

**RI**

**8649**

**Bureau of Mines Report of Investigations/1982**

*National Mine Health & Safety Academy  
Learning Resource Center  
**RESERVE COPY***

# **Silver Recovery From Cyanide Tailings Using an Acidic NaCl-FeCl<sub>2</sub> Leachant**

**By P. R. Bremner**



**UNITED STATES DEPARTMENT OF THE INTERIOR**





**Report of Investigations 8649**

# **Silver Recovery From Cyanide Tailings Using an Acidic NaCl-FeCl<sub>2</sub> Leachant**

**By P. R. Bremner**



**UNITED STATES DEPARTMENT OF THE INTERIOR**

**James G. Watt, Secretary**

**BUREAU OF MINES**

**Robert C. Horton, Director**

This publication has been cataloged as follows :

**Bremner, P. R. (Paul R.)**

Silver recovery from cyanide tailings using an acidic NaCl-  
FeCl<sub>2</sub> leachant.

(Report of investigations / Bureau of Mines ; 8649)

Bibliography: p. 7.

Supt. of Docs. no.: I 28.23:8649.

1. Silver--Metallurgy. 2. Tailings (Metallurgy)--Recycling. 3. Cyanides. 4. Chlorides. 5. Leaching. I. Title. II. Series: Report of investigations (United States. Bureau of Mines) ; 8649.

TN23.U43 [TN770] 622s [669'.23] 81-607161 AACR2

CONTENTS

	<u>Page</u>
Abstract.....	1
Introduction.....	1
Materials and procedure.....	2
Results and discussion.....	4
Summary and conclusions.....	6
References.....	7

TABLES

1. Spectrographic and chemical analysis of Millers tailings.....	3
2. Size distribution and silver assay of size fractions.....	3
3. Effect of fine grinding of tailings on silver recovery.....	4
4. Effect of ferrous chloride concentration on silver extraction.....	5
5. Effect of retention time on silver extraction.....	5
6. Effect of hydrochloric acid concentration on silver extraction.....	5
7. Effect of sulfuric acid concentration on silver extraction.....	6



# SILVER RECOVERY FROM CYANIDE TAILINGS USING AN ACIDIC NaCl-FeCl<sub>2</sub> LEACHANT

by

P. R. Bremner<sup>1</sup>

---

## ABSTRACT

In keeping with its mission to maximize mineral and metal recovery from domestic sources, the Bureau of Mines investigated a method to extract silver from tailings not amenable to cyanidation. Results of a laboratory study on the recovery of silver from cyanide tailings containing 1.7 ounces of silver per ton by leaching with an acidic ferrous chloride-sodium chloride solution are presented. The effects of reagent concentration and reaction time on the

leaching of silver were investigated. A leaching solution containing 5 wt-pct NaCl, 2.5 wt-pct FeCl<sub>2</sub>, and 1.2 wt-pct HCl (for acidity) extracted 82 pct of the silver from the tailings during a 24-hour leach. The amount of HCl consumed during the leach was 46 pounds of HCl per ton of feed. Only 23 pct of the silver was extracted by conventional cyanidation. Ninety-nine percent of the silver was recovered from the pregnant solution by cementation onto iron powder.

## INTRODUCTION

One of the goals of the Bureau of Mines is to develop technology for processing low-grade and difficult-to-treat ores and mine wastes. Because of recent metal price increases, old mill tailings that contain precious metals could be attractive economic ventures if metallurgical techniques can be developed to extract the metals profitably. Recycling mill tailings eliminates the expense of exploration, mining, crushing, and grinding.

Mineralogical studies of mill tailings conducted by previous investigators (1, 5, 8)<sup>2</sup> indicated that the

precious-metal values occur in diverse ways, including the following:

1. Free gold coated with iron or manganese oxides that cannot be recovered by amalgamation or cyanidation.
2. Gold and silver interlocked with sulfide minerals, such as pyrite, arsenopyrite, chalcopyrite, tetrahedrite, and galena.
3. Gold associated with carbonaceous material.
4. Silver and gold encapsulated within the siliceous gangue minerals.
5. Secondary silver in limonite and jarosite minerals.

---

<sup>1</sup>Chemist, Reno Research Center, Bureau of Mines, Reno, Nev.

<sup>2</sup>Underlined numbers in parentheses refer to items in the list of references at the end of this report.

6. Silver intimately associated with manganese oxides.

7. Disseminated silver in oxidized lead and zinc minerals.

A number of treatment schemes have been employed in the milling of silver and gold ores in the western United States. Most of the major operations have been reviewed in the scientific literature. Successful retreatment

operations include (1) cyanidation of tailings from amalgamation mills, (2) flotation of tailings containing residual gold associated with sulfides and carbonaceous material, and (3) cyanidation of flotation tailings (4, 7). The objective of this investigation was to evaluate an acidic ferrous chloride-sodium chloride ( $\text{FeCl}_2\text{-NaCl}$ ) leaching system for recovering silver from manganese oxide tailings that had been cyanided.

