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Bacterial Preoxidation of Stillwater Complex, MT, Platinum-Group Metal Flotation Concentrate and Recovery of Platinum-Group Metals by Cyanidation and Other Leachants

By D. L. Yopps and E. G. Baglin

UNITED STATES DEPARTMENT OF THE INTERIOR



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**UNITED STATES DEPARTMENT OF THE INTERIOR
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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mol/L	mole per liter
g	gram	mol pct	mole percent
g/L	gram per liter	mV	millivolt
g/mt	gram per metric ton	pct	percent
h	hour	psig	pound per square inch, gauge
L	liter	rpm	revolution per minute
L/h	liter per hour	tr oz	troy ounce
mg/L	milligram per liter	V	volt
mL	milliliter	wt pct	weight percent
μm	micrometer		

BACTERIAL PREOXIDATION OF STILLWATER COMPLEX, MT, PLATINUM-GROUP METAL FLOTATION CONCENTRATE AND RECOVERY OF PLATINUM-GROUP METALS BY CYANIDATION AND OTHER LEACHANTS

By D. L. Yopps¹ and E. G. Baglin²

ABSTRACT

In research conducted by the U.S. Bureau of Mines, platinum-group metal (PGM) flotation concentrate from the Stillwater Complex, MT, was subjected to biooxidation using *Thiobacillus ferrooxidans* in an effort to break down the sulfide minerals and liberate the associated PGM's for subsequent chemical leaching. Bacterial preleaching oxidized up to 94 pct of the sulfide present, destroyed the PGM-bearing pentlandite [(Ni,Fe)₉S₈] mineralization, and dissolved most of the nickel in the concentrate.

Cyanidation at 80° C proved to be the most attractive chemical leachant, removing 34 pct of the platinum, 76 pct of the palladium, 94 pct of the rhodium, and 97 pct of the gold from the biooxidized concentrate. Research also indicated that increased sulfide oxidation during the preleach phase led to improved PGM recovery in the subsequent chemical leaching phase.

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INTRODUCTION

The United States currently imports 93 pct of the 2 million tr oz of PGM's consumed domestically per year (1).³ Traditional processing of PGM ores includes flotation concentration, matte smelting, leaching, and refining steps. Previous U.S. Bureau of Mines research showed that over 95 pct of the PGM values could be recovered from Stillwater Complex flotation concentrates by matte smelting and leaching (2). To eliminate the smelting step, the Bureau investigated a procedure to recover PGM's directly from Stillwater Complex concentrates by oxidative leaching after a high-temperature roasting step (3). This technique produced platinum and gold recoveries comparable to matte leaching, but palladium recovery was only about 80 pct.

Biological oxidation of the sulfide minerals using the bacterium *Thiobacillus (T.) ferrooxidans* may also be an effective method to liberate the PGM's and gold in the Stillwater flotation concentrate. Biooxidation would eliminate the need for high temperatures required for smelting and would avoid emission control problems associated with the escape of SO₂ gas. Although the technology is relatively new, biooxidation is currently being used on

refractory gold ores that do not respond to direct cyanidation because the precious metals are locked inside a sulfide mineral matrix. After pretreatment with *T. ferrooxidans* in vat reactors, these ores can be successfully cyanided (4-5). For some ores, this technique is competitive with roasting (6-7) and pressure oxidation (8-9) as a means of breaking down refractory sulfides.

T. ferrooxidans is an aerobic, acidophilic bacterium that can utilize both sulfides and ferrous iron for its energy source. It can convert relatively insoluble metal sulfides by direct biological interaction into water-soluble metal sulfates and can also oxidize ferrous iron to ferric iron, which can chemically oxidize the metal sulfides to elemental sulfur and sulfate salts. During the biooxidation process, H₂SO₄ is also generated.

As part of its program to reduce the Nation's dependence on foreign sources of critical and strategic materials, the Bureau conducted research at the Reno Research Center to determine whether or not biooxidation is a feasible alternative for the treatment of sulfidic PGM concentrates. Methods studied for extracting the precious metals from the biooxidized concentrate are also discussed.

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The authors would like to thank the Stillwater Mining Co. (SMC), Nye, MT, for providing samples of flotation concentrate, and the Idaho National Engineering

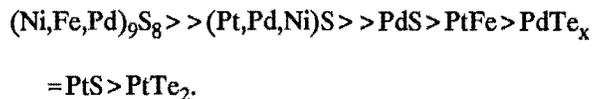
Laboratories, Idaho Falls, ID, for supplying bacterial cultures, nutrient media, and input on the biological aspects of the research.

