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# **Leaching Gold-Silver Ores With Sodium Cyanide and Thiourea Under Comparable Conditions**

**By J. A. Eisele, A. H. Hunt, and D. L. Lampshire**



**UNITED STATES DEPARTMENT OF THE INTERIOR**





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CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	2
Experimental procedures.....	2
Results and discussion.....	5
Conclusions.....	6
References.....	6

TABLE

1. Analyses and extraction of gold and silver from ores.....	4
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

g	gram	mV	millivolt
g/L	gram per liter	pct	percent
h	hour	tr oz/st	troy ounce per short ton
lb/st	pound per short ton	yr	year
mL	milliliter		

# LEACHING GOLD-SILVER ORES WITH SODIUM CYANIDE AND THIOUREA UNDER COMPARABLE CONDITIONS

By J. A. Eisele,<sup>1</sup> A. E. Hunt,<sup>2</sup> and D. L. Lampshire<sup>2</sup>

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## ABSTRACT

There is currently much interest in how extraction of gold and silver from ores with acidic thiourea solution compares with extraction using alkaline cyanide solution. Agitation leaching tests were performed by the Bureau of Mines on 14 precious metal ores using sodium cyanide (NaCN) and thiourea [(NH<sub>2</sub>)<sub>2</sub>CS] as extractants. The objective was to compare the results of the two extractants. NaCN was used at a concentration of 2 g/L with and without H<sub>2</sub>O<sub>2</sub> as an oxidant. (NH<sub>2</sub>)<sub>2</sub>CS was used at concentrations of 2 and 20 g/L, and the solution potential was controlled at 390 to 420 mV standard hydrogen electrode (Eh) with Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. With both reagents at 2 g/L extractant levels, NaCN extracted more gold and silver than (NH<sub>2</sub>)<sub>2</sub>CS from all of the ores. At 20 g/L (NH<sub>2</sub>)<sub>2</sub>CS compared with 2 g/L NaCN, (NH<sub>2</sub>)<sub>2</sub>CS extracted more gold than NaCN from two ores, the same amount from one ore, and more silver from one ore. NaCN extracted more gold than (NH<sub>2</sub>)<sub>2</sub>CS from 10 ores and more silver from 4 ores.

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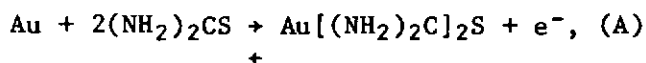
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## INTRODUCTION

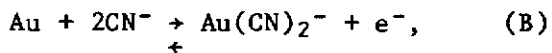
Cyanidation has been used almost exclusively for leaching gold and silver since its introduction 100 yr ago. Recently, there has been much interest in the mining and metallurgical processing industries in thiourea as an extractant for gold and silver (1-3, 6-14).<sup>3</sup> Thiourea extracts gold in an acidic medium (pH 1), and at a solution oxidation potential such that the dimer, formamidine disulfide, is formed and is the extractant.

Ferric sulfate is commonly used as an oxidant to achieve and maintain the oxidation potential of the solution in the proper range for dimer formation. The dissolution of gold by thiourea (formamidine disulfide) is expressed by



with gold solubilized as a cationic complex.

Cyanide extracts gold in an alkaline medium, and although no oxidant other than air from agitation is generally applied, addition of an oxidant may be beneficial (4). The dissolution of gold by cyanide is expressed by



with gold solubilized as an anionic complex.

This Bureau of Mines study was undertaken to compare the extraction of gold and silver from a variety of precious metal ores under comparable conditions of reagent concentrations, time of leaching, and at oxidant levels that enhance extraction for both cyanide and thiourea.

A NaCN concentration of 2 g/L (4 lb/st solution or 12 lb/st ore under test conditions) was used because this is a commonly used level in cyanidation of precious metal ores. For some ores that contain no constituents such as base metal sulfides or carbonaceous compounds, which interfere with cyanidation (clean oxide ores), a NaCN level as low as 0.17 g/L (0.33 lb/st solution or 1 lb/st ore) may be sufficient. However, for ores containing cyanicides, much higher levels than 2 g/L may be necessary to obtain good precious metal extraction. One ore used in this study required 100 g/L (200 lb/st solution or 600 lb/st ore) NaCN concentration to obtain over 90 pct gold extraction.