#### MATERIALS AND PROCEDURE

The cyanide mill tailings used were obtained from Millers, Nev., and represent an estimated 2-1/2 million tons of silver-bearing material (6). The origin of the tailings and history of the Tonopah mining district operations are well documented (2).

The Tonopah district consists of rhyolite and andesitic flows referred to as the "Mizpah trachyte." The silver-bearing materials are associated with quartz veins and sericitic and kaolinitic alteration products (9). The original ore, which had a silver-to-gold ratio of 92 to 1, occurred as replacement veins that followed faults and minor fractures classified as cemented breccias. The principal silver minerals were electrum, argentite, polybasite, arsenical pyrrargyrite, and cerargyrite.

The milling practice employed during the original treatment consisted of fine grinding followed by leaching with a warm, dilute cyanide solution (4). Lead acetate was added during cyanidation to improve silver recovery from the complex sulfide ores. An average of about 92 pct of the silver and 94 pct of the gold was extracted.

Microscopic examination of the tailings indicated that the material was predominantly quartz stained with manganese oxide. The tailings contained traces of pyrite and partially oxidized sulfides. Studies indicated that approximately two-thirds of the silver was associated with manganese oxide. Precious-metal values were determined by the fire assay method. Silver and gold assays were 1.7 and 0.015 oz/ton, respectively.

Spectrographic and chemical analyses were made on selected samples of tailings to determine the presence of other metallic constituents. These analyses are shown in table 1.

A wet-screen analysis of the tailings was made to determine the fineness of grind employed in the original cyanide operation and the distribution of the silver values. Table 2 lists the results. The screen analysis indicates that the ore was ground to approximately 70 pct minus 200 mesh. The minus 325-mesh fraction contained 59.8 pct of the silver values.

TABLE 1. - Spectrographic and chemical analysis  
of Millers tailings, percent

Constituent	Spectrographic analysis	Chemical analysis
Aluminum.....	4.0	ND
Calcium.....	.1	ND
Copper.....	.008	0.002
Iron.....	1.0	ND
Lead.....	.2	ND
Magnesium.....	.2	.12
Manganese.....	.4	.43
Silica.....	ND	79.9
Sodium.....	(1)	ND
Sulfur.....	ND	.35
Titanium.....	.05	ND
Vanadium.....	(2)	ND
Zinc.....	(3)	ND
Zirconium.....	(4)	ND

ND Not detected.

<sup>1</sup>Less than 0.3 pct.

<sup>2</sup>Less than 0.006 pct.

<sup>3</sup>Less than 0.1 pct.

<sup>4</sup>Less than 0.007 pct.

TABLE 2. - Size distribution and silver assay of size fractions

Tailings size, mesh	Tailings, wt-pct	Silver	
		Assay, oz/ton	Distribution, pct
Plus 35.....	1.0	3.0	1.7
Minus 35 plus 65.....	5.4	2.1	6.5
Minus 65 plus 100.....	6.3	1.5	5.4
Minus 100 plus 200.....	18.0	1.4	14.5
Minus 200 plus 325.....	11.6	1.8	12.1
Minus 325.....	57.7	1.8	59.8
Composite.....	100.0	1.7	100.0

The leaching experiments were performed on 200-gram charges in 2.5-liter Winchester<sup>3</sup> bottles. A dilution ratio of three parts of leaching solution to one of feed by weight was used. The slurry in the bottle was agitated by rotation on

<sup>3</sup>Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

a set of laboratory rolls. At the termination of the test, the slurry was filtered, the solids washed and assayed. Solutions were analyzed by atomic absorption. Chemical determination of ferrous and ferric iron was done by a standard procedure with potassium dichromate. Leached residues were analyzed by fire assay techniques. These experimental procedures are common to all tests.

## RESULTS AND DISCUSSION

Preliminary tests were made to evaluate the feasibility of recyaniding the mill tailings. Any silver-bearing sulfide minerals would have oxidized during the several decades since they were originally processed and would be recoverable by cyanide leaching. To determine the effect of finer grinding on silver extraction, portions of the tailings were reground to 100 pct minus 200 mesh and to 100 pct minus 325 mesh. The reground materials were leached for 72 hours with a solution containing 2.0 pounds of sodium cyanide (NaCN) per ton of solution and sufficient lime to maintain a pH of about 11. The results are summarized in

table 3. Silver recovery for the 100 pct minus 325-mesh fraction was double that of the as-received tailings. Fine grinding exposed more of the silver minerals to the NaCN solution. All the gold was extracted during recyanidation of the tailings. The leached residues assayed less than 0.005 ounce of gold per ton. Apparently, the oxidation of the pyrite exposed the gold particles. Cyanidation of the unground tailings yielded only 23 pct of the silver. Even with fine grinding, extraction was less than 50 pct. Consequently, other methods were investigated to increase silver extraction.

