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UNITED STATES DEPARTMENT OF THE INTERIOR



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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cm	centimeter	mm	millimeter
g/L	gram per liter	µm	micrometer
kg	kilogram	pct	percent
L	liter	ppm	part per million
m	meter	tr oz/st	troy ounce per short ton
mL/min	milliliter per minute	wt pct	weight percent

DUAL LEACHING METHOD FOR RECOVERING SILVER AND MANGANESE FROM DOMESTIC MANGANIFEROUS SILVER DEPOSITS

By John E. Pahlman,¹ Charles A. Rhoades,² and Peter G. Chamberlain³

ABSTRACT

The Bureau of Mines has conducted research on a dual leaching method that offers the potential for the economic recovery of the silver, as well as of the manganese, contained in some domestic manganiferous silver deposits. The method consists of an initial leach of manganese with aqueous sulfur dioxide (SO₂) followed first by a neutralization rinse, and then by a second leach with cyanide solution for the extraction of silver. Refractory silver in these ores was either (1) intimately associated with the manganese, (2) chemically resistant to cyanide leaching, or (3) rendered inaccessible to cyanide leach solution by the surrounding manganese mineralization. Less than 10 pct of the silver was extracted when minus 2.5- plus 1.3-cm ore pieces were leached directly with cyanide. However, extractions of 25 to 82 pct of the silver and 65 to 96 pct of the manganese were attained in laboratory column-leach tests using the dual leaching method on equivalent-sized ore pieces from seven domestic deposits.

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INTRODUCTION

In support of its goal of maintaining an adequate supply of minerals to meet national economic and strategic needs, the Bureau of Mines has investigated the feasibility of in situ and heap leaching to recover manganese from low- and medium-grade domestic manganese deposits and to also recover the silver found in some of these manganese deposits.

In situ leaching technology has been successfully used for uranium and copper. Heap leaching is an important method for recovery of gold, silver, and copper. These leaching technologies have the advantages over conventional mining of lower capital and operating costs, shorter startup times, and environmental and safety improvements. Thus, in situ or heap leaching is a favorable method for small and/or low-grade deposits that would not otherwise be mined. Most of the more than 2,100 low-grade manganese deposits in 35 States (6)⁴ fall into this category.

Previous Bureau research indicated the technical feasibility of recovering manganese from low-grade deposits by in situ leaching with aqueous SO₂ (1-2, 8). Manganese recovery ranged from 60 to 95 pct for oxide and carbonate deposits. As an offshoot of this project, the feasibility of recovering silver and manganese from refractory silver deposits was evaluated. These deposits are refractory because the silver is either bound with the higher order manganese oxides, rendered inaccessible to cyanide leach solutions by the surrounding manganese mineralization, or chemically resistant to cyanide leaching (3, 9). The evaluation was accomplished by conducting column-leach tests, using a dual leaching scheme in which silver is leached with cyanide solutions after an aqueous SO₂ leach of the manganese and an alkaline rinse to neutralize any residual acid (to assure that no toxic HCN gas forms). The results of this evaluation are described in this report.

Gaspirrini (5), in a study of the mineralogy of silver and its significance in metal extraction, including that by NaCN solutions, found that factors affecting the metallurgy of silver are (1) the silver-bearing minerals, (2) their grain size, (3) their host minerals, and (4) the association of the host minerals with the silver-bearing minerals. The common silver-bearing minerals native silver, electrum (AuAg), argentite-acanthite (Ag₂S), copper-silver minerals, and silver halides such as cerargyrite (AgCl), embolite [(Ag(Br,Cl))], bromyrite (AgBr), and iodyrite (AgI), etc., are readily dissolved in NaCN solutions, particularly when finely divided (<15 μm in size). The common silver-bearing minerals proustite (Ag₃AsS₃), pyragyrite (Ag₃SbS₃), stephanite (Ag₅SbS₄), polybasite [(Ag, Cu)₁₆Sb₂S₁₁], tennantite [(Cu, Ag, Fe)₁₂As₄S₁₃], and tetrahedrite [(Cu, Ag, Fe)₁₂Sb₄S₁₃] do not dissolve readily in NaCN. Preroasting may improve silver recovery in these cases. Lead-zinc minerals containing silver in solid solution and manganese-silver minerals and solid solutions are leached by NaCN solutions with great difficulty.