MATERIALS AND METHODS

DESCRIPTION OF STILLWATER CONCENTRATE

Samples of dried flotation concentrate, with a particle size of approximately 60 pct minus 75 μm, were obtained from SMC. Mineralogical analysis of the concentrate using scanning electron microscopy (SEM) shows a combination of host rock silicate minerals, including talc, along with base and precious metal sulfides. The PGM's are associated with iron, copper, and nickel sulfide minerals, with more than 80 pct of the palladium in solid solution in pentlandite (10). Six other PGM-bearing minerals are

prevalent in the Stillwater samples: braggite [(Pt,Pd,Ni)S], vysotskite [(Pd,Ni,Pt)S], ferroplatinum alloy (PtFe), moncheite (PtTe₂), cooperite (PtS), and kotulskite (PdTe). The relative preponderance, determined by an SEM image analysis technique, of PGM minerals in the concentrate is as follows:



The chemical analysis of the concentrate is shown in table 1.

³Italic numbers in parentheses refer to items in the list of references at the end of this report.

Table 1.—Chemical analysis of selected constituents in Stillwater flotation concentrate

Nickel pct ..	2.8	Al ₂ O ₃ pct ..	5.8
Copper pct ..	1.9	CaO pct ..	4.1
Iron pct ..	10.9	Palladium g/mt ..	1,142
Sulfur pct ..	5.9	Platinum g/mt ..	328
S ²⁻ pct ..	5.7	Gold g/mt ..	19
SiO ₂ pct ..	42.6	Rhodium g/mt ..	11
MgO pct ..	18.3		

BACTERIA DESCRIPTION AND CULTURING TECHNIQUES

Efforts to isolate native acidophilic bacteria that could use ferrous iron and/or sulfides for their energy source from ore and water samples collected at the mine site were unsuccessful, presumably because of the basic nature of the SMC ore body. Therefore, strains of the bacterium, *T. ferrooxidans*, were obtained from commercial sources and other biotechnology laboratories. Cultures included three American Type Culture Collection (ATCC) strains (19859, 13661, and 13598), one strain isolated from coal mine drainage, and four strains isolated from acid mine drainage high in manganese. The bacterial cultures were originally grown in 1X, a complex nutrient medium containing, in grams per liter, 7.46 FeSO₄·7H₂O, 0.15 (NH₄)₂SO₄, 0.15 KCl, 0.15 K₂HPO₄, 3.36 MgSO₄·7H₂O, 1.28 CaCl₂·2H₂O, 2.25 Al₂(SO₄)₃·18H₂O, and 0.12 MnSO₄·H₂O. Tests were conducted to determine if the medium could be simplified while maintaining bacterial activity. Results indicated that ATCC medium 64 (11), a four-component medium containing, in grams per liter, 20.00 FeSO₄·7H₂O, 0.80 (NH₄)₂SO₄, 0.40 KH₂PO₄, and 0.16 MgSO₄·7H₂O also supported biological growth.

Optimum growth conditions for *T. ferrooxidans* include a pH of about 2.5 and a temperature range of 30° to 35° C (12), although some strains have been adapted to grow at a lower pH and at higher temperatures. The thiobacillus cultures were maintained in an active growth phase by a biweekly transfer of 1 mL of culture into 10 mL of sterile nutrient media. Cultures were adapted to the concentrate over a period of several months by adding small amounts (approximately 0.1 g) of the substrate to the culture tubes and transferring biweekly until consistent growth in the presence of the concentrate was achieved. Stock cultures were maintained in an incubator at 30° C.

Inocula used for bioreactor leaching tests were prepared by adding 1 to 5 mL of bacterial culture to 100 to 500 mL of a nonsterile nutrient medium. In most cases, 10 to 50 g of nonsterile mineral concentrate was also

added to the inoculum to further adapt the culture. This mixture was grown in a 30° C incubator for 72 h prior to addition to leach tests. Average cell population in the inoculum, as determined by direct observation using a Petroff-Hausser⁴ counting chamber, was on the order of 2 - 4 × 10⁷ cells per milliliter.

SCREENING TESTS

Screening experiments were carried out in baffled 250-mL Erlenmeyer flasks containing 5 g of nonsterile flotation concentrate, 100 mL of nutrient medium, and 1 mL of bacterial inoculum of *T. ferrooxidans*. Flasks were loosely capped and placed in a constant temperature shaking water bath or in an environmentally controlled gyratory shaker operating at 200 rpm. Control tests were run under identical test conditions, but without bacterial inoculum to determine the extent of chemical leaching in the system. After 14 days, the slurries were filtered and washed with distilled water. Samples of the leach solution were analyzed for base metal concentrations, PGM's, total iron, and total sulfur by inductively coupled plasma (ICP) analysis, ferrous iron by a potassium dichromate titration, and sulfate by ion chromatography. Leach residues were analyzed for PGM's by a combined fire assay-ICP technique, base metals by ICP analysis, total sulfur using an oxygen combustion technique, sulfate using ion chromatography, and elemental sulfur using a carbon disulfide dissolution technique. The sulfide content of the residue was calculated as the difference between total sulfur and elemental and sulfate sulfur. Net sulfide oxidation in the solids was used as an indicator to determine the extent of biological activity.

