

# Ammonium Thiosulfate Ecological Viable Alternative to Replace Sodium Cyanide in Gold and Silver Dissolution Ores

María del Carmen Hernández<sup>1</sup>, María del Carmen Avitia<sup>1</sup>, Heriberto Peña<sup>1</sup>, Irma Leticia Gonzalez<sup>2</sup>, Nancy Verónica Torres<sup>3</sup>, Abdiel Rosaldo Félix<sup>3</sup>, Luis Miguel Rodríguez<sup>1</sup> and Laura Bibiana Hernández<sup>4</sup>

1. Department of Chemical and Biochemical Engineering, Technological Institute of Parral, Chihuahua 33850, Mexico

2. Department of Economic Administrative Department, Technological Institute of Parral, Chihuahua 33850, Mexico

3. Department of Industrial Engineering, Technological Institute of Parral, Chihuahua 33850, Mexico

4. Engineering and Independent Consultant, Palma Triangular 108, San José de Pozo Bravo, Aguascalientes 20126, México

**Abstract:** The southern region of the state of Chihuahua is mining by origin, as this has been proved ghost towns of Minas Nuevas, it is also called Villa Escobedo, Emerald and Blue. Minerals are nonrenewable resources. There are only reserves and waste deposited in tailings ponds of low-grade precious metals (gold and silver). A conventional method for recovering gold and silver ore is low-grade cyanidation and the solvent consider toxic and highly dangerous for the flora, fauna, humans and the environment. The mechanism of cyanide poisoning is inhibition of cytochrome oxidase—an enzyme needed for cell respiration. Without compromising efficiency, sensitivity and cost of the process, the toxic solvent is replaced by a less aggressive one, which helps the environment, public and occupational health.  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  has no appreciable damage to conservative amounts, is a selective aqueous solvent for leaching gold and silver, easy to get and manipulate. This work is done in the Technological Institute of Parral in a low-grade ore from the southern region of the state of Chihuahua. This document has been enriched presented in the IMEC 2014, with the increase of series V and VI.

**Key words:** Leaching, cyanide, ammonium thiosulfate.

## 1. Introduction

The mining industry in the extraction of gold and silver has been using sodium cyanide (NaCN) in production processes for centuries. The NaCN is essential in the modern world, but its effects on health and the environment have led to the recent public reaction to the use of NaCN.

The NaCN is one of the few chemical reagents, which dissolve the gold and silver in water and has been used in extracting them by an established technology since 1887. There are two general ways to leach gold and silver from an ore by NaCN: leaching tank and percolation leaching. Tank leaching is the

conventional method by which auriferous ore is crushed and ground to reduce it to less than 1 millimeter in diameter and is leached with cyanide solution typically between 0.01% and 0.05%. Safety measures in handling such salts are meticulous. Formal policies of companies that manufacture cyanide ensure that their product is only sold to companies that have the capacity and commitment to protect workers, the public and the environment. They hire selected carriers with safety records compatible with the rules of carriage manufacturers. Mining companies store the sodium cyanide in secure areas with controlled environment like dry, fresh, dark and airy, also, the boxes are stacked over impermeable floors, usually built with concrete adequate to contain any unlikely spillover.

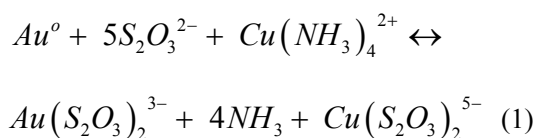
---

**Corresponding author:** María del Carmen Hernández, master, main research field: metallurgy.

Training programs are required for all employees who work with or near the cyanide. Companies have security plans and material handling in which the responsibilities to employees who control the management and use of cyanide from its arrival at the mine site and throughout the metallurgical process are assigned. Feature monitors gas area suitable protective clothing, autonomous breathing stations and first aid equipped with eyewash and showers. Toxic to 18.36 ppm causes mild symptoms after several hours, 135 ppm is fatal after 30 minutes and 270 ppm is immediately fatal [1]. The mechanism by which the cyanide causes poisoning is the inhibition of the oxidase cytochrome system, also other enzymatic systems are affected too much, but to a lesser grade.

