

ALKALINE SULFIDE RECOVERY OF GOLD UTILIZING NITROGEN SPECIES CATALYZED PRESSURE LEACHING

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Abstract

Over the past 15 years, numerous pressure oxidation plants for pretreatment of gold ores and concentrates have been installed throughout the world. While this technology is now established, it suffers in terms of the complex engineering and operational characteristics inherent in utilization of high temperatures (i.e. up to 225°C) and high pressures (i.e. > 3000 kPag). This paper outlines the application of an industrially proven pressure leaching methodology utilizing nitrogen species catalyzed pressure leaching and alkaline sulfide gold leaching. As such, it stands as an economic and engineering advancement in pressure leaching and non-cyanide treatment of gold ores and concentrates. In particular, the technology offers significant technical and economic advantages over traditional pressure oxidation and cyanide gold recovery in the treatment of gold bearing chalcopyrite ores and concentrates. An example of this will application will be delineated in this paper.

Introduction

The use of nitric acid in metal sulfide oxidation is not new. Many derivations of the technology have been researched and piloted [1,2,3,4]. However, as noted in Table I only the nitrogen species catalyzed (NSC) acid pressure leach has ever been built and operated successfully on an industrial scale [3]. Table II illustrates the comparative operating criteria for these technologies as well as some selected conventional pressure oxidation gold plants. As seen, NSC is advantageous over that others in that it is faster, uses lower temperatures, uses lower pressures, uses a small amount of nitrogen species regenerated in-situ and uses unlined 316L stainless steel autoclave.

Table I. -Nitrogen Species Pressure Leaching Historical Record

Process Name	Industrial Application	Operation	Other Applications
NSC	Ag, Cu	11 Years	PGM's, Au, Ni, Co, Zn
REDOX	Au	Pilot 1 Year	None
NITROX	None	None	Au

Table II.-Comparative Nitrogen Species Catalyzed and Selected Conventional Acid Pressure Leaching Gold Plant Operating Criteria

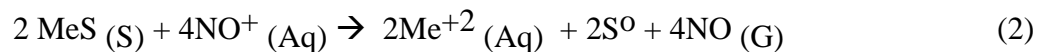
Name	Process Temperature	Process Pressure	Nitrogen Species Concentration	Nitrogen Species Regeneration Process	Nitrogen Species Residence Time,min	Materials of Construction
NSC	125-170 ^o C	625-975 kPag	2-3 g/L	In-situ	15-45	Stainless steel
REDOX	85-95 ^o C	Atmospheric	140-180 g/L	External	60	Titanium
REDOX	195-210 ^o C	1950 kPag	70-110 g/L	External	15	Titanium
NITROX	85-95 ^o C	Atmospheric	100-150 g/L	External	60	Stainless steel
McGlaughlin	180 ^o C	2200 kPag	None just O ₂	None just O ₂	90	Lead/ acid brick
Sao Bento	190 ^o C	1600 kPag	None just O ₂	None just O ₂	120	Lead/ acid brick
Goldstrike	225 ^o C	3000 kPag	None just O ₂	None just O ₂	75	Lead/ acid brick
Getchell	210 ^o C	3200 kPag	None just O ₂	None just O ₂	90	Lead/ acid brick

Fundamentals of Nitrogen Species Catalyzed Pressure Leaching

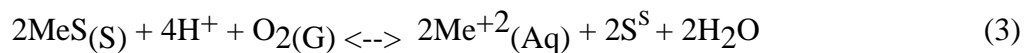
In order to understand the advantages of NSC pressure leaching, it is important to review the principles behind it. The commonly reported leach reaction of a sulfide mineral with nitric acid in conjunction with sulfuric acid is shown below:



However, it is postulated that the actual reaction species is NO⁺ and not NO₃⁻. The addition of, or presence of, NO₂⁻ instead of NO₃⁻ accelerates the formation of NO⁺ [4-6]. As seen in Table III [7], the NO⁺/NO couple is capable of an extremely high redox potential of about 1.45 V relative to hydrogen. The NO⁺ then reacts with the mineral and oxidizes the sulfide to sulfur.



