Industrial NSC Hydrometallurgical Precious Metals Recycle

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Abstract

In the processing of many concentrates and ores such as copper, zinc, nickel and cobalt hydrometallurgical methodologies are becoming more prominent. Among these, one industrially proven pressure leaching process is Nitrogen Species Catalyzed Pressure Leaching (i.e. NSC). This technology is applicable to many concentrates and ores. As well, it has been used on an industrial scale for the recycle of base and precious metals. This paper outlines the fundamentals and actual industrial application of this technology to the industrial recovery and recycle of precious metals.

Keywords: Precious metals; Recycle; Nitric acid; Nitrogen species; Hydrometallurgy; Pressure oxidation

Introduction

The use of nitric acid in metal sulfide oxidation is not new. Many derivations of the technology have been researched and piloted for applications such as copper, nickel and precious metals. Again, as noted in Table 1, and as specifically applied to copper concentrates and precious metals, only the nitrogen species catalyzed (NSC) acid pressure leach has ever been built and operated successfully on an industrial scale [1].

The NSC pressure oxidation system offers several definitive and industrially proven advantages. First of all it is the only proven industrial process over the long term for pressure leaching of precious metal bearing sulfides and can be used to partially or fully oxidize the contained sulfide. Second, the rate of reaction is much faster and subsequent required reactor volume is thus smaller. Third, the process does not require excessively high temperatures or pressures. Fourth, the ORP 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 and the like. 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 an 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 and any sulfur produced is effectively utilized as both a gold lixiviant and ultimately as a value added by-product so there are no major economic or environmental issues.

Industrial NSC Plant Operation

Nitrogen species catalyzed pressure leaching was first industrially applied almost 20 years ago. Thus a brief synopsis of the industrial facilities present at that site is in order. These industrial operations, and their inherent applications, have been the direct subject of several other publications [2-6]. Therefore, in depth detail will not be covered in this discussion.

First started in 1984, this patented nitrogen species catalyzed pressure leach was the only commercial operation of its type in the world [7]. In essence, it was a low pressure and temperature leaching operation relying on a small amount of nitrogen species as an oxidizer. In this process, the nitrogen species facilitate the oxidation of sulfides and metals. This results in the solubilization of silver, copper, iron and other less noble metals. If noble metals such as gold and platinum are present in the concentrate, they are not dissolved and tend to remain in the solid phases such as sulfur [8-10]. The typical precious metals bearing copper

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

Table 1: Nitrogen species pressure leaching technology historical record.

Product Type	Ag, g/Tonne	Cu, %	Sb, %
Refinery Feed	43,000	24.0	0.5

Table 2: Typical composition of NSC plant copper concentrate.

concentrate feed assay is listed in Table 2 and the operating leach conditions used are presented in Table 3.

The key to the process is the leach reaction mechanism. Its unique characteristic is the use of relatively low levels (i.e. 2 to 3 g/L) of nitrogen species and their continuous in-situ regeneration. Besides greatly enhancing the kinetics of the reaction, a much higher redox potential occurs in reaction with the sulfide than would be realized with oxygen pressure alone.

Originally, nitric acid was used as the oxidizer, but in-house research efforts determined that sodium nitrite was superior [11]. Recent work by other researchers has verified this [12]. The commonly reported leach reaction with nitric acid is shown below.

It is now postulated that the actual reaction species is NO^+ and not NO_3^- . The addition of NO_2^- instead of NO_3^- accelerates the formation of NO^+ . NO^+ is readily formed from nitrous rather than nitric acid. A convenient source of nitrous acid is sodium nitrite. When it is added to an acidic solution, nitrous acid is readily formed.

Nitrous acid further reacts to form NO^+

The NO^+ then reacts with the mineral and oxidizes the sulfide to sulfur.

Of course, at higher temperatures and/or nitrous acid concentrations the sulfide would be fully oxidized to sulfate, an advantage when processing gold concentrates for example.

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. In the pressure leach system, a closed vessel with an oxygen overpressure is used. 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. The NO is then regenerated to NO^+ . Overall this can be viewed as:

Since the nitrogen species 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 some elemental sulfur.

As seen in Table 4 the NO^+/NO couple is capable of an extremely high redox potential of about 1.450 V relative to hydrogen.

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. In essence, the silver, copper and less noble metals are solubilized in the leach. The hot slurry is then transferred from the reactor to screening, thickening and filtration. Typical assays and mass

Leach Batch Size	18,000Liters
Initial Cupric Ion	15 g/L
Initial Free Sulfuric Acid	200 g/L
Preleach Temperature	90°C
Preleach Time	1 Hour
Reactor Working Pressure	620 kPag
Slurry Solids Content	8 - 20% by weight
Working Temperature Range	50°C to 155°C
Nitrogen Species Concentration	2.0 to 3.0 g/L

Table 3: Pressure leach plant conditions.

