0 - 2.1
Stabilized yttrium - zirconium oxide	ZrO ₂ (95%) - Y ₂ O ₃ (5%)	3.6 - 3.8
Stabilized cerium - zirconium oxide	ZrO ₂ (80%) - CeO ₂ (20%)	3.9 - 4.0
Stabilized magnesium - zirconium oxide	ZrO ₂ (97%) - MgO (3%)	3.2 - 3.4
Zirconium silicate	ZrO ₂ (69%) - SiO ₂ (31%)	2.2 - 2.4



Figure 2.13 Grinding media used in stirred mills

2.3.4 Atmospheric Leaching

For the atmospheric oxidation process to be autogenous, the grade of sulfur as sulfide must exceed 14%, this way the leaching stage can operate at 95°C. The pyrite/arsenopyrite oxidation occurs at a neutral pH between 5-7, in order to form goethite (FeOOH), which is stable in cyanide solutions; so that, a countercurrent washing system will not be necessary as in the case of base metals where it is necessary to use an acid medium to obtain a washed overflow rich in metals and an underflow free of base metals. The neutral oxidation of pyrite/arsenopyrite requires the continuous addition of an alkalinizing medium such as limestone CaCO_3 (Hourn, 2012).

The production of goethite or ferric hydroxide depends on the pH and temperature as shown in Figure 2.14. Where at $\text{pH} > 1.5$ and temperatures below 100°C goethite is formed preferentially for the atmospheric leaching. This figure also explains the pressure oxidation product is preferentially basic ferric sulfate (BFS) at temperatures about 220°C and pH below 1.5 (Fleming, 2009).

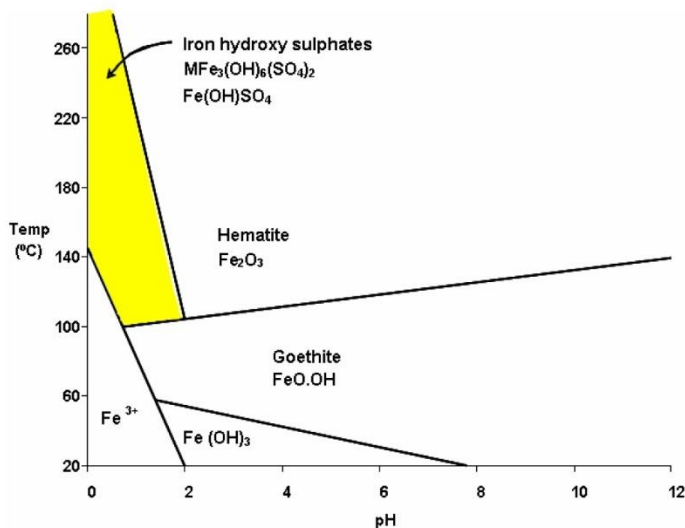


Figure 2.14 Stability areas of the system Fe-S-O (Fleming, 2009)

Reaction R2.1 shows that pyrite initially forms ferrous iron, then oxidized to ferric iron as observed in reaction R2.2. Finally, the desired product from ferric sulfate is goethite shown in reaction R2.3 which is formed at pH about 5 and low oxidation potentials as shown in the Eh-pH diagram (Figure 2.15). Similarly, the R2.4 reaction shows the oxidation of arsenopyrite to arsenate and elemental sulfur, this reaction occurs at slightly acidic pH around 4 depending on the arsenic concentration according to experience (Hourn, 2012).

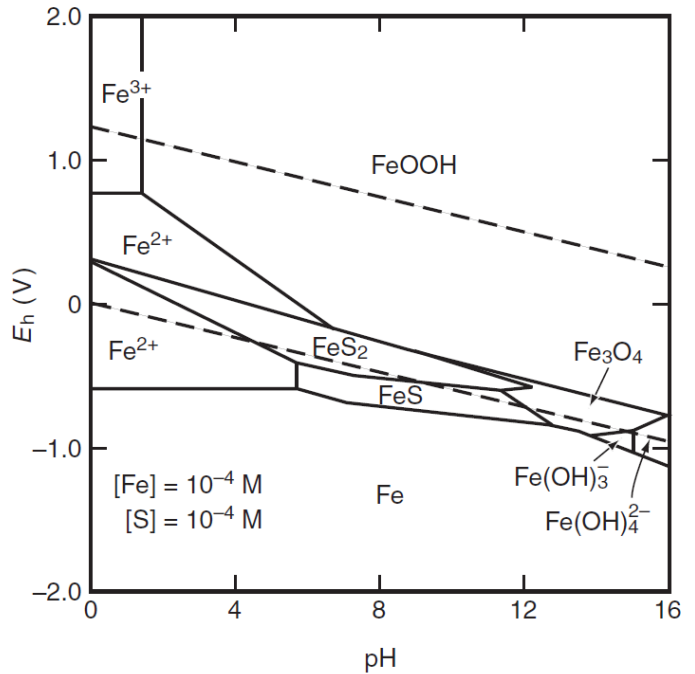
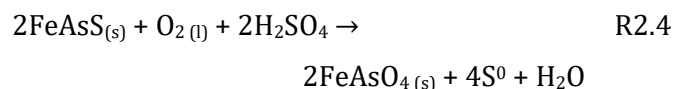
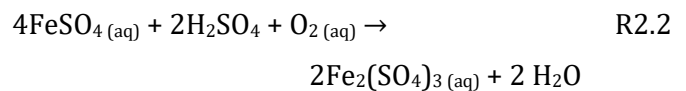
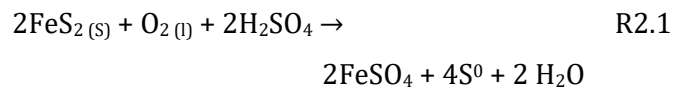
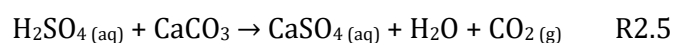


Figure 2.15 Eh-pH for the system Fe-S-H₂O at 25 °C (Marsden, 2006)



The generation of the neutral medium with limestone can be seen in the reaction R2.5, this addition allows the generation of pH conditions for the formation of goethite, As it forms elemental sulfur in the oxidizing environment, this sulfur is oxidized to sulfuric acid as observed in reaction R2.6. Additionally, to provide the oxidizing medium, it is necessary to solubilize the gaseous oxygen in an aqueous oxygen, as can be seen in reaction R2.7.





