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High-Temperature Cyanide Leaching of Platinum-Group Metals From Automobile Catalysts—Process Development Unit

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UNITED STATES DEPARTMENT OF THE INTERIOR

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CONTENTS

ILLUSTRATIONS

TABLES

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mg/L	milligram per liter
cm	centimeter	min	minute
g	gram	mL	milliliter
gal	gallon	mm	millimeter
g/L	gram per liter	μm	micrometer
h	hour	pct	percent
in	inch	ppm	part per million
kg	kilogram	psig	pound per square inch, gauge
L	liter	tr oz	troy ounce
lb	pound	tr oz/st	troy ounce per short ton
lb/st	pound per short ton	$/tr oz	dollar per troy ounce
m^2/g	square meter per gram		

HIGH-TEMPERATURE CYANIDE LEACHING OF PLATINUM-GROUP METALS FROM AUTOMOBILE CATALYSTS—PROCESS DEVELOPMENT UNIT

By R. J. Kuczynski,[1] G. B. Atkinson,[2] and L. A. Walters[3]

ABSTRACT

The U.S. Bureau of Mines operated a 2,000-g (4.4-lb) batch process development unit for recovering platinum-group metals (PGM) from automobile catalysts. Virgin monolith, used pellet, and used monolith catalyst samples were tested. Leaching twice with 1-pct sodium cyanide (NaCN) solution at 160° C for 1 h dissolved more than 95 pct of the PGM from virgin catalysts and more than 90 pct from used pellet catalysts. More than 85 pct of the PGM was dissolved from used monolith catalysts when a third autoclave step was added. Solid PGM concentrates containing more than 99.8 pct of the dissolved PGM and analyzing greater than 70 pct PGM were recovered by heating the pregnant leach solutions from virgin catalysts to 250° C and used catalyst to 275° C for 1 h. The solution after heating contained less than 0.2 ppm total cyanide. The virgin residues passed the EPA Extraction Procedure Toxicity Test (EP Tox Test), the EPA Toxicity Characteristic Leaching Procedure (TCLP), and the California Waste Extraction Test (WET) for all elements except Ba. Adding sodium sulfate (Na_2SO_4) to the virgin leach residues reduced the amount of Ba dissolved to an acceptable level. The used leach residues passed the EP Tox Test for all elements but failed the WET and TCLP for Pb.

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INTRODUCTION

Automobile catalysts continue to be one of the largest demand sectors for platinum-group metals (PGM). More than 1.3 million tr oz of Pt, 230,000 tr oz of Pd, and 330,000 tr oz of Rh were used in the manufacture of automotive catalysts in 1990 (*1*).[4] In the United States, an estimated 1 million tr oz of PGM is used annually by the automotive industry in the manufacture of catalysts. The United States relies on foreign sources for its PGM needs, importing an estimated 95 pct of its PGM in 1990.

Scrap automobile catalysts are an underutilized aboveground source of PGM. They can contain up to 30 tr oz of PGM per short ton of catalyst. At current prices, this translates to $15,000 of PGM per short ton of catalyst. Current estimates are that 50 pct of the scrapped catalysts available in the United States are being collected (*2*). Of these scrapped catalysts, only 30 pct are processed domestically for recovery of their PGM content. The remaining balance is shipped to Japan or Europe for processing (*2*).

The number of catalysts collected and processed for PGM recovery has increased steadily over the last few years. This is due in part to increases in the number of catalyst-equipped vehicles being scrapped and the number of States requiring automobile dismantlers to remove catalysts prior to shredding. Increased demand for scrap automobile catalysts by collectors and decanners is due to increased PGM loadings and higher PGM prices.

Steps in current PGM recovery practices include collecting used converter canisters, cutting the canisters to physically remove the monolith support or pellets from the metal shell, and processing the monolith or pellets at a central facility. Hoffman (*3*) published a review article describing proposed or current hydrometallurgical and pyrometallurgical methods 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 about 20 pct of the alumina from monolith catalysts using aqua regia. Pyrometallurgical methods include plasma fusion, Cu collection, and addition of crushed catalysts to Cu smelter feed. Each method has its disadvantages, which range from high reagent consumption and corrosion to variable recoveries. The range of average recoveries is 86 to 93 pct for Pt and Pd and 81 to 87 pct for Rh.

