

**RI 8970**

Bureau of Mines Report of Investigations/1985

# Recovery of Platinum, Palladium, and Gold From Stillwater Complex Flotation Concentrate by a Roasting-Leaching Procedure

By E. G. Baglin, J. M. Gomes, T. G. Carnahan, and J. M. Snider



UNITED STATES DEPARTMENT OF THE INTERIOR



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**BUREAU OF MINES**  
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Library of Congress Cataloging in Publication Data:

Recovery of platinum, palladium, and gold from Stillwater Complex flotation concentrate by a roasting-leaching procedure.

(Bureau of Mines report of investigations ; 8970)

Bibliography: p. 12.

Supt. of Docs. no.: I 28.23:8970.

1. Platinum--Metallurgy. 2. Palladium--Metallurgy. 3. Gold--Metallurgy. 4. Roasting (Metallurgy). 5. Leaching. 6. Flotation. I. Baglin, E. G. (Elizabeth G.). II. Series: Report of investigations (United States. Bureau of Mines) ; 8970.

TN23.U43 [TN799.P7] 622s [669'.2] 85-600085

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mL	milliliter
g	gram	oz/ton	ounce per ton
h	hour	pct	percent
L	liter	psig	pound (force) per square inch, gauge
<u>M</u>	gram mole per liter	µm	micrometer
mg	milligram	V	volt

# RECOVERY OF PLATINUM, PALLADIUM, AND GOLD FROM STILLWATER COMPLEX FLOTATION CONCENTRATE BY A ROASTING-LEACHING PROCEDURE

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## ABSTRACT

The Bureau of Mines devised a procedure for selectively extracting platinum-group metals (PGM) and gold from Stillwater Complex flotation concentrate. The Stillwater Complex is the only major U.S. PGM resource. Development of a suitable extraction technique will contribute to its exploitation. The concentrate was roasted at 1,050° C to convert host base-metal sulfides to oxides and the PGM from sulfide minerals to their elemental states. The roasted concentrate was preleached with dilute sulfuric acid to remove easily soluble gangue minerals. After preleaching, the concentrate was slurried with 6M HCl and leached at ambient temperature and pressure with a strong oxidizing agent. Hydrogen peroxide, chlorine, sodium hypochlorite, nitric acid, and a persulfate salt were the oxidants investigated. The two-stage leaching scheme extracted up to 97 pct of the platinum, 92 pct of the palladium, and 99 pct of the gold from the roasted concentrate. The base metals were not solubilized and reported to the residue. No attempt was made to devise a procedure to recover the copper and nickel because they comprise less than 5 pct of the value of the concentrate. Viable techniques for recovering the precious metals from the pregnant solution were sulfide precipitation, cementation with nickel, or adsorption on activated carbon.

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## INTRODUCTION

For several years the Bureau of Mines has been investigating methods for concentrating and recovering platinum-group metals (PGM) and associated base metals from ores from the Stillwater Complex, Montana, because it is the only major U.S. PGM resource (1-4).<sup>4</sup> The most significant PGM mineralization occurs in conjunction with iron, nickel, and copper sulfides which are found in mineralized layers of the Banded Zone of the Complex. Because of this sulfide association, the Bureau's studies focused on traditional techniques for treating sulfide ores. Samples of Stillwater Complex ores were beneficiated by froth flotation (1-3) and matte smelting-leaching (4).

Because of long processing times encountered with conventional treatment of

PGM sulfide concentrates and the ultimate probable dependence on a foreign smelter and refinery to produce the platinum-group metals, alternative processing of Stillwater Complex concentrates is being considered. The objective of the current investigation was to determine the feasibility of hydrometallurgical techniques to recover PGM from Stillwater Complex concentrates. Ore samples were obtained from the Minneapolis Adit on the Howland Reef and the West Fork Adit on the J-M Reef. Geological, stratigraphical, petrographical, and mineralogical descriptions of these zones of PGM concentration are discussed elsewhere (5-7).

## ACKNOWLEDGMENT

The authors gratefully acknowledge the assistance of Anaconda Minerals Co. (Atlantic Richfield Corp.) and Johns-

Manville Corp. for providing ore and concentrate samples used in this investigation.

## SAMPLE DESCRIPTION

Table 1 summarizes chemical and size distribution data for the four flotation concentrates used in this study. The ore from which concentrates MA, MB, and MC were prepared originated in Anaconda's Minneapolis Adit. These samples are representative of the concentrates generated by pilot mills operated by the Bureau and Anaconda Minerals Co. MA is a cleaner concentrate prepared from anorthositic ore in the Bureau's pilot mill using an acidified pulp and mercaptobenzothiazole (MBT) as the collector (2). MB resulted from flotation of a mixture of anorthositic and serpentized ores using a natural pH-xanthate circuit which included three cleaning cycles. This concentrate

was prepared in Anaconda Minerals Co. pilot mill at Tucson, AZ. MC was prepared by twice cleaning rougher concentrates recovered from serpentized ore in the Bureau's pilot mill. A sodium isobutyl xanthate-normal dodecylmercaptan collector combination was used at a natural pH of 8.2 (3). Sample WF was prepared from anorthositic ore from Johns-Manville's West Fork exploration adit. The WF concentrate was recovered by bench-scale flotation using an acid-MBT flotation circuit (1).