For the oxygen mass transfer to be efficient, the stirring power is very important, for which the rheological properties of the pulp must be taken into account. Due to the fact that the particles have an ultrafine size, the viscosity is high. Therefore, to keep the ultrafine particles in suspension it is necessary to use higher agitation power than for those with coarse particle sizes.

Figure 2.16 graphically illustrates the oxidation of the particle. Initially a solid particle and later after oxidation. Oxidation products are generated around the particle, which later in the cyanidation stage facilitate the access of solution to dissolve the fine gold contained inside the particle (Hourn, 2005).

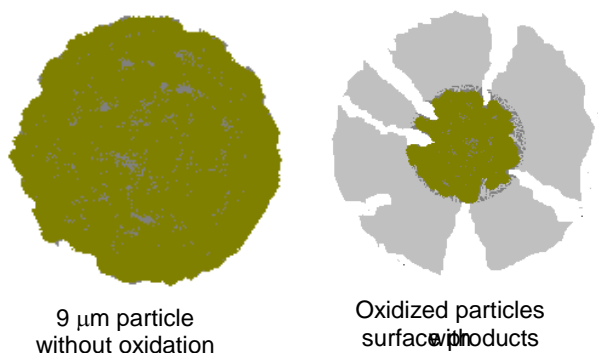
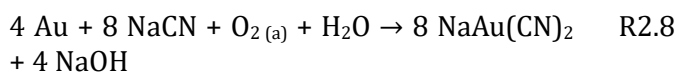


Figure 2.16 Pyrite leaching from particle to oxidized particle (Hourn, 2005)

2.3.5 CIL Leaching

More than 200 years ago the solubility of gold in cyanide was known. It was Elsner who in 1894 defined the reaction R2.8, although it is known that this reaction actually occurs in several stages (Marsden, 2006)



Cyanide hydrolyzes in aqueous solution, when equilibrium is established and depending on the pH, HCN can be formed according to reaction R2.9. In Figure 2.17 can be seen that the formation of HCN is favored at pH less than 9.2. This figure also shows that thermodynamically cyanide is unstable in water and undergoes spontaneous oxidation to cyanate, that oxidation is favorable for gold extraction. Returning to the generation of HCN and depending on the

temperature, HCN can be hydrolyzed to ammonium formate according to reaction R2.10.

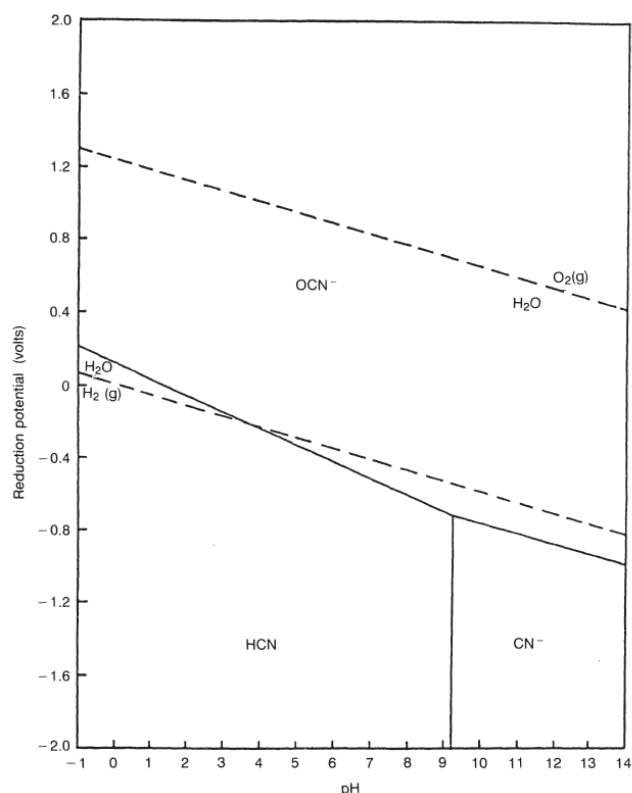


Figure 2.17 Redox potential versus pH for the system CN-H₂O at 25°C (Yannopoulos, 1990)

As aeration is an integral part of cyanidation in stirred tanks, the presence of CO₂ is unavoidable. Therefore, it is necessary to maintain alkaline radicals that react with carbonic acid and maintain the dissociation of HCN. If the neutralization reagent is hydrated lime, CaCO₃ will be formed, which precipitates on the carbon surface, an effect known as fouling, this can be seen in reaction R2.11.



Because gold is a noble metal, there are very few solvents that can dissolve gold. Solutions capable of dissolving gold usually have an oxidant and a reagent capable of forming a complex with gold. In cyanidation, oxygen is the oxidant and cyanide is the complexing agent, which forms Au(CN)₂⁻, as shown in Figure 2.18 and is stable over the entire pH range.

