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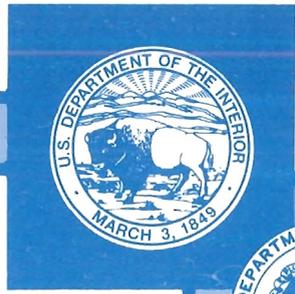
REPORT OF INVESTIGATIONS/1995

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Report of Investigations 9543

**High-Temperature Cyanide Leaching
of Platinum-Group Metals
From Automobile Catalysts—Pilot
Plant Study**

By R. J. Kuczynski, G. B. Atkinson, and W. J. Dolinar

**UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary**

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

With Factors for Conversion of Selected Units to U.S. Customary Units

g	gram	mL	milliliter
g/L	gram per liter	mm	millimeter
g/t	gram per metric ton	N	normal concentration
h	hour	pct	percent
kg	kilogram	ppm	part per million
kg/t	kilogram per metric ton	r/min	revolution per minute
kPa	kilopascal	tr oz	troy ounce
L	liter	tr oz/st	troy ounce per short ton
lb	pound	μm	micrometer
m	meter	°C	degree Celsius
mg/L	milligram per liter	\$/t	dollar per metric ton
min	minute		

To convert from—	To—	Multiply by—
gram	troy ounce	31.1035
gram per metric ton	troy ounce per short ton	34.24
kilogram	pound	2.2046
kilogram per metric ton	pound per short ton	2.0
kilopascal	pound (force) per square inch, gauge	0.1450
liter	gallon	0.2642
meter	foot	3.28
millimeter	inch	0.0394
degree Celsius	degree Fahrenheit	1.8 and add 32

HIGH-TEMPERATURE CYANIDE LEACHING OF PLATINUM-GROUP METALS FROM AUTOMOBILE CATALYSTS—PILOT PLANT STUDY

By R. J. Kuczynski,¹ G. B. Atkinson,² and W. J. Dolinar¹

ABSTRACT

The U.S. Bureau of Mines Reno Research Center investigated, developed, and patented a high-temperature cyanide leaching process for recovering platinum-group metals (PGM) from automobile catalysts. A batch pilot plant was constructed at the center and operated to demonstrate this technology to industry. Approximately 1,600 kg of used pellet, monolith, and metal support catalysts containing 1,700 g (54 tr oz) of PGM was processed. Forty-five-kilogram batches of used catalysts were leached with sodium cyanide solution at 160 °C for 1 h in a countercurrent processing sequence. This selectively dissolved the PGM. Average extractions from the used pellet catalyst were 96 pct Pt, 95 pct Pd, and 73 pct Rh. Average extractions from the used monolith catalyst were 84 pct Pt, 81 pct Pd, and 66 pct Rh. Heating the pregnant leach solutions to 275 °C for 4 h destroyed the PGM-cyanide complexes, causing over 99.7 pct of the PGM to precipitate from solution. The PGM precipitate was predominantly a metallic powder concentrate, typically analyzing greater than 50 pct PGM. Heating destroyed the cyanide to less than 0.2 mg/L free and total cyanide. Both the pellet and monolith residues were evaluated for disposal using the toxicity characteristic leaching procedure developed by the U.S. Environmental Protection Agency.

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INTRODUCTION

In the early 1960's, the State of California enacted legislation requiring yearly reductions in automobile exhaust emissions. These exhaust emissions were known to be a significant contributor to southern California's serious air pollution problem. To meet the yearly emission reduction standards, the State was granted permission by the Federal Government to require the installation of emission control devices on all new automobiles sold in that State.

Prior to 1974, California's emissions standards could be met by installing various antipollution devices and making minor engine adjustments. To meet emission standards set forth for the years 1974 and later, automobile manufacturers turned to oxidation catalysts containing platinum-group metals (PGM). These catalysts offered the most cost effective and reliable technology available to decrease automobile exhaust emissions. Catalytic converter-equipped vehicles were first introduced in California during the 1973 model year, and by 1976, all of the new automobiles sold in the State were catalyst equipped.

It was not until passage of the Clean Air Act of 1970, however, that yearly reductions in motor vehicle exhaust emissions were mandated for the rest of the country. These yearly reductions followed a similar format, but delayed the timetable used by the State of California. Installation of oxidation catalysts for new automobiles sold in the rest of the Nation began with the 1975 model year. By 1978, nearly all new automobiles sold in the United States were catalyst equipped. In addition to the United States, Japan (1975), Canada (1977), Australia (1986), and the European Community (1988) have also mandated the use of catalytic converters for automobile exhaust emissions control (1).³ More recently, concern over automobile exhaust emissions in Brazil, Hong Kong, Mexico, Singapore, South Korea, and Taiwan has resulted in legislation mandating the use of catalytic converters beginning with the 1993 model year. All of these areas appear to be following an emissions reduction format and timetable similar to that in the United States (1).

Since 1975, demand for PGM for use in automobile catalysts has tripled, making automobile catalysts the largest demand sector for Pt and Rh today (1). In 1992, the amount of PGM used in automobile catalysts as a percentage of total world demand for each metal was 34 pct Pt, 13 pct Pd, and 87 pct Rh. This translates to approximately 48,200 kg (1.55 million tr oz) Pt, 15,700 kg (505,000 tr oz) Pd, and 9,400 kg (303,000 tr oz) Rh (2). In the United States alone, an estimated 1 million tr oz of PGM are used annually by the automotive industry in the

manufacture of catalysts. Unfortunately, the United States is a net importer of PGM, relying on foreign sources for almost 90 pct of its PGM needs (3).

Scrap catalysts represent a large above-ground source of PGM. They contain an average of 1,000 g/t (30 tr oz/st) PGM with a value of \$15,000 at current prices. Current estimates are that 60 pct of the catalysts scrapped in the United States are being collected. Of these scrapped catalysts, less than a third is processed domestically for recovery of their PGM content. The remaining catalysts are shipped to Japan or Europe for processing.

The quantity of scrapped catalysts collected and processed for PGM recovery has increased steadily over the last few years. In 1982, about 1,600 kg (50,000 tr oz) of PGM was recovered from scrap catalysts collected in the United States. By 1992, this figure increased to 11,400 kg (367,000 tr oz) (2). Legislation requiring automobile dismantlers to remove catalysts from catalyst-equipped vehicles prior to shredding and an increase in the dollar value paid for scrapped automobile catalysts due to increased PGM loadings and high PGM prices have increased the demand for scrap automobile catalysts by collectors and decanners.

Steps in current PGM recovery practices include collecting used converter canisters, cutting the canisters to physically remove the ceramic monolith support or pellets from the metal shell, and processing the monolith or pellets at a central facility. Hoffmann (4) and Mishra (5) published review articles describing proposed or current hydrometallurgical, pyrometallurgical, and gas-phase volatilization processes for recovering PGM from spent automobile catalysts. Hydrometallurgical methods include dissolving the pellet substrate with sulfuric acid (H_2SO_4) or dissolving the PGM and a portion of the alumina from monolith catalysts using aqua regia. Pyrometallurgical methods include plasma fusion, where the decanned catalyst material is heated to extremely high temperatures in a plasma and the PGM are collected in an Fe alloy; Cu collection, where the PGM are recovered by fluxing, smelting, and collection with Cu; and Cu-Ni smelting, where the decanned catalyst material is fed into non-ferrous smelting operations as incremental slag tonnage. Gas-phase volatilization methods utilize selective chlorination of the PGM and a portion of the catalyst substrate to form volatile PGM and Al compounds and condensing them in a cooler zone. Each method has its own disadvantages, such as high reagent consumption, chemical side reactions, corrosion, toxic emissions, and variable recoveries. Average recoveries for these methods range from 86 to 93 pct for Pt and Pd and 81 to 87 pct for Rh.

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

As part of its mission to help ensure a domestic supply of strategic and critical minerals, the U.S. Bureau of Mines (USBM) investigated, developed, and patented a process for recovering PGM from scrapped automobile catalysts (6). In the process, a high-temperature cyanide solution under basic conditions selectively leaches PGM from the catalyst substrate. PGM recovery from solution is accomplished by thermal treatment at even higher temperatures to decompose cyanide complexes and free cyanide. Use of the process was intended to provide an economic incentive for increasing the amount of catalytic converters collected and processed domestically for PGM recovery.

Initial research (7) investigated leaching virgin monolith catalysts with cyanide solutions to establish baseline leaching parameters. Results from this investigation showed that a basic solution containing sodium cyanide (NaCN) and an oxidation promoter commonly used in Au cyanidation operations dissolved over 90 pct of the PGM from virgin catalysts. Chemical reduction of the PGM with hydrogen (H_2) before leaching was critical for high recoveries, and air treatment before reduction was beneficial. Leaching with a 5-pct NaCN and 1-pct promoter leach solution at a pH of 12 at 80 °C for 1 h dissolved more than 95 pct of the PGM.

Laboratory tests showed that applying this method on used catalysts dissolved less than 75 pct of the PGM. Additional research showed that greater PGM recoveries were obtained by leaching with NaCN solution at elevated temperatures in a pressure vessel (autoclave) (8). Best leaching results were obtained with a 5-pct NaCN solution for 1 h at 160 °C and 520 kPa pressure. This dissolved over 97 pct of the PGM contained in the virgin monolith, over 85 pct of the PGM contained in the used monolith, and 90 pct of the PGM contained in the used pellet catalyst. The best method for fast and almost complete recovery of the dissolved PGM and the destruction of cyanide was heating the solution to 250 °C or higher and 6,200 kPa pressure for 1 h in an autoclave. This thermally decomposed the cyanide complexes and removed over 99.8 pct of the metals from solution.