Oxidant	Redox Equation	E^0_{h} ($p^{\text{H}} = 0$, H_2 ref.)
Fe^{+3}	$\text{Fe}^{+3} + \text{e}^- \rightarrow \text{Fe}^{+2}$	0.770 V
HNO_3	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^- \rightarrow \text{NO}_{(g)} + 2\text{H}_2\text{O}$	0.957 V
HNO_2	$\text{NO}_2^- + 2\text{H}^+ + \text{e}^- \rightarrow \text{NO}_{(g)} + \text{H}_2\text{O}$	1.202 V
$\text{O}_{2(g)}$	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$	1.230 V
$\text{Cl}_{2(g)}$	$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.358 V
NO^+	$\text{NO}^+ + \text{e}^- \rightarrow \text{NO}_{(g)}$	1.450 V

Table 4: Relative potentials of hydrometallurgical oxidizers.

Assay	Ag	Cu	Fe	Pb	Sb	As	Zn
Solution	6 g/l	45 g/l	25 g/l	1 ppm	1 ppm	2 g/l	2 g/l
Residue	2.7%	1%	3%	35%	4%	1%	0.1%
S° Pellets	-	0.5%	1%	0.1%	0.1%	0.1%	0.1%

Table 5: Assay of nitrogen species catalyzed acid pressure oxidation plant leach products.

Assay	Ag	Cu	Fe	Pb	Sb	As	Zn
Solution	96%	99%	93%	-	-	85%	99%
Residue	4%	0.5%	6%	100%	100%	15%	1%
S° Pellets	-	0.5%	1%	-	-	-	-

Table 6: Mass distribution of nitrogen species catalyzed acid pressure oxidation plant leach products.

balances of the industrial plant leach process are illustrated in Tables 5 and 6.

The pregnant, filtered leach solution is stripped efficiently and selectively of its silver using NaCl solution to precipitate AgCl. This is illustrated as:

The solid AgCl precipitate is filtered from the pregnant solution and washed thoroughly. Then, the silver chloride is reduced by methods that are covered elsewhere in this paper. The silver is further electrorefined to a purity of 99.95%, 99.99%, or 99.999%. In 1990, bench scale testing was completed on a new process to replace metal powder reduction of silver chloride [13]. In essence, the system revolves around the use of an alkaline hydrometallurgical reduction scenario. While this concept has been tried before, this particular system is distinct in itself because it relies initially on carbonate rather than hydroxide as a source of alkalinity and because it is done on a production scale.

The reagents used in the process chemistry are soda ash and dextrose. Heating to a temperature of 85-95°C is required for completion of the reaction. The perceived reactions are:

In plant practice clean AgCl solids from the horizontal belt filter are mixed in batch in a glass-lined tank with water. The appropriate amount of dextrose is added and allowed to dissolve while the slurry mixes. Then, the soda ash is added carefully as a solid. As it dissolves and reacts, its exothermic nature provides some of the heat necessary to drive the reaction. To supplement this steam is used to bring the reaction to temperature. Essentially, if the stoichiometry is correct, the reaction is complete at this point. If necessary a platinum redox probe can be used to indicate the endpoint. From this process a high quality silver sponge of above 99% purity is readily produced.

What remains of the silver free pregnant solution contains considerable quantities of copper, iron and free sulfuric acid. To save acid, one third of this stream is recycled back to the leach area for make up solution. However, it contains a significant amount of chloride ion due to silver stripping. It is cleaned up by precipitation. This entails using some of the silver containing pregnant stream to react with the chloride ion in the recycle stream. Filtering of the contained solid AgCl leaves a liquid with a slight excess of silver in solution. This process assures that no chloride ion is transferred to the 316L stainless steel pressure leach vessels. This is important for two reasons: First, the potential for corrosion using this type of pressure vessel in chloride environments is immense. Furthermore, it insures that silver solubilization in the leach will not be inhibited by AgCl precipitation.

The other two thirds of the silver free leach solution is treated with slaked limed to reduce much of the acidity. The copper is then recovered using conventional solvent extraction and electrowinning technology. High-grade copper metal cathodes are produced.

As currently experienced in other industrial systems, gold can accumulate in the elemental sulfur that is produced [6,7,8]. 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. 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 ($\text{Na}_2\text{S}_2\text{O}_3$) are created along with sulfide. This is illustrated simplistically in the following scenario.