Although several laboratory tests have been successfully conducted on leaching of manganese with SO₂ solutions followed by leaching of silver with cyanide solutions (4, 10-11), the present study has several key differences from earlier studies. In the present study, percolation SO₂ and CN leaching tests were conducted on larger ore pieces (minus 2.5- plus 1.3-cm) rather than fine ore particles (<0.210 mm) to simulate in situ and/or heap leaching conditions. A 5-wt-pct-SO₂ solution was used to preferentially leach most of the manganese while leaving most of the iron in the residue. In other studies employing high concentrations of SO₂ (8 to 9 wt pct SO₂), most of the iron was leached along with the manganese. Another difference from past studies is the elimination of calcining of the ore to improve permeability or to decompose carbonates.

⁴Underlined numbers in parentheses refer to items in the list of references at the end of this report.

CHARACTERISTICS OF DEPOSITS

The manganese deposits that were sampled and tested in the column leaching experiments are characterized in table 1. The deposits are of hydrothermal vein origin and contain predominately the higher order oxide minerals: pyrolusite and psilomelane. The samples were

obtained mostly from waste rockpiles and lean ore dumps around mine sites in the listed districts. Chemical analyses of the samples, partially given in table 2, indicated that they contained between 1.8 and 7 tr oz/st Ag.

EXPERIMENTAL METHOD

Manganese extraction was determined on 3.5-kg samples of minus 2.5- plus 1.3-cm pieces in 10-cm-diam Plexiglas acrylic columns that were 1 m long. A 5-wt-pct-SO₂ solution was applied at a rate of 1 mL/min. This rate approximates the application rates in commercial gold-silver and copper heap leaching operations and resulted in an unsaturated column of ore. Effluent from the column was collected and analyzed for manganese, iron, calcium, and silver by atomic absorption (AA) spectroscopy. Although the AA readings are accurate to ±1 ppm, calculated

recovery values are probably accurate to 5 pct of the reported values. The tests were usually run until the manganese in the effluent from the column dropped to 1 g/L. Initial manganese concentrations in the effluent ranged from 2.7 g/L for sample AZ-3 to 12.0 g/L for sample AZ-2. At least 50 L of solution was applied to each ore sample during any one test.

After leaching an amount of manganese that would simulate the recovery in a heap or in situ leaching operation (65 to 95 pct), the material remaining in the column was rinsed with a 0.3-wt-pct-NaOH

TABLE 1. - Manganese ore characteristics¹

Sample	District	County and State	Manganese minerals ²	Principal gangue minerals ²
AZ-1..	Harshaw....	Santa Cruz, AZ	Psilomelane, pyrolusite, braunite.	Anglesite, quartzite, feldspar, rhyolite, galena.
AZ-2..	...do.....	...do.....	Psilomelane, pyrolusite.	Quartzite, anglesite, feldspar, rhyolite, galena.
AZ-3..	Tombstone..	Cochise, AZdo.....	Quartz, calcite, dolomite.
AZ-4..	...do.....	...do.....	...do.....	Do.....
CO-1..	Leadville..	Lake, CO.....	Psilomelane, pyrolusite, manganosiderite.	Quartz, calcite, hematite, goethite.
CO-2..	Silvercliff	Custer, CO....	Cryptomelane.	Quartz, hematite.
NV-1..	Pioche.....	Lincoln, NV...	Manganite, braunite.	Goethite, quartz, calcite.

¹All manganese oxides of hydrothermal vein origin.

²Listed in order of decreasing abundance.

TABLE 2. - Partial chemical analyses of ore samples

Sample	Fe, pct	Ca, pct	Mn, pct	Ag, tr oz/st
AZ-1.....	3.3	0.5	10.6	2.9
AZ-2.....	6.9	1.0	27.7	2.4
AZ-3.....	2.5	25.1	2.0	2.4
AZ-4.....	1.9	<.5	9.8	7.0
CO-1.....	6.0	9.9	10.2	4.0
CO-2.....	3.5	.6	4.6	1.8
NV-1.....	22.8	3.2	10.6	3.3

solution to neutralize any acidity. This was necessary to prevent formation of toxic HCN gas, which occurs if cyanide encounters acidic solutions.