Microprobe examination showed that the concentrates were composed primarily of sulfide minerals in siliceous gangues. Although the mineralogy of the individual concentrates differed somewhat, the principal accessory minerals were pentlandite [(Fe,Ni)<sub>9</sub>S<sub>8</sub>], pyrite (FeS<sub>2</sub>), and chalcopyrite (CuFeS<sub>2</sub>), with minor to trace amounts of heazlewoodite (Ni<sub>3</sub>S<sub>2</sub>), galena

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

(PbS), sphalerite (ZnS), and millerite (NiS). The PGM were distributed partly in the form of platinoid minerals (Pt-Fe alloys, PGM sulfides) and partly in solid-solution in the pentlandite, with palladium partially replacing nickel in the crystal lattice. The other principal PGM minerals observed in these samples were vysotskite (PdS) and braggite (Pt,PdS). The gangue minerals consisted of Al, Ca, Fe, and Mg silicates. Analyses of gangue materials are reported in table 1 and throughout the paper as oxides of aluminum, calcium, magnesium, and silicon.

Because of a large supply of concentrate from the Bureau's pilot mill, most of the experimental work was carried out on sample MA. After the details of the procedure for recovering precious metals had been worked out, the method was tested on MB, MC, and WF which were available only in limited quantities. All experiments were conducted on a bench-scale. The concentrate samples used in leaching ranged from 25 to 300 g.

TABLE 1. - Analysis of flotation concentrates

Sample.....	Minneapolis Adit			West Fork Adit
	MA	MB	MC	WF
Analysis, oz/ton:				
Pt.....	8.79	8.76	3.05	3.57
Pd.....	16.21	33.21	8.62	11.38
Au.....	0.43	0.40	0.17	0.41
Analysis, pct:				
Cu.....	1.4	2.0	0.6	1.9
Ni.....	0.8	2.5	0.7	3.4
Fe.....	8.2	12.0	7.4	13.9
S.....	5.9	8.7	2.8	10.3
Al <sub>2</sub> O <sub>3</sub> .....	7.1	4.3	4.9	3.9
CaO.....	3.3	3.0	5.0	1.3
MgO.....	20.3	20.8	24.1	20.6
SiO <sub>2</sub> .....	46.7	40.7	48.1	32.7
Size distribution, pct:				
+200 mesh <sup>1</sup> .....	1.5	4.6	1.2	0.3
-200, +270 mesh <sup>1</sup>	2.9	6.3	3.3	3.5
-270, +325 mesh <sup>1</sup>	5.7	2.7	3.8	2.9
-325 mesh <sup>1</sup> .....	89.9	86.4	91.7	93.3

<sup>1</sup>Tyler standard screen sieves.

#### TEST SCHEME DEVELOPMENT AND EXPERIMENTAL PROCEDURES

Because of the complex nature of the Stillwater concentrate, it was anticipated that severe reaction conditions would be required to achieve good extraction of the metal values. Preliminary leaching experiments employed strong reagent concentrations, high temperatures, and sometimes high pressures. Pressure leaching experiments were performed in a glass-lined, 2-L Parr<sup>5</sup> titanium autoclave or in a modified 500-mL Parr hydrogenation reactor. Atmospheric pressure leaching was conducted in glass resin kettles which ranged in capacity from 500 mL to 4 L. Each reactor was fitted with a sealed-shaft stirrer, thermometer and thermocouple, and reflux condenser. Reactor temperature was maintained with a

heating mantle and temperature was controlled with a chromel-alumel thermocouple controller.

Preliminary studies revealed that roasting the concentrate made the PGM more amenable to oxidative leaching in strong HCl solutions. Roasting was conducted in a muffle furnace equipped with a thermocouple controller which maintained the temperature to  $\pm 5^\circ$  C of the set point. A rabble was used to stir the samples periodically to insure uniform oxidation throughout the bed, and a thermocouple was inserted into the sample bed to monitor the temperature. The usual procedure for conducting oxidative leaching was to slurry the roasted concentrate in a solution containing the desired acid concentration, and add oxidant dropwise until a constant solution redox potential, measured by a Pt-Ag/AgCl electrode couple, was attained. The observed potential was increased by the amount of

<sup>5</sup>Reference to specific products does not imply endorsement by the Bureau of Mines.

the reference electrode potential (0.20 V), and all values reported in this manuscript are relative to the standard hydrogen electrode. After leaching, the slurries were filtered, washed, and the residues oven-dried at 110° C. Solids and liquids were submitted for chemical analysis.

Subsequent experiments delineated the effects of reagent concentration and roasting and leaching temperatures on the selectivity of metal extraction. Finally, an H<sub>2</sub>SO<sub>4</sub> preleaching step was implemented into the processing scheme to remove easily soluble base metals and gangue mineral constituents which otherwise would contaminate the PGM-bearing pregnant solutions. Preleaching was conducted by heating a slurry containing 10 pct roasted solids in 1M H<sub>2</sub>SO<sub>4</sub> at 70° C for 4 h.