Information from the laboratory tests was used to develop, design, operate, and evaluate a process development unit (PDU) capable of treating 2,000-g batches of virgin and used catalyst material (9-10). Treating this amount of catalyst material in the PDU accomplished three objectives. First, a larger volume of pregnant solution was generated for testing and evaluating PGM-recovery methods. Second, the effectiveness of the countercurrent leaching procedure was evaluated. Third, a sufficient quantity of solid residue was produced to evaluate the environmental impacts.

Over 95 pct of the PGM was dissolved from virgin monolith and over 90 pct from used pellet catalysts by using a two-stage autoclave leach at 160 °C for 1 h with a

0.1N NaOH and 1-pct NaCN leach solution. Between 85 and 90 pct of the PGM was dissolved from used monolith catalyst by leaching three times at 160 °C for 1 h with a 0.1N NaOH and 1-pct NaCN solution. Sodium cyanide consumption was 20 kg/t of catalyst for each leach. Sodium hydroxide (NaOH) requirements were 8 kg/t of catalyst. The differences between the results from leaching virgin and used monolith catalysts were due to contamination from combustion byproducts and the sintering of the used catalyst substrate, which decreased solution-to-solids contact. Pretreating the catalysts prior to leaching to improve PGM extraction was not effective. For example, preleaching the catalyst material with 1.0N NaOH solution to dissolve the alumina wash coat and theoretically expose more PGM to the leach solution did not increase the amount of PGM leached. Crushing catalyst material to increase the surface area to minus 65 mesh did not increase PGM recovery.

PGM were recovered from pregnant leach solutions by thermal decomposition of the cyanide complexes. Over 99.8 pct of the PGM contained in the solutions was recovered as a precipitate, analyzing over 60 pct metallic PGM. Pregnant solutions from virgin and used catalysts were decomposed at 250 and 275 °C for 1 h, respectively. Thermal treatment also decreased the concentration of total cyanide in solution to less than 0.2 mg/L.

The virgin catalyst residue passed the California waste extraction test (WET) for all elements, but failed the U.S. Environmental Protection Agency's (EPA's) toxicity characteristic leaching procedure (TCLP) for Ba. The addition of sodium sulfate (Na_2SO_4) at a rate of 7.5 kg/t of virgin catalyst residue stabilized Ba so that the residue passed the TCLP. The used catalyst residue failed both the WET and TCLP for Pb. Attempts to stabilize the Pb were not successful. Because of this, the catalyst residue would be considered a hazardous waste and must be disposed of accordingly.

To better understand the leaching process, a detailed investigation of PGM dissolution chemistry in cyanide solutions was undertaken (11). Cyanide decomposition, PGM species present in solution and their geometry, and the rate of PGM dissolution were investigated.

The rapid decomposition of cyanide at elevated temperatures was determined to be due to hydrolysis of cyanide to formate and ammonia. The half life of cyanide was determined to be about 7 min at 160 °C, and as a result, it was concluded that very little would be gained by leaching for extended periods of time at elevated temperatures. The Pt and Pd cyanide complexes were identified as square planar tetracyanoplatinate(II) and tetracyanopalladate(II) by their distinctive ultraviolet spectra. The Rh cyanide complex was identified as octahedral hexacyanoorhodate(III), although its ultraviolet spectrum was less distinctive. The rate of dissolution of the PGM

was investigated using a rotating disk technique, and dissolution rates were determined to increase in the order of Rh, Pt, and Pd. It was concluded that the rate of pore diffusion was the limiting step for PGM dissolution from catalyst samples. Although diffusion rates can be increased by increasing temperature, the instability of the Pd cyanide complex at temperatures above 160 °C determines the upper temperature limit to be 160 °C.

The feasibility of this leaching technology was demonstrated to industry by including cooperators in the operation of a 45-kg batch pilot plant. The pilot plant was constructed at the Reno Research Center and operated by the center's staff. Participating process cooperators

provided representative samples of catalysts for testing and evaluating the pilot plant. Process cooperators also supplied \$10,000 to help defray processing costs. In return, the cooperators received a description of the process and operational information. The PGM recovered during processing were returned to the cooperator, with the exception of material required for analysis and evaluation. AC Rochester-Division of General Motors Corp. (Flint, MI) and Heraeus Precious Metals Management, Inc. (New York, NY), were process cooperators. Johnson Matthey (West Deptford, NJ) was a refiner-cooperator and agreed to evaluate the PGM concentrate.

SAMPLE DESCRIPTION AND PREPARATION

There are two basic types of catalysts—oxidation and three way. Oxidation catalysts first appeared in late 1973 and contained either Pt or Pt and Pd and were used for the catalysis of carbon monoxide (CO) and hydrocarbons to carbon dioxide (CO₂) and H₂O. More stringent emission standards required the reduction of nitrous oxides (NO_x) emissions, in addition to CO and hydrocarbon emissions. This resulted in three-way catalysts being required on new automobiles sold, beginning with the 1980 model year. Three-way catalysts contain either Pt and Rh or Pt, Pd, and Rh for the additional catalysis of NO_x to nitrogen (N₂) (1, 4, 12). By 1982, the oxidation-only catalytic converters were completely phased out and replaced by combination oxidation and three-way catalytic converters (1, 4).

Automobile catalytic converters consist of an AISI Type 409 stainless steel canister containing the monolith or pellet catalysts. Combined weights of the canister and catalyst range from 2 to 10 kg. The monolith catalysts are honeycomb structures with a circular or elliptical cross section typically measuring 100 to 150 mm in width and 100 to 200 mm in length and weighing from 400 to 1,400 g (12). The monolith structure is composed of synthetic cordierite, a porous ceramic material, which serves as a support. The cordierite support is coated with a high-surface-area wash coat composed of gamma alumina and rare earths. This wash coat acts as a substrate for the PGM and accounts for almost 15 pct of the total catalyst weight (12).

Similar in size, shape, and appearance to the ceramic monolith catalysts are metal support catalysts. These are corrugated stainless steel rolls or coils with a wash coat similar to that found on ceramic monolith catalysts. The wash coat is estimated to account for 20 pct of the catalyst's weight. Metal support catalysts are used primarily to treat emissions from sources, such as stationary engines used to generate electricity. These catalysts currently make up a small percentage of the total automobile catalysts manufactured, but their market share is expected

to significantly increase. When compared to ceramic monolith catalysts, metal support catalysts have the advantage of faster light-off times, i.e., the time required for a catalyst to reach its operating temperature, about 250 °C (1). This is an important factor, since most of the pollution emitted by an automobile occurs during the first few moments of operation as the catalyst heats up to this operating temperature (1). Metal support catalysts have higher physical and chemical stability at extreme temperatures because of their ability to dissipate heat much more efficiently than ceramic catalysts (13). The unique corrugated and rolled structure of metal support catalysts enables them to withstand excessive vibration and shock when compared to other catalysts (13).

The pellet catalysts are spheres or prills about 2 mm in size. A typical pellet charge weighs from 1,800 to 3,200 g and is composed entirely of high-surface-area gamma alumina. The gamma alumina acts as both support media and substrate for the PGM (12). Current estimates are that monolith automobile catalysts, including the metal support type, comprise 60 pct of the scrapped catalyst market. Monolith catalysts tend to have PGM concentrations almost three times that of older pellet catalysts and, because of this, are more valuable to the collector and processor.

During its operational life, a catalyst undergoes many physical and chemical changes. These changes are the result of extreme temperature cycles and chemical contaminants. Temperatures greater than 1,100 °C sinter the alumina support, decrease the surface area, and reduce the catalytic ability of the PGM. Lead, carbon, hydrocarbons, and sulfates are the most significant chemical contaminants. From a leaching and disposal standpoint, Ba, Pb, Ni, and S in the form of sulfates were the contaminants of most concern. The presence of Ba and Pb in the leached residue can create disposal problems. Nickel tends to consume large quantities of cyanide during low-temperature leaching at the expense of PGM-cyanide

complexation. Reaction of the PGM with Pb and sulfate can form compounds that are refractory to cyanide solutions.

AC ROCHESTER CATALYST

AC Rochester provided two 225-kg lots of used catalyst. The catalyst was from its warranty reject program and included both pellet and monolith catalysts. The pellet catalyst was screened to minus 4 mesh to remove tramp metal fragments and insulation material. The screened catalyst was thoroughly mixed and split using a Jones splitter. This resulted in five batches weighing approximately 45 kg each. A sample for analysis was split from the original lot and from each of the individual batches. Table 1 shows the concentration of PGM in the pellet catalyst, based on multiple analyses. Average PGM concentrations were within ± 0.5 standard deviation for Pd and Rh. The PGM concentration in used pellet catalysts was higher than that previously observed in earlier pellet samples, indicating that the catalysts came from newer model automobiles where higher PGM concentrations are required. Table 2 shows the concentrations of other elements found in the pellet catalyst. Most concentrations were comparable to those previously reported in used pellet catalysts (8-10). Exceptions were lower concentrations of Pb, Ni, and P. The pellet catalyst contained about 500 g of tramp metal pieces that ranged in size from 10 to 100 mm.