Following the rinse phase, 1 kg of the material was put into another 10-cm-diam Plexiglas acrylic column and leached with about 4 L of solution containing 0.3 wt

pct NaCN and 0.3 wt pct NaOH applied at a rate of 1 mL/min. Effluent solution was collected and analyzed for iron, silver, and cyanide by AA methods. Control samples (no SO₂ preleach to remove manganese) were leached with cyanide in an identical manner.

RESULTS

MANGANESE EXTRACTION TESTS

In previous column leaching tests (8), manganese extractions of 70 to 95 pct have been obtained from samples containing pyrolusite, psilomelane, and/or wad.

The manganese-extraction curves as a function of volume of solution applied to the column are shown in figure 1 for the seven silver-bearing samples. The manganese in all the samples except NV-1 was predominately psilomelane and pyrolusite; therefore, it readily leached to the 80- to 95-pct extraction level. The manganese in sample NV-1 was predominately manganese and was leached at a slower rate.

SILVER EXTRACTION TESTS

Results of cyanide leaching tests on the control samples and the samples that had been leached with SO₂ are summarized in table 3. Silver-extraction rates are displayed in figure 2 for both control and post-SO₂-leach samples. Cyanide leaching without SO₂ preleaching resulted in silver extractions of 0.7 to 8.5 pct. The SO₂ leaching step, intended to remove manganese, also resulted in significant silver extraction in most samples. These

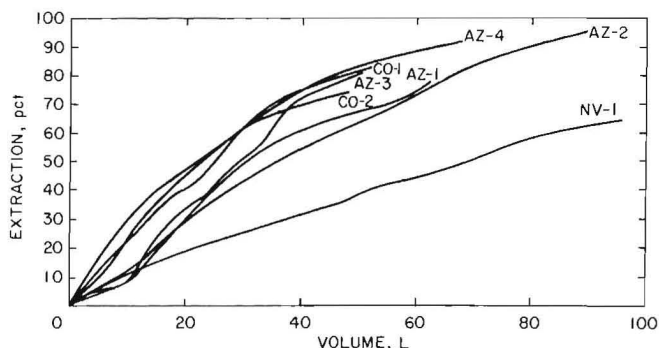


FIGURE 1.—Manganese-extraction curves for seven silver-containing ore samples.

silver values can be recovered either by chloride precipitation or by cementation. Cyanide leaching of the samples after the SO₂ leach resulted in additional silver extractions ranging from 2 to 80 pct. The total silver recovered during SO₂ leaching and cyanide leaching after the SO₂ leach was 8 to 110 times greater than the silver extraction for cyanide leaching alone.

The refractory nature of some silver deposits with regards to extraction by cyanide solutions could be due to several factors. A major factor is the silver mineralization. Some silver minerals are resistant to leaching or leached only to a small extent with cyanide solutions. Another major factor is the intimate association of silver with the manganese

TABLE 3. - Silver-extraction test results, percent

Sample	Cyanide direct	SO ₂ extraction	Cyanide after SO ₂ leach	Total extraction
AZ-1...	3.3	43.	23.	66.
		43.	25.	68.
AZ-2...	.7	14.	64.	78.
		14.	66.	80.
		14.	68.	82.
AZ-3...	1.0	2.	22.	24.
		2.	23.	25.
AZ-4...	1.3	13.	46.	59.
		13.	59.	72.
		13.	63.	76.
		13.	65.	78.
		13.	67.	80.
CO-1...	8.5	2.	65.	67.
		2.	76.	78.
		2.	80.	82.
CO-2...	1.4	38.	2.	40.
NV-1...	4.5	40.	12.	52.
		40.	14.	54.