Since the nitrosyl ion is continuously regenerated, its role in the overall reaction as the actual oxidizer is not obvious. The net overall reaction has the sulfide mineral reacting with the acid solution and oxygen to solubilize the metal value into the sulfate solution and form elemental sulfur (at low temperatures and/or low nitrogen species concentrations):



or sulfate (at high temperatures and/or high nitrogen species concentrations):

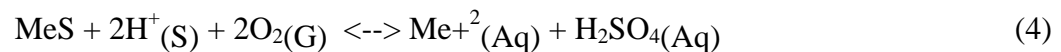
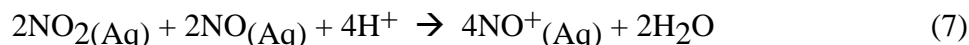
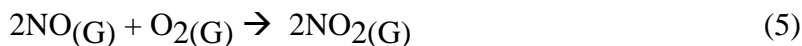


Table III.-Relative Potentials of Hydrometallurgical Oxidizers [7]

Oxidant	Redox Equation	E^0_H (pH = 0, H ₂ ref.)
Fe ⁺³	Fe ⁺³ + e ⁻ → Fe ⁺²	0.770 V
HNO ₃	NO ₃ ⁻ + 4H ⁺ + 3e ⁻ → NO(g) + 2H ₂ O	0.957 V
HNO ₂	NO ₂ ⁻ + 2H ⁺ + e ⁻ → NO(g) + H ₂ O	1.202 V
O ₂ (g)	O ₂ + 4H ⁺ + 4e ⁻ → 2H ₂ O	1.230 V
Cl ₂ (g)	Cl ₂ (g) + 2e ⁻ → 2 Cl ⁻	1.358 V
NO ⁺	NO ⁺ + e ⁻ → NO(g)	1.450 V

As can be seen, nitric oxide gas, NO, is produced from the oxidation of sulfides. As this gas has a limited solubility in aqueous solutions, it tends to transfer out of solution. The nitric oxide gas emanating from the leach slurry accumulates in the headspace of the reactor where it reacts with the supplied oxygen to form nitrogen dioxide gas, which reacts further to regenerate.



Overall, the nitrogen intermediates serve as an expedient means to transport oxygen to the surface of the solid particle and allow the resulting reaction to take place at a heightened redox potential. Complete oxidation of sulfide to sulfate can be achieved without the excessive conditions found in other pressure leach systems.

NSC Application to a Gold Concentrate

An example of the NSC complete sulfide oxidation process application to gold is listed in Tables IV, V and VI. In this case, the sulfides are completely oxidized to sulfate due to high temperatures and long leaching times used. The gold is recovered via conventional carbon in leach cyanidation of the leached solids.

Table IV.-Assay of Gold Concentrate Treated With Complete NSC Sulfide Oxidation

Gold = 35 g/T	Iron = 25.0%
Arsenic = 6.31 %	Total Sulfur = 24.0%

Table V.-NSC Complete Sulfide Oxidation Leach Conditions

Initial Free Sulfuric Acid = 20 g/L
 Reactor Working Pressure = 975 kPag
 Slurry Solids Content = 100 g/L
 Solids Size = 80 % minus 10 micron
 Maximum Temperature = 170 °C
 Nitrogen Species Concentration = 2.0 g/L
 Reaction Time = 45 minutes

Table VI.-CIL Gold Recovery From NSC Complete Sulfide Oxidation

CIL Au recovery = 94.2 %

Fundamentals and Applications of Alkaline Sulfide Gold Recovery.

Another potential methodology with this technology is the partial oxidation of the sulfide to elemental sulfur instead of sulfate. In this case, a lower temperature is used and subsequently less oxygen is consumed. As currently experienced in other industrial systems, the majority of the gold tends to accumulate in the elemental sulfur that is produced [8-10]. As practiced in industry, this product can be readily screened or floated away from the other leached solids. Then, the gold can be leached via alkaline sulfide lixiviation whereby the sulfur containing the gold is dissolved in an alkaline solution. To better illustrate this, Figure 1 [11] shows the equilibrium sulfur system while Figure 2 [12] shows the meta stable species sulfur system. In reality, the species shown in Figure 2. dominate as the alkaline sulfide system is slow to reach equilibrium .