Precious metals were recovered from pregnant solutions by three techniques: (1) A 500-mL sample of pregnant solution containing the precious metals was allowed to drip at 1.3 mL/min from a reservoir through a column of minus 12- plus 30-mesh activated coconut charcoal. The column measured 1.6 cm ID and contained 30 mL of charcoal. Effluent from the column was passed through a second column of fresh charcoal to remove traces of metals not adsorbed by the first column. Effluent samples were collected during of the experiment and analyzed for precious metals. (2) A 200-mL sample of pregnant solution was stirred with 20 g of granular nickel for 3 h. The cementation

product containing the precious metals was collected on glass-fiber filter paper and the depleted solution was analyzed for precious metals. (3) A 5-L sample of pregnant solution was sparged with gaseous H<sub>2</sub>S for 10 min. The black precipitate composed of precious metal sulfides was removed by filtration, and the depleted solution was analyzed for precious metals.

Spent H<sub>2</sub>SO<sub>4</sub> preleaching solution was neutralized by reaction with flotation tailings which were basic because of the presence of talc. Experiments were conducted by gradually adding tailings to 250 mL-samples of preleaching solution. The slurries were stirred and the pH measured after each addition of solids. The pH was topped off by adding lime.

Samples were analyzed for base metal and gangue mineral oxides by inductively coupled plasma (ICP) spectroscopy. Determination of Pt, Pd, and Au was accomplished by a fire assay-ICP technique (8). Dore' beads were produced by fuming solid samples or evaporated liquid samples after inquarting with silver, which acted as a collector for the precious metals. The beads were dissolved in acid, and the resulting solutions analyzed by ICP. Sulfur was determined by a standard combustion technique. A scanning electron microscope (SEM) equipped with microprobe and X-ray diffraction spectroscopy were used to identify elements and compounds in solid samples.

## RESULTS AND DISCUSSION

### PRELIMINARY TESTS

Preliminary tests were undertaken to evaluate the leachability of Stillwater flotation concentrates. Most of the leaching solutions were mixtures of common oxidizing agents and strong mineral acids. Results are summarized in table 2. An effective leaching system should solubilize all of the valuable metals in the concentrate--in this case, the copper, nickel, and precious metals--or selectively remove the different metals or metal groups in a series of stages. None

of the media in table 2, except NaCl-O<sub>2</sub>, effectively separated the copper and nickel from the precious metals, and none solubilized high percentages of platinum and palladium.

A more effective technique was roasting followed by oxidative leaching. Data showing the effect of roasting temperature on the extraction of metal values and major gangue minerals from an orthositic concentrate with strong HCl and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) are summarized in table 3. Ninety percent or more of the Pt, Pd, and Au were extracted by the

TABLE 2. - Concentrate leaching - screening tests<sup>1</sup>

Lixiviant	Temp, °C	Pressure, psig	Extraction, pct					
			Pt	Pd	Au	Cu	Ni	Fe
H <sub>2</sub> O <sub>2</sub> -HCl.....	105	0	<0.1	<0.04	<0.9	77	70	65
H <sub>2</sub> O <sub>2</sub> -H <sub>2</sub> SO <sub>4</sub> .....	105	0	<.1	<.03	<.9	33	16	39
NaOCl-HCl.....	105	0	33	61	62	94	90	80
NaOCl-H <sub>2</sub> SO <sub>4</sub> .....	105	0	34	69	31	>99	98	90
NaCl-Cl <sub>2</sub> -O <sub>2</sub> .....	110	<sup>2</sup> 50	.7	16	<.9	95	93	.3
NaCl-Cl <sub>2</sub> .....	95	<sup>3</sup> 50	31	74	38	>99	99	89
NaCl-O <sub>2</sub> .....	110	<sup>2</sup> 50	.2	8.7	<.6	94	87	.1
CuCl <sub>2</sub> -NaCl-O <sub>2</sub> .....	100	<sup>2</sup> 60	3.9	28	17	74	73	1.5
FeCl <sub>3</sub> -HCl.....	100	0	20	26	2.6	74	61	47
Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub> ..	100	0	0	0	0	34	10	33
H <sub>2</sub> SO <sub>4</sub> -O <sub>2</sub> .....	150	<sup>2</sup> 100	<.1	26	<.9	>99	>99	>99
NH <sub>3</sub> -O <sub>2</sub> .....	80	<sup>2</sup> 60	.9	52	6.0	94	93	.2

<sup>1</sup>Concentrate MB used for tests.

<sup>2</sup>O<sub>2</sub> pressure.

<sup>3</sup>Cl<sub>2</sub> pressure.

TABLE 3. - Effect of roasting temperature on H<sub>2</sub>O<sub>2</sub>-6M HCl leaching of Stillwater concentrate at 105° C<sup>1</sup>

Roasting temp, °C	Extraction, pct									
	Pt	Pd	Au	Cu	Ni	Fe	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SiO <sub>2</sub>
NR.....	4.7	16	75	91	76	67	92	76	38	0.23
500.....	51	35	94	99	89	82	91	74	36	.20
600.....	78	74	97	96	92	82	90	73	36	<.01
750.....	72	86	93	85	94	83	88	73	43	.29
800.....	95	92	>99	47	91	84	81	69	52	.17
960.....	90	96	>99	50	87	81	80	69	49	.30

NR Not roasted.

<sup>1</sup>Leaching conditions: 50-g roasted concentrate MA, 840 mL of 0.7M H<sub>2</sub>O<sub>2</sub>-6M HCl leaching solution, 105° C, 6 h.

hot H<sub>2</sub>O<sub>2</sub>-6M HCl solution when the roasting temperature was 800° C or higher. These extractions are comparable to those from conventional matte smelting leaching (4). Appreciable quantities of base metals and gangue minerals were also solubilized. Magnesium solubilization is a concern because the flotation concentrates contained approximately 20 pct MgO. The decreased solubility of copper at higher roasting temperatures is ascribed to increasing formation of refractory copper ferrites at the higher roasting temperatures.