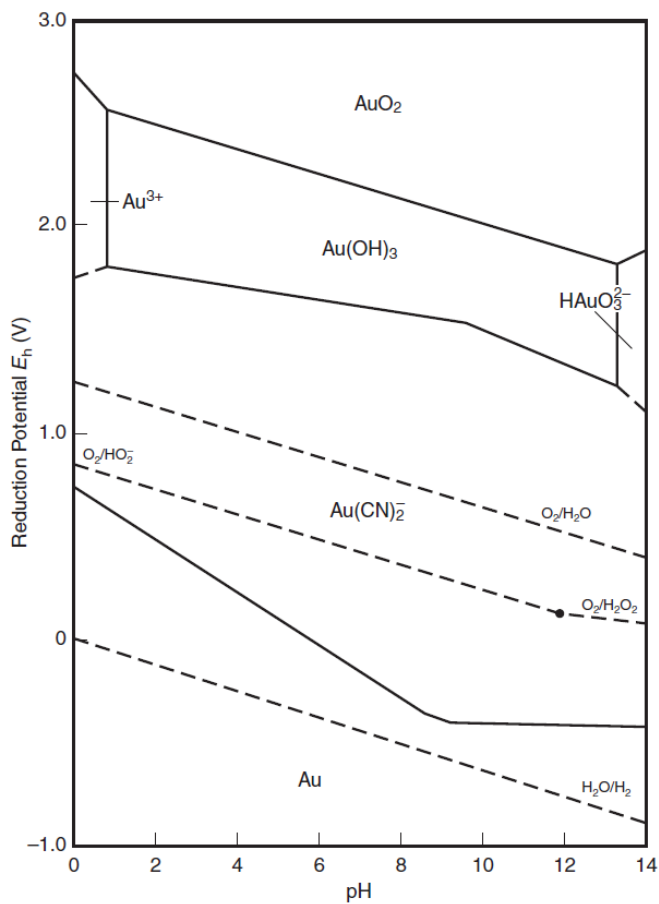
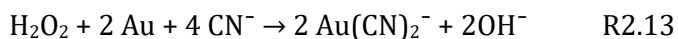
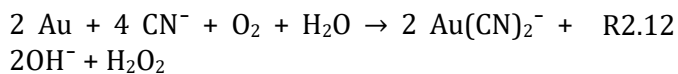
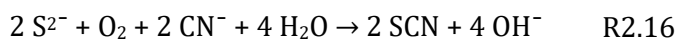
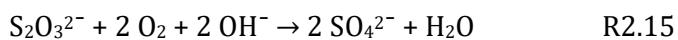
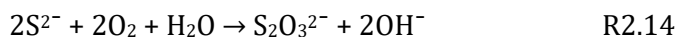


Figure 2.18 Eh-pH diagram for the system Au-H₂O-CN at 25 °C (Marsden, 2006)

To understand the complete mechanism of gold dissolution by cyanide-oxygen, the Elsner equation can be divided into two consecutive reactions R2.12 and R2.13.



Due to the incomplete oxidation of pyrite, during cyanidation these residual sulfides break down into sulfide ions with or without the formation of metal cyanides. Once the sulfide is in solution, it can form thiosulfates (R2.14), sulfates (R2.15), and thiocyanates (R2.16).



Reactions R2.14, R2.15, and R2.16 show that the presence of soluble sulfides during leaching results in oxygen and cyanide consumption; however, neither such reaction is detrimental to gold dissolution as long

as sufficient oxygen and cyanide are provided. The addition of lead salts could inhibit the formation of thiocyanate (R2.38) and accelerate the oxidation of sulfide to thiosulfate (R2.36) and sulfate (R2.37) according to Hedley and Tabachnik (1968)

Additionally, pyrite is a source of iron, which is why it is necessary to review the thermodynamic stability conditions of the goethite formed during atmospheric oxidation. Figure 2.19 suggests not to cyanide between pH 8-10, since goethite would consume additional cyanide which would form iron WAD cyanide upon decomposition.

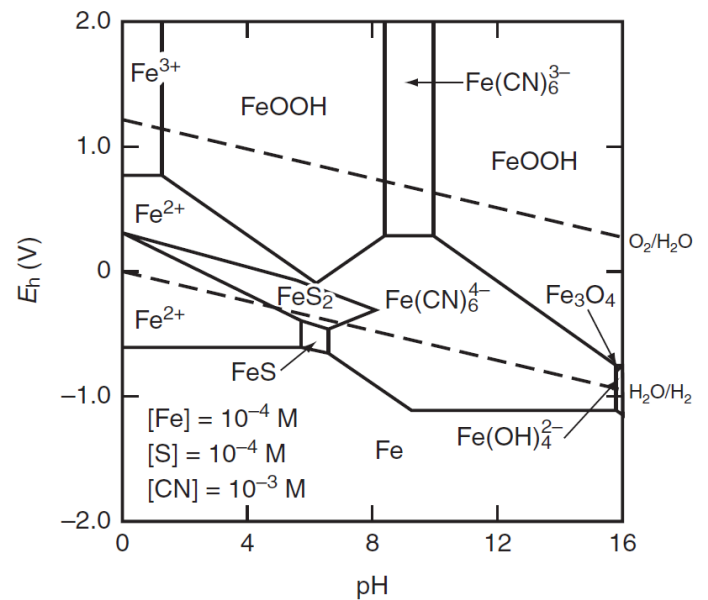


Figure 2.19 Eh-pH diagram for the system Fe-S-CN-H₂O at 25 °C (Marsden, 2006)

3 Experimental

The Salave project is located on the north coast of Spain, near the Bay of Biscaya, two kilometers east of the city of Villa Tapia de Casariego, in the western part of the Principality of Asturias. The mining of the Salave project will be carried out through underground galleries, since the area of influence restricts activities in the surface due to agriculture and recreation. Mining in the region dates back to Roman times in the 1st century BC, and possibly before the Celts. It is estimated that production during Roman times was six million tons, with a production of 5,000 to 7,000 kilograms of gold. Recent explorations began in 1960 by IMEBESA, and after several explorers, in 2010 Astur acquired the Salave property and drilled holes totaling 3,031 meters, IMEBESA carried out metallurgical studies in 1971, determining its refractoriness, for which flotation tests were carried out, followed by pressure oxidation to release the fine gold and then CIL. The application of bacterial oxidation was also studied, and it was found that both methods help to

recover gold significantly. At 106 μm there is a recovery of gold over 95% by flotation and in the pressure oxidation of this concentrate values of 98% oxidation were achieved. Bacterial oxidation achieved 97% oxidation (Black Dragon 2017). The present work investigates the alternative of the ultrafine grinding and atmospheric oxidation process to extract fine gold from the refractory Salave deposit.