As part of its mission to help ensure a domestic supply of strategic and critical minerals, the U.S. Bureau of Mines investigated development of a process for recovering PGM from scrapped automobile catalysts. The process was intended to provide an economic incentive for increasing the amount of catalytic converters collected and processed domestically for PGM recovery.

Initial Bureau research (*4*) investigated leaching virgin monolith catalysts with cyanide solutions to establish baseline leaching parameters. Results from this investigation showed that a solution containing sodium cyanide (NaCN) and a promoter dissolved a high percentage of the PGM from the virgin catalysts. Chemical reduction of the PGM with H_2 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 its natural pH of about 11.8 at 80° C for 1 h dissolved greater than 95 pct of the PGM.

Laboratory tests showed that using this method on used catalysts dissolved less than 75 pct of the PGM. Continued research showed that greater PGM recoveries were obtained by leaching with NaCN at elevated temperatures in an autoclave (*5*). Best results were obtained by leaching with a 5-pct NaCN solution for 1 h at 160° C. This dissolved more than 97 pct of the PGM contained in the virgin monolith, more than 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 for 1 h in an autoclave. This thermally hydrolyzed the cyanide complexes and removed more than 99.8 pct of the PGM from solution.

Information from laboratory tests was used to develop, design, operate, and evaluate a process development unit (PDU) capable of treating 2,000-g (4.4-lb) batches of virgin and used catalyst material. Treating this amount of catalyst material in the PDU accomplished three objectives. A larger volume of pregnant solution was generated for testing, the effectiveness of the countercurrent leaching procedure was evaluated, and a sufficient quantity of solid residue was produced to evaluate the environmental impacts.

SAMPLE DESCRIPTION

Automobile makers began installing oxidation catalysts on their vehicles in 1974. The oxidation catalysts contained either Pt or Pt and Pd and were used for the catalysis of CO and hydrocarbons to CO_2 and H_2O. Application of more stringent emission standards led to the gradual implementation of three-way catalysts containing Pt and Rh or Pt, Pd, and Rh for the additional catalysis of nitrogen oxides (NO_x) to N_2 (*6*). By 1982, the oxidation-only catalytic converters were completely phased out and

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

replaced by combination oxidation and three-way catalytic converters (*3, 6*).

Automobile catalytic converters consist of a type-409 stainless steel canister (10 to 12 pct Cr) containing the monolith or pellet catalyst. Combined weights of canister and catalyst range from 1.8 to 10.8 kg (4 to 24 lbs). The monolith catalysts are honeycomb structures with a circular or elliptical cross section typically measuring 10 to 15 cm (4 to 6 in) in width and 10 to 20 cm (4 to 8 in) in length and weighing from 0.4 to 1.4 kg (0.9 to 3 lb) (*6*). The monolith structure is composed of either an Fe or Mg cordierite support, coated with a high-surface-area gamma-alumina washcoat, which acts as substrate for the PGM. This washcoat accounts for almost 15 pct of the total catalyst weight. Monoliths tend to have PGM concentrations almost three times that of the pellets and because of this are of more value to the collector and processor. The pellet catalysts are spheres or prills about 3 mm (1/8 in) in size. A typical pellet charge weighs from 1.8 to 3.2 kg (4 to 7 lb) and is composed entirely of high-surface-area gamma-alumina. The gamma-alumina acts as both support media and substrate for the PGM (*3, 6*). Pellet catalysts are used almost exclusively by one automobile manufacturer. Canister size constraints and mechanical difficulties plagued the earlier pellet catalysts and almost led to their complete abandonment. As operating performance improved and the mechanical difficulties were eliminated, pellet catalysts continued to find limited applications in trucks and larger vehicles where canister size was not a significant concern.

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, decreasing the surface area and masking the PGM. Lead, carbon, hydrocarbons, and sulfates are the most significant chemical contaminants. The Pb is from leaded gasoline, in which it is used as an anti-knock compound. A small amount of Pb is also inadvertently present in unleaded gasoline. The C and hydrocarbons are from inefficient engine operation. Sulfur and sulfur compounds occur naturally in petroleum-based fuels and remain after refining. After combustion in the engine, some of the S compounds are removed from the exhaust and deposited on the catalyst. Manganese, which is added to gasoline as a Pb substitute, and P, which is added as a fuel system detergent, also occur in significant concentrations on the catalyst (*7*). Metals such as Cr, Fe, Mg, Ni, and Zn are from the operation and degradation of the engine and automobile exhaust system. Barium, zirconium and rare-earth oxides are often added by the catalyst manufacturer to retard sintering and promote catalytic properties (*7*).