Further investigation indicated that leaching temperature had a significant effect on the selectivity of metal extraction. The data in table 4 show that leaching at ambient temperature (~25° C)

preferentially extracted the precious metals from the concentrate and left almost all of the base metals in the residue. When the leaching temperature was increased from 25° to 105° C, PGM extraction increased 8 to 20 pct but coextraction of base metals and gangue minerals increased several-fold. This preferential extraction of the precious metals at 25° C would simplify processing of the roasted concentrate, because the precious metals can be solubilized without requiring processing stages for base metal recovery. Loss of the copper and nickel in the tailings represents less than 5 pct of the monetary value of the concentrate, and their recovery would be undertaken only if the economics were favorable.

TABLE 4. - Effect of leaching temperature on H<sub>2</sub>O<sub>2</sub>-6M HCl leaching of 800° C roasted concentrate<sup>1</sup>

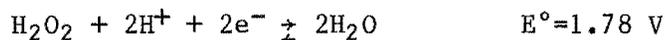
Leaching temp, °C	Extraction, pct									
	Pt	Pd	Au	Cu	Ni	Fe	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SiO <sub>2</sub>
225.....	87	72	96	3.6	2.5	2.8	32	42	11	0.6
70.....	98	82	>99	18	50	37	55	57	22	1.3
105.....	95	92	>99	47	91	84	81	69	52	.2

<sup>1</sup>Leaching conditions: 50-g roasted concentrate MA, 840 mL of 0.7M H<sub>2</sub>O<sub>2</sub>-6M HCl leaching solution, 6 h. 222 h.

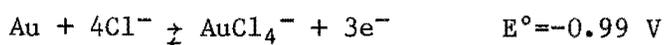
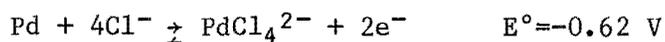
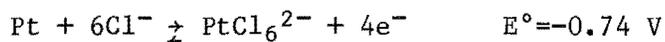
X-ray diffraction examination of concentrates roasted at temperatures greater than 800° C showed a ferrite-type major phase MFe<sub>2</sub>O<sub>4</sub> (M-Cu and/or Ni) possibly mixed with maghemite (αFe<sub>2</sub>O<sub>3</sub>), which has a very similar crystal structure. Microprobe studies identified a number of nickel, iron, and nickel-iron oxidic phases. The PGM were converted from sulfide minerals to their elemental states by the roasting process. Some very small palladium-rich particles existed as relatively pure inclusions in the nickel-iron oxide phase. These inclusions sometimes contained small concentrations of platinum. Larger discrete grains of Pt°-Pd° particles, which ranged in size up to 15 μm, were also observed. These particles exhibited varying ratios of palladium to platinum. Thus, both locked and liberated grains of palladium occurred in the roasted concentrate, but platinum existed primarily in liberated form.

According to thermodynamic corrosion diagrams (9), platinum and palladium metals can be dissolved only under very acid conditions with strong oxidizers. The corrosion domain for platinum is below pH 0 and an oxidizing potential of 1.0 to 1.2 V must be applied to cause the metal to dissolve. Palladium is soluble at potentials above 0.8 V if the solution pH is below 2. Under conditions outside of the corrosion domains, the metals are either immune to attack or passivated by oxide films which protect the metal surfaces. The corrosion domains can be enlarged significantly by the presence of complexing agents, such as chloride ion, which stabilize the dissolved metal ions.

Gold exhibits a larger corrosion domain than platinum and palladium, but it too is not attacked by acidic reagents unless they are both oxidizing and complexing. This explains the dissolution of platinum, palladium, and gold in aqua regia and the solubilization of the precious metals from roasted concentrate by H<sub>2</sub>O<sub>2</sub> in 6M HCl. The half-reaction potential relative to a standard hydrogen reference electrode, E°, for H<sub>2</sub>O<sub>2</sub> acting as an oxidizing agent increases with acidity:



However, half reactions for the dissolution of PGM and gold in chloride media are not dependent on pH but are strongly dependent on chloride concentration. High concentrations of chloride ion promote the oxidation of the precious metals:



The HCl provides both the high acidity required to promote the H<sub>2</sub>O<sub>2</sub> half-reaction and the complexing ions required to enhance the oxidation of the PGM by stabilizing the dissolved precious metal ions. Therefore, HCl-H<sub>2</sub>O<sub>2</sub> leaching generates high solution potentials in a strongly acid medium and leads to corrosion of the mineral surface and solubilization of the precious metals.

Experimentally, leaching was effective only when solution potentials were above 1.1 V,  $E_h$ . In fact, as will be discussed later in this report, high extraction can be achieved in strong HCl with other oxidizers, such as sodium hypochlorite (NaOCl) persulfate salts,  $HNO_3$ , or chlorine. Most of the experimental data was collected with  $H_2O_2$  as the oxidant because it was easy to handle and because it is nonpolluting, its reduction product being water.