STIRRED BIOREACTOR TESTS

Stirred bioreactor experiments were conducted in jacketed 1- to 5-L reactors, as shown in figure 1, with a 10-wt pct pulp of concentrate in the nutrient medium and a 10-wt pct inoculum of *T. ferrooxidans* culture. Reactors were sparged with air containing 5 mol pct CO₂ to enhance the rate of biooxidation and to provide a source of cellular carbon. The gas mixture was bubbled through a water column placed in line ahead of the bioreactor to minimize evaporative losses. The water-saturated air-CO₂ mixture was then sparged into the bioreactor through capillary tubes at a rate of approximately 1.2 L/h, which

⁴Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

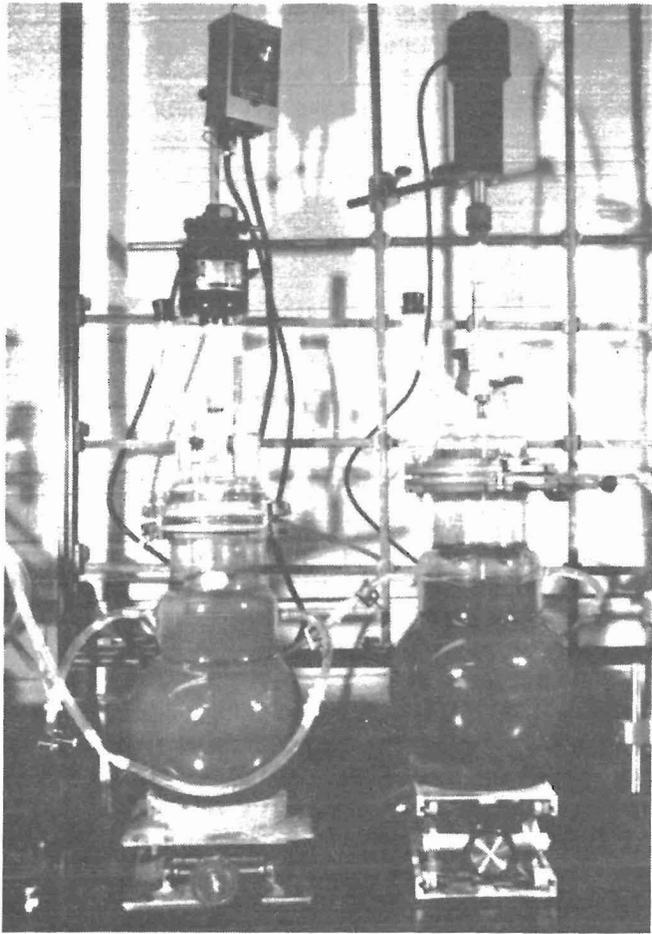


Figure 1.—Constant temperature stirred bioreactor.

produced a dissolved oxygen content of approximately 2 to 3 mg/L in the solution. According to the literature, a dissolved oxygen concentration of at least 2.0 mg/L ensures that the availability of dissolved oxygen does not limit biological oxidation of refractory sulfide gold ores (13-14).

Reactors were continuously stirred at approximately 200 rpm, a rate fast enough to keep the slurry well suspended, and the temperature was maintained at 30° C. Tests were generally 21 to 35 days long, with samples taken periodically to monitor ferrous iron, sulfate, copper, and nickel concentrations in the solutions and sulfide content of the solids. The pH and oxidation potential (Eh) of the slurries were also monitored.

THIOUREA LEACH TESTS

Tests were conducted in stirred beakers for 5 h at ambient temperature (~23° C) with 50 g of concentrate or biooxidized material added to 150 mL of distilled water. The pH was adjusted between 1.0 and 2.0 with dilute H₂SO₄, after which thiourea was added to make a 5-pct solution. The slurry potential was maintained in the range recommended for gold extraction, 0.39 to 0.42 V versus standard hydrogen electrode (SHE) (15), by the periodic addition of Fe₂(SO₄)₃.

OXIDATIVE CHLORIDE AND AQUA REGIA LEACH TESTS

Tests were carried out in stirred beakers for 6 h at ambient temperature with 10 g of concentrate or biooxidized material in 200 mL of either 6 mol/L HCl or aqua regia. Concentrated H₂O₂ (30 pct by volume) was added to the HCl experiments as necessary to maintain the solution potential above 1.00 V versus SHE in the oxidative chloride system. The solution potential in the aqua regia system remained above 1.00 V versus SHE without the addition of supplementary oxidizers.