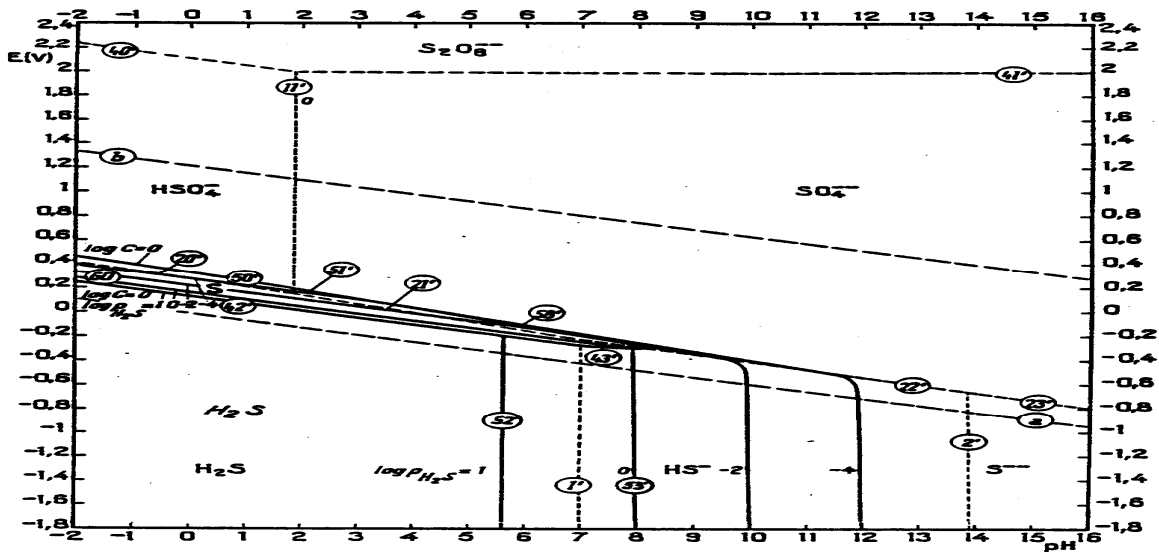


Figure 1: Equilibrium Eh-pH diagram for Sulfur.

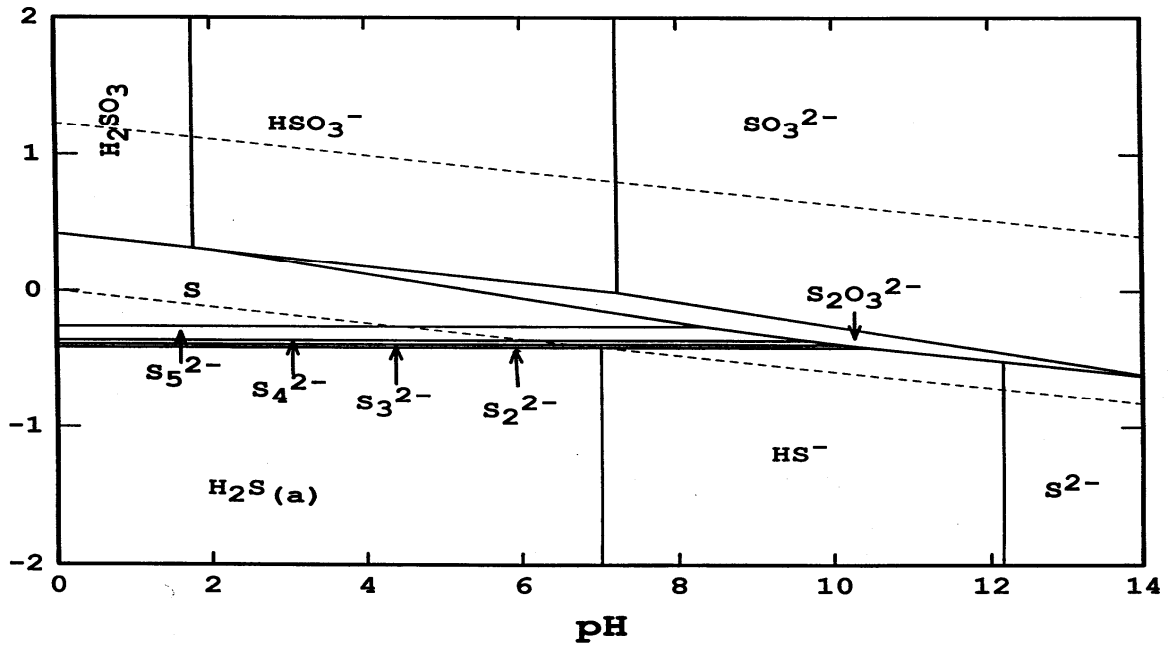
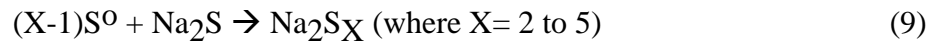
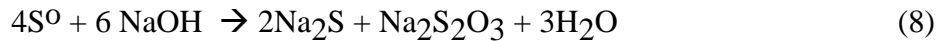
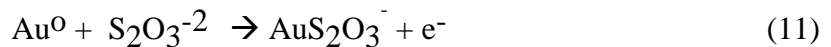