Barium, lead, nickel, and sulfur 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.

Both monolith and pellet catalyst types were processed in the PDU. Tables 1 and 2 show PGM and other metals found in the catalysts tested in the PDU. A 68.1-kg (150-lb) sample of virgin monolith was obtained from rejects during a catalyst manufacturer's production run. Two used monolith samples were treated in the PDU. One sample was a 90.8-kg (200-lb) mix of used oxidation and three-way monolith obtained from a commercial decanner located in Chicago. The other sample was an 18.0-kg (40-lb) monolith composite of used oxidation and three-way catalysts obtained from scrapped converters collected locally and decanned by the Bureau's Reno Research Center staff. The used pellet sample was a 29.5-kg (65-lb) mixture of oxidation and three-way catalyst obtained from a commercial decanner.

Table 1.—PGM concentrations in catalyst samples, troy ounces per short ton

Catalyst	Pt	Pd	Rh
Virgin 3-way monolith	43.6	NP	7.9
Used Chicago monolith	23.4	8.3	1.5
Used monolith composite . . .	27.4	5.3	2.6
Used pellet	8.4	3.3	.13

NP Not present.

Table 2.—Analysis of catalyst samples, percent

Element or contaminant	Virgin monolith	Used Chicago monolith	Used monolith composite	Used pellet
Ba	0.36	0.15	0.32	0.02
C	NP	.63	NA	1.10
Ca	.26	.18	.28	.31
Cr	.01	.02	.02	.10
Fe	2.10	.83	.91	1.75
Mg	5.30	7.20	6.50	.21
Mn	.25	.16	.03	.18
Na	.04	.20	.20	.48
Ni	.01	.22	.26	.01
P	.25	.48	.32	.66
Pb	.01	.86	.21	1.10
Zn	.21	.25	.14	.42
SO_4	NP	.61	.58	.82

NA Not available.
NP Not present.

EQUIPMENT AND PROCEDURE

Figure 1 is the standard flowsheet for the PDU. The PDU flowsheet design was based on data generated in earlier bench-scale laboratory leaching tests. The design consisted of two-stage cyanide leach steps in autoclaves followed by two repulp wash steps. The PDU was operated in countercurrent mode to generate a higher concentration of PGM in the pregnant solution and to decrease the amount of water required.

Catalyst material was processed in the PDU following the standard conditions outlined in the flowsheet in figure 1. The monolith catalysts were stage crushed to minus 8 mesh. Crushing eliminated the large pores present in the monolith structure, which could trap air bubbles during leaching and result in solution entrapment during filtering and washing. The catalyst was thoroughly mixed and split into 2,000-g (4.4-lb) lots for treating in the PDU. Pellet catalysts were mixed and split into 2,000-g (4.4-lb) lots and treated without crushing.

Each 2,000-g (4.4-lb) sample was loaded into a basket fabricated from 100-mesh stainless steel screen and lowered into the autoclave. This allowed for easier loading and unloading of the autoclave. An 8.5-L (2 gal) stainless steel autoclave was used for leaching without agitation. The catalyst material was leached with 4 L (1.1 gal) of a 1-pct NaCN solution at temperature for 1 h. A 2:1 solution-to-solids ratio was maintained for leaching. Sodium hydroxide (NaOH) was used for pH adjustment. Most of the PGM were leached in the first autoclave, but because of the high dollar value of the material, the residue was leached again to increase PGM recovery. One hour was required for the autoclave to reach a temperature of 160° C. A pressure of 75 psig was measured. The autoclave was held at temperature for 1 h then allowed to cool overnight to room temperature for unloading and filtering.