CYANIDE LEACH TESTS

Pressurized cyanide leach tests were conducted in a 250-mL Teflon fluorocarbon polymer-lined autoclave. Twenty grams of concentrate or biooxidized material was added to 100 mL of distilled water. The pH was adjusted using NaOH to approximately 10.0, after which NaCN was added to form a 2-wt pct cyanide solution. The reactor was sealed and heated to 160° C and maintained at temperature for 1 h. The pressure in the autoclave was about 75 psig. After cooling, the slurry was filtered and washed with distilled water, and the solutions and solids were analyzed.

Atmospheric cyanidation tests utilized a 1-L controlled temperature, stirred reactor. Thirty grams of concentrate or biooxidized material was added to 600 mL of distilled water. The pH was adjusted using NaOH to approximately 10.0, after which NaCN was added to form a 1- to 2-wt pct cyanide solution. These tests were conducted for 23 to 48 h at varying temperatures and cyanide concentrations. The reactor was vented through a condenser tube to minimize water losses.

RESULTS AND DISCUSSION

SCREENING TESTS

Shake-flask and culture-tube screening tests were performed to determine conditions for operating the larger bioreactors. The effects of temperature, nutrient medium, and acidity were investigated. Abiotic control tests were conducted to determine the extent of chemical oxidation of the sulfide minerals in the absence of bacteria.

The eight *T. ferrooxidans* strains were inoculated into sterile nutrient medium 1X containing flotation concentrate and 1.5 g/L ferrous iron, the latter added as a supplemental energy source. The cultures were incubated at three temperatures, 30° C, 35° C, and ambient (~23° C) to determine the best temperature for biological activity, as determined by visual inspection of culture growth and ferrous iron oxidation rates. Results showed that the bacteria were more active at 30° C than at either ambient temperature or 35° C, and that all strains oxidized the iron at approximately the same rate for any given temperature.

Screening tests also showed that sulfide oxidation of the Stillwater concentrate was as good or better with medium 64 as with medium 1X. Therefore, all bacterial cultures were adapted to grow in medium 64.

It is known that pH control is critical for maintaining biological activity of *T. ferrooxidans* bacteria. The pH was particularly important in the present research because the basic mineral talc [$Mg_3Si_4O_{10}(OH)_2$] comprised over 50 pct of the Stillwater concentrate and acted in a buffering capacity, partially neutralizing the H_2SO_4 generated during the biooxidation process. If the pH of the biooxidation slurry rose above about 2.5, not only did biological activity decrease, but ferric iron produced during the biooxidation of ferrous iron precipitated in the form of jarosite and hydroxy sulfate compounds. These precipitates could inhibit leaching by coating the concentrate particles. However, if the nutrient solution was acidified to pH 2.0 before use by adding dilute H_2SO_4 , the bacteria could maintain the pH below 2.5 during biooxidation and the precipitation problem was eliminated.

Test conditions to be used in batch stirred bioreactors were selected from the information obtained in the screening experiments. Since all strains of bacteria oxidized ferrous iron at approximately the same rate, *T. ferrooxidans* strain A-6 was selected at random for subsequent testing. ATCC medium 64 at a pH of 2.5 or lower was used as the growth medium, and the tests were conducted at 30° C.

Abiotic control tests were conducted to ensure that chemical leaching did not contribute significantly to the

overall sulfide oxidation. Results from shake-flask tests that used flotation concentrate slurried in sterile ATCC nutrient medium 64 showed that less than 1 pct of the sulfide was oxidized in 14 days at any of the three temperatures tested, compared with approximately 50 pct oxidation for biologically active experiments.

STIRRED BIOREACTOR STUDIES

Unadapted strains of *T. ferrooxidans* were used in the initial batch-bioreactor tests. Biooxidation stopped after about 65 pct of the sulfide in the concentrate had been converted to sulfate. Adapting the bacteria by adding substrate to the culture tubes and the inoculum led to progressively higher levels of sulfide oxidation. Abiotic control tests conducted in the stirred reactors confirmed the previous finding that chemical leaching was not an important factor in the overall sulfide oxidation.

Results obtained from a typical biological leach of the Stillwater flotation concentrate using an adapted *T. ferrooxidans* culture are presented in figure 2. The sulfide concentration in the solid was reduced to approximately 1 pct in 35 days, corresponding to 83 pct sulfide oxidation.