A  $(\text{NH}_2)_2\text{CS}$  concentration of 2 g/L was used to give a direct comparison with NaCN. A second level of  $(\text{NH}_2)_2\text{CS}$  concentration, 20 g/L, was also used because most previous leaching studies had used concentrations of 1 pct and higher, and it is of interest to know if increasing the reagent level tenfold greatly increases the gold and silver extraction.

## EXPERIMENTAL PROCEDURES

Thiourea leaching solutions were prepared by dissolving reagent-grade  $(\text{NH}_2)_2\text{CS}$  in water and acidifying with  $\text{H}_2\text{SO}_4$  to pH 1. Fifty-gram samples of ore

and 150 mL of leaching solution were agitated in a beaker by magnetic stirring. Ferric sulfate was added as needed to maintain the potential of the slurry between 390 and 420 mV Eh, which is a suitable range for gold extraction by thiourea (1). Leaching was at ambient temperature for 5 h.

<sup>3</sup>Underlined numbers in parentheses refer to items in the list of references at the end of this report.



Cyanide leaching tests were performed by adding reagent-grade NaCN and NaOH to 50-g samples of ore and 150 mL of water to bring the pH of the slurry to about 11. Slurries were agitated as above for 5 h at ambient temperature. In some cyanide leaches, hydrogen peroxide was added in small increments to bring the redox of the solution to the desired level.

After the leaching period, slurries were filtered and the residues were washed. Precious metal contents of head samples and residues were determined by fire assay. The gold and silver content of pregnant solutions was determined by atomic absorption spectrometry. When using atomic absorption analysis care must be taken to obtain correct values (5). Background absorption can cause a false, high reading unless background corrections are properly made, especially in the case of thiourea solutions containing dilute sulfuric acid. Another source of possible error in atomic absorption analysis was the following: after prolonged use of an atomic absorption analyzer for gold analyses, mostly in alkaline cyanide solution, the stainless steel internal lining of the nebulizer was gold plated. This can result in error in two ways, first, low values for the sample from which gold is cemented, and second, possible dissolution of gold by following samples and resultant false high value. The possible dissolution is more likely by a thiourea solution sample because thiourea is known to dissolve a gold disk more rapidly than cyanide (7). The use of a Teflon<sup>4</sup>

fluorocarbon polymer nebulizer avoids such a problem.

Percent extraction was calculated from the amount of gold in the pregnant solution and in the calculated head; i.e., the amount in the pregnant solution determined by atomic absorption plus the amount in the residue determined by fire assay. When the amount in the pregnant solution was below the detection limit, extraction was considered to be zero. Values of less than 0.5 tr oz/st Ag were not considered in extraction calculations because material balances are difficult to obtain and the monetary value is very low.

All oxidation potential measurements were made with Ag-AgCl and Pt electrodes, but are reported in terms of Eh.

Fourteen samples used for the tests had a range of gold and silver values and of base metal content. Analyses of the ores are given in table 1. Particle size of the samples was nominally 100 mesh. The minerals listed were identified by X-ray diffraction, which detects only those present in large amounts; small quantities would go unreported. For example, sample 8, which contains 2.8 pct As and 2.0 pct S, is a material from an area noted for its orpiment and realgar minerals, although none were identified in the X-ray scan. Table 1 shows some were gold ores with very little silver, one was a silver ore with no gold, and several contained significant values of both. Samples 1 through 7 represent clean oxide ores, which should be readily amenable to cyanidation. Samples 8 through 14 contain metallic and non-metallic elements that are known to interfere with cyanidation.

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<sup>4</sup>Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 1. - Analyses and extraction of gold and silver from ores