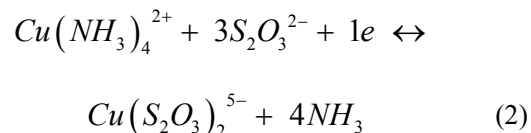
The current problematic is the replacement of sodium cyanide by ammonium thiosulfate, minimizing the toxic risk to the environment including the public and occupational health. Ammonium thiosulfate does not cause appreciable damage using conservative quantities in addition it has the benefit of being an aqueous solvent for leaching gold and silver, which selectively dissolves with high probabilities of replacing cyanide at low cost and with the conventional infrastructure.

Reaction leaching of precious metals with ammonium thiosulfate: add copper with thiosulfate and ammonia produce that the gold is dissolved quickly in comparison with the process that uses cyanide. The gold leaching is produced according to the reaction in Eq. (1) [2]:



The metallic gold is oxidized to  $Au^+$  by effect of the copper complex  $Cu(NH_3)_4^{2+}$ , then the thiosulfate ions

complexed the  $Au^+$  formed to integrate the complex  $Au(S_2O_3)_2^{3-}$ . The  $Cu(NH_3)_4^{2+}$  ( $Cu^{2+}$ ) complex in presence of  $S_2O_3^{2-}$  form the  $Cu(S_2O_3)_2^{5-}$  complex according to the reaction in Eq. (2):



## 2. Experimental Work

This paper emerges from an academic commitment to provide safe procedures to protect workers in the mining industry from the public and the environment.

It is performed in the laboratories of the Technological Institute of Parral, mainly in the metallurgy laboratory, which has equipment for mechanical preparation consisting of 2 crushers jaw, 2 cone crushers, pulverize and set of meshes from 45 U.S. (0.038 inches) to 325 U.S. (0.0017 inches) and Ro-Tap for particle size control. The study conduct the whirling in a roller table using amber bottles with acid (leaching capacity 1,000 mL) at 56 revolutions per minute.

The research used a sample of 64 kilograms which was prepared 100% passing by the mesh number 10, the granulometry of the sample is determined, including the specific gravity and the assay of gold and silver. The constants to determine the process of cyanide were probable consumption of lime, grinding, protector alkali, pulp dilution, cyanide concentration and stirring time. It was taken as basis of the procedure to determine the parameters in the process of cyanidation developed by David, C. C. [3], which method consist in determining one variable at time. The constants show in Table 1.

To control the cyanidation process, valuations are made of cyanide and free calcium oxide with silver

**Table 1 Constants determined for cyanidation.**

Probable consumption of lime	Grinding (mesh)	Alkali protector (%) CaO	Dilution water: ore	Cyanide concentration		Time stirring (h)	Recovery (%)
				(%) CN	g/t		
0.026 g/T	100% a-100	0.10	2:1	0.15	1,060	48	37.2

nitrate and oxalic acid, respectively, using phenolphthalein as an indicator in the case of CaO. To facilitate the process, the solutions were precipitated using zinc powder and lead acetate, melting the precipitated sample through a basic flux mixture.

Based on the results, cyanidation proceeded to design tests for ammonium thiosulfate. To which some patents and related studies were reviewed sodium thiosulfate [4-10].

The ammonium thiosulfate is used in solution with a concentration of 56%, yellow and with a density of 1.32 grams per cubic centimeter. For the first series,

200 g of sample were used. The activator of copper sulfate was used in a 1:1 with ammonium thiosulfate. Dilution pulp was 2:1 (Table 2).

In the second series, the influence of pH was considered, the concentration of ammonium thiosulfate and copper sulfate maintain constant leaching time 3 hours (Table 3).

In the third series of tests, it is considered the influence of the agitation, the particle size and time, keeping the pH constant at 10, ammonium hydroxide and the sample at 200 grams and dilution of 2:1 per bottle (Table 4).