Table 1.—PGM concentration in AC Rochester catalyst, grams per metric ton

Catalyst	Pt	Pd	Rh
Monolith	1,050	154	88.0
Pellet	658	336	49.0

The monolith catalyst was crushed before shipment to the Reno Research Center. Typical particle size was 80 pct minus 35 mesh, and 10 pct of the sample was plus 25 mm. The monolith catalyst was screened to minus 10 mesh, and the oversize was stage crushed to minus 10 mesh. The crushed monolith was thoroughly mixed and split into five batches weighing approximately 45 kg each. A sample for analysis was split from the original lot and each of the individual batches. Table 1 shows the concentration of PGM in the monolith catalyst, based on an average of multiple analyses. Average concentrations were within ± 1.0 standard deviation for Pt and ± 0.5 standard deviation for Pd and Rh. The Pt and Pd levels were comparable to those previously reported in the monolith catalyst (8-10), whereas the level of Rh was almost twice as high. Again, this catalyst came from newer model cars where higher Rh concentrations are required. Table 2 shows the concentrations of other elements found in the monolith catalyst. Concentrations were comparable to

those previously observed in used monolith catalysts (8-10). The crushed monolith catalyst contained about 900 g of tramp metal pieces that ranged in size from 10 to 20 mm.

Table 2.—Analysis of AC Rochester catalyst, parts per million

Component	Monolith	Pellet
Al	¹ 14.6	¹ 45.3
As	91	610
Ba	¹ 0.26	54
C _(Total)	¹ 0.24	¹ 0.37
Ca	¹ 0.17	¹ 0.11
Ce	¹ 2.5	¹ 2.3
Co	39	16
Cr	340	260
Cu	44	75
Fe	¹ 0.90	¹ 0.42
K	¹ 0.30	¹ 1.0
La	700	¹ 0.29
Mg	¹ 5.5	510
Mn	325	430
Na	¹ 0.75	890
Nb	25	590
Ni	¹ 0.42	<30
P	¹ 0.20	¹ 0.27
Pb	¹ 0.28	¹ 0.22
Sb	<180	<180
Si	¹ 20.00	¹ 1.23
Ti	¹ 0.31	57
W	190	200
Zn	300	¹ 0.11
CO ₃ ²⁻	¹ 0.12	¹ 0.30
HCO ₃ ⁻	ND	ND
S _(Total)	¹ 0.20	¹ 0.10
SO ₄ ²⁻	¹ 0.50	¹ 0.30

ND Not determined.

¹Percent.

HERAEUS CATALYST

Heraeus provided eight different types of used catalysts weighing a total of 1,040 kg. The catalysts were obtained from both domestic and European sources and included pellet, monolith, and metal support catalysts. The pellet catalyst was screened to minus 4 mesh to remove tramp metal fragments and insulation material. The screened catalyst was thoroughly mixed and split using a Jones splitter. This resulted in equal batches weighing approximately 45 kg each. A sample for analysis was split from each of the individual batches. Table 3 shows the concentration of PGM in the pellet catalysts. These concentrations are the average of multiple analyses. Standard deviations compared favorably to the AC Rochester pellet catalyst. The concentrations of PGM in used pellet catalysts were comparable to the AC Rochester pellet catalyst. Table 4 shows the concentrations of other elements found in the Heraeus pellet catalyst. Most concentrations were comparable to the AC Rochester pellet

catalyst. Exceptions were lower concentrations of Pb, Ni, and P. The Heraeus pellet catalyst contained an average 120 g of tramp metal for every 45 kg of catalyst. The metal pieces ranged in size from 10 to 100 mm.

The monolith catalyst was crushed prior to processing. Typical as received particle size was 95 pct plus 25 mm. The remaining 5 pct was minus 20 mesh. The monolith catalyst was stage crushed to 100 pct minus 8 mesh. The crushed monolith was thoroughly mixed and split into sample batches weighing approximately 45 kg each. A sample for analysis was split from each of the individual batches. Table 3 shows the average concentration of PGM in the monolith catalyst. These concentrations were the average of multiple analyses. Standard deviation of the PGM concentrations compared favorably to the AC Rochester monolith catalyst. The PGM concentrations for the domestic monolith samples were comparable to the AC Rochester monolith catalyst. Significantly higher concentrations of Pt and Rh were found in the European monolith sample. Table 4 shows the concentrations of other elements found in the monolith catalysts. Concentrations were comparable to those previously observed in the AC Rochester monolith catalyst. The monolith catalyst contained an average 250 g of tramp metal for every 45 kg of catalyst. The metal pieces ranged in size from 10 to 20 mm.

The metal support samples were processed as is. Because of the difficulty in sampling and analyzing the metal catalyst, PGM concentrations were estimated based on analysis of the wash coat, which according to the manufacturer, Heraeus, accounts for 20 pct of the catalyst's weight. Table 3 shows estimated PGM concentration, and table 4 shows the concentration of other elements from the metal support catalyst wash coat. Based on this method of analysis, estimated PGM concentrations compared favorably to the other AC Rochester and Heraeus monolith catalysts.

Table 3.—PGM concentration in Heraeus catalyst, grams per metric ton

Catalyst	Pt	Pd	Rh
European monolith	1,442	45.5	260
U.S. monolith 1	832	277	65.4
U.S. monolith 2	853	373	139
U.S. monolith 3	1,068	209	125
U.S. pellet 1	442	270	23
U.S. pellet 2	331	181	16.1
U.S. pellet 3	384	259	17.8
European metal ¹	726	0	125

¹Estimated. Based on wash coat analysis and assumption that wash coat is 20 pct of catalyst weight.

Table 4.—Analysis of Heraeus catalyst, percent

Component	Monolith				Pellet			European metal ¹
	European	U.S. 1	U.S. 2	U.S. 3	U.S. 1	U.S. 2	U.S. 3	
Al	16.6	19.3	20.2	20.3	43.5	47.5	43.5	22.0
As	² 426	² <230	² 240	² 240	3.0	2.9	² 250	² 270
Ba	² 613	0.20	0.59	0.21	² 170	² 137	² 10	² 600
C _(Total)	0.25	0.30	0.30	0.40	0.60	0.61	0.50	ND
Ca	0.21	0.15	0.10	0.10	0.28	0.30	² 336	2.3
Ce	2.9	1.0	0.9	1.9	1.2	0.9	0.9	ND
Co	² 76	² <23						
Cr	² 575	² 395	² 460	² 394	0.14	² 945	² 78	3.5
Cu	² 657	² 30	² 32	² <31	² 394	² 375	² <31	² 75
Fe	1.0	1.0	1.2	1.0	0.26	0.30	0.23	12.0
K	0.25	² 1,100	² 1,800					
La	² 965	² 301	0.11	0.24	0.69	0.17	0.39	ND
Mg	5.7	5.7	4.7	5.7	0.28	0.25	² 190	0.37
Mn	² 119	² 589	² 238	² 320	² 375	² 408	² 640	ND
Na	0.3	0.33	0.28	0.31	0.36	² 849	0.28	3.0
Nb	² 500	² 340	² 300	² 300	² 250	² 250	² 260	² 35
Ni	² 498	0.27	0.27	0.24	² 151	² 362	² 95	1.6
P	0.12	0.54	0.38	0.51	0.30	0.15	0.26	0.38
Pb	² 300	0.30	² 701	² 261	0.46	0.93	² 981	0.5
Sb	² 205	² <180	² <180	² <180	² 190	² 210	² 190	1.6
Si	19.8	20.0	20.1	20.3	1.6	0.53	1.5	10.5
Ti	0.40	0.25	0.25	0.30	² 60	² 60	² 80	0.30
W	² 200	² 200	² 200	² 180	² 200	² 200	² 190	² 250
Zn	² 800	0.24	0.18	0.13	0.37	0.34	0.16	1.0
CO ₃ ²⁻	0.13	0.09	0.3	0.19	0	0.39	0.48	ND
HCO ₃ ⁻	0	0	0	0	0	0	0	ND
S _(Total)	0.1	0.2	0.2	0.1	0.1	0.1	0.1	ND
SO ₄ ²⁻	0.1	0.5	0.5	0.3	0.1	0.1	0.1	ND

ND Not determined.

¹Wash coat analysis.

²Parts per million.

EQUIPMENT AND PROCEDURES

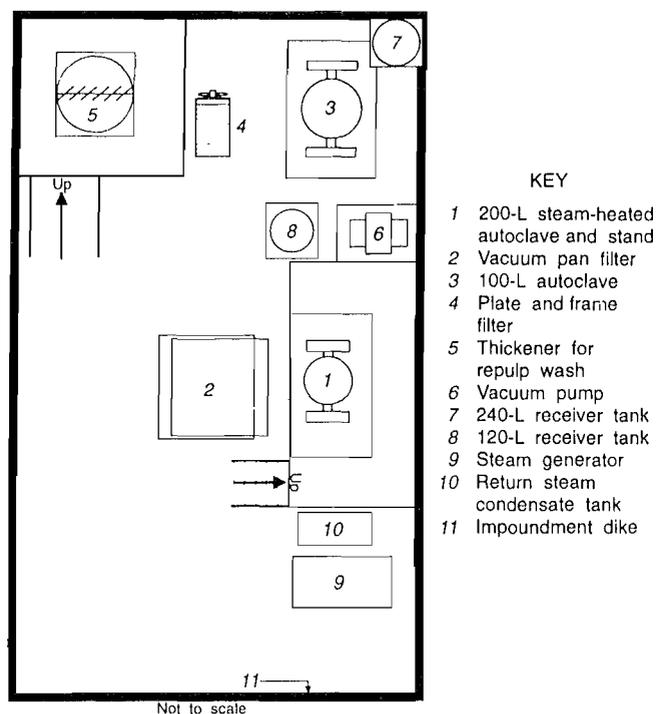
Figure 1 shows a floor plan of the pilot plant and the location of all major pieces of equipment. The autoclaves, filters, vacuum system, and receiver tanks were all constructed of carbon steel. Catalyst leaching was carried out in a double-wall, 200-L steam-heated autoclave (1)⁴ without agitation. A natural gas-fired boiler provided the steam. The autoclave was emptied by rotating the reactor on a trunnion to dump the liquid and wet solids onto the moveable vacuum pan filter (2).