#### STUDY OF PROCESS VARIABLES

Table 5 shows the effects of HCl and  $Cl^-$  concentrations on the  $H_2O_2$ -acid chloride leaching of 800° C roasted concentrate. Chloride levels were maintained, where necessary, by adding NaCl to the HCl solutions. Extraction of the precious metals increased with acidity, chloride concentration, and solution potential. For experiments 1-5, a large excess of  $H_2O_2$  was used and the potentials remained within a few millivolts of the values shown. At lower acid and salt concentrations (experiments 1-3), potentials stabilized in the 0.8 to 0.9 V range and could not be increased by adding more oxidant. In more acidic solutions, potentials exceeded 1.1 V and extractions improved. The highest PGM extraction was achieved in 12M HCl, but it was only minimally more than 6M HCl

which was used in subsequent leaching research.

Peroxide concentration was not important if a sufficiently high solution potential was maintained. Peroxide additions totaling 0.005 to 0.03M were sufficient to maintain the oxidation potential. Comparison of experiments 5 and 7 in table 5 shows that 0.03M  $H_2O_2$  is as effective as 0.7M  $H_2O_2$  for leaching the PGM from roasted concentrate in 6M HCl.

Figure 1 and table 6 show the effect of roasting temperature on the extraction of precious metals during ambient temperature leaching. Extraction increased with temperature up to 1,050° C and decreased at higher temperatures owing to fusing of the furnace charge. Maximum platinum, palladium, and gold extractions of 95, 90, and 99 pct, respectively, occurred after roasting at 1,050° C. There are two reasons for the lower solubility of palladium than of platinum and gold:

1. Palladium locked inside acid-resistant, nickel-iron oxide mineral grains would be less accessible to the leaching solution than the discrete, liberated, platinum-rich metallic particles. This was confirmed by SEM examination of leached solids, which showed the presence of ferrite-locked palladium-rich grains that were less than 1  $\mu m$  in size. The larger metallic Pt<sup>0</sup>-Pd<sup>0</sup> particles in the roasted concentrate were not observed. Tests showed that grinding to minus 400

TABLE 5. - Effects of HCl and  $Cl^-$  concentrations on  $H_2O_2$ -acid chloride leaching at ambient temperature of 800° C roasted concentrate<sup>1</sup>

Experiment	Concentration, M		$E_h$ , V	Extraction, pct									
	HCl	$Cl^-$		Pt	Pd	Au	Cu	Ni	Fe	$Al_2O_3$	CaO	MgO	$SiO_2$
1.....	0.6	0.6	0.80	9.6	39	21	1.9	1.2	0.8	24	41	9.2	5.1
2.....	.6	3.8	.89	31	57	68	1.7	<.1	.5	4	18	8.6	1.4
3.....	3.0	3.0	.88	36	62	61	4.7	1.7	2.0	44	61	14	2.8
4.....	3.6	5.2	1.11	78	71	97	4.2	2.0	2.1	27	40	12	1.4
5.....	5.7	5.7	1.20	87	72	96	3.6	2.5	2.8	32	42	11	.6
<sup>2</sup> 6.....	12.0	12.0	1.12	92	76	99	3.7	3.8	8.8	13	26	12	.1
<sup>2</sup> 7.....	6.0	6.0	1.18	90	73	99	3.3	<.1	1.8	28	42	11	1.2

<sup>1</sup>Leaching conditions: 25-g roasted concentrate MA, 420 ml of 0.7M  $H_2O_2$ -HCl-NaCl leaching solution, 25° C, 22 h.

<sup>2</sup>0.03M  $H_2O_2$ -HCl, 6 h.

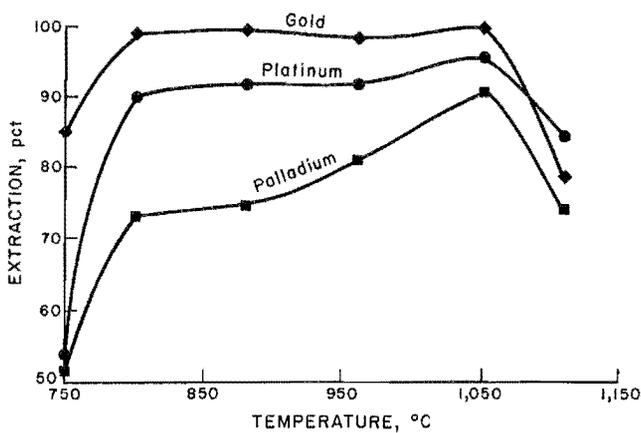


FIGURE 1. - Effect of roasting temperature on the extraction of precious metals with  $H_2O_2$ -6M HCl at ambient temperature.

mesh did not liberate the ferrite-locked grains.

2. The roasted concentrates may have contained some of the palladium as insoluble oxide, while the platinum and gold were present in the leachable elemental form. Oxides of platinum and palladium can form during roasting, while gold, which is a more noble metal, is not attacked by oxygen. Although  $PtO_2$ , the most stable oxide of platinum, decomposes to metal and oxygen at temperatures above  $650^\circ C$ ,  $PdO$ , the most stable oxide of palladium, can exist at red heat (10). This oxide is insoluble in minerals acids including aqua regia. Higher roasting temperatures favor decomposition of  $PdO$  to metal, which could result in increased

palladium extraction during leaching as shown in figure 1.

Roasting temperature affected base-metal and gangue mineral attack. Coextraction of base metals after roasting at  $1,050^\circ C$  was lower than after roasting at lower temperatures, and magnesium extraction decreased to approximately 1 pct. Since  $MgO$  comprises about 20 pct of the concentrate, any decrease in solubilization is of significance to the overall process. The principal contaminants of the pregnant solution were dissolved  $Al^{3+}$  and  $Ca^{2+}$  ions.