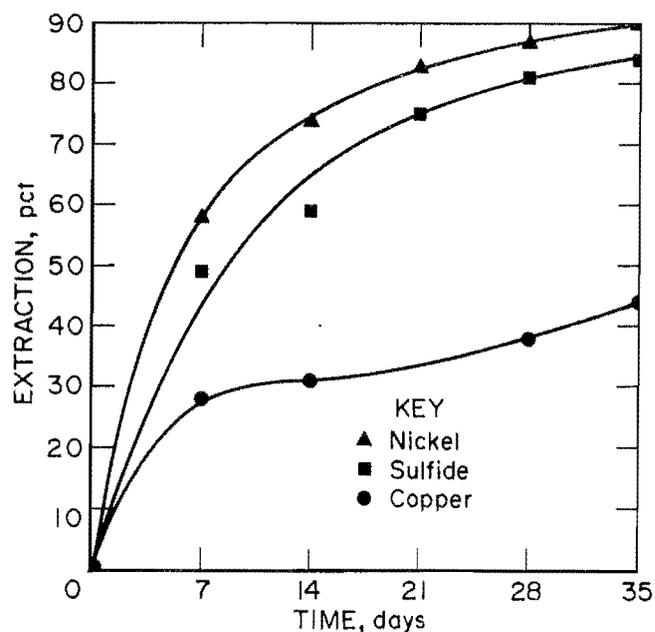


Figure 2.—Biooxidation of Stillwater flotation concentrate. Stirred bioreactor leach test using an adapted strain of *T. ferrooxidans* in ATCC medium 64.

In the same time, 44 pct of the copper and 90 pct of the nickel were solubilized. The redox potential of the system rose from 0.52 to 0.81 V versus SHE, indicating strong oxidizing conditions, while the pH remained relatively constant at 2.4.

Results from several batch reactor experiments showed that the rate of sulfide oxidation decreased after approximately 28 days of leaching. To investigate the possibility that biological inhibition was occurring because of ion or metabolite buildup in the leach solution, tests were conducted in which the nutrient medium was replaced periodically with fresh medium. Medium replacement would also provide additional nitrogen and phosphorus, necessary to fulfill the nutritional requirements of the bacteria. A summary of the results obtained are presented in table 2.

Table 2.—Effect of periodic medium replacement on biooxidation of Stillwater flotation concentrate, percent

	No replacement	Weekly replacement
Sulfide in solids:		
7 days	5.6	5.2
14 days	4.2	2.3
21 days	1.6	NR
28 days	1.4	.9
35 days	1.1	.3
Total sulfide oxidized	83	94
NR	No reading.	

NOTE.—Conditions: 3-L stirred reactor, ATCC medium 64, 10 pct pulp, 10 pct inoculum, sparged with air containing 5 pct CO₂, 30° C.

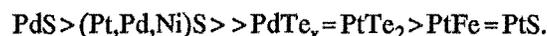
Weekly medium replacement did improve the sulfide oxidation somewhat. The experiment in which the medium was not replaced achieved 83 pct sulfide oxidation in 35 days, while the test with replacement achieved 94 pct in the same time. The rate of sulfide oxidation still decreased toward the end of the test, indicating rate-inhibiting factors other than ion buildup or nutrient depletion may exist.

Solution and solids analyses indicated that some of the ferrous iron in the ATCC 64 nutrient medium precipitated from solution during the first 7 days of biooxidation. Tests were conducted to determine if such high concentrations of ferrous iron were essential for bioleaching. If the ferrous iron additions could be decreased or eliminated, problems associated with iron precipitation would be decreased, and reagent costs would be reduced.

The ferrous iron in the nutrient medium was decreased from 4 to 0 g/L, generally with no deleterious effect on

sulfide oxidation. However, maintaining active stock cultures in iron-free media proved to be difficult, and sometimes the bacteria died. Further research showed that growing cultures in medium containing 4.0 g/L ferrous iron and inoculating into iron-free media in the bioreactor provided active bacterial populations and at the same time significantly decreased the overall amount of ferrous sulfate required.

Mineralogical analysis of the residues after bioleaching showed a nearly complete removal of pyrite, chalcopyrite, and the palladium-bearing pentlandite. The PGM sulfides are more stable than the base metal sulfides and were much more difficult to oxidize (16-17). The relative preponderance, determined by an SEM image analysis technique, of PGM's after bioleaching to 94 pct sulfide oxidation is as follows:



Comparison of these results with the sequence before biological treatment indicates that palladium in the pentlandite was transformed to palladium sulfide (PdS) during the biooxidation process.

Research was undertaken to determine whether or not destruction of the sulfide matrix during biooxidation liberated these PGM grains sufficiently to allow extraction by chemical means.

PGM AND GOLD EXTRACTION

Several lixivants were tested to determine their effectiveness for the removal of the PGM's and gold from the bioleached residue. Lixivants that are used in an acidic environment would be preferred since they would be more compatible with the acidic conditions established during the biooxidation process and would not necessitate neutralization before use.