A 0.9- by 0.9-m vacuum pan filter (2) was used for catalyst filtration. The pan filter was fitted with casters and flexible tubing to permit easy movement across the pilot plant floor. A tilting mechanism allowed dumping of the solids from the pan. An ASTM Type 33 twill cotton fabric was used for the filter cloth. A vacuum pump (6) transferred the solution into a 240-L receiver tank (7). Clear flexible hoses were used so that the flow of liquid could be observed as it was filtered from the solids.

A 100-L electrically heated autoclave (3) was used to heat the pregnant leaching solution. No agitation was necessary. This resulted in destruction of cyanide and precipitation of the PGM as a solid. No agitation was used.

⁴Bold numbers in parentheses refer to location of pilot plant equipment in figure 1.

Figure 1



Floor plan of pilot plant and location of all major pieces of equipment. (Approximate area = 6 by 9 m.)

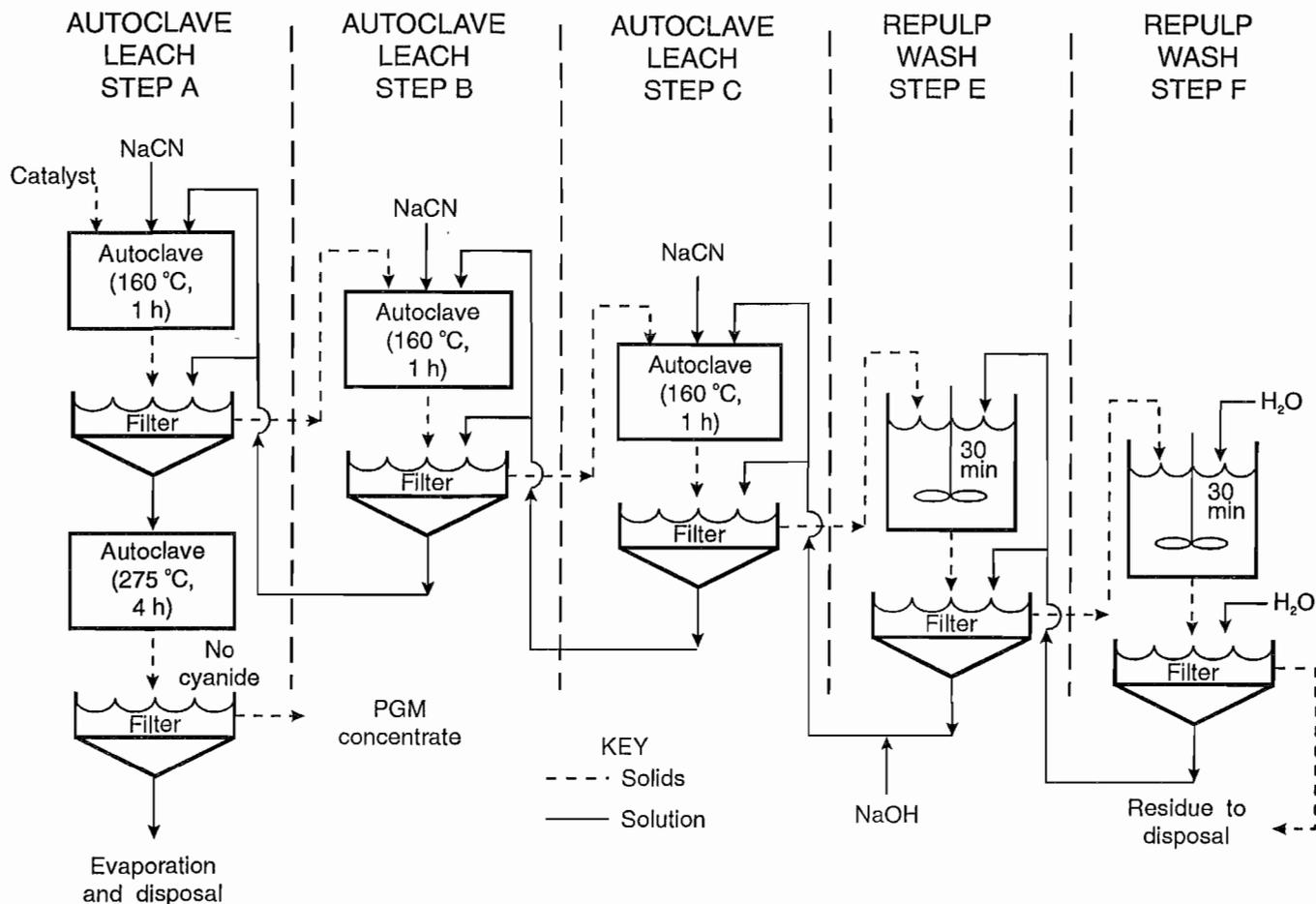
A suction tube was used to remove the solution and powder PGM precipitate from the autoclave. The tube was connected to a 200-mm square plate and frame filter (4) fitted with 20 plates. Two-micrometer filter paper was used to separate the PGM precipitate from solution. A 0.2- μm canister filter with a 1- μm prefilter was used as a polishing filter. The vacuum pump (6) transferred the solution through the filters and into a separate receiver tank (8). Using separate receiver tanks eliminated cross contamination between liquids with high (800 mg/L) and low (less than 1 mg/L) concentrations of PGM.

A 0.9-m-diam thickener (5) with a 100-mm discharge in the bottom was elevated 1.5 m and used for the repulp washes. Agitation was accomplished by rotation of the thickener rake at 2.5 r/min. The thickener was emptied by removing a rubber stopper fitted into the 100-mm bottom opening. This allowed bottom discharge directly onto the pan filter. The pilot plant processing area was enclosed by a 130-mm-high impoundment dike to prevent the escape of solution that might be spilled. An overhead crane served the pilot plant area. Pilot plant ventilation was provided by large volume exhaust fans.

Reagent-grade NaCN was used to dissolve the PGM. The use of cyanide requires that trained personnel be employed and safety precautions be observed. The pH of the solution must be maintained above 11, preferably between 12 and 13, to prevent the formation of poisonous hydrogen cyanide (HCN) gas. Good hygiene must be practiced to prevent ingestion and repeated contact with the skin (14).

The catalyst was processed in the pilot plant following the typical processing sequence shown in figure 2. The plant was operated in a countercurrent mode to decrease water requirements and to increase the concentration of PGM in the processing solution as it advanced from right to left through the process. The solid catalyst entered the process on the left side of figure 2 at step A. It was leached with filtration solution exiting step B. The ratio of solution to solids in step A was 1.5:1. Any excess solution from step B was used to displacement wash the solids after leaching and filtering in step A. This allowed control of the solution-to-solids ratio in the reactor and helped push the dissolved PGM toward recovery. If no solution from a previous step was available, i.e., during the initial start up, tap water was used. Before fresh tap water was used in any of the leaching steps, it was made 0.1N NaOH to ensure a pH between 12 and 13 to prevent formation of HCN gas. Fresh NaCN was added to each autoclave leaching solution at a rate of 20 kg/t of catalyst to replace the cyanide that was 98 pct destroyed by heat in the previous leaching operation. After leaching in step A, the charge was filtered. The pregnant solution was sent to PGM recovery and the solids were sent to leaching in step B. The process continued in this manner.

Figure 2



Typical processing sequence of pilot plant.

During a typical operation for processing pellet catalyst in step A, the 200-L autoclave was first loaded with the pellet catalyst and then the solution. Cyanide briquettes were added last. For processing the monolith catalyst, the solution was first pumped into the 200-L autoclave and cyanide briquettes were dissolved in the solution. The monolith catalyst was carefully added to the leach solution containing the dissolved NaCN. A solution-to-solids ratio of 1.5:1 was used for all step A tests. Each method produced similar extractions. The catalyst and cyanide solution were heated to an operating temperature of 160 °C and 520 kPa pressure. This was achieved in about 90 min. After 1 h at 160 °C, the steam was turned off and the autoclave was allowed to cool overnight. By the following morning, the solution had cooled to 30 °C. The autoclave lid was removed and the contents were poured onto the vacuum pan filter. The odor of ammonia from cyanide decomposition was noticeable, but it was easily controlled. Typical free cyanide concentration decreased from 5,300 to 50 mg/L after each autoclave leach at 160 °C for 1 h

because of the decomposition of free cyanide. Vacuum filtration continued until no flow of solution could be observed through the clear vacuum hoses. Typical time requirements for filtration were 90 min for the pellet catalyst and 30 min for the monolith catalyst. The filter cake in step A was displacement washed with solution remaining from step B.

Following filtration, the pregnant solution continued to step R for PGM recovery and the solids continued to step B for additional leaching. In step R, the solution from step A was pumped into the 100-L autoclave. Care was taken to allow for the expansion of the solution at elevated temperatures without rupturing the pressure vessel. An operating temperature of 275 °C and 6,200 kPa pressure was reached in approximately 3 h. Time at temperature ranged from 1 to 4 h. After heating, the autoclave was allowed to cool overnight. By the following afternoon, the solution had cooled to a temperature of 35 °C. The autoclave was then opened and the contents were suctioned through the plate and frame filter to separate the PGM

precipitate from the liquid. The precipitate was recovered from the plate and frame filter after processing five pellet batches and again after five monolith batches.