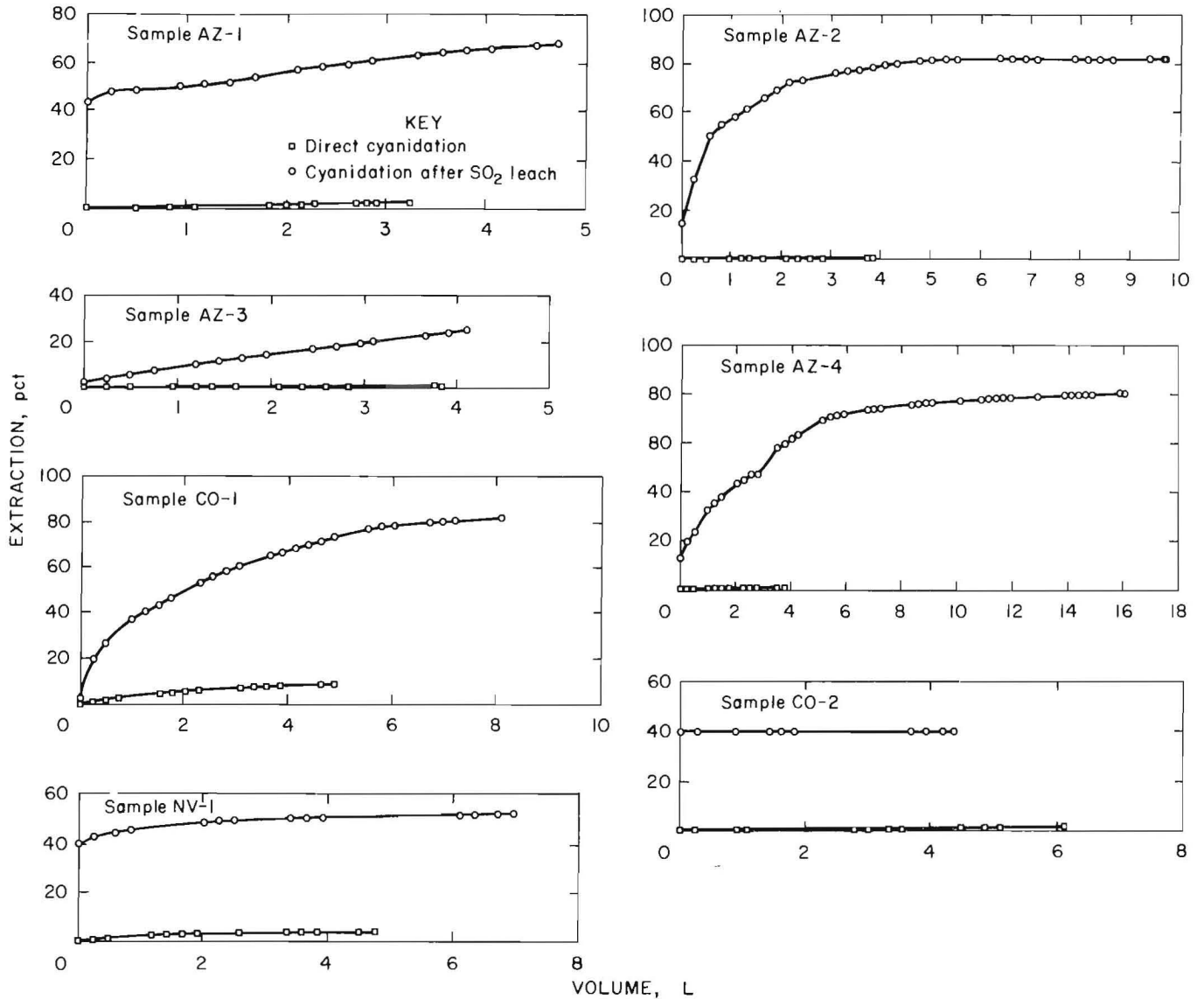


FIGURE 2.—Silver-extraction curves.

oxides in the ore. It is these deposits that are the target of the methods presented herein; in such deposits the manganese must be dissolved before the silver can be solubilized. Yet another factor is the accessibility of the silver mineralization to the cyanide leach solution.