Samples of previously concentrated tailings from Mina Salave Gold located in northern Spain were received by Envirogold-Las Lagunas, Dominican Republic, to study the feasibility of extracting gold from previously concentrated ore by flotation. The sampling was classified into two zones: Upper Zone and Lower Zone. The classification was decided due to the fact that material in the upper zone could present oxidation due to exposure to the atmosphere. The material was conventionally floated by Black Dragon Gold Corp. The next section presents the characterization of the concentrates, ultrafine grinding tests, atmospheric leaching tests, CIL and finally the justification of the experimental design.

3.1 Concentrate Characterization

Six 20-liter containers of refractory gold concentrate sample were received, three from the Upper Zone and three for the Lower Zone. After homogenizing them separately by zones, representative samples were taken to analyze the humidity, specific gravity of the solid and chemical analysis of both two zones.

3.2 Experimental Design

According to previous experiences, it is known that the energy consumption to achieve a P_{80} of 8-12 μm is 35 kWh/t (Hourn, 2006 and 2005) and in real operation, Isamill of Envirogold-Las Lagunas consumes 35 kWh/t. Taking these considerations into account, it was decided to work at 30 kWh/t since the chemical analysis showed that it had arsenic, and knowing that the arsenopyrites are less hard compared to the dominant pyrite in Envirogold-Las Lagunas.

The residence time for the atmospheric leaching is considered to be 48 hours which is the actual residence at Envirogold-Las Lagunas. The pH maintained during the atmospheric oxidation at Envirogold-Las Lagunas is about 5.3. For this Salave sample, it is recognized that it has arsenopyrite, which is why a pH of 4.4 to 5.5 should be explored.

Due to the arsenic content in the Salave sample, the acidification reaction could be faster; so that, the neutralization agent during atmospheric oxidation was decided to operate with a mixture of limestone and sodium carbonate in a 90/10 ratio. Envirogold-Las

Lagunas uses only limestone because pyrite predominates largely in its composition.

The CIL residence time considered was 30 hours according to laboratory experience (Hourn, 2006) and actual operation at Envirogold-Las Lagunas. pH of 11 in all CIL cases to keep goethite stable without forming iron WAD cyanide. Solids content 30% with 30 g/L of activated carbon, thus keeping the carbon distributed in the pulp without floating/sinking the carbon. Free cyanide in excess of 700 ppm to minimize consumption by cyanicides.

Table 3.1 shows the experimental design summarizing the conditions mentioned above. Three tests at different pH in atmospheric leaching and two tests without atmospheric leaching to compare CIL gold recoveries from concentrate and CIL after ultrafine grinding. This matrix is for both Upper Zone samples and Lower Zone samples as well. In this way, at least 10 tests would be carried out. However, during Lower Zone sample testing, gold recoveries were so low that two additional tests were done using 60 kWh/t to obtain smaller particle sizes than the obtained at 30 kWh/t. This is the reason why two tests were added to the original program.

Table 3.1 Conditions for the ultrafine grinding-atmospheric leaching and CIL process test

Test →	1	2	3	4	5
Energy (Kwh/t)	30	30	30	-	30
Atmospheric leaching residence time (h)	48	48	48	-	-
Atmospheric leaching pH	4.40	4.80	5.50	-	-
Atmospheric leaching solids content (%)	10%	10%	10%	-	-
Atmospheric leaching $\text{CaCO}_3/\text{Na}_2\text{CO}_3$	90/10	90/10	90/10	-	-
CIL residence (h)	30	30	30	30	30
CIL pH	11	11	11	11	11
CIL solids content (%)	30	30	30	30	30
CIL free CN (ppm)	700	700	700	700	700
CIL activated carbon (g/L)	30	30	30	30	30

3.3 Ultra-fine Grinding

A Grinding Solutions Ltd. laboratory stirred mill was used for ultrafine grinding of the two concentrate samples, as shown schematically in Figure 3.1. It has a vertical axis with horizontal pins that allow the mixture of pulp and grinding media to be stirred. The container

has a capacity of 5 litres. This equipment has an electronic load cell and an instantaneous power meter to calculate the specific energy of ultrafine grinding.

Keramax MT1 2.0 mm ceramic grinding media provided by Magotteaux was used as a grinding medium, which contains Al_2O_3 79%, SiO_2 6.5% and ZrO_2 14%. This grinding media has a solid specific gravity of 2.7 and hardness according to the manufacturer of 1300-1400 HV.

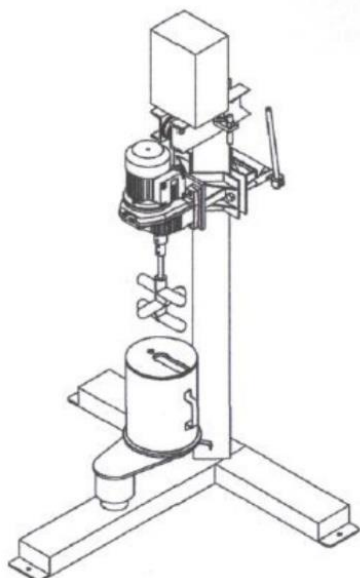


Figure 3.1 Stirred mill from Grinding Solutions™ used for ultrafine grinding testing.

The ultrafine grinding process was performed at 50% volume of 2.0 mm ceramic media. For a 5-liter container, the effective volume is 2112 mL, so the ceramic half and the 50% solids pulp will occupy 1056 mL each. With the above data and knowing that the specific gravity of the solid sample is 3.0, the required grinding time is estimated to achieve 30 kWh/t (time calculated using the data mentioned above). In turn, in this total time, sampling is carried out to see the kinetics of energy consumption versus product size, basically, particle size distribution.