A 10-in-diam pressure filter with 15 psig pressure was used for filtering. In all cases, the slurry was filtered and then displacement washed with 1 L of solution. Because of the porosity of the pellet and monolith catalyst material, filter cake moisture content ranged between 22 and 25 pct. Typical filtration times were 30 min for autoclave

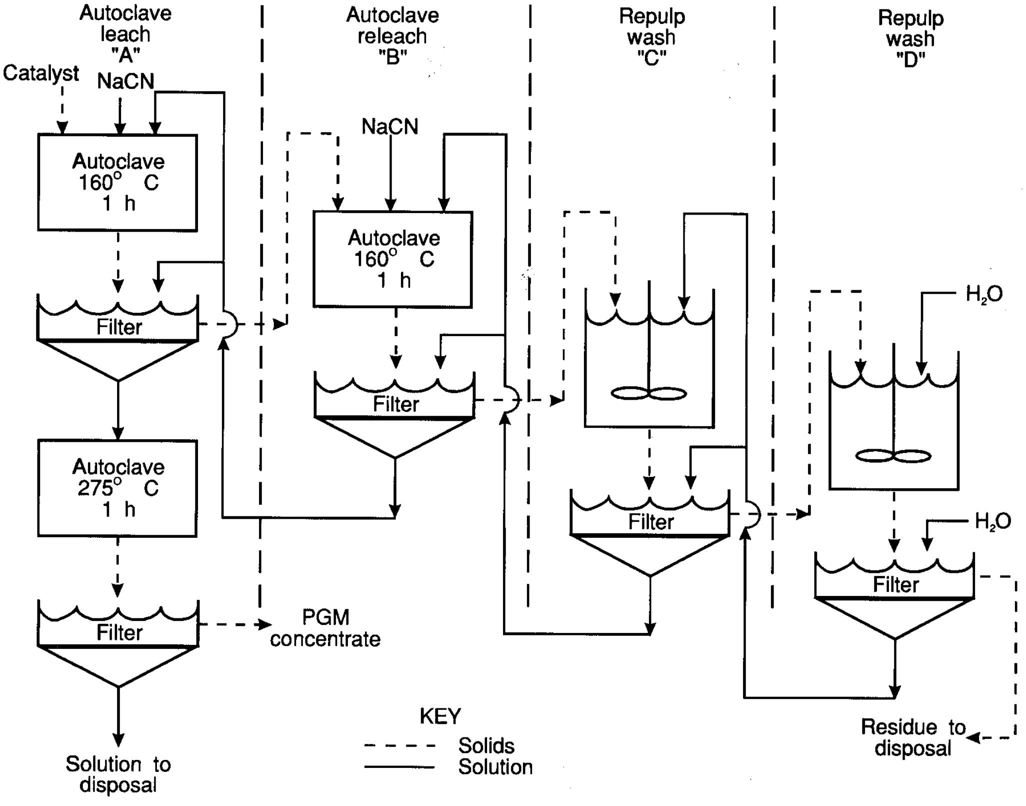

Figure 1.—Standard process development unit flowsheet.

slurries and 45 min for repulp wash slurries. Increasing filter times to 60 min and 90 min, respectively, did not appear to decrease filter cake moisture content. The catalyst material was washed by repulping with 4 L (1.1 gal) of solution in an 18.9-L (5-gal) stainless steel kettle with mild agitation for 1 h. A 2:1 solution-to-solids ratio was maintained for each repulp washing stage.

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 to prevent the formation of poisonous hydrocyanic gas (HCN). Good hygiene must be practiced to prevent ingestion and repeated contact with the skin (*8*). PDU solution flow streams were analyzed for strong acid dissociable (total) cyanide concentration. All PGM extraction results were calculated from the PGM analysis of the leaching solutions and the leach residue. A metallurgical balance was always within 10 pct and usually within 5 pct of an independent head analysis. The discrepancy in the metallurgical balance was due to the sample's not being homogenous and analysis difficulties because of the small amount of PGM present in the residues. Solutions were analyzed for PGM and other metals using sequential inductively coupled plasma (ICP) spectroscopy. Residues were analyzed for PGM by fire assaying the solids, dissolving the doré bead, and analyzing the solution by sequential ICP (*9*). The total cyanide concentration was determined by acidifying a 500-mL solution sample with 51 mL of 1:1 concentrated H_2SO_4, refluxing for 1 h, trapping the HCN liberated in a NaOH solution, and analyzing the solution for cyanide by spectrophotometry.