The linearity of plots of $\ln [(1+f)/(1-f)]$ versus time for SO₂ leaching of the ores is exemplified in figure 3 for ores CO-1 and NV-1 and evidenced for all seven ores by the near-unity correlation

coefficients for a linear fit of the data (table 4) and proves that the rate data follow the rate expression for autocatalytic reactions:

$$kt = \ln[(1+f)/(1-f)] \quad (1)$$

where k = rate constant,

t = time,

and f = fraction of manganese leached at time t .

TABLE 4. - Coefficients for linear fit ($y = A + Bx$) of kinetic plots $\ln[(1+f)/(1-f)]$ versus time

Sample	A coefficient	B coefficient	Correlation coefficient
AZ-1.....	-6.121×10^{-2}	3.474×10^{-5}	0.9906
AZ-2.....	-2.312×10^{-1}	3.906×10^{-5}	.9865
AZ-3.....	2.138×10^{-1}	4.824×10^{-5}	.9906
AZ-4.....	-4.765×10^{-2}	4.862×10^{-5}	.9984
CO-1.....	6.007×10^{-3}	4.777×10^{-5}	.9981
CO-2.....	2.491×10^{-1}	3.578×10^{-5}	.9917
NV-1.....	5.020×10^{-2}	1.558×10^{-5}	.9985

DISCUSSION

Since the solubilization of manganese upon contact with SO_2 was observed to be rapid in previous work on sea nodules (7) and in batch-leaching tests on fine particles of manganese ores, the rate of leaching of manganese from ores is dependent upon the rate at which the leach solution can penetrate the ore.

Microscopic examination of the ores in this investigation showed that the manganese mineralization had precipitated in and closed capillaries, coated interiors of pores, and precipitated at matrix-grain boundaries. This accounts for the

low water permeabilities observed for these ores (as low as 10^{-2} to 10^{-4} darcy) and indicates why most silver mineralization in the bulk of the ore pieces, even though amenable to direct cyanidation, was not leached until after a preliminary SO_2 leach. Without removal of manganese to open up pores and capillaries, there is no penetration of any leach solution into the ore pieces.

Since SO_2 solutions rapidly leach manganese upon contact, the pores and capillaries are opened up commensurate with the fraction of manganese leached. This is in agreement with the autocatalytic rate expression given in equation 1. Microscopic examination of X-ray diffraction of ore pieces after leaching with SO_2 solutions showed that most of the manganese was removed by SO_2 leaching.

A parallel situation occurs for ores with high calcite contents. The calcite, like the manganese mineralization, either surrounds the silver mineralization or fills the voids, grain boundaries, and capillaries of the ore, thus preventing cyanide solution from reaching and dissolving the silver.

Minerals that fill fissures and pores to such an extent that the solution is physically blocked from attacking the silver can have a profound influence on silver leachability. If manganese is the primary mineral blocking cyanide-solution access to the silver, the SO_2 preleach again offers potential.

Clues to the reason for the refractoriness of the manganese-silver ores AZ-1, AZ-2, AZ-3, AZ-4, CO-1, CO-2, and NV-1 are found in the data in table 3 and

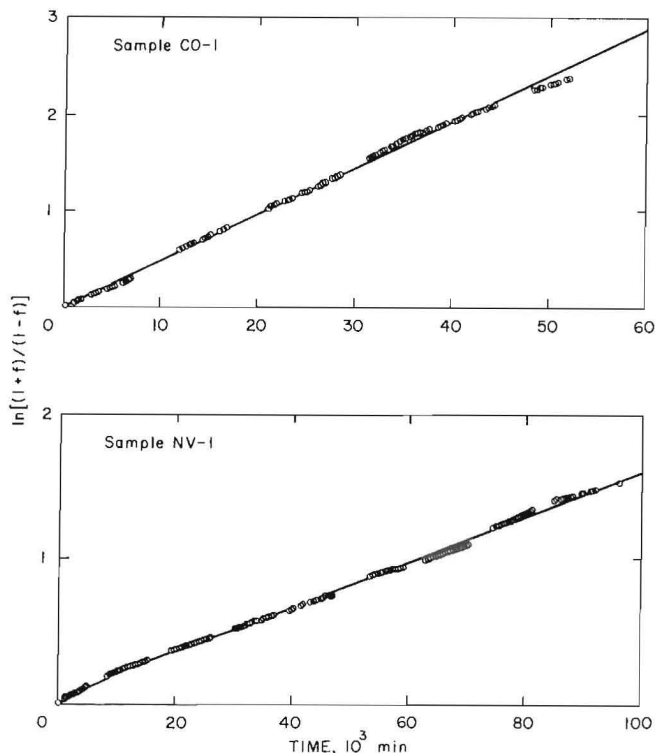


FIGURE 3.—Kinetic plots for samples CO-1 and NV-1.