Figure 2: Meta-stable Eh-pH diagram for Sulfur.

The combination of sodium hydroxide and elemental sulfur results in the formation of species other than just sulfide (S^{2-}). Both sodium polysulfide (Na_2S_X) and sodium thiosulfate ($Na_2S_2O_3$) are created along with sulfide. This illustrated simplistically in the following scenario:



Initially gold lixiviation was thought to be the result of leaching by polysulfides and thiosulfates:



Currently, collaborative studies between The Department of Chemical Engineering at Monash University in Australia and the Center for Advanced Mineral and Metallurgical Processing are underway on the actual kinetics and mechanism of the alkaline sulfide system [13,14]. A rotating electrochemical quartz crystal microbalance (REQCM) is being utilized to study the system. The current work, as shown in Figure 3., suggests that complexation of gold may be by sulfide after oxidation by polysulfide [15].

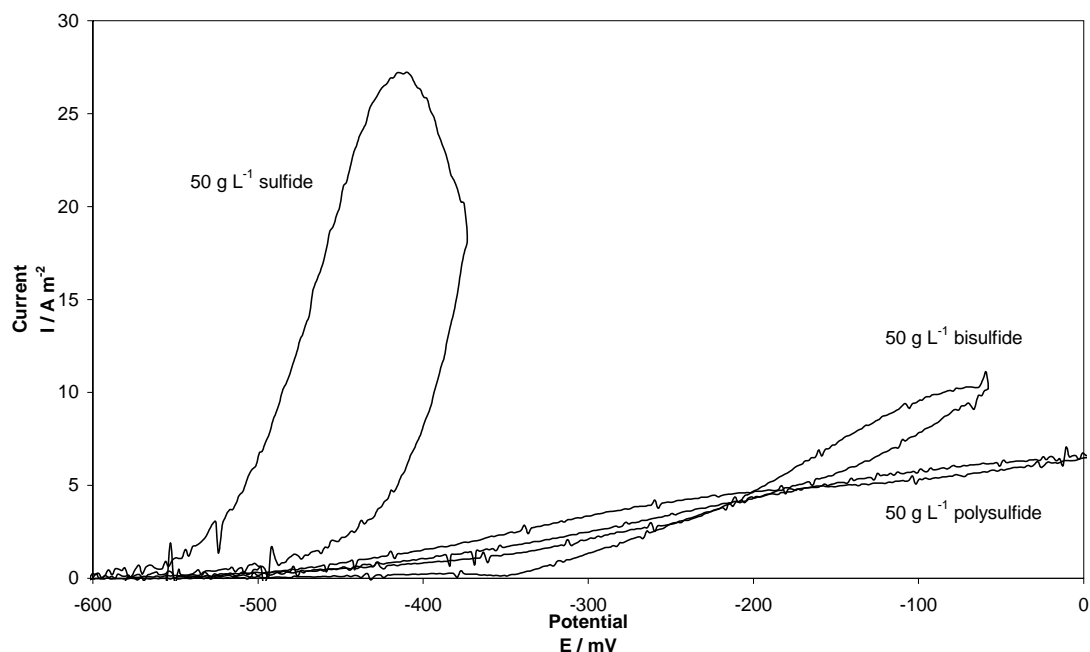


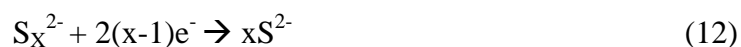
Figure 3: REQM Reverse potential sweeps and calculated current for potential lixiviants at a concentration of 50 g L^{-1} and at a temperature of 30°C

Figure 3 shows a comparison of sulfide, bisulfide and polysulfide as potential lixiviants for the alkaline sulfide system. The large calculated current for sulfide in comparison to those of bisulfide and polysulfide, suggests that sulfide is the dominant lixiviant of the system, and that bisulfide and polysulfide are poor lixiviants. The actual leaching occurring in the polysulfide and bisulfide system may be attributable to the presence of some sulfide in equilibrium with the bisulfide and polysulfide. A number of ligands form stable compound with the aurous cations, including sulfide and bisulfide. From the data below it can be seen that sulfide forms a more stable complex with gold than bisulfide as shown by the larger stability constant, confirming what was seen experimentally.

Table VII.-Stability Constants and Standard Reduction Potentials for Sulfur Containing Gold Complexes

Complex	β	Reaction	E^0 / mV
AuS^-	2×10^{36}	$\text{AuS}^- + e^- \rightarrow \text{Au} + \text{S}^{2-}$	- 460