Sample	Analysis								Minerals identified	Extraction, pct							
	Calc, oz/ton		pct							NaCN leach, 2 g/L, 5 h				Thiourea leach, 5 h			
	Au	Ag	As	Cu	Fe	Pb	Zn	S		No oxidant		With H <sub>2</sub> O <sub>2</sub>		2 g/L		20 g/L	
	Au	Ag	Au	Ag	Au	Ag	Au	Ag		Au	Ag	Au	Ag	Au	Ag		
1.....	0.22	<0.5	0.05	<0.05	2.1	<0.05	<0.05	0.6	Nap.....	92	Nap	96	Nap	<sup>1</sup> 70	Nap	70	Nap
2.....	.13	0	<.05	<.05	2.2	<.05	<.05	.3	Nap.....	82	Nap	93	Nap	0	Nap	60	Nap
3.....	.13	<.5	<.05	<.05	10.5	.08	.06	<.1	Nap.....	{ 69 282	{ Nap Nap	{ Nap Nap	{ Nap Nap	<sup>1</sup> 50	Nap	50	Nap
4.....	.09	<.5	<.05	<.05	1.6	<.05	<.05	<.1	Nap.....	82	Nap	89	Nap	<sup>3</sup> 78	Nap	100	Nap
5.....	.09	<.5	<.05	<.05	3.5	.11	<.05	.2	Nap.....	100	Nap	100	Nap	<sup>3</sup> 0	Nap	82	Nap
6.....	.06	.6	<.05	<.05	3.5	<.05	<.05	1.3	Nap.....	{ 86 286	{ 100 273	{ Nap Nap	{ Nap Nap	40	<sup>4</sup> 2	80	100
7.....	.03	<.5	.10	<.05	3.1	<.05	<.05	.2	Nap.....	67	Nap	100	Nap	<sup>3</sup> 0	Nap	100	Nap
8.....	.03	<.5	2.8	<.05	.6	<.05	<.05	2.0	Nap.....	67	Nap	100	Nap	0	Nap	<sup>5</sup> 0	Nap
9.....	.03	8.7	.05	.38	.4	1.1	.17	.1	Nap.....	{ 67 2100	{ 57 264	{ Nap Nap	{ Nap Nap	<sup>3</sup> 0	<sup>3</sup> <1	44	77
10....	0	16.8	<.05	.05	.6	1.1	1.8	1.4	Sphalerite.....	{ Nap Nap	{ 65 274	{ Nap Nap	{ Nap Nap	Nap	4	Nap	65
11....	.64	5.1	.10	.68	28.0	<.05	.59	18.0	Pyrrhotite, chalcopyrite.	64	25	83	63	<sup>6</sup> 18	<sup>6</sup> 7	49	28
12....	.95	4.9	11.4	.24	12.7	1.8	1.8	12.3	Arsenopyrite, marcasite-pyrite	4	10	5	16	11	<sup>1</sup> <1	4	10
13....	.68	<.5	<.05	.07	17.5	<.05	<.05	20.1	Pyrite.....	32	Nap	34	Nap	<sup>3</sup> 1	Nap	18	Nap
14....	.37	7.1	<.05	2.6	2.5	18.2	.56	1.5	Cerrusite, galena	{ 7 29	{ <1 2<1	{ Nap Nap	{ Nap Nap	<sup>3</sup> 0	<sup>3</sup> <1	<sup>3</sup> 11	<sup>3</sup> 48

Nap Not applicable.

<sup>1</sup>No oxidant added, Eh of slurry above 390 mV at start and during leach; subsequent test with oxidant brought Eh of slurry to around 500 mV, gold-silver extraction did not increase.

<sup>2</sup>Duplicate test, Eh of slurry in 110- to 220-mV range.

<sup>3</sup>No oxidant added, Eh of slurry above 390 mV.

<sup>4</sup>Oxidant addition to raise Eh to 500 mV extracted 50 pct Au, 11 pct Ag.

<sup>5</sup>Material balance bad, tailings assay 0.01 tr oz/st, but no Au detected in solution.

<sup>6</sup>Oxidant addition to raise Eh above 500 mV did not increase Au, Ag extraction.

## RESULTS AND DISCUSSION

The results of extraction tests are given in table 1. Cyanide leaches were done at a concentration of 2 g/L NaCN (12 lb/st ore) and two conditions. One condition was that no oxidant was added other than the air contacting the slurry during agitation. Since addition of an oxidant may improve precious metal extraction, the second condition was with  $H_2O_2$  added to the slurry. A test was run on ore that did not respond well to cyanidation to determine what level of  $H_2O_2$  addition would be beneficial. The test showed that when the redox of the slurry was maintained in the range between 110 and 220 mV Eh, gold extraction increased from the baseline value of less than 30 pct to more than 50 pct. Above 250 mV Eh extraction decreased, and, above 290 mV Eh, cyanide was consumed and no free cyanide was detected in solution. On the basis of this test,  $H_2O_2$  was added to cyanide leaching slurries to maintain the potential between 110 and 220 mV Eh. Ideally, such a test series would be run for each ore sample to determine the proper level of oxidant; however, this level probably gave a good first approximation.