Tests for the recovery of PGM by thermal hydrolysis were conducted in a 2-L (0.5-gal) autoclave. Pregnant leach solution was added to the autoclave and heated to 200°, 225°, 250°, and 275° C without agitation. The residue was collected on filter paper and analyzed for PGM and trace metals. Comparative analysis of the solution was used to calculate PGM recovery.

PDU solid residues were evaluated for disposal. The residues were tested using three methods: the EPA Extraction Procedure Toxicity Test (EP Tox Test), the State of California Waste Extraction Test (WET), and the Toxicity Characteristic Leaching Procedure (TCLP). The EP Tox Test leaches solids with a 0.5*N* (normal) acetic acid solution at a pH of 5 for 24 h. The WET leaches solids with a 0.2*M* (molar) sodium citrate solution at a pH of 5 for 48 h. The TCLP leaches solids with an acetic acid solution at a pH of 4.98 for 18 h. In all tests, the filtered solution is analyzed, and to pass the test, the solution must contain less than the threshold concentration for each metal.

RESULTS AND DISCUSSION

Bench-scale leaching tests, conducted with autoclave temperatures between 105° and 200° C, indicated that the highest percentage of PGM was dissolved from virgin and used catalyst material at an autoclave temperature of 160° C for 1 h (*5*) (fig. 2). From these and other bench-scale tests, it was concluded that the rate of formation of PGM-cyanide complexes was faster at higher temperatures. Higher temperatures also accelerated the thermal hydrolysis of free cyanide and initiated the destruction of the PGM-cyanide complexes. A balance was achieved among PGM-cyanide formation, thermal hydrolysis of cyanide, and the stability of PGM-cyanide complexes. This balance resulted in maximum leaching of PGM at about 160° C. The Pd-cyanide complex appeared to be the least thermally stable as the concentration of Pd in solution quickly decreased at temperatures greater than 160° C. The Pt- and Rh-cyanide complexes appeared to be most stable, as evidenced by the slow decrease in Pt and Rh concentrations at temperatures greater than 160° C.

Table 3 shows the effectiveness of leaching virgin three-way monolith, used monolith, and used pellet catalyst material under standard conditions in the 8.5-L reactor. These results compared favorably with the best results obtained from earlier bench-scale testing. Under these conditions, 97 pct Pt and 87 pct Rh were leached from virgin monolith catalyst; and 82 pct Pt, 72 pct Pd, and 77 pct Rh were leached from used Chicago monolith catalyst. Leaching used pellet material under these same standard conditions resulted in PGM extractions of 94 pct Pt, 94 pct Pd, and 92 pct Rh. Because of the small

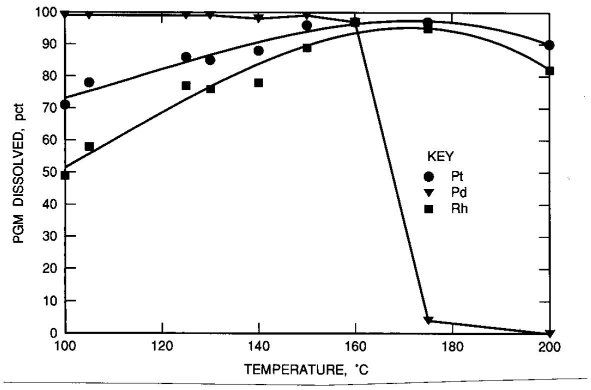

Figure 2.—Effect of leaching virgin oxidation catalyst at elevated temperatures.

amount of Rh present in the pellet head sample (0.13 tr oz/st Rh), the percentage of Rh dissolved is questionable.

Table 3.—Leaching catalysts in process development unit with 1-pct NaCN solution at 160° C for 1 h

	Pt	Pd	Rh
Virgin 3-way monolith:			
Head . . . . tr oz/st . .	43.6	NP	7.9
Residue . . . . tr oz/st . .	1.15	NP	1.04
PGM dissolved . . . . pct . .	97	NP	87
Used Chicago monolith:			
Head . . . . tr oz/st . .	23.4	8.3	1.5
Residue . . . . tr oz/st . .	4.11	2.29	0.35
PGM dissolved . . . . pct . .	82	72	77
Used pellet:			
Head . . . . tr oz/st . .	8.4	3.3	0.13
Residue . . . . tr oz/st . .	0.55	0.19	0.01
PGM dissolved . . . . pct . .	94	94	92

NP Not present.