The solids from step A proceeded to steps B and C. In step B, the solids from step A were leached with part of the filtration solution exiting step C. A solution-to-solids ratio of 2:1 was used. In step C, the solids from step B were leached with part of the filtration solution from step E. A solution-to-solids ratio of 2:1 was used. Before the repulp wash water from step E was used in leaching step C, it was made 0.1*N* NaOH to ensure a pH between 12 and 13 to prevent the formation of HCN gas. Additional NaCN was added to each autoclave leaching step at the

rate of 20 kg/t catalyst. The solution-to-solids ratio took into account the moisture content of the catalyst.

In step E, the solids from step C were repulp washed with part of the filtration solution exiting step F. In step F, the solids from step E were repulp washed with tap water. Each repulp wash used a 2:1 solution-to-solids ratio and lasted 30 min. Filtration after repulp washing was accomplished using the vacuum pan filter described previously. Filtration times after washing increased to 120 min for monolith catalyst and 180 min for pellet catalyst because of the generation of fines by agitation during the repulp step.

ANALYSIS OF SOLUTIONS AND SOLIDS

Extractions of PGM were calculated using analyses of the leaching solutions and leached residues. Concentrations of PGM in the solutions were determined using a sequential inductively coupled plasma (ICP) spectrometer. Concentrations of PGM in solid samples were determined by fire assaying the solids, dissolving the dore bead in an acid solution, and analyzing the solution by ICP spectroscopy.⁵ All solids were dried at 110 °C for 20 h before analyses. Referee analyses were performed on select AC Rochester pellet and monolith head and residue samples by LeDoux & Co. (Teaneck, NJ), a widely recognized expert in PGM analysis. Free cyanide concentration was determined by analyzing a 5-mL sample of solution directly with a spectrophotometer. Weak acid dissociable (WAD) cyanide was determined by acidifying a 500-mL sample of solution to a pH of 5 with H₂SO₄, refluxing for 1 h, trapping the HCN gas liberated in an NaOH solution, and analyzing the NaOH solution using a spectrophotometer. Total cyanide concentration was determined by acidifying a 500-mL sample of solution with 51 mL of 1:1 concentrated H₂SO₄:H₂O solution, refluxing for 1 h, trapping the HCN gas liberated in an NaOH solution, and analyzing the NaOH solution using a spectrophotometer.

Residues from pellet and monolith catalysts were evaluated for disposal. Although WAD and total cyanide standards for solids have not been found, the residues were still tested for the presence of soluble WAD and total cyanide. The residues were also tested for disposal suitability by the EPA's TCLP.

Soluble WAD cyanide was determined by adding a 500-g sample of wet catalyst residue to 2.5 L of deionized H₂O at a pH of 7 in an air-tight, zero-head space container. The contents are then stirred mildly for 24 h at room temperature. The pulp or slurry was then filtered and the filtrate analyzed for WAD cyanide with a spectrophotometer. Soluble total cyanide was determined similarly, the only exception being the adjustment of the deionized H₂O pH from 7 to 5 with H₂SO₄. The filtrate was analyzed for total cyanide with a spectrophotometer.

The TCLP test leached solids with a buffered acetic acid solution at a pH of 4.98 for 18 h. The filtrate was analyzed by ICP spectroscopy. To pass the test, the filtrate must contain less than the published threshold concentration for each metal.

RESULTS AND DISCUSSION

LEACHING AC ROCHESTER CATALYST

Each of the five batches of AC Rochester used pellet and used monolith catalyst was processed in the pilot plant following the flowsheet in figure 2. Table 5 shows results from these tests and includes the analyzed concentration of PGM remaining in each residue, the percentage PGM leached from each batch calculated from the solution and

residue analysis, and the head for each batch calculated from these same analyses. The calculated head was usually within 10 pct of an analytically determined head analysis for PGM. Reasons for discrepancies in the mass balance include difficulties in analyzing PGM concentrations in both solids and solutions and the potential for nonhomogeneous solid samples.

An example of typical solution analysis used for these calculations is shown in table 6. These data were obtained from processing the third batch of pellet catalyst, experiment AC-3, and the third batch of monolith catalyst,

⁵OFR 130-92. Bureau of Mines Practice in Fire Assaying, by W. L. Barry.

Table 5.—Results from leaching AC Rochester catalyst with NaCN

Test	Residue, g/t			PGM leached, pct			Calculated head, g/t		
	Pd	Pt	Rh	Pd	Pt	Rh	Pd	Pt	Rh
MONOLITH ¹									
AC-6	36.3	166	32.2	81	83	72	174	949	113
AC-7	35.3	165	31.8	77	84	65	142	1,041	93.5
AC-8	36.6	171	31.2	78	83	75	165	1,014	123
AC-9	30.1	164	33.2	83	86	72	180	1,171	119
AC-10	34.0	164	33.2	82	86	72	196	1,202	119
Average	34.6	166	32.3	80	85	71	171	1,075	114
PELLET ²									
AC-1	16.4	26.7	15.4	95	96	73	311	692	56.8
AC-2	15.1	22.6	15.4	96	93	68	317	610	48.6
AC-3	16.8	22.6	14.7	96	97	73	336	668	54.4
AC-4	17.5	20.9	12.7	94	96	74	244	579	52.4
AC-5	33.9	25.3	13.4	89	96	75	267	603	52.4
Average	19.9	23.6	14.3	94	96	73	295	630	52.9

¹Average monolith head, grams per metric ton: 154 Pd, 1,048 Pt, and 88.0 Rh.

²Average pellet head, grams per metric ton: 336 Pd, 657 Pt, and 49.0 Rh.

Table 6.—PGM concentrations in solution from AC Rochester monolith test AC-8 and pellet test AC-3

Step	Catalyst	Concentration, mg/L						Volume, L	
		Pd		Pt		Rh		Entering	Leaving
		Entering	Leaving	Entering	Leaving	Entering	Leaving		
A	Monolith	62	133	186	670	14	59	75	64
	Pellet	105	293	200	551	10	30	78	42
B	Monolith	23	44	55	139	3.8	18	76	73
	Pellet	41	146	79	262	6	17	75	72
C	Monolith	7	12	21	36	1.7	3.2	86	83
	Pellet	17	54	32	110	2	7	82	81
E	Monolith	0.9	1.0	2.6	3.0	0.4	0.4	86	84
	Pellet	4	22	8	42	0.5	3	78	77
F	Monolith	(¹)	0.4	(¹)	0.6	(¹)	0.4	88	86
	Pellet	(¹)	6	(¹)	12	(¹)	0.6	85	83
R	Monolith	139	0.9	696	0.6	63	0.2	45	43
	Pellet	305	0.3	550	0.6	34	0.3	31	30

¹Fresh tap water for final wash step.

experiment AC-8. PGM leaching results from used pellet catalyst AC-3 were 97 pct Pt, 96 pct Pd, and 73 pct Rh. Previous experience in the PDU showed similar Pt and Pd extractions, but greater Rh extractions for used pellet catalyst (9-10). The average PGM metallurgical balance for the pellet catalysts was within 4 pct for Pt, 12 pct for Pd, and 7 pct for Rh of the average head analysis. PGM leaching results from processing used monolith catalyst AC-8 were 83 pct Pt, 78 pct Pd, and 75 pct Rh. The average PGM balance for monolith catalyst was within 3 pct for Pt, 10 pct for Pd, and 22 pct for Rh of the average head analysis.

Typical PGM extractions from processing 2,000-g samples in the PDU are shown in table 7. When the PGM extractions in table 7 are compared to the average PGM extractions from the pilot plant for AC Rochester pellet catalyst, average pilot plant extractions were 2 pct higher for Pt, 1 pct lower for Pd, and 17 pct lower for Rh. Average extractions from processing the AC Rochester monolith catalyst in the pilot plant were about 3 pct lower for

Pt, 2 pct lower for Pd, and 14 pct lower for Rh when compared to PDU extractions in table 7.

Table 7.—Comparison of PGM extractions for monolith and pellet catalysts in PDU (9-10) and pilot plant

Catalyst	Location	Extraction, pct		
		Pd	Pt	Rh
Used monolith	PDU	82	88	85
Do.	Pilot plant	80	85	71
Do.	..do.	82	83	59
Do.	..do.	81	84	66
Virgin monolith	PDU	NP	98	90
Used pellet	PDU	95	94	90
Do.	Pilot plant	80	85	72
Do.	..do.	95	96	73
Do.	..do.	95	96	73

Do. Same as above.

NP Not present.

¹AC Rochester.

²Heraeus.

³Average.

In addition to determining PGM recoveries, cyanide was also monitored to determine its disposition. Table 8 shows free cyanide concentration in solutions leaving processing steps from the same pellet experiment AC-3 and monolith experiment AC-8. Free cyanide concentrations after the autoclave leaching in steps A, B, and C were typically 50 mg/L. At 160 °C, free cyanide has a theoretical half-life of 7 min. Assuming an initial free cyanide concentration before each autoclave leach of about 5,000 mg/L, greater than 98 pct of the initial free cyanide was hydrolyzed or complexed after 1 h at 160 °C. The hydrolysis reaction often generated detectable amounts of ammonia.