So, gold lixiviation is the result of leaching by polysulfides and thiosulfates.

A rotating electrochemical quartz crystal microbalance (REQCM) is being utilized to study the system. The initial work suggests that complexation of gold may be by sulfide after oxidation by polysulfide [14].

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. 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. The assay of the solution tested is shown in Table 7, and the assays of the final

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 7: Alkaline sulfide gold leach head solution 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 8: Alkaline sulfide gold solution final assay.

	Liquid	Solid
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%

Table 9: Overall gold selectivity and recovery.

products are shown in Table 8. The overall results are presented in Table 9.

Finally the alkaline sulfide solutions that are barren of gold can be recycled for further gold leaching or further processed with low temperature oxidation to sodium sulfate, Na_2SO_4 . This has been routinely practiced in industry. 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 to and utilized in industries such as pulp and paper, glass, ceramics, detergents, mineral feed supplements, textile dyes, bleach and photography. As such, there is no environmental or toxicological issue in the use of alkaline sulfide gold recovery as the waste products becomes value added, marketable by-products. As a courtesy to the reader, additional references delineating NSC and related technologies are provided [15-113].

Industrial Plant Recycle Applications

Silver Bearing Photographic Ash: In the photographic industry, silver and silver halides play a major technological role. Most of the silver utilized is recycled in some fashion. This requires burning of the film to concentrate the precious metals. Then it is generally sent to a pyrometallurgical smelter for recovery. Using NSC pressure leaching, this material was industrially blended with silver bearing copper sulfide concentrates and leached for recovery. The experimental results are presented in Tables 10 and 11.

AgCl content is first removed by reacting it with sodium sulfide as;

The resultant silver sulfide is the feed for the nitrogen species catalyzed pressure leach system and it is easily recycled back through the system.

The percentage of silver that reported to the leach solution was 96.5%. Using the plant scale technology outlined before, the silver can be processed from this solution to a final product of up to 99.999% purity.

Silver Bearing Canister Waste Materials from Film Processing: In the processing of photographic and x-ray film, many waste solutions are generated. These are treated by cementation silver using iron bearing cartridges or canisters. These are generally recycled to a pyrometallurgical facility. Using NSC pressure leaching, the material was blended with silver bearing copper sulfide concentrates and leached for recovery.

Ag	AgCl
7.9 %	1.3 %

Table 10: Silver film ash assay .

Assay	Ag	Cu	Fe
Solution	96.5%	99.90%	99.28%
Residue	3.4%	0.09%	0.67%
S° Pellets	0.1%	0.01%	0.05%

Table 11: NSC pressure oxidation recovery of combined film ash and copper concentrate.

Ag	Fe
4.1%	31.7 %

Table 12: Silver canister material assay.

Assay	Ag	Cu	Fe
Solution	94.30%	99.90%	97.22%
Residue	3.92%	0.09%	2.73%
S° Pellets	0.05%	0.01%	0.05%

Table 13: NSC pressure oxidation recovery of combined canister and copper concentrate.

Ag	Au, g/Tonne
13.1 %	141.3

Table 14: Silver Chemical Production Waste Assay.

Assay	Ag	Cu	Fe	Au
Solution	97.45%	99.90	99.28%	0.0%
Residue	2.48%	0.09%	0.67%	3.1%
S° Pellets	0.07%	0.01%	0.05%	96.9%

Table 15: NSC pressure oxidation recovery of combined silver waste and copper concentrate.

The experimental results are presented in Tables 12 and 13.

The percentage of silver that reported to the leach solution was 94.30%. Using the plant scale technology outlined before, the silver can be processed from this solution to a final product of up to 99.999% purity.

Gold and Silver Bearing Wastes from Silver Chemical Production: In the production of silver nitrate and other chemicals, solids wastes can accumulate. These often are high in both silver and gold. Using NSC pressure leaching, this material was industrially blended with silver bearing copper sulfide concentrates and leached for silver and gold recovery. The experimental results are presented in Tables 14 and 15.

The percentage of silver, which reported to the leach solution, was 97.45%. Using the plant scale technology outlined before, the silver can be processed from this solution to a final product of up to 99.999% purity. As seen previously, most of the gold reported to the sulfur pellet product. Gold could be recovered from the sulfur product utilizing alkaline sulfide gold leaching

and recovery along with value added by-product sodium sulfate technology that was illustrated in equations 14 through 21 and Tables 7, 8 and 9.

Summary

The industrial NSC pressure oxidation system was successfully utilized for recycling of secondary materials. This paper details these applications and the technologies underlying this successful undertaking.

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