**Table 2 Test conditions ammonium thiosulfate SERIE I.**

Number	pH	NH <sub>4</sub> OH (mL)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (mL)	CuSO <sub>4</sub> 3% (mL)	Time (h)	Recovery (%)	
						Au	Ag
1	10	160	80	80	48	95	62
2	10	160	80	80	3	84	83
3	10	160	80	80	3	80	59
4	8.5	80	40	40	1.5	60	69

**Table 3 Test conditions ammonium thiosulfate SERIE II.**

Number	Sample (g)	pH	NH <sub>4</sub> OH (mL)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (mL)	CuSO <sub>4</sub> 3% (mL)	Recovery (%)	
						Au	Ag
1	200	Nat*	-	80	80	99	4
2	200	10	10	40	40	99	-
3	200	10	10	10, 10% weight	10	100	34
4	200	10	10	11.7 10% vol.	11.7	99	35
5	200	Nat*	-	11.7 10% weight	11.7	100	32
6	200	Nat*	-	80	-	100	33

\*Natural, without addition of reagent pH modifier.

**Table 4 Test conditions of ammoniumthio sulfate SERIE III.**

Number	Stirring	Particle size (mesh)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (mL)	CuSO <sub>4</sub> 3% (mL)	Time (h)	Recovery (%)	
						Au	Ag
1	With	-100	10, 10% weight	10	6	99	32
2	With	-100	10, 10% weight	-	6	100	36
3	With	-100	10, 10% weight	10	48	100	33
4	With	-100	10, 10% weight	10	12	100	22
5	Without	-100	10, 10% weight	10	24	100	38
6	Without	-100	10, 10% weight	10	48	100	32
7	With	-35	10, 10% weight	10	24	100	37
8	With	-35	80	80	24	99	58

### Ammonium Thiosulfate Ecological Viable Alternative to Replace Sodium Cyanide in Gold and Silver Dissolution Ores

The fourth series was time constant to 24 hours. The bottles 5 and 6 correspond to sample Band C respectively for the behavior of ammonium thiosulfate at higher grade ores (Table 5).

In the fifth series of leach tests, they were conducted for samples A, B and C. The conditions were absence of oxygen, aqueous dilution 2:1 and 48 hours of treatment as shown in Table 6.

The sixth test series includes the three samples A, B and C in Table 7 shows that the test conditions are

presented, pH 9, dilution of 2:1 and the leaching time was variable to establish one where greater solution is obtained.

### 3. Results and Discussion

From the results, it has laws observable head in Table 8. The sample for the study prepared 100% passing 10 mesh US. The particle size of the sample prepared for the cyanidation 100% passing the 35 mesh US. The particle size used in determining cyanidation

**Table 5 Test conditions ammonium thiosulfate SERIES IV.**

Number	Particle size (mesh)	pH	NH <sub>4</sub> OH (mL)	(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>3</sub> (mL)	CuSO <sub>4</sub> 3% (mL)	Recovery (%)	
						Au	Ag
1	-35	10 Ca(OH) <sub>2</sub>	-	80	80	75.6	98.2
2	-100	7	40	80	80*	91.2	98.2
3	-100	7	10	40	40	87.6	98.2
4	-100	7	10	40	20	87.0	98.2
5	-35	-	40	80	80	95.1	89.3
6	-35	-	40	80	80	12.5	69.3

\*This test is performed with CuSO<sub>4</sub> 1%.

**Table 6 Test conditions ammonium thiosulfate SERIES V.**

Number	Particle size (mesh)	pH	NH <sub>4</sub> OH (mL)	NH <sub>4</sub> (S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> 100% (mL)	CuSO <sub>4</sub> 3% (mL)	Recovery (%)	
						Au	Ag
1	-100	9	40	80	80	100	100
2	-35	9	40	80	80	100	84
3	-35	9	40	80	80	66	66

**Table 7 Test conditions ammonium thiosulfate SERIES VI.**

Number	Particle size (mesh)	NH <sub>4</sub> (S <sub>2</sub> O <sub>3</sub> ) <sub>2</sub> (mL)	CuSO <sub>4</sub> 3% (mL)	Time (h)	Recovery (%)	
					Au	Ag
1A	-100	80	80	4	100	100
1B	-35	80	80	5	100	100
1C	-35	80	80	7	100	100
2A	-100	80	80	8	100	100
2B	-35	80	80	3	89	77
2C	-35	80	80	4	100	78
3A	-100	80	80	5	85	79
3B	-35	80	80	6	77	81
3C	-35	80	80	24	91	88
4A	-100	80	80	3	87	63
4B	-35	80	80	4	83	60
4C	-35	80	80	5	**	63
5B	-35	80	80	6	83	68
5C	-35	80	80	24	71	66

\* Inconsistent, higher than the value of his head.