#### PRELEACHING

Incorporating an  $H_2SO_4$  preleaching stage into the processing scheme significantly decreased contamination of the pregnant solution by removing easily soluble gangue minerals and other metals prior to oxidative leaching. Table 7 shows the selectivity of two-stage leaching, and table 8 compares analyses of the pregnant solutions and tailings obtained by oxidative leaching of the concentrate with and without  $H_2SO_4$  pretreatment. The precious metals content exceeded 60 mg/L in both pregnant solutions, but contamination by base metals and gangue minerals was decreased from a total of 3.2 g/L to less than 110 mg/L when the concentrate was preleached prior to oxidative leaching.

TABLE 6. - Effect of roasting temperature on  $H_2O_2$ -6M HCl leaching of Stillwater concentrate at ambient temperature<sup>1</sup>

Roasting temp, °C	$E_h$ , V	Extraction, pct									
		Pt	Pd	Au	Cu	Ni	Fe	$Al_2O_3$	CaO	MgO	$SiO_2$
NR <sup>2</sup> ....	1.12	1.2	8.9	40	12	14	21	42	30	7.4	1.8
750.....	1.14	54	52	85	20	8.9	6.3	36	47	22	.8
800.....	1.18	90	73	99	3.3	<.1	1.8	28	42	11	1.2
880.....	1.18	92	75	99	3.0	3.5	2.0	33	40	7.6	1.6
960.....	1.18	92	81	98	1.3	<.1	.8	32	40	3.3	1.2
1,050...	1.17	95	90	99	.9	<.1	1.1	38	40	1.0	1.0
1,110...	1.20	83	74	78	2.3	1.8	3.7	20	21	.7	.5
1,130...	1.20	86	78	82	6.9	6.9	7.0	3.2	3.3	2.0	.1

NR Not roasted.

<sup>1</sup>Leaching conditions: 25-g roasted concentrate MA, 420 ml of 0.03M  $H_2O_2$ -6M HCl leaching solution,  $25^\circ C$ , 6 h.

<sup>2</sup>0.2M  $H_2O_2$ -6M HCl.

TABLE 7. - Two-stage leaching of  
1,050° C roasted concentrate

	Extraction, pct	
	Stage 1 (1M H <sub>2</sub> SO <sub>4</sub> )	Stage 2 (H <sub>2</sub> O <sub>2</sub> -6M HCl)
Pt.....	0.2	97
Pd.....	.3	92
Au.....	<.5	99
Cu.....	5.1	.06
Ni.....	3.2	.13
Fe.....	3.9	.62
Al <sub>2</sub> O <sub>3</sub> ....	49	.17
CaO.....	56	1.6
MgO.....	4.0	.20
SiO <sub>2</sub> .....	4.6	.01

Leaching conditions: Stage 1.  
300-g roasted concentrate MA, 2.8 L  
of 1M H<sub>2</sub>SO<sub>4</sub>, 70° C, 4 h. Stage 2.  
150-g preleached concentrate, 2.5 L  
of 0.03M H<sub>2</sub>O<sub>2</sub>-6M HCl leaching solu-  
tion, 27° C, 6 h.

TABLE 8. - Analysis of products from  
single- and two-stage leaching of  
1,050° C roasted concentrate<sup>1</sup>

	Pregnant solution analysis, mg/L		Tailings analysis, pct	
	Single- stage	Two- stage	Single- stage	Two- stage
Pt.....	21.8	24.6	20.59	20.34
Pd.....	37.5	42.2	22.3	21.8
Au.....	1.1	1.2	2.004	2.004
Cu.....	11	<.5	2.0	1.3
Ni.....	<.7	<.7	1.1	.9
Fe.....	72	40	11	11
Al <sub>2</sub> O <sub>3</sub> ....	1,800	20	5.3	4.5
CaO.....	880	16	2.3	1.6
MgO.....	140	28	23	22
SiO <sub>2</sub> ....	300	<2	51	52

<sup>1</sup>Leaching conditions: 150-g roasted  
concentrate MA, 2.5 L of 0.03M H<sub>2</sub>O<sub>2</sub>-6M  
HCl leaching solution, 27° C, 6 h.

<sup>2</sup>oz/ton.

Preleaching was normally conducted by heating a pulp containing 10 pct solids in 1M H<sub>2</sub>SO<sub>4</sub> at 70° C for 4 h. The resulting preleaching solutions were supersaturated with CaSO<sub>4</sub> as a result of the reaction of the H<sub>2</sub>SO<sub>4</sub> with calcium in the gangue. In practice, use of dilute H<sub>2</sub>SO<sub>4</sub> and a low percent solids pulp would be

required to prevent precipitation of CaSO<sub>4</sub> during preleaching. If the solubility of CaSO<sub>4</sub> is exceeded, the CaSO<sub>4</sub> will precipitate in the preleach residue, and will dissolve with the precious metals during the oxidative leaching stage.

Sulfuric acid consumption during preleaching would depend on the nature of the gangue minerals in the concentrate leached and the duration and temperature of the preleaching operation. Acid consumption for the samples tested ranged from 0.04 to 0.22 g of H<sub>2</sub>SO<sub>4</sub> per gram of concentrate.