Table 8.—Concentration of free cyanide in solution from AC Rochester monolith test AC-8 and pellet test AC-3

Step	Catalyst	Free cyanide concentration exiting process step, mg/L
A	Monolith	38
	Pellet	45
B	Monolith	58
	Pellet	26
C	Monolith	26
	Pellet	17
E	Monolith	3.4
	Pellet	4.0
F	Monolith	0.3
	Pellet	1.8
R	Monolith	0.2
	Pellet	0.1

Free cyanide concentration in solution after the final repulp wash step F was 1.8 mg/L for pellet experiment AC-3. Since processed pellets typically contain, on average, 43 pct moisture, free cyanide concentration in the entrapped solution might be too high for discharge of the pellet residue. An additional repulp wash of the pellet catalyst with water resulted in free cyanide concentration in solution exiting the wash of less than 0.2 mg/L. Concentration of free cyanide in solution after step F for monolith experiment AC-8 was 0.3 mg/L, which indicates better washing. Table 9 shows total cyanide concentrations in solution after final repulp wash step F were 2.0 mg/L for the pellet experiment AC-3 and 1.1 mg/L for monolith experiment AC-8. Table 10 shows WAD and total cyanide concentrations for the final residue from pellet experiment AC-3 and monolith experiment AC-8. Although no regulatory standards for cyanide in solids have been found, these levels of cyanide are believed to be low enough for disposal.

PROCESS MODIFICATIONS FOR AC ROCHESTER CATALYST

The low extractions of Rh from the AC Rochester pellet catalyst and Pt, Pd, and Rh from the AC Rochester

monolith catalyst were a concern. The low extractions were originally considered to be analytical in nature. Reference analyses of pellet and monolith head samples and leach residues were performed by LeDoux. Analytical results are shown in table 11 and were comparable to USBM analyses for the same samples.

Table 9.—Free and total cyanide concentrations in solution after process steps F and R from AC Rochester monolith test AC-8 and pellet test AC-3

Step	Catalyst	Cyanide concentration, mg/L	
		Free	Total
F	Monolith	0.3	1.1
	Pellet	1.8	2.0
R	Monolith	0.2	0.2
	Pellet	0.1	0.2

Table 10.—WAD and total cyanide concentrations of final residues from AC Rochester monolith test AC-8 and pellet test AC-3

Catalyst	Cyanide concentration, ppm	
	WAD	Total
Monolith	9.4	11.5
Pellet	1.5	5.9

Table 11.—Results from USBM and LeDoux analysis of solids from AC Rochester tests AC-8, AC-8 releach, and AC-3

	USBM			LeDoux		
	Pd	Pt	Rh	Pd	Pt	Rh
AC-8 MONOLITH						
Head, g/t	153	1,048	88.0	158	1,038	95.9
Residue, g/t	36.6	171	31.2	34.4	175	28.1
PGM removed, pct	76	84	65	78	83	71
Releach residue, g/t	25.3	126	21.6	24.0	122	21.9
PGM removed, pct ¹	84	88	76	85	88	77
AC-3 PELLET						
Head, g/t	336	657	49.0	360	661	50.3
Residue, g/t	16.8	22.6	14.7	14.0	21.2	9.93
PGM removed, pct	95	97	70	96	97	80

¹After releaching.

Extensive laboratory-scale experiments were conducted on 50-g samples of each head and residue in an attempt to increase extractions. Variables tested were longer leaching time, higher NaCN concentration, higher and lower leaching temperatures, oxygen overpressure, CO overpressure, and barium chloride addition. Also tested were pretreatment by H₂ reduction, borohydride reduction, NaOH preleach to dissolve the alumina wash coat, and pulverization. Results from most of these tests showed little or no improvement in extractions. A slight improvement in PGM extractions was observed when the monolith

catalyst was pulverized before leaching. Pulverization of the catalyst to a particle size of less than 300 mesh created significant problems in the laboratory in liquid solid separation. Because of these problems, it was decided that the small increase in extractions would not justify the added difficulties of processing in the pilot plant or in a larger plant. Crushing the catalyst to a particle size between the minus 10 mesh tested in the pilot plant and the 300 mesh tested in the laboratory did not improve extractions during laboratory leaching tests.

Some improvement in extractions was obtained by leaching the AC Rochester monolith residue with a solution-to-solids ratio of 1:1 and increasing the NaCN concentration in solution to 5 pct. Laboratory results indicated that this would improve PGM extractions about 5 pct. This was tested in the pilot plant by re-leaching the residue from monolith test AC-8. Results from this test are also shown in table 11. Final extraction of Pt from the monolith sample was equal to those from the PDU in table 7, while the extraction of Pd increased by 2 pct. The extraction of Rh was still 9 pct less than the PDU results. Using one additional leach with the higher NaCN concentration did not appear to cause any processing problems. However, if more than one additional leach using the higher reagent concentration was conducted, there would be a high potential for the salt content of the solution to exceed its solubility and start to precipitate from solution, usually at some undesirable step in the process. The salt is composed primarily of NaCN decomposition products such as sodium carbonate (Na_2CO_3) and sodium bicarbonate (NaHCO_3).

Another problem besides low Rh extractions was the high moisture content of the filter cake. Typical time requirements for filtration were 120 min for the pellet catalyst and 60 min for the monolith catalyst. Average residual moisture content was 43 pct for pellet catalyst and

25 pct for monolith catalyst. The difference in moisture content was due to the greater internal pore volume of the pellet catalysts when compared to monolith catalysts and the fact that pellet catalysts were more susceptible to attrition scrubbing during repulp washing, steps E and F. The fines generated by attrition scrubbing coat the filter media and eventually restrict the flow of the solution during liquid-solid separation. This results in increased moisture content of the solids.

Attempts were made to decrease the residual moisture content of the catalyst filter cake. The options for decreasing moisture content were limited. Increased filtration times, the use of filter aids, and covering the pan filter to evacuate the entire catalyst were tested. Increasing the filtration times to 4 h did not significantly decrease the moisture content. Coating the filter media with a filter aid such as diatomaceous earth and covering the pan filter were also ineffective. No further attempts were made to decrease the moisture content of the catalyst.

LEACHING HERAEUS CATALYST

At least one batch from each sample of used Heraeus catalyst was processed in the pilot plant following the flowsheet in figure 2. Table 12 shows results from these baseline tests. For the metal support catalyst, the percentage leached and the calculated head were estimated based on the analysis of the wash coat residue and assuming the wash coat represents 20 pct of the catalyst weight.

Average results from leaching the pellet catalysts showed that more than 95 pct of the Pt and Pd was dissolved. Rhodium extractions were much lower and averaged 73 pct. Results from leaching the four types of monolith catalyst showed that Pt extractions ranged from 75 to 90 pct and averaged 83 pct, Pd extractions ranged

Table 12.—Results from leaching used Heraeus catalyst with NaCN under baseline conditions

Test	Catalyst	Residue, g/t			PGM leached, pct			Calculated head, g/t			Analytical head, g/t		
		Pd	Pt	Rh	Pd	Pt	Rh	Pd	Pt	Rh	Pd	Pt	Rh
METAL SUPPORT													
H-61	European metal ¹	0	117	35.6	0	84	72	0	726	125	0	726	125
MONOLITH													
H-51	European	7.19	195	91.8	88	88	68	32.9	1,736	346	45.5	1,442	260
H-58	U.S.-1	62.7	165	26.4	78	80	59	300	726	72.3	277	832	66.8
H-59	U.S.-2	75.7	204	78.8	79	75	43	401	949	209	373	853	139
H-60	U.S.-3	32.9	107	43.1	84	90	65	216	1,113	118	209	1,068	125
Average		37.1	168	60.0	82	83	59	238	1,131	186	226	1,049	148
PELLET													
H-55	U.S.-1	13.4	22.6	5.82	95	95	74	320	500	54.9	270	442	22.6
H-56	U.S.-2	6.16	4.45	3.42	95	96	81	184	408	134.6	181	331	15.1
H-57	U.S.-3	13.7	9.93	6.85	95	97	64	284	346	13.0	259	384	17.8
Average		11.1	12.3	5.36	95	96	73	263	418	34.2	237	386	18.5

¹Estimated. Based on wash coat residue analysis and assumption that wash coat is 20 pct of catalyst weight.

from 78 to 88 pct and averaged 82 pct, and Rh extractions ranged from 43 to 68 pct and averaged 59 pct. Estimated Pt and Rh extractions from the metal support catalyst were 84 and 72 pct, respectively. Palladium was not present in the metal support catalyst samples. The calculated head was usually within 10 pct of an analytically determined head analysis for PGM.

As in the case of the AC Rochester catalyst, cyanide was also monitored to determine its disposition. Free cyanide concentrations after the autoclave leaching in steps A, B, and C were typically 50 ppm. Table 13 shows free and total cyanide concentration in solutions leaving processing steps F and R from tests H-51, H-55, H-58, and H-61.

Table 13.—Free and total cyanide concentrations in solution after process steps F and R from Heraeus tests

Step	Test	Catalyst	Cyanide concentration, mg/L	
			Free	Total
F	H-51	European monolith	0.2	0.2
	H-55	U.S. pellet 1	0.1	0.2
	H-58	U.S. monolith 1 . .	0.2	0.3
	H-61	European metal . .	0.2	0.3
R	H-51	European monolith	0.1	0.1
	H-55	U.S. pellet 1	0.1	0.1
	H-58	U.S. monolith 1 . .	0.1	0.1
	H-61	European metal . .	0.1	0.1

A comparison of PGM extractions for PDU and Heraeus pilot plant tests is shown in table 7. When average PGM extractions for the Heraeus pellet catalyst are compared to the PDU pellet extractions, Pt extractions increased slightly from 94 to 96 pct, while Pd extractions remained unchanged at 95 pct. Rhodium extractions decreased from 90 to 73 pct. When compared to the AC Rochester pellet extractions, Heraeus pellet extractions were nearly identical. When PGM extractions for the Heraeus monolith catalyst are compared to the PDU monolith extractions, Pt extractions decreased from 88 to 83 pct, while Pd extractions remained unchanged at 82 pct. Rhodium extractions decreased significantly from 85 to 59 pct. When compared to the AC Rochester monolith extractions, Heraeus Pt extractions decreased by 2 pct, but Pd extractions increased by 2 pct. Rhodium extractions were 12 pct lower than AC Rochester monolith catalyst.