**Table 8 Head laws samples investigated.**

Sample	Assay (g/T)					Laws (%)			
	Au	Ag	Al	As	Cu	Fe	Mn	Sb	Zn
A	1.91	55.6	3.67	0.01	0.009	2.62	0.01	0.004	0.01
B	7.83	131	-	0.01	0.008	4.31	-	0.002	0.02
C	0.08	238	-	0.03	0.029	4.81	-	0.018	0.06

**Table 9 Sieve Analysis Sample.**

Particle size (mesh)	100%-10 mesh		100%-35 mesh			100%-100 mesh		
	weight (%)	Cumulative	weight (%)	Cumulative	Mesh	weight (%)	Cumulative	
	+	-	+	-		+	-	
-10 + 35	58.36	58.36	41.64					
-35 + 45	7.04	65.40	34.60	13.44	13.44	86.56		
-45 + 70	7.18	72.58	27.42	20.01	33.45	66.55	-100+140 13.99 13.99 86.01	
-70 + 100	3.74	76.32	23.68	11.20	44.65	55.35	-140+200 17.25 31.24 68.76	
-100 +140	3.00	79.32	20.68	7.18	51.83	48.17	-200+270 11.59 42.83 57.17	
-140 +200	2.82	82.14	17.86	7.20	59.03	40.97	-270+325 2.50 45.33 54.67	
-200	17.86	100.00	0.00	40.97		0.00	-325 54.67 100.00 0.00	
	100.00			100.00			100.0	

which is constant 100% to less 100% mesh was made to US (Table 9).

The first series (Table 2) shows that the leaching time is decisive for the dissolution of gold. On the three samples at the 48 hours, the recovery only increased 6%, from one and a half to three hours, increased 16%. For this reason, in the second set time (Table 3), it remains at three hours and six tests behavior is observed when changing the pH to 10 while natural pH being 7, the sample fed the ammonium thiosulfate in different concentrations trying to find a similar procedure in the control of solutions used in the cyanidation. The results show a complete dissolution in ones and almost complete in other tests.

From these results, the question arises about the particle size and the third experimental series is prepared (Table 4), where the agitation and static leaching tests are included, with a particle size of 100% passing through the 100 mesh and 100% passing the 35 mesh. Then a test without copper sulphate is prepared immediately to observe the effects on the solution. From these tests, it is observed that for gold dissolution, it is completed from six hours of leaching,

showing complete solution for 12 hours, 24 hours and 48 hours.

The results of the four series shown in Table 5, where time keep constant at 24 h, the pH of the test is 7-10 and the additions of ammonium hydroxide, copper sulfate and ammonium thiosulfate are shown.

Recoveries of the first fore tests decrease in values with respect to the III series, regarding silver show no appreciable difference, concerning gold recoveries is decreased according to this series.

Number 5 of the same series is corresponding to other mineral (sample B), in which high recovery of Au and Ag can be seen. The number 6 (sample C) indicates otherwise the recovery of Au decreases while that silver increases less than expected and recovering only 69.3%.

In the fifth series, leaching results show that the gold dissolves almost completely in the samples A and B, even when the particle size is coarser in the sample B, sample C in the recovery of gold and silver decreases as shown in Table 6. The assay results showed traces, so the recovery reservedly taken as 90% as atomic absorption in previous tests for zero gold is reported.

**Table 10** Summary of test results per sample SERIES VI.

Bottles	Particle size (mesh)	Tail (g/T)		Recovery (%)	
		Au	Ag	Au	Ag
1A	-100	0.0	0.0	100	100
2A	-100	0.0	0.0	100	100
3A	-100	0.0	0.0	100	100
4A	-100	0.0	0.0	100	100
1B	-35	0.5	29	89	77
2B	-35	0.0	27	100	78
3B	-35	0.7	26	85	79
4B	-35	1.10	24	77	81
5B	-35	0.40	15	91	88
1C	-35	0.2	75	87	63
2C	-35	0.27	82	83	60
3C	-35	0.27	66	83	68
5C	-35	0.45	77	71	66

The results of the sixth series of tests that have different particle size, respecting the leaching conditions and varying time reveal certain assaying the dissolution of gold and silver. To clarify this point, the data obtained are summarized in Table 10.