3.4 Atmospheric Oxidation Leaching

The concentrate, after grinding at 30 kWh/t, undergoes atmospheric oxidation tests in a stirred reactor equipped with a heater to maintain the pulp temperature, an oxygen injector, and the addition of the $\text{CaCO}_3/\text{Na}_2\text{CO}_3$ mixture through of a condenser. Figure 3.3 shows the distribution and connection of equipment and instruments. The agitation was maintained at a constant 600 rpm for all cases, the addition of oxygen constant at 90 mL/min in all cases. The addition of the alkalizing pulp ($\text{CaCO}_3/\text{Na}_2\text{CO}_3$) is done by automatic control to maintain the pH at the target (4.4, 4.8, 5.5). This pulp of limestone and sodium carbonate tends to settle, so the container that

contains it is agitated and by means of a peristaltic pump it is pumped continuously to the top where an automatic valve diverts the pulp towards the agitated reactor through the condenser for this way to maintain the required pH. The container containing the $\text{CaCO}_3/\text{Na}_2\text{CO}_3$ pulp is mounted on a balance that records the consumption of this mixture in order to indirectly determine the oxidation of sulfur as sulfide. This indirect way of calculating oxidation is provided by chemical analyzes of sulfur as sulfide before and after atmospheric leaching. Figure 3.2 shows the arrangement of equipment and instruments used at Envirogold–Las Lagunas. Figure 3.3 shows the loop control and instruments used for the atmospheric leaching test.



Figure 3.2 Arrangement of equipment and instruments for the atmospheric leaching test at the Envirogold facility in the Dominican Republic.

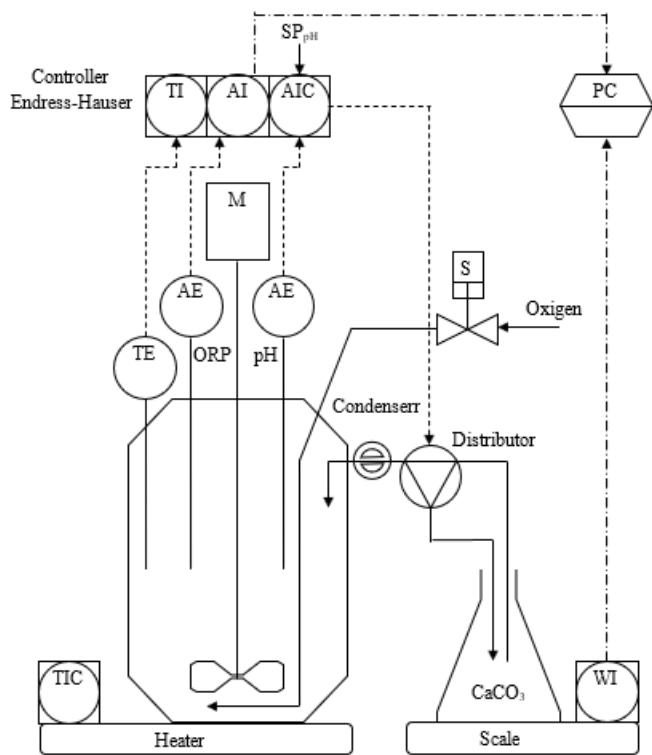


Figure 3.3 Equipment and instruments used during the atmospheric leaching testing at Envirogold.

3.5 CIL Testing

After atmospheric oxidation, the pulp is filtered and repulped to 30% solids to proceed with CIL tests on bottles at room temperature around 25°C. The pulp is regulated at pH 11 and then sodium cyanide is added to initially have 700 ppm of free cyanide. Subsequently, 30 g/L of virgin activated carbon is added, in all cases, previously soaked. After 30 hours of agitation on rotating rollers, the content of gold in activated carbon, gold in solution and gold in solid is analyzed in order to determine the CIL recovery, all the CIL tests were carried out in duplicates.

4 Results

The results of the characterization of the sulfide concentrates of the Salave sample are presented below.

4.1 Concentrate Characteristics

Table 4.1 shows the chemical analysis of the samples after homogenization. The high content of arsenic in the samples can be noted. The Upper Zone shows 5.5% As and the Lower Zone 9.19%. These high Arsenic contents are indicative that the operating pH, based on previous tests, should be slightly acidic with pH values between 4.4 and 5.5. The specific gravity of the Upper Zone and Lower Zone samples was determined to be 3.0 and this value was used for solids content estimation.

Table 4.1 Chemical analysis of the homogenized composite samples

	Au (g/t)	ST (%)	As (%)	Sb (%)
Upper Zone	35.0	19.5	5.50	0.21
Lower Zone	38.0	12.7	9.19	0.53

The mineralization of the Salave project is related to a hydrothermal alteration within a granodiorite. High gold grades are associated with intense albite-sericite alterations with finely grained arsenopyrite, disseminated in the form of needles, in addition to the presence of pyrite and stibnite according to geological studies presented by Black Dragon (CSA Global, 2018). IMEBESA carried out metallurgical studies in 1971, determining its refractoriness, for which flotation tests were carried out, followed by pressure oxidation to release the fine gold and then CIL (Prenn et al, 2017). The P80 of Upper Zone and Lower Zone was 75 and 60 µm.

4.2 Ultra-fine Grinding

A representative sample was taken from each zone after homogenization and subjected to ultrafine grinding. The results can be seen for the Upper Zone in Figure 4.3 and Figure 4.4. The kinetic results show the grain size curve shifting to the left (finer) from the feed on the right. The P80 at 30 kWh/t was 8 µm for the Upper Zone sample.