Average free cyanide concentration in solution after the final repulp wash step F was less than 0.2 mg/L for all of the catalyst test samples. An additional repulp wash of the catalyst with water could lower this even further. Concentration of total cyanide in solution after step F for the same tests was less than 0.3 mg/L. Free and total cyanide concentrations after thermal decomposition step R were always less than 0.1 mg/L. Table 14 shows WAD and

total cyanide concentrations for the final residue from the same tests. These levels are also believed to be low enough for disposal.

Table 14.—WAD and total cyanide concentrations of Heraeus final residues

Test	Catalyst	Cyanide concentration, ppm	
		WAD	Total
H-51	European monolith . . .	7.80	9.60
H-55	U.S. pellet 1	0.43	0.99
H-58	U.S. monolith 1	2.30	4.70
H-61	European metal ¹	4.50	ND

ND Not determined.

¹Wash coat residue.

PROCESS MODIFICATIONS FOR HERAEUS CATALYST

Like the previously discussed AC Rochester catalyst, the observed low extractions of Rh from the Heraeus pellet catalyst and Pt, Pd, and Rh from the Heraeus monolith catalyst were a concern. Extensive laboratory-scale experiments were conducted on 50-g samples of each head and residue in an attempt to increase extractions. These laboratory tests identified promising and practical modifications to the standard leaching conditions. Decreasing the volume of leaching solution and increasing the concentration of NaCN from 1 to 5 pct increased PGM extractions in the laboratory by as much as 5 pct. When tested in the pilot plant, a 5-pct increase in PGM extractions was also observed. Several problems were encountered when NaCN concentration was increased in the pilot plant, which included the precipitation of carbonate compounds that interfered with the filtering and recovery of the PGM concentrate. Higher NaCN concentration also increased the amount of ammonia and formate generated during hydrolysis.

Previous research (9-10) had shown that additional pressure leaches could increase PGM extractions by as much as 10 pct when compared to two pressure leaches. These tests also showed that a maximum amount of leachable PGM was reached after the fifth leach. Additional autoclave leaches on monolith and metal support samples were tested in the pilot plant. For the monolith sample, the amount of PGM leached was maximized after the fifth leach. PGM extractions increased from 78, 75, and 54 pct Pt, Pd, and Rh, respectively, after three leaches to 81, 78, and 61 pct Pt, Pd, and Rh, respectively, after the fifth leach. No increase in PGM extractions was observed when the metal support catalyst was released.

Another change to the leaching technique that gave PGM extractions similar to the standard leaching procedure, but may offer easier processing, was to inject the required fresh cyanide as a concentrated solution into the

leaching reactor while it was at the processing temperature of 160 °C. This was first tested in the laboratory on a small scale before it was tested in the pilot plant. Injection of NaCN by this method would improve the efficiency of the leaching operation by eliminating the intermediate cooling and filtering now required to achieve maximum PGM recovery. Sodium cyanide injection was successfully tested in the pilot plant and resulted in extractions similar to those obtained with standard leaching conditions. This modification shows promise for decreasing the amount of handling required and increasing throughput.

High residual moisture contents and long filtration times were observed during the processing of several Heraeus catalyst samples. These problems were due to unusually high concentrations of fines present in the catalyst, in addition to the fines generated by particle attrition during repulp washing. In an attempt to decrease some of the fines and lessen their effect on filtration time, samples of the catalysts were displacement washed while on the pan filter bed in place of repulp washing. This significantly decreased the catalyst handling requirements and decreased the total time required to wash the material. This bed washing method was conducted on Heraeus pellet and monolith samples. However, to achieve PGM concentrations comparable to those after repulp washing, the number of washes required would have to be increased. This would increase the water inventory for the process and the amount of time that the PGM remain in inventory as part of the processing solution. Therefore, it is possible to lessen the effect of fines on filtration times with bed washing. However, to achieve PGM concentrations comparable to repulp washing, water requirements and solution inventory would increase significantly.

PLATINUM-GROUP METALS RECOVERY FROM PREGNANT LEACH SOLUTION

Powdered PGM concentrates were recovered from pregnant leach solution in laboratory tests by heating the solution to 275 °C for 1 h and filtering. This resulted in barren solutions with PGM concentrations of less than 1 mg/L. The heat thermally decomposed the metal cyanide complexes and destroyed cyanide. Without cyanide available to complex the PGM, the PGM precipitated from solution as a powder. Treatment of pregnant solutions in the pilot plant at 275 °C for 1 h resulted in decreasing the Pt concentration from 500 to 50 mg/L. Because of the dollar value of this solution, this concentration was not acceptable. The same pregnant leach solution was heated in the laboratory to 275 °C for 1 h. This resulted in a Pt concentration of less than 0.5 mg/L. The difference between pilot plant and laboratory results was believed to be due to the slow heat transfer inside the larger pilot plant autoclave. Increasing the time at temperature from

1 to 2 h in the pilot plant autoclave resulted in a Pt concentration of 5 ppm. Increasing the time at temperature to 4 h resulted in a Pt concentration of less than 1 ppm. A time at temperature of 4 h was used to treat all other pregnant leach solutions in the pilot plant. Table 15 shows typical percentages of PGM removed from both monolith and pellet pregnant leach solutions. Over 99 pct of the PGM were removed from monolith pregnant leach solutions. Over 99 pct of the Pt and Rh and over 98 pct of the Pd were removed from pellet pregnant leach solutions.

Table 15.—Typical removal of PGM from AC Rochester pregnant leach solutions, percent

Catalyst	Pd	Pt	Rh
Monolith	99.1	99.8	99.8
Pellet	98.2	99.9	99.1

All solutions exiting the decomposition reactor in step R were analyzed. Results showed that occasionally the concentration of Pd in the barren solution was higher than expected, sometimes as high as 7 to 10 mg/L. The concentrations of Pt and Rh were always less than 1 mg/L. The reason for the occasionally high concentration of Pd was not determined. The loss of Pd at 10 mg/L in solution would amount to less than \$50 t of catalyst or less than 0.3 pct of the total PGM value. Tables 7 and 8 show free and total cyanide concentrations for the AC Rochester barren leach solutions after step R. Free cyanide concentration was 0.2 mg/L or less for the barren solutions from both the pellet and monolith. Total cyanide concentration was 0.2 mg/L or less for the AC Rochester pellet and monolith solutions, even when high Pd concentrations were determined. Table 13 shows free and total cyanide concentrations for the Heraeus barren solutions were 0.1 mg/L or less.

The solids were filtered from the step R process solution onto filter paper in the plate and frame filter. The solids were leached with H₂SO₄ to dissolve residual Na₂CO₃ and some of the base metal contaminants. Sulfuric acid leaching dissolved less than half of the concentrate weight, and the solution contained less than 1 mg/L PGM after filtering. The filtrate was then evaporated and the residue analyzed for disposal by the TCLP. For some unexplainable reason, one batch of concentrate after H₂SO₄ leaching could not be filtered. The slurry was dried and returned to the cooperator without any additional treatment. Table 16 shows a partial analysis of a typical concentrate recovered from thermal treatment of the solutions. The PGM were in the elemental state. Analysis showed that the concentrate contained greater than 50 pct PGM. A scanning electron microscope examination showed that the powder was composed of nominal 1- μ m size particles that were agglomerated together. The

resulting PGM concentrate was sent to Johnson Matthey for evaluation. Johnson Matthey's analysis showed that the concentrate contained 65 pct PGM plus some Fe, Al, and Ni. No deleterious elements were found. Johnson Matthey concluded that the USBM's PGM concentrate dissolved easily and would fit into its current refinery sweeps stream.

Table 16.—Partial analysis of recovered concentrate, percent

Component:		Component:—Continued	
Al	4.2	P	0.9
As	1.5	Pb	1.0
Ca	2.0	Pd	9.1
Cu	1.0	Pt	42.1
Fe	1.0	Rh	3.0
Mn	0.2	Sb	0.1
Na	0.9	Zn	0.5
Ni	5.0		

DISPOSAL OF SOLUTIONS AND RESIDUES FROM CATALYST PROCESSING

The only solutions to leave the process were the barren leach solutions. Table 17 shows concentration of metals, total carbon, carbonate, total S, and sulfate concentrations for AC-8 monolith barren leach solution and AC-3 pellet. Table 18 shows typical concentrations of metals, total carbon, carbonate, total S, and sulfate concentrations for barren leach solutions from processing Heraeus catalysts.

Table 9 shows free and total cyanide concentrations for the AC Rochester barren solutions. Table 13 shows free and total cyanide concentrations for the Heraeus barren solutions. Because the barren solutions have a high Na concentration of greater than 20 g/L, the solutions cannot be recycled back into the process. Recycling of solution would result in precipitation of Na_2CO_3 and other salts in the process equipment. The high concentration of total

dissolved solids in the barren solutions also prevented discharge into the sewer. The best method for disposal of the barren solution appears to be by evaporation to produce an impure Na_2CO_3 - NaHCO_3 residue. All barren processing solutions from processing the pellet and monolith catalysts were evaporated. A total of 37 kg of solids were recovered after evaporation of AC Rochester barren solutions and 107 kg of solids was recovered after evaporation of Heraeus barren solutions. Table 19 shows an analysis of the recovered solids. The PGM content in the recovered solids was high because of the experimental nature of some of the tests. Even at these levels, the amount of PGM present in the evaporation residue represent about 2 pct of the PGM in the feed.