#### 4. Conclusions

Ores treated in this study belong to the Southern region of the state of Chihuahua, which would need to apply in ores mineralogically different.

The research for cyanidation lasted three months with a recovery of 37.2% for silver, for gold, appreciable results in the assay was not obtained by dry process. Tests with ammonium thiosulfate require less time and work with more confidence in handling the reagents, there was no difference in precipitating solutions for both leaching methods.

To perform the test with ammonium thiosulfate, it took into account the optimal particle size used in the cyanidation. Those are 100% to less than 100 mesh and a dilution 2: 1.

The results obtained by atomic absorption showed a nearly complete recovery of gold, the solution of which is deduced to 100% of that in the ammonium thiosulfate solution. While the results for silver are inconsistent.

Regarding the pH, it was maintained at baseline in

10 and the end at 7, from which the authors conclude that the pH is not a determining factor in the dissolution of gold and silver with ammonium thiosulfate.

Copper sulfate on the sample A does not showed appreciable change in the recovery of precious metals.

The chemical reagents added and doses do not show impact in increasing dissolution tests with ammonium thiosulfate.

The optimal time for ammonium thiosulfate leaching is in the range of 3 hours to 6 hours of treatment.

By varying the particle size, it was observed that the size is inconsequential as passing 100% through a 35 mesh recovery, which was similar to the 100% pass 100 mesh.

As a general conclusion, it was noted that different sets of gold dissolution test was always higher than that of silver, with a time of less than cyanide agitation, as shown in Table 10.

It should be noted that the repeatability of the results are regardless of the analyst, analytical method and equipment used.

For the second stage of research tests at the pilot level, it is intend to establish the ongoing process contemplated with a high probability of replacing cyanide at low cost and with conventional infrastructure.

## References

- [1] Contreras Castro, D. 1967. *Experimentation Minerals Gold and Silver for the Cyanidation Process*. México, D.F: CFM.
- [2] Delgado Alfaro, E., and Michel, D. 2011. "Ores Gold Leaching Using Thiosulphate: An Alternative Technology to Gold Ores Cyanidation." Accessed February 20, 2014. <http://documents.mx/documents/lixivacion.html>.
- [3] Hernández, J. 2013. "Kinetic Study of the Leaching of Silver in the System  $S_2O_3^{2-}-O_2-Cu^{2+}$ , Contained in Mining-Metallurgical Waste." Accessed February 21, 2014. [http://www.scielo.cl/scielo.php?pid=S0718-07642013000100007&script=sci\\_arttext](http://www.scielo.cl/scielo.php?pid=S0718-07642013000100007&script=sci_arttext).
- [4] Genik-Sas-Berezowsky, R., Sefton V., and Gormely L. 1978. Recovery of Precious Metals from Metal Sulphides. US Patent 4,070,182 A, filed August 13,1976, and issued January 24, 1978.
- [5] Kerley, B. 1981. Recovery of Precious Metals from Difficult Ores. US Patent 4,269,622 A, filed December 28, 1979, and issues May 26, 1981.
- [6] Kerley, J. 1983. Recovery of Precious Metals from Difficult Ores. US Patent 4,369,061 A, filed October 20, 1980, and issues January 18, 1983.
- [7] Laurel Gómez, M. 2014. "Perspective of the Employment of Alternative Lixiviantes Agents to the Cyanide for the Recovery of Gold and Silver." CIPIMM. Accessed March 12, 2015. <http://www.cipimm.co.cu/revista-info/descargas/2-2014/13-RESE%C3%91A%20pp.74-84.pdf>.
- [8] Melo Halmenschlager, P. 2015. "Leaching of Gold and Silver from Printed Circuit Board of Mobile Phoes." Metallurgy and Materials. Accessed April 16, 2015 <http://www.redalyc.org/pdf/564/56438403008.pdf>.
- [9] Pérez, A., and Galaviz, H. 1987. Method for Recovery of Precious Metals from Difficult Ores with Copper-Ammonium Thiosulfate. US Patent 4654078 A, filed July 12, 1985, and issues March 31, 1987.
- [10] Teijón Rivera José, M. 2006. *Fundamentals of Structural Biochemistry*. Madrid: Ed. Tébar.