Thiourea

Considerable research has been conducted with thiourea as an alternative to cyanidation for extracting precious metal values from gold ores (13, 18). Tests were performed to determine if thiourea would be an effective lixiviant for PGM extraction. The results, presented in table 3, show that thiourea proved ineffective for PGM solubilization. Extraction from both the biooxidized and as-received samples was similar. Based on the poor recoveries, thiourea was eliminated as a possible lixiviant for PGM extraction.

Table 3.—Thiourea leaching of Stillwater PGM concentrate, percent

Sample	Sulfide oxidized	Extraction			
		Platinum	Palladium	Rhodium	Gold
As received . .	0	5	8	20	49
Biooxidized . .	60	0	0	26	46

NOTE.—Conditions: 50 g concentrate, 150 mL distilled water, pH 1 to 2, Eh 390 to 420 mV versus SHE, 5 pct thiourea, ambient temperature, 5 h.

Oxidative Chloride Leaching

Previous Bureau research showed that oxidative chloride leaching was effective for solubilizing PGM's from roasted Stillwater concentrates (3). Tests were conducted to determine if the oxidative chloride leach would also be effective for extracting PGM's from the biooxidized material.

The results obtained from the oxidative chloride leaching tests are summarized in table 4. The pH of the acid chloride system was compatible with the biooxidation process, but the high acidity solubilized base metals and gangue in addition to the PGM's, producing a complex leach solution. Biological pretreatment of the concentrate made it more amenable to chemical extraction as compared with the untreated sample, and in general, the greater the extent of sulfide oxidation in the preleach, the higher the subsequent PGM extraction. Rhodium was not extracted using the oxidative chloride leach.

Table 4.—Oxidative chloride leaching of Stillwater PGM concentrate, percent

Sample	Sulfide oxidized	Extraction			
		Platinum	Palladium	Rhodium	Gold
As received . .	0	2	8	0	43
Biooxidized . .	60	3	46	0	73
Do.	79	10	62	0	81
Do.	94	24	65	0	88
Roasted					
1,060° C . . .	99+	69	72	0	88

NOTE.—Conditions: 10 g concentrate, 200 mL of 6-mol/L HCl, ambient temperature, 6 h.

Overall extractions were much lower than those reported in the previous roasting-leaching research, which showed greater than 90 pct extraction of platinum and gold, and about 80 pct extraction of the palladium from a

concentrate that had been roasted to remove the sulfides. A sample of as-received concentrate was treated under conditions similar to those used in the previous research to compare results. The sample was roasted at 1,060° C for 6 h and then subjected to the oxidative chloride leach. Table 4 shows that platinum extraction increased significantly as compared with the extraction from the biooxidized material, but was still less than reported earlier, indicating a possible change in mineralogy between the samples obtained for current research and those obtained for the previous work.

Aqua Regia

Aqua regia is widely used by industry to extract PGM's from anode slimes and matte products (19-20) and would be compatible with the acidic biooxidation procedure. A set of tests was conducted under the same conditions used in the oxidative chloride tests, with the exception of the chemical lixiviant, to determine if aqua regia would be a more suitable agent for PGM extraction.

Results, presented in table 5, show that the biological preleach did not lead to improved PGM extraction. In this case, similar recoveries were obtained with the as-received and biooxidized concentrate. Like oxidative chloride leaching, significant improvements in platinum extraction were obtained when the concentrate was roasted to remove the sulfides prior to chemical leaching.

Neither acid leach system removed high enough concentrations of PGM's, especially platinum or rhodium, from the biooxidized concentrate. Extensive base and gangue mineral solubilization occurred, which would create solubility problems in recycled solutions used in an operating metals recovery plant.

Table 5.—Aqua regia leaching of Stillwater PGM concentrate, percent

Sample	Sulfide oxidized	Extraction			
		Platinum	Palladium	Rhodium	Gold
As received . .	0	36	69	0	98
Biooxidized . .	60	33	69	0	97
Do.	79	26	67	0	95
Do.	94	28	67	0	97+
Roasted					
1,060° C . . .	99+	87	75	0	96

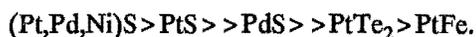
NOTE.—Conditions: 10 g concentrate, 200 mL aqua regia, ambient temperature, 6 h.

Cyanidation

Current research at the Reno Research Center has shown that high PGM extractions can be obtained from automobile catalytic converters using high-temperature cyanidation (21). Tests were conducted to determine if the PGM's could be extracted from the biooxidized residue using cyanide. Temperature, pressure, duration of leach, cyanide concentration, and extent of sulfide oxidation during the biological pretreatment were considered. Since cyanide must be used in a basic environment, at a pH of 10 or higher to avoid the production of HCN gas, both the as-received and biooxidized samples required pH adjustment prior to the addition of cyanide.