Residues from pellet and monolith experiments were evaluated for disposal. The residues were analyzed for WAD and total cyanide, total carbon, carbonate, and sulfate and evaluated by the TCLP. Since the metal support catalysts would most likely be recycled after the PGM were removed, they were not evaluated for disposal. Table 10 shows typical WAD and total cyanide concentrations for AC Rochester pellet and monolith residues. Table 20 shows total carbon, carbonate, bicarbonate, S, and sulfate concentrations for these same residues. Table 14 shows typical WAD and total cyanide concentrations for Heraeus pellet, monolith, and metal support residues. Table 21 shows typical total carbon, carbonate, S, and sulfate concentrations for these same residues.

All residues from AC Rochester pellet and monolith tests passed the TCLP for all metals. Of the 20 Heraeus pellet and monolith catalyst batches processed, only 3 head and residue samples failed the TCLP. U.S. monolith 1 (H-58), U.S. pellet 1 (H-55), and U.S. pellet 2 (H-56) failed the TCLP for Pb by exceeding the 5-mg/L leach solution Pb standard. For the failed samples, the concentrations of Pb in the TCLP leach solutions were typically greater than 20 mg/L.

Table 17.—Concentration of components in solution leaving AC Rochester step R, milligrams per liter

Component	Catalyst		Component	Catalyst	
	AC-8 monolith	AC-3 pellet		AC-8 monolith	AC-3 pellet
Al	28.3	30	P	140	100
As	8.9	10	Pb	<1.4	<1
Ba	<1	<1	Pd	0.9	0.3
Ca	<30	<30	Pt	0.6	0.6
Ce	0.3	0.2	Rh	0.2	0.3
Co	<1	<1	Ti	<3	<3
Cr	<4	<4	W	<30	<30
Cu	16	<6	Zn	5.5	6.1
Fe	4.7	5.0	$\text{C}_{(\text{Total})}$	¹ 8.76	¹ 8.62
K	75	110	$\text{CN}^{\text{I}}_{(\text{Free})}$	0.2	0.1
La	7.6	<1	$\text{CN}^{\text{I}}_{(\text{Total})}$	0.2	0.2
Mg	<10	<10	CO_3^{2-}	¹ 15	¹ 19
Mn	0.12	<0.10	HCO_3^-	¹ 9.2	¹ 11
Na	¹ 23	¹ 20	$\text{S}_{(\text{Total})}$	¹ 1.32	¹ 1.58
Nb	<2	<2	SO_4^{2-}	¹ 2.79	¹ 3.28
Ni	<3	<3			

¹Grams per liter.

Table 18.—Concentration of components in solution after leaving Heraeus step R, milligrams per liter

Component	Catalyst			
	European monolith, H-51	U.S. pellet 1, H-55	U.S. monolith 1, H-58	European metal, H-61
Al	290	2.76	26	11.2
As	31.7	0.80	2.34	0.6
Ba	2.38	0.34	0.07	0.06
Ca	10	8.63	1.5	1.3
Cd	0.6	0.1	0.1	0.1
Ce	5	5	5	5
Co	<5	<5	<5	<5
Cr	3.5	0.46	0.40	0.38
Cu	1.3	5.57	0.20	7.58
Fe	0.87	0.66	0.70	0.98
K	103	166	53	7.23
La	10	10	10	10
Mg	8.9	3.23	0.98	0.92
Mn	0.14	0.02	0.02	0.02
Na	¹ 8.3	¹ 13.9	¹ 19.7	¹ 13.6
Ni	2.6	2.4	1.83	5.06
P	8.4	16	127	357
Pb	8.6	0.80	0.74	0.78
Pd	0.3	0.4	1.3	0.51
Pt	0.1	0.5	0.7	0.54
Rh	0.3	0.3	0.1	0.30
Sb	31.3	0.89	0.95	0.99
Si	3.5	3.21	38.1	0.54
Zn	5.6	1.74	0.95	1.11
C _(Total)	¹ 2.43	¹ 19.9	¹ 6.5	¹ 4.8
CN _(Free)	0.1	0.1	0.1	0.1
CN _(Total)	0.1	0.1	0.1	0.1
CO ₃ ²⁻	¹ 14.0	¹ 48.0	¹ 21.0	¹ 20
HCO ₃ ⁻	ND	¹ 23.0	¹ 14.0	¹ 5.9
S _(Total)	¹ 0.30	¹ 1.0	¹ 1.0	¹ 0.10
SO ₄ ²⁻	¹ 0.77	¹ 3.0	¹ 3.09	¹ 0.22

ND Not determined. ¹Grams per liter.

Table 19.—Analysis of evaporation residue, parts per million

Component	AC Rochester ¹	Heraeus ²
Al	³ 0.28	³ 0.15
As	<150	700
Ca	250	300
Cr	270	200
Cu	<20	60
Fe	800	³ 0.2
K	³ 0.1	³ 0.1
Mg	500	500
Mn	5.1	10
Mo	<21	<21
Na	³ 36	³ 35
Ni	600	400
Pb	<100	<100
Pd	⁴ 2.7	⁴ 2.4
Pt	⁴ 5.6	⁴ 3.2
Rh	⁴ 0.9	⁴ 0.3
Si	³ 0.6	³ 0.6
Zn	200	200
C _(Total)	³ 10	³ 11
CO ₃ ²⁻	³ 23	³ 43
HCO ₃ ⁻	³ 13	³ 8.7
S _(Total)	³ 1.9	³ 1.7
SO ₄ ²⁻	³ 6.1	³ 4.7

¹Residue weight, 37 kg (82 lb).²Residue weight, 107 kg (238 lb).³Percent.⁴Grams per metric ton.

Table 20.—Carbon, carbonate, bicarbonate, S, and sulfate concentrations for AC Rochester monolith and pellet residues, percent

	AC-8 monolith	AC-3 pellet
C _(Total)	0.23	0.25
CO ₃ ²⁻	0.01	0.50
HCO ₃ ⁻	0	0.35
S _(Total)	0.05	0.02
SO ₄ ²⁻	0.10	0.01

Table 21.—Carbon, carbonate, bicarbonate, S, and sulfate concentrations for Heraeus pellet and monolith residues

Component	Concentration, pct		
	European mono- lith, H-51	U.S. pellet 1, H-55	U.S. monolith 1, H-58
C _(Total)	0.13	0.63	0.20
CO ₃ ²⁻	0	1.26	0.14
HCO ₃ ⁻	0	0.75	0.10
S _(Total)	0.10	0.10	0.10
SO ₄ ²⁻	0.10	0.10	0.10

SUMMARY AND CONCLUSIONS

A 45-kg batch pilot plant was operated at the Reno Research Center to test high-temperature cyanide leaching of automobile catalysts to recover PGM. Batches of used pellet, monolith, and metal support automobile catalysts were processed. Results from operation of the pilot plant showed that NaCN solution selectively dissolved the PGM. Three stages of autoclave leaching of the pellet catalyst with NaCN at 160 °C for 1 h dissolved from 93 to 97 pct of the Pt, 89 to 95 pct of the Pd, and 64 to 82 pct of the Rh. Leaching the monolith catalyst under the same conditions dissolved from 75 to 90 pct of the Pt, 77 to 88 pct of the Pd, and 43 to 72 pct of the Rh. Rhodium extractions were much lower than predicted by small-scale laboratory and PDU test results. Extraction of Pt and Rh from the metal support sample was estimated at 84 pct Pt and 72 pct Rh.

Extraction of Pt, Pd, and Rh from an AC Rochester monolith sample was increased from 84 to 88, 76 to 84, and 70 to 76 pct, respectively, by re-leaching the residue from three leaches with a solution-to-solids ratio of 1:1 and an NaCN concentration of 5 pct. Increasing NaCN concentration to 5 pct and decreasing the solution-to-solids ratio to 1:1 increased PGM extractions from a Heraeus sample by 5 pct, but caused carbonate precipitation problems during the PGM-recovery tests. Additional autoclave

leaches on another Heraeus sample showed an increase in PGM extractions by as much as 5 pct was possible, and the maximum amount of leachable PGM was reached after the fifth leach. Addition of cyanide by injection of concentrated NaCN while the leaching autoclave was at temperature showed promise from an economic standpoint. The need for intermediate cooling and filtering was eliminated, which increased throughput without affecting PGM extractions.

Sodium cyanide consumption for each of the original three leaches was 20 kg/t catalyst-autoclave leach. The additional leach at the 5 pct NaCN concentration required 50 kg/t catalyst. Typical free cyanide concentration after each autoclave leaching step was 50 mg/L.

Heating the pregnant leach solutions to a temperature of 275 °C for 4 h completely destroyed the cyanide to a concentration of 0.2 mg/L and produced a powder metallic PGM concentrate analyzing greater than 50 pct PGM. All AC Rochester pellet and monolith residues passed the EPA's TCLP for all metals. Head and process residues from Heraeus tests H-55 (U.S. pellet 1), H-58 (U.S. monolith 1), and H-56 (U.S. pellet 2) failed the TCLP for Pb by exceeding the 5-mg/L Pb leach solution standard. The remaining head and process residues passed the TCLP for all metals.

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