$\text{Au}(\text{HS})_2^-$	1.3×10^{30}	$\text{Au}(\text{HS})_2^- + e^- \rightarrow \text{Au} + 2\text{HS}^-$	- 90

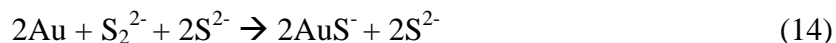
Thus, the reduction of polysulfide when acting as an oxidizer may be represented by the below half reaction:



For a polysulfide with x equals 2:



Thus, assuming that sulfide is the complexing lixiviant and polysulfide (S_2^{2-}) the oxidant, the overall reaction can be written as:



Gold leached by the alkaline sulfide system is readily recoverable by several means including electrowinning, gaseous precipitation, chemical precipitation, cementation, solvent extraction and ion exchange. The use of electrowinning for recovery of gold leached in alkaline sulfide solutions is illustrated in Table VIII.

Table VIII.-Gold Electrowinning Recovery from Alkaline Sulfide Solutions

Initial Gold Tenor in Solution = 0.983 g/L
Initial Total Sulfur in Solution = 52.3 g/L
Initial Free Hydroxide in Solution = 15 g/L
Cathode Current Density = 600 A/m ²
Anode Current Density = 1000 A/m ²
Voltage = 4.1 Volts
Final Gold Tenor in Solution = 0.010 g/L
Gold Recovery = 99.0 %
Current Efficiency = 47.3 %

Further, a novel gold recovery method has been adopted to quantitatively and selectively recover leached gold from complex alkaline sulfide solutions. This is illustrated by selectively removing gold from an alkaline sulfide leach solution containing impurities such as Hg, As, Sb and Sn, which are the only other possible elements soluble in this lixiviant. The assay of the solution tested is shown in Table IX and the assays of the final products are shown in Table X. The overall results are presented in Table XI.

Table IX.-Alkaline Sulfide Gold Leach Head Solution Assay

Volume L	Au	Sb	As	Hg	Sn
0.5	88.7 ppm	21.0 g/L	5.31 g/L	274 ppm	1.84 g/L

Table X.-Alkaline Sulfide Gold Solution Final Assay

Volume, L	Au	Sb	As	Hg	Sn
0.5	1.5 ppm	21.1 g/L	5.21 g/L	274 ppm	1.89 g/L

Final Au Solid Sorbent Assay = 1561.4 g/T

Table XI.-Overall Gold Selectivity and Recovery

	<u>Liquid</u>	<u>Solid</u>
Gold	1.7%	98.3%
Antimony	100.0%	0.0%
Arsenic	100.0%	0.0%
Tin	100.0%	0.0%
Mercury	100.0%	0.0%