TABLE 3. - Effect of fine grinding of tailings on silver recovery<sup>1</sup>

Feed size	Assay of leached residue, oz/ton	Extraction, pct
70 pct minus 200 mesh <sup>2</sup> .....	1.3	23
100 pct minus 200 mesh.....	1.0	41
100 pct minus 325 mesh.....	.9	47

<sup>1</sup>Feed assay was 1.7 ounces of silver per ton.

<sup>2</sup>Unground feed.

Cyanidation of Nevada silver ores generally does not produce tailings containing less than 1 ounce of silver per ton. This silver content is either encapsulated in silica or associated with manganese minerals in the ore. A sample was leached with aqua regia to determine how much of the silver in the tailings was actually encapsulated in the quartz. The leached residue assay showed that 0.25 ounce of silver per ton of original tailings was insoluble and presumably encapsulated within the siliceous gangue. The removal of manganese during the aqua regia digestion and subsequent silver extraction indicated that nearly two-thirds of the silver in the tailings was associated with the manganese oxide. The occurrence of silver in the crystal lattice of manganese oxide minerals will prevent silver recovery by cyanidation (3).

Studies were made to determine if the silver in the tailings could be

extracted with an acidic chloride leachant. Twenty-four-hour leaching tests were made employing a solution containing 5 wt-pct NaCl and 1.2 wt-pct hydrochloric acid (HCl). Silver extraction was 47 pct. Silver extraction was improved by adding  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  to the 5-wt-pct-NaCl-1.2-wt-pct-HCl leaching solution. The ferrous ion reduced and solubilized the manganese oxides associated with silver. The amounts of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  employed were equivalent to 1, 2.5, and 5 wt-pct  $\text{FeCl}_2$ . Leaching duration was 24 hours. Results are given in table 4. The data indicate that the  $\text{FeCl}_2$  additive increased silver extraction. All of the manganese and nearly all of the silver that was not encapsulated in the gangue were extracted. Leached residues contained less than 0.001 pct manganese. Acid consumptions were 40 to 46 pounds of HCl per ton of feed.

Bureau of Mines  
Report of Investigations 8649

SILVER RECOVERY FROM CYANIDE TAILINGS  
USING AN ACIDIC NaCl-FeCl<sub>2</sub> LEACHANT

by

P. R. Bremner

---

---

ERRATA

On page 5, the last boxhead in table 6 should read as follows: HCl consumed,  
lb/ton of feed

TABLE 4. - Effect of ferrous chloride concentration on silver extraction<sup>1</sup>

FeCl <sub>2</sub> , wt-pct	Leached residue oz/ton	Extraction, pct
1.....	0.4	76
2.5.....	.3	82
5.....	.3	82

<sup>1</sup>A leach solution containing 5 wt-pct NaCl and 1.2 wt-pct HCl was used for 24 hours at ambient temperature. Acid consumption was 40 to 46 pounds per ton of feed.

The effect of duration of leach on silver extraction was investigated. In these tests, 200 grams of tailings were leached with 600 ml of solution containing 2.5 wt-pct FeCl<sub>2</sub>, 5 wt-pct NaCl, and 1.2 wt-pct HCl (3.2 tons of leaching solution per ton of feed). Leaching times

were 1, 2, 4, 8, and 24 hours. After the leach was completed, the residues were filtered, washed with water, dried, and analyzed. Table 5 summarizes the results. In 1 hour, 59 pct of the silver was leached. A leaching period of 24 hours extracted 82 pct of the silver.

TABLE 5. - Effect of retention time on silver extraction<sup>1</sup>

Retention time, hr	Leached residue, oz/ton	Extraction, pct
1.....	0.7	59
2.....	.7	59
4.....	.6	65
8.....	.5	71
24.....	.3	82

<sup>1</sup>The leach solution contained 5 wt-pct NaCl, 2.5 wt-pct FeCl<sub>2</sub>, and 1.2 wt-pct HCl. Tests were conducted at ambient temperature.

Table 6 summarizes data showing the effect of HCl concentration on silver extraction. The tailings were agitated along with a leach solution containing 2.5 wt-pct FeCl<sub>2</sub> and 5 wt-pct NaCl

acidified with HCl. Silver extraction increased with increasing acid addition to 82 pct at an addition of 77 pounds of HCl per ton of feed.