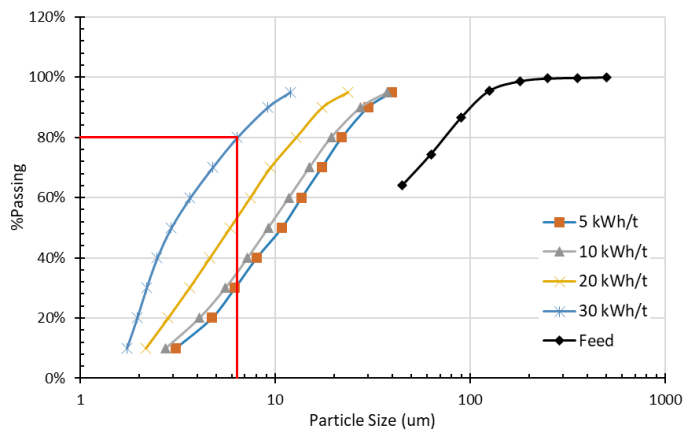


Figure 4.1 Particle size distribution after ultrafine grinding of the Upper Zone sample at different specific energies 5, 10, 20 y 30 kWh/t

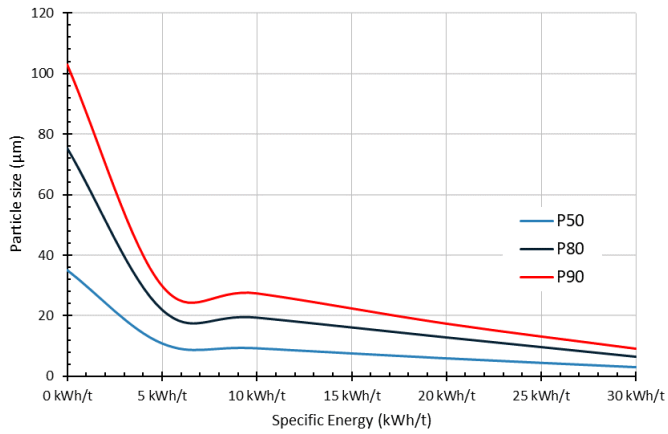


Figure 4.2 Particle size product after ultrafine grinding (P50, P80 and P90) of the concentrate of the Upper Zone relative to specific energy consumption

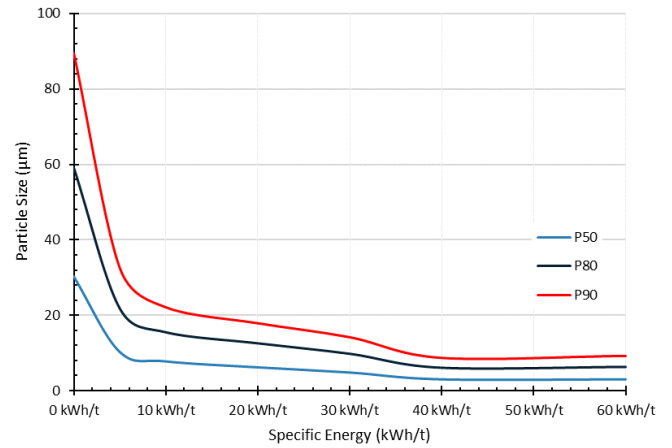


Figure 4.4 Particle size product after ultrafine grinding (P50, P80 and P90) of the concentrate of the Lower Zone relative to specific energy consumption

Figure 4.3 shows the grinding kinetics where the displacement of the granulometric curve from the feed on the right to the left (greater power applied) is observed. The P80 at 60 kWh/t was about 8 µm. Greater energy was needed to obtain a granulometry close to the Upper Zone. This energy demand is due to the higher content of Arsenic (presence of arsenopyrite) which is less hard than pyrite.

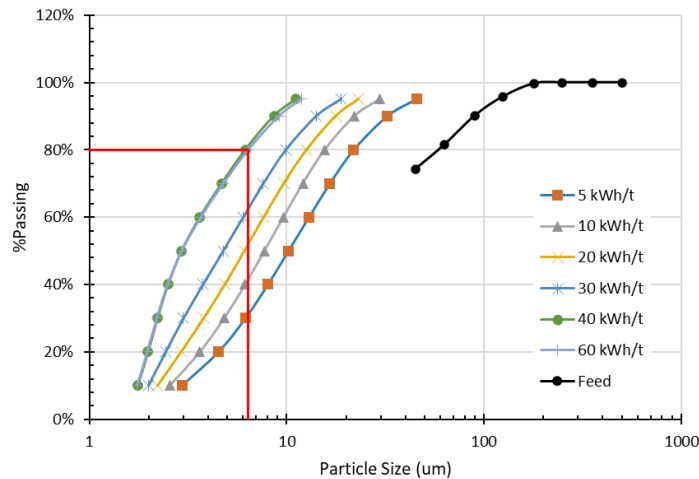


Figure 4.3 Particle size distribution after ultrafine grinding of the Lower Zone sample at different specific energies 5, 10, 20 y 30 kWh/t

4.3 Atmospheric Leaching

The results of the atmospheric leaching show that for a sample from the Upper Zone produced by grinding with 30 kWh/t, the highest oxidation of 83% was obtained at pH 4.4, as can be seen in Figure 4.5.

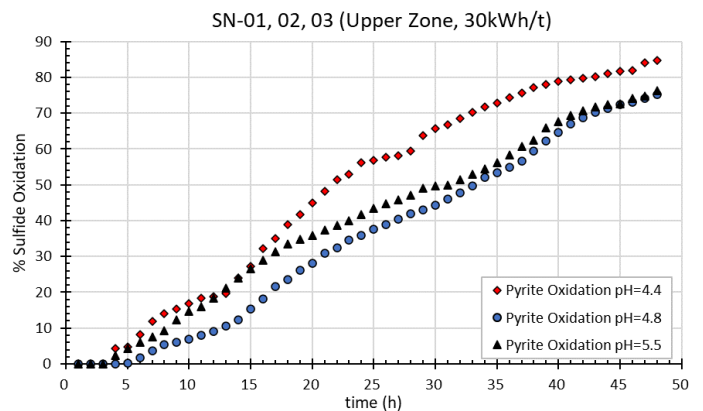


Figure 4.5 Sulfide oxidation of the Upper Zone sample at pH 4.4, 4.8 and 5.5 at 30kWh/t

Figure 4.6 shows that for a milled product at 30 kWh/t from the Lower Zone sample the maximum oxidation with Sulfur Oxidation from Upper Zone sample at pH 4.4, 4.8 and 5.5 at 30kWh/t a value of 64% at pH 4.8 . Due to this low oxidation, new tests were carried out at higher grinding power.