Dilute H<sub>2</sub>SO<sub>4</sub> for preleaching could be produced from the SO<sub>2</sub> in the roaster off-gas. For example, the Hitachi and Lurgi Sulfacid (11) processes produce dilute H<sub>2</sub>SO<sub>4</sub> by adsorption of SO<sub>2</sub> on activated carbon in the presence of oxygen and water. The solution obtained from washing the carbon contains 7 to 65 pct H<sub>2</sub>SO<sub>4</sub>, depending on reactor design and the nature of the stack gases treated, and would be suitable for preleaching.

Because Stillwater ore contains high concentrations of talc, a basic mineral, the possibility exists that spent preleaching solution can be neutralized by contact with tailings from the flotation mill. Bench-scale experiments demonstrated that a tailings to solution ratio of 2 g/mL increased the solution pH from 0.2 to 4.4 if tailings produced by floating a serpentinitic ore were used. Tailings from anorthositic ore increased the pH to 3.3. The pH was adjusted to pH 6 with lime.

#### ALTERNATE OXIDANTS

Oxidizers other than H<sub>2</sub>O<sub>2</sub> may be used to extract PGM from roasted concentrates. Table 9 compares the results of leaching a roasted and preleached concentrate with H<sub>2</sub>O<sub>2</sub>, NaOCl, (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Cl<sub>2</sub>, and HNO<sub>3</sub> oxidants in 6M HCl solution. Sufficient oxidizing agent was added to maintain solution potentials above 1.1 V. All of the oxidants produced similar results. For NaOCl, the E<sub>h</sub>-pH diagram (12) shows that at pH <0, hypochlorite is converted to chlorine and HCl at potentials below about 1.7 V, so that the actual oxidant in the NaOCl-6M HCl system is chlorine.

TABLE 9. - Leaching of 1,050° C roasted and preleached concentrate with different oxidants<sup>1</sup>

Oxidant	E <sub>h</sub> , V	Extraction, pct									
		Pt	Pd	Au	Cu	Ni	Fe	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SiO <sub>2</sub>
0.03M H <sub>2</sub> O <sub>2</sub> .....	1.17	97	92	99	0.06	0.13	0.62	0.71	1.6	0.20	0.01
.002M NaOCl.....	1.19	97	92	99	.06	.13	.48	.11	.28	.01	.01
.014M (NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> .....	1.19	97	92	99	.07	.14	.47	.11	13	.19	.01
.71M HNO <sub>3</sub> .....	1.17	96	91	99	.06	.13	.58	.11	4.8	.01	.01
Cl <sub>2</sub> .....	1.20	97	92	99	.06	.14	.64	.17	1.7	.19	.01

<sup>1</sup>Leaching conditions: 25-g roasted and preleached concentrate MA, 420 mL of oxidant-6M HCl leaching solution, 25° C, 6 h.

<sup>2</sup>Leaching conditions: 150-g roasted and preleached concentrate MA, 2.5 L of H<sub>2</sub>O<sub>2</sub> 6M HCl solution, 27° C, 6 h.

Likewise, chlorine is generated by HNO<sub>3</sub>-HCl mixtures. On the basis of cost and selectivity, NaOCl, chlorine, and H<sub>2</sub>O<sub>2</sub> are the most favorable reagents. If NaOCl were used for leaching, control of sodium ion buildup in the pregnant solution would be necessary. Peroxide and chlorine add no contaminating ions to the leaching solution.

#### LEACHING OF CONCENTRATES MB, MC, AND WF

Since only limited quantities of samples MB, MC, and WF were available, pre-leaching of these concentrates and a thorough investigation of leaching extraction as a function of roasting temperature was not possible. Table 10 compares the leachabilities of MB and MC with MA in H<sub>2</sub>O<sub>2</sub>-6M HCl solutions after roasting at 800°, 960°, and 1,050° C.

Data for 1,050° C roasted WF are also included. Increasing the roasting temperature to 1,050° C improved the precious metals extraction and appreciably decreased coextraction of CaO and MgO from samples MA, MB, and MC. However, palladium was consistently less soluble than platinum and gold. Palladium extraction from the WF sample was only 58 pct.

SEM comparison of the 1,050° C roasted MA and WF concentrates showed that sample WF possessed fewer large, discrete and easily leached Pt°-Pd° grains, and the palladium-rich locked inclusions were associated with iron-rich ferrite material, while in sample MA the ferrite material was nickel-rich. The iron-rich ferrite was probably more effective in encapsulating the palladium inclusions and retarded their solubilization. Extraction of precious metals from concentrates

TABLE 10. - Effect of roasting temperature on H<sub>2</sub>O<sub>2</sub>-6M HCl leaching of different Stillwater concentrates<sup>1</sup>

Concentrate	Roasting temp, °C	Extraction, pct									
		Pt	Pd	Au	Cu	Ni	Fe	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	SiO <sub>2</sub>
MA.....	800	90	73	99	3.3	<0.1	1.8	28	42	11	1.2
	960	92	81	98	1.3	<.1	.8	32	40	3.3	1.2
	1,050	95	90	99	.9	<.1	1.1	38	40	1.0	1.0
MB.....	800	76	45	92	5.9	4.0	4.2	20	53	20	2.0
	960	68	60	91	1.3	.8	.6	18	20	2.6	.9
	1,040	89	75	96	.8	.6	.5	20	19	1.4	1.0
MC.....	800	89	48	99	7.8	5.3	5.5	29	60	9.8	1.6
	960	85	72	99	<.2	<.2	1.2	22	36	2.7	.7
	1,050	90	82	98	.1	1.0	.2	26	27	2.5	1.7
WF.....	1,050	86	58	94	<.04	.3	.3	21	38	.2	.6

<sup>1</sup>Leaching conditions: 25-g roasted concentrate, 420 mL of 0.03M H<sub>2</sub>O<sub>2</sub>-6M HCl leaching solution, 25° C, 6 h.