TABLE 6. - Effect of hydrochloric acid concentration on silver extraction<sup>1</sup>

HCl addition, lb/ton of feed	Leached residue, oz/ton	Extraction, pct	H <sub>2</sub> SO <sub>4</sub> consumed, lb/ton of feed
9.....	1.3	24	9
19.....	.7	59	19
29.....	.7	59	26
38.....	.6	65	36
48.....	.5	71	40
58.....	.4	76	43
77 <sup>2</sup> .....	.3	82	46

<sup>1</sup>Leach solutions containing 5 wt-pct NaCl, 2.5 wt-pct FeCl<sub>2</sub>, and various amounts of HCl were used for 24 hours at ambient temperature.

<sup>2</sup>Equivalent to 1.2 wt-pct HCl.

A study using sulfuric acid ( $H_2SO_4$ ) instead of HCl in the NaCl- $FeCl_2$  leaching system was made. Two-hundred grams of tailings were leached for 24 hours with solutions containing 5 wt-pct NaCl, 2.5 wt-pct  $FeCl_2$ , and various concentrations of  $H_2SO_4$ . The pulps were filtered, and the leach residue washed, dried, and

assayed. Results are shown in table 7. Less HCl was consumed than  $H_2SO_4$  for comparable silver extraction. For example, 43 pounds of HCl compared to 72 pounds of  $H_2SO_4$  was consumed in achieving 76-pct extraction. The  $FeCl_2$ -NaCl- $H_2SO_4$  solution dissolved 76 pct of the silver in the tailings.

TABLE 7. - Effect of sulfuric acid concentration on silver extraction<sup>1</sup>

$H_2SO_4$ addition, lb/ton of feed	Leached residue, oz/ton	Extraction, pct	$H_2SO_4$ consumed, lb/ton of feed
20.....	1.1	35	20
39.....	.6	64	38
59.....	.5	70	48
78.....	.5	70	55
98.....	.4	76	72

<sup>1</sup>Leach solutions containing 5 wt-pct NaCl, 2.5 wt-pct  $FeCl_2$ , and various amounts of  $H_2SO_4$  were used for 24 hours at ambient temperature.

The following test indicates that silver can be readily recovered from the pregnant solution by iron cementation. The pregnant leach solution used was comprised of 200 grams of tailings and 600 ml of leaching solution containing 2.5 wt-pct  $FeCl_2$ , 5 wt-pct NaCl, and 1.2 wt-pct HCl, which are the optimum leach conditions shown in table 6.

Sufficient iron powder was added to the spent liquor to precipitate essentially 98 pct of the silver. All of the iron in the leach solution was converted to the ferrous state (no ferric iron could be detected by chemical analysis), indicating that the barren solution could be recycled to the leaching step after adding makeup HCl.

#### SUMMARY AND CONCLUSIONS

A  $FeCl_2$ -NaCl leaching system containing  $H_2SO_4$  or HCl effectively extracted the silver from tailings containing manganese oxide and 1.7 ounces of silver per ton. Maximum silver extraction was 82 pct, with a leaching time of 24 hours and acid consumption of

46 pounds of HCl per ton of feed. More than 99 pct of the leached silver was recovered by cementation on iron powder. The leaching technique can be used to recover silver from ores and tailings containing silver-bearing manganese oxide minerals.

## REFERENCES

1. Adamson, R. J. Gold Metallurgy in South Africa. Cape and Transvaal Printers Ltd., Cape Town, South Africa, 1972, 452 pp.
2. Carpenter, J. A., R. R. Elliott, and B. F. W. Sawyer. The History of Fifty Years of Mining at Tonopah, 1900-1950. Univ. Nev. Bull., v. 45, No. 3, 1953, 153 pp.
3. Clevenger, G. H., and M. H. Caron. The Treatment of Manganese-Silver Ores. BuMines Bull. 226, 1925, 110 pp.
4. Dorr, J. V. N., and F. L. Bosqui. Cyanidation and Concentration of Gold and Silver Ores. McGraw-Hill Book Co., Inc., New York, 1950, 511 pp.
5. Henley, K. J. Gold-Ore Mineralogy and Its Relation to Metallurgical Treatment. Miner. Sci. Eng., v. 7, No. 4, 1975, pp. 289-312.
6. Jacobson, I. N. Construction Starts on New Mill at Millers Property. Min. Record, Apr. 28, 1976, p. 1.
7. Leaver, E. S., and J. A. Woolf. Re-Treatment of Mother Lode (California) Carbonaceous Slime Tailings. BuMines Tech. Paper 481, 1930, 20 pp.
8. Lloyd, P. J. D. Maximizing the Recovery of Gold From Witwatersrand Ores. Miner. Sci. Eng., v. 10, No. 3, 1978, pp. 208-221.
9. Nolan, T. B. The Underground Geology of the Western Part of the Tonopah Mining District, Nevada. Univ. Nev. Bull., v. 24, No. 4, 1930.