A summary of the test results is shown in table 6. In all cases, biological pretreatment of the ore improved its amenability to cyanidation. In general, PGM extraction increased with increased sulfide oxidation during the pretreatment phase, and solubilization of gangue minerals was minimal. The data indicate that cyanidation under atmospheric pressure conditions at 60° and 80° C was as effective as the tests run at 160° C under a pressurized environment. Cyanide concentration and leach time did not greatly affect PGM extraction for the combinations tested. The best results obtained using the cyanide lixivant extracted 75 pct of the palladium and more than 94 pct of the rhodium and gold, but only 34 pct of the platinum.

A mineralogical inspection of the 94 pct oxidized residue after cyanidation showed the relative order of PGM's remaining in the material as follows:



When the order of species before cyanidation is compared, it can be seen that cyanide attacks PdS preferentially over the platinum-bearing sulfides, which accounts for the difference in extraction between palladium and platinum.

Results of this study indicate that complete sulfide oxidation may be required during the biological treatment stage to achieve suitable PGM extractions from the Stillwater flotation concentrate. This is in contrast to gold ores, which generally require only 30 to 50 pct sulfide

oxidation during bioprocessing to obtain acceptable gold extraction during cyanidation. It is entirely possible that *T. ferrooxidans* may not be capable of oxidizing the extremely stable platinum sulfide minerals. Screening of chemical lixiviants will continue and tests will be performed to identify the upper limit of PGM extraction based on the maximum obtainable sulfide oxidation in the preleach process.

Table 6.—Cyanidation of Stillwater PGM concentrate, percent

Sample	Sulfide oxidized	Extraction			
		Platinum	Palladium	Rhodium	Gold
PRESSURE CYANIDATION: 160° C, 1 h, 2 pct CN ⁻					
As received ..	0	6	11	5	23
Biooxidized ..	70	14	71	87	77
Do.	79	18	74	89	94
Do.	94	29	76	100	97
ATMOSPHERIC CYANIDATION: AMBIENT TEMP, 23 h, 2 pct CN ⁻					
As received ..	0	5	14	0	96
Biooxidized ..	17	8	36	0	97
Do.	24	9	40	27	100
Do.	60	10	72	75	59
Do.	83	9	75	67	95
ATMOSPHERIC CYANIDATION: 60° C, 23 h, 2 pct CN ⁻					
As received ..	0	12	24	21	79
Biooxidized ..	17	16	44	0	88
Do.	24	18	63	63	95
Do.	60	19	76	89	96
Do.	79	21	75	91	97
Do.	94	28	76	94	97
Roasted	99	70	77	0	95
ATMOSPHERIC CYANIDATION: 80° C, 23 h, 2 pct CN ⁻					
As received ..	0	19	58	79	93
Biooxidized ..	17	20	71	88	100
Do.	24	11	37	25	76
Do.	60	25	76	83	96
Do.	79	22	74	93	97
Do.	94	28	76	94	97
Roasted	99	79	84	21	97
ATMOSPHERIC CYANIDATION: 80° C, 23 h, 1 pct CN ⁻					
Biooxidized ..	79	23	74	82	99
Do.	94	35	76	90	99
ATMOSPHERIC CYANIDATION: 80° C, 48 h, 1 pct CN ⁻					
Biooxidized ..	79	25	73	92	97
Do.	94	34	75	94	97

SUMMARY AND CONCLUSIONS

Biological oxidation of sulfide minerals present in Stillwater Complex flotation concentrate with *T. ferrooxidans* has been demonstrated. Up to 94 pct sulfide oxidation was achieved in 35 days of leaching in a stirred tank bioreactor. Weekly medium replacement and sparging with air enhanced biological oxidation of the sulfide minerals.

Decreasing the medium iron concentration did not adversely affect the extent of sulfide oxidation and eliminated the problems associated with iron precipitation.

The potential for extracting PGM's from the biooxidized residue was assessed. Increased sulfide oxidation in the biological preleach led to increased PGM extraction

during subsequent oxidizing acidic chloride or cyanide leaching. Cyanidation was determined to be more attractive because acid leaching solubilized excessive amounts of gangue constituents. The most successful test, an

80° C cyanide leach, removed 34 pct of the platinum, 75 pct of the palladium, 94 pct of the rhodium, and 97 pct of the gold from the biooxidized concentrate.