Figure 4.7 shows the oxidation of the Lower Zone sample product of grinding at 60 kWh/t. Only pH 4.8 and 5.5 were chosen because at 30 kWh/t the greatest oxidation was obtained at pH 4.8 followed by 5.5. Sulfur oxidation was indistinct at both pHs with a value of 85%

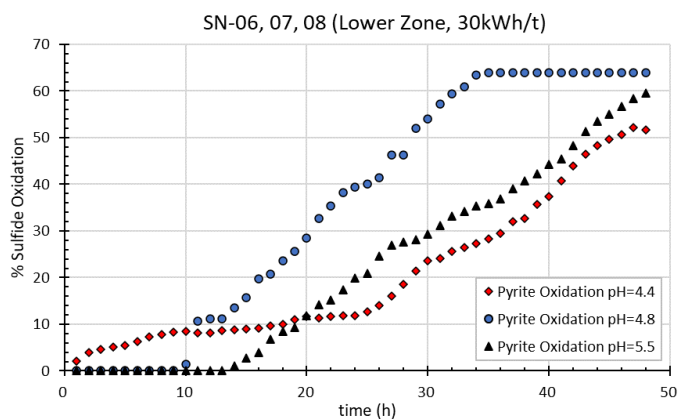


Figure 4.6 Sulfide oxidation of the Lower Zone sample at pH 4.4, 4.8 and 5.5 at 30kWh/t

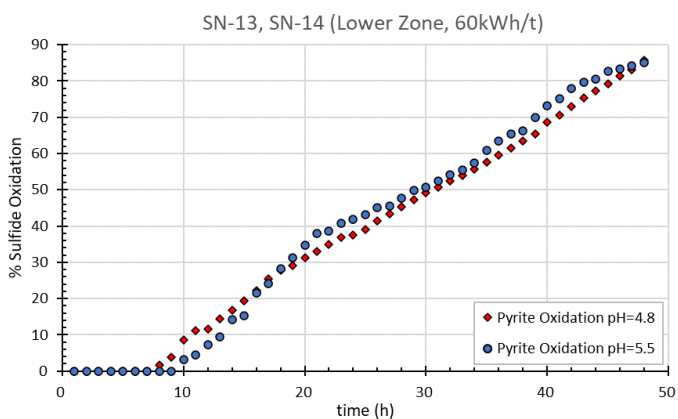


Figure 4.7 Sulfide oxidation of the Lower Zone sample at pH 4.8 and 5.5 at 60kWh/t

4.4 Carbon in Leach

Figure 4.8 below shows the CIL results for Salave Upper Zone concentrate after atmospheric leaching at pH 4.4, 4.8 and 5.5 after grinding at 30 kWh/t, where the highest recovery was obtained after atmospheric leaching at pH 4.4 with a value of 96%. These recoveries are confirmed after the chemical analysis carried out on the feed to the CIL processes and the discharge or CIL tails, as can be seen in the gray-colored bars and black bars, respectively.

Additionally, Figure 4.8 shows a comparison with samples of concentrate without atmospheric oxidation that have CIL recovery of 35% gold at P80 of 75 µm and after performing ultrafine grinding with 30 kWh/t and applying CIL, 50% gold recovery is obtained. These last two tests confirm that the Salave Upper Zone samples require a pyrite and arsenopyrite oxidation process to extract the gold contained in these samples.

Figure 4.9 shows a comparison of CIL tests on Salave Lower Zone samples produced by atmospheric oxidation at pH 4.4, 4.8 and 5.5 after applying 30 and 60 kWh/t in the mill. The best gold recovery was obtained in CIL after atmospheric leaching at pH 5.5 after grinding at 30kWh/t with a value of 86%. The CIL

recovery results are highly favored after applying atmospheric oxidation at pH 4.8 and grinding at 60 kWh/t with a value of 95% gold recovery.

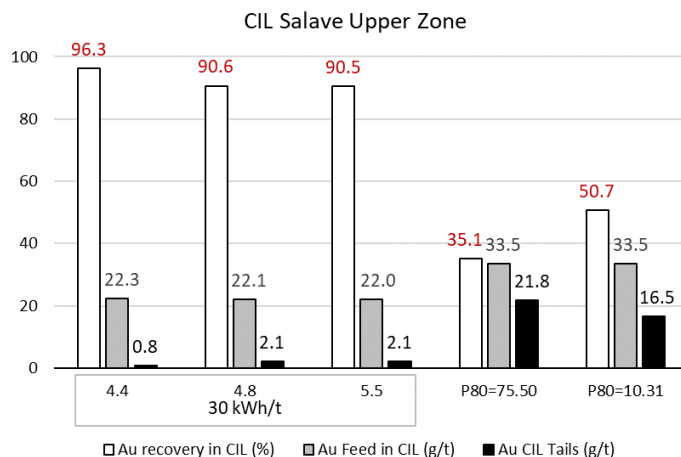


Figure 4.8 Comparison of CIL recoveries of atmospheric oxidation products (after 30kWh/t) at different pHs as well as direct CIL of the concentrate (P₈₀=75.5 µm) and CIL of ultrafine (P₈₀=10.3 µm) at 30 kWh/t

Additionally, Figure 4.9 shows the importance of oxidizing pyrite/arsenopyrite to release the fine gold contained within them. Thus, the CIL gold recovery of the concentrate at a P80 of 59 µm is 41%. Gold recovery of 38% was obtained after grinding the sample at 30 kWh/t and subjecting it to CIL.