EFFECT OF AUTOCLAVE TEMPERATURE ON PGM EXTRACTION

Tests with virgin catalyst material were conducted in the PDU at autoclave leaching temperatures of 150° and 160° C. It was speculated that at 150° C, higher PGM extractions might be possible, since cyanide has a longer half-life at lower temperatures. Because of this longer half-life, more cyanide would be available to complex the PGM. Table 4 shows that the highest recoveries of Pt and Rh were obtained at an autoclave temperature of 160° C. The amount of Pt and Rh leached increased from 95 and 85 pct, respectively, at 150° C to 97 and 87 pct, respectively, at 160° C.

Tests were conducted in the PDU with used Chicago monolith material at autoclave temperatures of 150° and 160° C. Table 4 shows the percentages of PGM leached. The amount of Pt and Pd leached decreased from 83 and 75 pct, respectively, at 150° C to 82 and 72 pct, respectively, at 160° C. The amount of Rh leached increased from 73 pct at 150° C to 77 pct at 160° C.

EFFECT OF pH ON PGM EXTRACTION

Under standard conditions, PDU leach solutions had a measured pH between 10.5 and 11.5. In order to provide an added margin of safety, the pH of autoclave solution "A" was increased to a theoretical pH of 13. NaOH was added at rate of 4 g/L of solution to autoclave leach solution "A." The end result was a 1-pct NaCN and 0.1*N* NaOH leach solution with a measured pH of 12.5.

Table 4.—Leaching catalysts in process development unit with 1-pct NaCN solution at 150° and 160° C for 1 h

	Pt	Pd	Rh
VIRGIN 3-WAY MONOLITH			
Average temperature, 150° C:			
Head . . . . tr oz/st . .	43.6	NP	7.9
Residue . . . . tr oz/st . .	2.26	NP	1.15
PGM dissolved . . . . pct . .	95	NP	85
Average temperature, 160° C:[1]			
Head . . . . tr oz/st . .	43.6	NP	7.9
Residue . . . . tr oz/st . .	1.36	NP	1.04
PGM dissolved . . . . pct . .	97	NP	87
USED CHICAGO MONOLITH			
Average temperature, 150° C:			
Head . . . . tr oz/st . .	23.4	8.3	1.5
Residue . . . . tr oz/st . .	4.00	2.07	0.40
PGM dissolved . . . . pct . .	83	75	73
Average temperature, 160° C:[1]			
Head . . . . tr oz/st . .	23.4	8.3	1.5
Residue . . . . tr oz/st . .	4.11	2.29	0.35
PGM dissolved . . . . pct . .	82	72	77

NP Not present.

[1] Standard conditions.

Table 5 shows that NaOH addition to the first autoclave leach solution does not significantly affect the amount of PGM leached from virgin catalyst material. For used catalyst material, the amount of PGM leached increased when NaOH was added to the first autoclave solution. Table 5 shows that when compared with standard conditions, Pt extractions increased from 82 to 84 pct, Pd extractions increased from 72 to 76 pct, and Rh extractions increased from 77 to 80 pct when NaOH was added.

Table 5 shows that when compared with standard conditions, the amount of Pt leached from used pellets decreased slightly from 94 to 93 pct when NaOH was added to the first autoclave solution. The amount of Pd leached increased from 94 to 96 pct after the NaOH addition. Because of the small amount of Rh present in both the head sample and residue, the effectiveness of the NaOH addition is questionable.

EFFECT OF NaOH PRETREATMENT OF CATALYST MATERIAL ON PGM EXTRACTED

Results from earlier bench-scale and PDU tests indicated that only a portion of the PGM present could be leached. This was true for both new and used catalyst types. These lower extractions are possibly due to the chemical state of the PGM and their accessibility to cyanide leaching solutions. For used catalysts, this lack of accessibility could be due to high-temperature sintering of the catalyst during its operational life. Another possible explanation could be the presence of Pb and SO_4 compounds that are refractory to cyanide solutions.