REFERENCES

1. Loebenstein, J. R. Platinum-Group Metals. Sec. in BuMines Mineral Commodity Summaries 1989, p. 120.
2. Baglin, E. G., J. M. Gomes, and M. M. Wong. Recovery of Platinum-Group Metals From Stillwater Complex, Mont., Flotation Concentrates by Matte Smelting and Leaching. BuMines RI 8717, 1982, 15 pp.
3. Baglin, E. G., J. M. Gomes, T. G. Carnahan, and J. M. Snider. Recovery of Platinum, Palladium, and Gold From Stillwater Complex Flotation Concentrate by a Roasting-Leaching Procedure. BuMines RI 8970, 1985, 12 pp.
4. Brynesteyn, A. Bioleaching of Refractory Gold/Silver Ores and Concentrates. Paper in CIM—Leaching, Unit Operations and Processes (Pres. at 14th CIM Annu. Hydrometallurgy Meet., Timmins, Ontario, Canada, Oct. 14-17, 1984). CIM, 1984, pp. 1-9.
5. Hutchins, S. R., J. A. Brierley, and C. L. Brierley. Microbial Pretreatment of Refractory Sulfide and Carbonaceous Gold Ores. Soc. Min. Eng. AIME preprint 87-143, 1987, 16 pp.
6. Jha, M. C., and M. J. Kramer. Recovery of Gold From Arsenical Ores. Precious Met.: Min., Extr., and Process., AIME (New York), 1987, pp. 337-365.
7. Arriagada, F. J., and K. Osseo-Asare. Gold Extraction From Refractory Ores: Roasting Behavior of Pyrite and Arsenopyrite. Precious Met.: Min., Extr., and Process., AIME (New York), 1987, pp. 367-385.
8. Muir, C. W. A., L. P. Hendriks, and H. W. Gussman. The Treatment of Refractory Gold-Bearing Flotation Concentrates Using Pressure Leaching Techniques. Precious Met.: Min., Extr., and Process., AIME (New York), 1987, pp. 309-322.
9. Argall, G. O. Perseverance and Winning Ways at McLaughlin Gold. Eng. and Min. J., v. 187, No. 10, 1986, pp. 26-32.
10. Hodges, G. J., and R. K. Clifford. Recovering Platinum and Palladium at Stillwater. J. Met., v. 40, June 1988, pp. 32-35.
11. Cole, R. (ed.). Catalogue of Bacteria and Phages. Am. Type Cult. Collect., 17th ed., 1989, p. 293.
12. Kelly, D. P., and P. P. Harrison. Bergey's Manual of Systematic Bacteriology. Williams and Wilkins, v. 3, 1989, pp. 1842-1858.
13. Gormely, L. S., and R. M. R. Branion. Engineering Design of Microbiological Leaching Reactors. Paper in Biohydrometallurgy (Proc. Int. Symp., Jackson Hole, WY, Aug. 13-18, 1989). Can. Cent. Miner. and Technol., 1989, pp. 499-518.
14. Griffin, E. A., and L. Luinstra. Bioreactor Scaleup: Practical Considerations for Biologically Assisted Gold Recovery. Paper in Biohydrometallurgy (Proc. Int. Symp., Jackson Hole, WY, Aug. 13-18, 1989). Can. Cent. Miner. and Technol., 1989, pp. 221-230.
15. Eisele, J. A., A. H. Hunt, and D. L. Lampshire. Leaching Gold-Silver Ores With Sodium Cyanide and Thiourea Under Comparable Conditions. BuMines RI 9181, 1988, 7 pp.
16. Southwood, M. J. Bacterial Leaching: Some Mineralogical Constraints in the Selection of Low-Grade Nickel Ores. Mintek Rev., v. 1, 1985, pp. 25-30.
17. Natarajan, K. A. Electrochemical Aspects of Bioleaching Multi-sulfide Minerals. Miner. & Metall. Process., v. 5, May 1988, pp. 61-65.
18. Schultze, R. G. New Aspects in Thiourea Leaching of Precious Metals. J. Met., v. 36, June 1984, pp. 62-65.
19. Demopoulos, G. P. Refining of Platinum-Group Metals. CIM Bull., v. 82, March 1989, pp. 165-171.
20. Lanham, R. D., and E. D. Zysk. Platinum-Group Metals. Ch. in Kirk-Othmer Encyclopedia of Chemical Technology. Wiley, v. 18, 1982, pp. 228-253.
21. Atkinson, G. B., D. P. Desmond, R. J. Kuczynski, and L. A. Walters. Recovery of PGM From Virgin Automotive Catalysts by Cyanide Leaching. Paper in Platinum Group Metals and the Quality of Life, ed. by A. Austin, C. M. Barnard, and G. E. Haslam (Proc. Semin. Int. Precious Met. Inst., Las Vegas, NV, Jan. 29-31, 1989). Int. Precious Met. Inst., 1989, pp. 109-115.