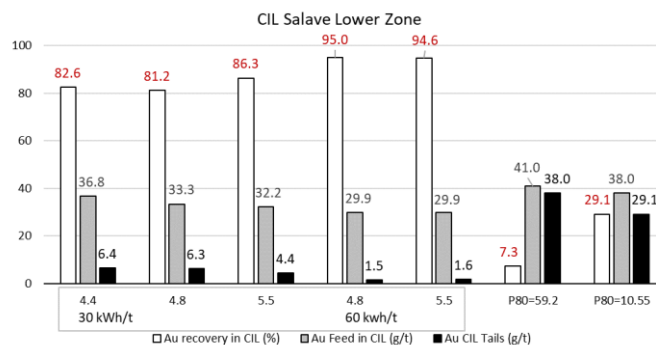


Figure 4.9 Comparison of CIL recoveries of atmospheric oxidation products (after 30 and 60 kWh/t) at different pHs as well as direct CIL of the concentrate (P₈₀=60 µm) and CIL of ultrafine (P₈₀=10.5 µm) at 30 kWh/t

Next, Figure 4.10 presents the oxidation of sulfur (lead-colored bars) and the CIL recovery after oxidation of the grinding product at 30 kWh/t for the Salave Upper Zone sample, where it can be seen that the release or oxidation is consistent with the CIL gold recoveries

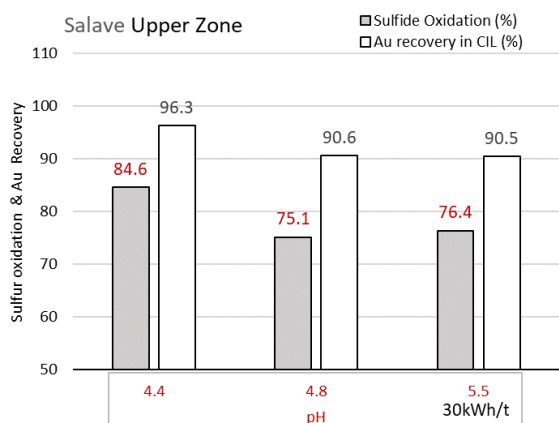


Figure 4.10 Sulfide oxidation Oxidación de azufre a diferentes pH y Au recuperación CIL a 30 kWh/t Upper Zone

Finally, Figure 4.11 shows the oxidation of sulfur and CIL recovery after atmospheric at different pH and at 30 and 60 kWh/t applied in grinding prior to atmospheric oxidation in the Salave Lower Zone sample. In this figure it can be seen that the oxidation of the grinding product at 30 kWh/t at pH 4.8 and are high compared to pH 5.5; however, the CIL recovery of gold does not agree, because the high arsenopyrite of 9% softer than pyrite did not allow greater size reduction, for which it is believed that it has formed a passivating layer to atmospheric oxidation pH 4.4. at 60 kWh/t there is a very valid correlation of sulfur oxidation and gold recovery during CIL.

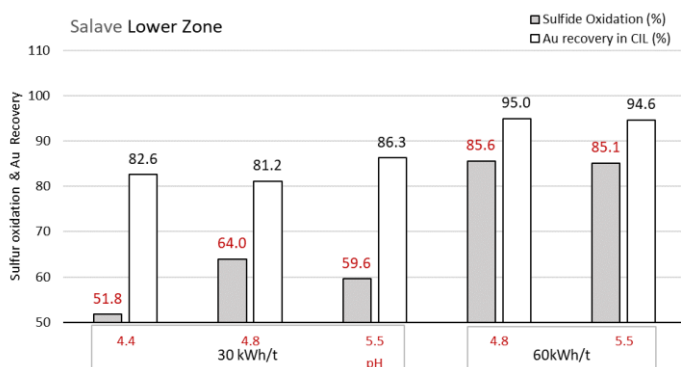


Figure 4.11 Oxidation from sulfur to differences pH and Au recuperation CIL a 30 y 60 kWh/t samples Lower Zone

Table 4.2 Summary of conditions of atmospheric leaching conditions, sulfide oxidation results and gold CIL recoveries

Sample	Test	Specific energy (kWh/t)	Atmospheric leaching pH	Sulfide Oxidation (%)	Au Recovery in CIL (%)
Upper Zone	SN-01	30	4.4	84.6	96.3
	SN-02	30	4.8	75.1	90.6
	SN-03	30	5.5	76.4	90.5
	SN-04	-	P80=75.50	-	35.0
	SN-05	30	P80=10.31	-	50.0
Lower Zone	SN-06	30	4.4	51.8	82.6
	SN-07	30	4.8	64.0	81.2
	SN-08	30	5.5	59.6	86.3
	SN-13	60	4.8	85.6	95.0
	SN-14	60	5.5	85.1	94.6
SN-09	-	P80=59.2	0.0	7.0	
SN-10	30	P80=10.55	0.0	29.0	

5 Conclusions

Table 4.2 summarizes the results of the principal conditions. In conclusion, after performing several tests of ultrafine-grinding, atmospheric oxidation and CIL, it was found that the following results:

The optimal extraction of gold from the Salave Upper Zone is applying ultrafine-grinding with 30 kWh/t, accompanied by an atmospheric oxidation at pH 4.4 (10% solids) using as neutralizing agent $\text{CaCO}_3/\text{Na}_2\text{CO}_3$ in a ratio 90/10 with 48 hours of residence and CIL at pH 11 (30% solids), with 700 ppm free cyanide, 30 g/L activated carbon and a residence time of 30 hours.

The best gold extraction conditions for the Salave Lower Zone sample were found by applying 60 kWh/t for ultrafine-grinding, followed by atmospheric oxidation at pH 4.8 (10% solids), with a neutralizing agent ratio of 90/10 of $\text{CaCO}_3/\text{Na}_2\text{CO}_3$ with 48 hours residence time and finally the CIL step at 30% solids with pH 11, at 700 ppm free cyanide, 30 g/L activated carbon and 30 hours residence time.

Acknowledgment

I appreciate the Envirogold lab facility very much for the instrumental and analytical support during the testing and the guidance of Dean Young for the ultrafine grinding and atmospheric oxidation technology support. Thanks to Diana Florez for the long hours testing carried out at Envirogold in the Dominican Republic.

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