figure 2, respectively. Silver not solubilized by the dual-leaching system is probably very slowly leached or resistant to cyanide leaching or is still not accessible to cyanide solutions owing to blockage by calcite or remaining manganese mineralization. Silver cosolubilized with manganese during SO₂ leaching is most likely intimately associated with the manganese oxides in the ore. Silver extracted by the cyanide solution after manganese removal by SO₂ solutions was previously not accessible to the cyanide solution owing to the presence of manganese mineralization in pores and fluid channels.

About 13 to 14 pct of the silver in ores AZ-2 and AZ-4 (fig. 2) was co-leached with the manganese by SO₂ solutions and therefore is intimately associated with the manganese mineralization, while about 67 to 68 pct of the silver was not accessible by cyanide solutions until after the manganese mineralization was removed. The remaining 18 to 20 pct of the silver is either (1) still encapsulated or intimately associated with the manganese mineralization remaining in the ore, (2) very slowly leached by cyanide, or (3) non-leachable by cyanide. Assuming a homogeneous distribution of the silver throughout the ores, from 1 to 5 pct additional silver should be recovered if the manganese leaching with SO₂ is allowed to be completed.

Ore CO-1 (fig. 2) has little silver in the manganese mineralization, as evidenced by the 2 pct of the silver

co-leached with the manganese (table 3). About 80 pct of the silver was amenable to cyanide leaching after manganese removal, making the silver mineralization accessible to cyanide solutions. Less than 18 pct of the silver is either slowly leached or not leached by cyanide solutions.

Ore AZ-3 (fig. 2) also had little silver in the manganese mineralization (2 pct) (table 3). The linearity of the silver-extraction curves (percent extraction versus volume cyanide solution applied) after 82-pct manganese extraction indicates that much of the refractory nature of this ore is due to the presence of calcite.

Much of the silver in ores AZ-1, CO-2, and NV-1 (fig. 2) is intimately associated with the manganese mineralization as 43, 40, and 38 pct of the silver (table 3) was coextracted with 78, 82, and 75 pct of the manganese, respectively. An additional 25, 14, and 2 pct of the silver was made accessible to cyanidation by removing manganese. Some of the remaining 32, 46, and 60 pct Ag in these ores is probably either slowly leached with cyanide solutions or not leachable with either SO₂ or cyanide solutions; however, extraction of more silver is probable if the SO₂ leaching of manganese is continued longer. Assuming a homogeneous distribution of silver throughout the ores about 12, 18, and 13 pct additional silver, respectively, would be extracted with the SO₂ solutions upon extraction of the remaining manganese.

CONCLUSIONS

Column-leaching tests were conducted on minus 2.5- plus 1.3-cm ore pieces to evaluate a dual in situ or heap leaching method for the recovery of manganese and silver from domestic manganese deposits. The method features an initial leach of the manganese with a 5-wt-pct-SO₂ solution followed by a neutralization rinse, and then a second leach of the silver with a 0.3-wt-pct-caustic-cyanide solution. Silver-leaching tests were conducted on materials from domestic

manganese deposits that contained silver ranging from 1.8 to 7.0 tr oz/st. Direct cyanide leaching of these samples resulted in only 0.7- to 8.5-pct silver extraction. Leaching with cyanide after SO₂ leaching resulted in silver extractions ranging from 2 to 80 pct in addition to the 2 to 40 pct recovered during the SO₂ leach. Overall silver recovery was 25 to 80 pct.

The dual leaching method appears suitable for deposits in which the silver is

intimately associated with the manganese mineralization prohibits the cyanide and for deposits in which manganese solution from attacking the silver.

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