Finally the alkaline sulfide solutions, which are barren of gold, can be recycled for further gold leaching or further processed with low temperature oxidation to sodium sulfate, Na₂SO₄. This has been routinely practiced in industry [16]. The resultant sodium sulfate is further treated by purification and crystallization to produce high grade, marketable sodium sulfate. This process is illustrated simplistically in the following scenario:



This versatile and environmentally benign chemical is then sold and utilized in industries such as pulp and paper, glass, ceramics, detergents, mineral feed supplements, textile dyes, bleach and photography. As such, there are no environmental or toxicological issues in the use of alkaline sulfide gold recovery because the waste products become value-added, marketable by-products.

An example of this application of partial oxidation of a gold concentrate by NSC is illustrated in Tables XII, XIII and XIV.

Table XII.-Gold Concentrate Treated With Partial NSC Sulfide Oxidation

Gold = 35 g/T	Iron = 25.0 %
Arsenic = 6.31 %	Total Sulfur = 24.0 %

Table XIII.-Nitrogen Species Catalyzed Partial Sulfide Oxidation Leach Conditions

Initial Free Sulfuric Acid = 50 g/L
Reactor Working Pressure = 620 kPag
Slurry Solids Content = 100 g/L
Solids Size = 80 % minus 10 micron
Maximum Temperature = 125° C
Nitrogen Species Concentration = 2.0 g/L
Reaction Time = 30 minutes

Table XIV.-Alkaline Sulfide Recovery With NSC Partial Sulfide Oxidation

Alkaline Sulfide Au Leach Recovery = 93.3 %

Moreover, NSC partial sulfide oxidation pressure leaching followed by alkaline sulfide gold leaching and recovery is an advantageous application for treatment of copper sulfide gold ores and concentrates. First of all, primary sulfide copper ores and concentrates such as chalcopyrite can be effectively treated at low temperatures and pressures. Then, the sulfur produced can be used to directly leach and recover the gold. This is particularly advantageous in that it avoids the large reagent consumptions found when treating copper ores and concentrates with cyanide. The following example illustrates the treatment of a gold bearing chalcopyrite ore [17].

500 tonnes per day of a gold bearing chalcopyrite ore has been proposed to be treated by NSC partial sulfide oxidation pressure leaching followed by SX-EW production of copper. The gold will be recovered via alkaline sulfide leaching followed by electrowinning. Table XV illustrates the plant conditions utilized while Table XVI shows result of NSC partial sulfide oxidation on the chalcopyrite concentrate. Table XVII delineates the site-specific economics of the application for treatment of the chalcopyrite ore. Figure 4 illustrates the proposed flowsheet. A key aspect here is to minimize sulfide oxidation to elemental sulfur. This minimizes oxygen consumption, reduces in-situ acid production and the closed circuit process causes in-situ iron precipitation. This limits the amount of iron and acid build up in the process circuit thereby by limiting amount of the circuit impurity bleed stream. As well, the elemental sulfur produced, acts as a non-cyanide lixiviant for gold in the alkaline sulfide recovery system. Another key aspect is that the solutions recycled do not buildup nitrates or nitrites, which could be damaging to the solvent extraction reagents. Continuous closed circuit testing and analysis of the flowsheet has consistently shown both nitrogen species solution concentrations of less than 0.1 ppm. Thus, by in-situ methods, the closed circuit NSC system does not allow any buildup of nitrogen species in the recycled solutions, which may be harmful.