For samples 3, 6, 9, 10, and 14 no oxidant was added to the second NaCN leach (with  $H_2O_2$  column). Since the redox potential for the slurry was already in the desired range, these tests are duplicates of the first series. A range of extraction values are observed when a leaching test is repeated several weeks later. The difference for sample 3 is unusually large for material with a relatively high head value. For sample 9 the difference between 67 and 100 pct extraction for gold is large, but for material with such a low head assay the percent extraction is very sensitive to small changes. In this case, the same amount of gold was found in each pregnant solution, 0.02 tr oz/st ore, but the tailings assayed 0.01 tr oz/st for the first test and none in the second test.

The same type of situation was true for the silver extraction of sample 6, the same amount of silver was found in each pregnant solution, but, in one case, no

silver was found in the tailings and in the other case a small amount, 0.2 tr oz/st. In general, addition of an oxidant did not improve gold or silver extraction, with the exception of sample 11, which contained pyrrhotite and chalcopyrite. The ores that contained arsenopyrite, pyrite, and cerrusite responded poorly to cyanidation and were not helped by the oxidant. The test conditions--agitation in an open beaker--supplied sufficient oxygen. For sample 14, increasing the NaCN concentration to 20 g/L and leaching for 4 h extracted 23 pct of the Au and 51 pct of the Ag. Increasing the NaCN concentration to 100 g/L (600 lb/st ore) and leaching for 24 h extracted 92 pct of the Au and 87 pct of the Ag. Cyanide consumption was not measured.

Thiourea leaches were done at two reagent concentration levels with the redox potential of the slurry maintained between 390 and 420 mV Eh. The 2 g/L thiourea level gave a direct comparison of extraction with the cyanide leaching tests. On a molar basis the  $(NH_2)_2CS$  solution is weaker (0.026M) than the NaCN (0.041M) because of the higher molecular weight of  $(NH_2)_2CS$ . If the dimer is considered the extractant, the thiourea solution would be approximately 0.013M. However, this should provide enough extractant to adequately dissolve the precious metals, because even the highest grade ore at 17tr oz/st Ag contains 0.0003 mole of Ag in 50 g of ore and 150 mL of the thiourea solution contains about 0.002 mole of formamidine disulfide. One-hundred-fifty milliliters of cyanide solution contain 0.006 mole of NaCN. If base metals are consuming cyanide or thiourea, these levels may be inadequate. This is well illustrated by the cyanide level required for sample 14, 100 g/L NaCN, mentioned above. Thiourea leaching was also done with a solution containing 20 g/L, which corresponds to levels reported giving good gold extraction, generally between 1 and 5 pct thiourea.

Examination of the extraction values in table 1 shows that at the 2-g/L level

thiourea had mixed success in extracting gold from the clean oxidized ores, samples 1 through 7. Extraction was almost the same as cyanide for one ore, less than cyanide for two ores, and negligible for the other ores. When the thiourea level was increased to 20 g/L for the same ore samples, results were again mixed, although gold extractions generally increased. For all the samples of this group (1 through 7), gold extraction at 20 g/L thiourea was less than at 2 g/L NaCN, except for sample 4 where it was higher.

Examination of the refractory group of samples (8 through 14) shows that at the

2-g/L level thiourea did not leach gold or silver from several ores that had responded to cyanidation, samples 8 through 11. For the remaining three ores (samples 12-14) neither cyanide nor thiourea extracted much gold or silver. At 20 g/L thiourea, gold and silver extractions increased over the 2-g/L level, but were less than with 2 g/L cyanide, except for sample 14. Ore sample 14, containing a large amount of lead carbonate and significant amounts of Cu and Fe, had almost half of its silver content extracted; gold extraction was similar to that obtained with cyanide.

### CONCLUSIONS

A cursory investigation was made to determine the extraction of gold and silver from 14 ores with cyanide or thiourea. The research indicated that if most ores cannot be cyanided they will not be leached any better with thiourea. Ores that are amenable to cyanidation generally give poorer extraction with thiourea. Thiourea will probably find application as a leachant for gold only under special conditions; for example,

when an acidic medium is desired to co-extract a metal that is not leached in alkaline cyanide, such as uranium. Another special case where thiourea found application was in leaching a gold-bearing antimony concentrate (10). The faster leaching rate of gold, compared to antimony, in thiourea solution allowed the gold to be extracted before the antimony was attacked.

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