MB, MC and WF could in all likelihood be increased if the effects of roasting temperature, comminution, and leaching temperature were optimized.

#### PGM AND GOLD RECOVERY FROM SOLUTION

Platinum, palladium, and gold were recovered from the pregnant solution by three techniques: (1) precipitation as sulfides by sparging the solution with  $H_2S$ , (2) cementation on nickel granules, and (3) collection on a column of activated coconut charcoal. Sulfide precipitation and cementation decreased the PGM and gold contents to less than the detection limits (0.04 mg/L), and a two-column carbon train removed all of the gold and all but approximately 0.1 mg/L of the platinum and palladium. Thorough removal of precious metals from the pregnant solution required a long retention time on the carbon columns. Best results were achieved at flow rates of less than three bed volumes per hour. Since the HCl would be recycled to leaching, any PGM or gold left in solution could be reclaimed on subsequent passes through the leaching system.

McDougall and Hancock (13) reported that activated carbon chemically adsorbs gold from a chloride medium by a reductive mechanism. Because of their similar reduction potentials, it is probable that the chloro-complexes of platinum and palladium are also reduced by carbon. If the precious metals are present in metallic form, carbon stripping would be difficult and the values could be recovered only by burning the carbon. An acid-tolerant anion exchange resin, such as the Monivex resin developed by Warshawsky

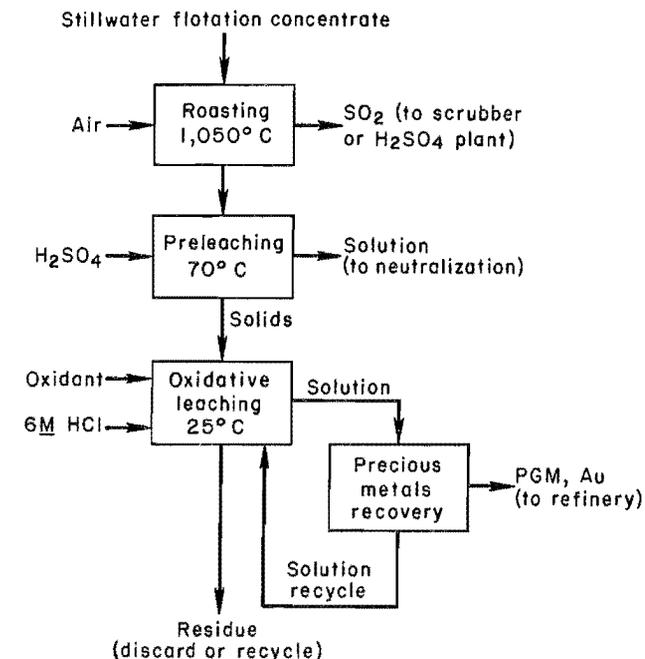


FIGURE 2. - Flow diagram for roasting-leaching procedure.

(14), would be more amenable to continuous processing than carbon because the PGM could be easily stripped with thiourea and the resin could be reused.

#### FLOW DIAGRAM FOR ROASTING-LEACHING PROCEDURE

Based on the experimental results described in this report, a flow diagram for the roasting-leaching procedure was devised and is presented in figure 2. Flotation concentrate is roasted at  $1,050^{\circ}C$  and then preleached in  $H_2SO_4$  to dissolve impurity elements. Oxidative leaching in  $6M$  HCl is conducted on the solids to extract the PGM and gold. The precious metals are recovered from solution for treatment at a refinery.

#### SUMMARY

A procedure was developed for selectively extracting platinum-group metals and gold from Stillwater Complex flotation concentrate. Roasting the concentrate at  $1,050^{\circ}C$  converts the precious metals from sulfide minerals to their elemental states. After preleaching with dilute  $H_2SO_4$  to remove easily soluble gangue minerals, the roasted concentrate

is slurried with  $6M$  HCl and leached at ambient temperature and pressure in the presence of an oxidizing agent. Hydrogen peroxide is the preferred oxidant, but other reagents, such as chlorine,  $NaOCl$ ,  $HNO_3$ , or persulfate salts, are also effective.

The two-stage leaching scheme extracts up to 97 pct of the platinum, 92 pct of

the palladium, and 99 pct of the gold from roasted concentrate. These extractions are comparable to conventional matte smelting-leaching procedures. The roast-leach procedure allows a high-grade precious metals refinery feed material to be produced directly from concentrate rather than relying on a toll smelter as in the conventional method. The base

metals, which comprise less than 5 pct of the value of the Stillwater Complex concentrates, are not solubilized and remain in the residue. The pregnant solutions contain more than 60 mg/L Pt, Pd, and Au and less than 110 mg/L other metals. The precious metals can be recovered from the solution by cementation, sulfide precipitation, or loading on activated carbon.

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