Table XV.-Nitrogen Species Catalyzed Partial Oxidation Leach Conditions with In-Situ Iron Precipitation

Initial Free Sulfuric Acid = 15 g/L
Reactor Working Pressure = 620 kPag
Slurry Solids Content = 100 g/L
Solids Size = 80% -10 micron
Maximum Temperature = 125° C
Nitrogen Species Concentration = 2.0 g/L

**Table XVI.-Summary of Nitrogen Species
Catalyzed Partial Oxidation Leach**

Composition of Chalcopyrite Ore				
	Cu, %	Fe, %	Total S, %	Au, g/T
	3.2	4.1	5.7	11.0
NSC Partial Oxidation Leach Elemental Distribution				
	Cu, %	Fe, %	Total S, %	Au, %
Solution	99.0	8.3	3.4	0.0
Residue	1.0	91.7	96.6	100.0

Both sulfuric acid generation and iron dissolution are minimized along with production of elemental sulfur to be utilized in non-cyanide gold recovery.

Alkaline Sulfide Gold Leaching with Electrowinning Recovery = 93.1 %

**Table XVII.-Summary of Site Specific Economics for NSC
Partial Oxidation of a Gold Bearing Chalcopyrite Ore**

NSC Chalcopyrite Ore Partial Oxidation Cost = \$ 3,500,000.00 USD

NSC Chalcopyrite Partial Oxidation Operating Cost = \$0.056 USD/lb Cu or \$ 0.36 USD/g Au

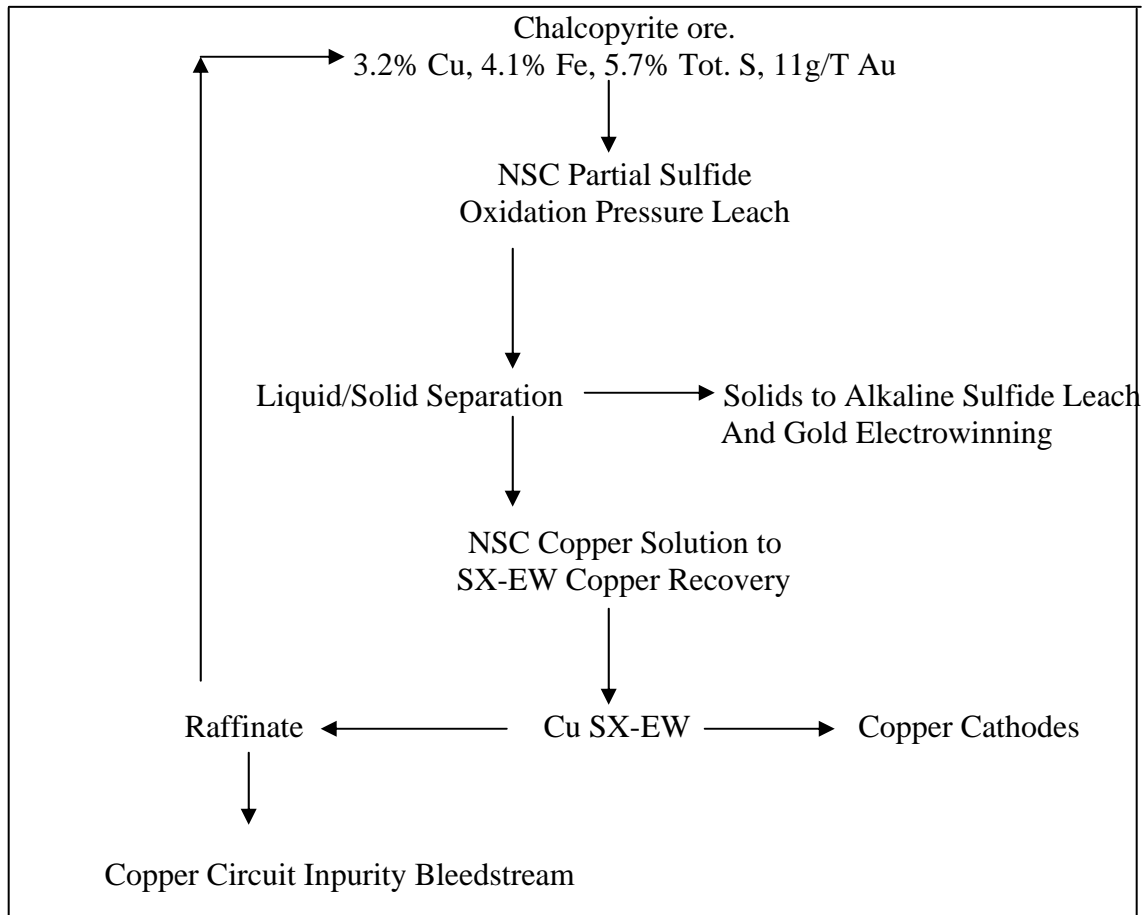


Figure 4: Flowsheet of NSC Partial Sulfide Oxidation of a Gold Bearing Chalcopyrite Ore

Moreover, the relative economics of the NSC pressure oxidation methodologies are better than that of conventional pressure leaching. This is illustrated by an order of magnitude economic analysis of various pressure oxidation pretreatment options subject to the following:

- The treated material is of the quality listed in Tables IV and XII.
- The plant is located in the Western United States treating 250 tonnes per day
- The costs include all normal unit operations involved in pressure leaching.

Operating costs are expressed as dollars per % contained sulfide in the concentrate being oxidized. Based on this, the order of magnitude capital and operating costs for NSC compared to conventional pressure leaching are summarized in Tables XVIII and XIX.

Table XVIII.-Comparative Order of Magnitude Capital Cost Estimate

<u>Type of Process</u>	<u>USD</u>
Conventional Complete Sulfide Pressure Oxidation	\$12,500,000
Complete NSC Sulfide Oxidation Process	\$10,000,000
Partial NSC Sulfide Oxidation Process	\$ 7,500,000

Table XIX.-Comparative Order of Magnitude Operating Cost Estimate

<u>Type of Process</u>	<u>USD/% Contained Sulfide Oxidized</u>
Conventional Pressure Oxidation	\$2.75
Complete NSC Sulfide Oxidation Process	\$2.00
Partial NSC Sulfide Oxidation Process	\$1.50

Finally, the relative reagent costs of sodium cyanide versus alkaline sulfide produced from sulfur are illustrated in Table XX. This does not include the by-product revenues available when using the alkaline sulfide system or the costs associated with destruction of waste cyanide. Thus, as seen, there are significant economic incentives with the use of alkaline sulfide leaching of gold instead of cyanide. This advantage was illustrated before in the treatment of gold bearing chalcopyrite where conventional pressure leaching followed by cyanidation is far more expensive.

Table XX.-Comparative Cost of Gold Leaching Reagents

<u>Reagent Type</u>	<u>Cost</u>
Sodium Cyanide	\$ 1.00 - \$ 2.25 USD/Kg
Alkaline sulfide	\$ 0.05 - \$ 0.30 USD/Kg

Summary

In summation, the NSC pressure oxidation system offers several definitive and industrially proven advantages. First it is the only proven industrial process for pressure leaching of precious metal bearing sulfides. Second, the rate of reaction is much faster and the required reactor volume is thus smaller. Third, the process does not require excessively high temperatures or pressures. Fourth, the solution potential is extremely high so it oxidizes almost any sulfide at low oxygen overpressures. Fifth, the materials of construction are readily available stainless steels, so there is no need for titanium, cladding or brick with lead liners. Thus, the capital and maintenance costs are less. Also, because of the simpler internal design, direct heat exchange can be utilized in-situ for optimal temperature control. Further, in a manner analogous to existing Ni/Co laterite HPAL systems, the energy from the in-situ heat exchange can be readily utilized for optimizing the plant heat balance or co-generating electrical power resulting in significant process operating cost savings. Sixth, there is no need for a dip tube or special design radial agitators with cowlings. Oxygen transfer is innate with the enhanced nitrogen species chemistry. So, with no titanium, and no titanium dip tube in particular, there is much less oxygen fire danger. Seventh, the design of the feed pump system is far less of a challenge as is the flash system and the choke system. Eighth, like a smelter, precious metals recovery can be high and direct. Ninth, there are no sophisticated chloride chemistries or resultant corrosion issues to deal with. Tenth, sulfur production and materials handling is readily accomplished. Further, any elemental sulfur that is produced can be used as a cost effective lixiviant for gold production and waste streams from this can be further processed to produce value added by-product sodium sulfate. Finally, there is both a minor amount of nitrogen species utilized, which can be controlled by commercially available systems so there are no major economic or environmental issues.

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