Table 5.—Leaching catalysts pretreated with NaOH in process development unit with 1-pct NaCN solution at 160° C for 1 h

	Pt	Pd	Rh
VIRGIN 3-WAY MONOLITH			
Head . . . . tr oz/st . .	43.6	NP	7.9
Standard conditions:			
Residue . . . . tr oz/st . .	1.15	NP	1.04
PGM dissolved . . . . pct . .	97	NP	87
0.1*N* NaOH primary autoclave solution:			
Residue . . . . tr oz/st . .	1.16	NP	0.95
PGM dissolved . . . . pct . .	97	NP	88
1.0*N* NaOH pretreatment:			
Residue . . . . tr oz/st . .	2.93	NP	1.74
PGM dissolved . . . . pct . .	93	NP	78
USED CHICAGO MONOLITH			
Head . . . . tr oz/st . .	23.4	8.3	1.5
Standard conditions:			
Residue . . . . tr oz/st . .	4.11	2.29	0.35
PGM dissolved . . . . pct . .	82	72	77
0.1*N* NaOH primary autoclave solution:			
Residue . . . . tr oz/st . .	3.77	2.03	0.30
PGM dissolved . . . . pct . .	84	76	80
1.0*N* NaOH pretreatment:			
Residue . . . . tr oz/st . .	4.00	2.08	0.40
PGM dissolved . . . . pct . .	83	75	73
USED PELLET			
Head . . . . tr oz/st . .	8.4	3.3	0.13
Standard conditions:			
Residue . . . . tr oz/st . .	0.55	0.19	0.01
PGM dissolved . . . . pct . .	94	94	92
0.1*N* NaOH primary autoclave solution:			
Residue . . . . tr oz/st . .	0.56	0.15	.01
PGM dissolved . . . . pct . .	93	96	92
1.0*N* NaOH pretreatment:			
Residue . . . . tr oz/st . .	0.69	0.17	0.02
PGM dissolved . . . . pct . .	92	95	85

NP Not present.

Results from bench-scale testing indicated that PGM extractions appeared to improve after pretreatment with 1*N* NaOH solution at 80° C for 1 h (*5*). Improvements in PGM extractions by as much as 5 pct were observed. A benefit of the NaOH pretreatment would be the dissolving of a portion of the alumina washcoat without dissolving any of the PGM. This would result in the exposure of more PGM to the cyanide leach solution and increase the amount of PGM extracted. A second benefit would be that the NaOH solution entrapped within the pretreated catalyst would raise the pH of the autoclave solutions.

Testing NaOH pretreatment in the PDU was conducted by leaching 2,000-g (4.4-lb) samples of catalyst material with 4 L (1.1 gal) of a 1.0*N* NaOH solution at a pH of 14 and a temperature of 60° C. An 18.9-L (5-gal) covered stainless steel vat was used for the NaOH pretreatment. After treatment, the slurry was cooled to a temperature safe for handling and filtered. No displacement wash was used. This allowed a portion of the NaOH solution to remain with the catalyst and be carried over to the subsequent autoclave treatment steps.

Results in table 5 show that the amount of PGM leached from virgin catalyst material decreased after pretreatment with 1*N* NaOH solution when compared with results from tests using standard conditions and results from tests using a 0.1*N* NaOH primary autoclave leach solution. The amount of Pt leached decreased from 97 to 93 pct, and the amount of Rh leached decreased from 87 to 78 pct. In addition, NaOH pretreatment resulted in the generation of fines. This was from the dissolution of the alumina washcoat and support structure. Because of these fines, the autoclave and repulp wash slurries required additional time for filtering. In a few instances, up to 90 min was required to produce a filter cake with a moisture content between 20 and 25 pct.

The NaOH pretreatment was expected to dissolve some of the alumina washcoat and fused material and expose more of the PGM to the leach solution. Results in table 5 show that the amounts of Pt and Pd leached from used monolith catalyst increased slightly after pretreatment with 1*N* NaOH solution when compared with results from tests using standard conditions. Extractions were less than those obtained when using a 0.1*N* NaOH primary leach solution. The amount of Pt leached increased from 82 to 83 pct, while the amount of Pd leached increased from 72 to 75 pct. The amount of Rh leached decreased from 77 to 73 pct. Bench-scale tests indicated that no further advantage would be gained if the NaOH concentration was increased for the pretreatment solution. Filtering time increased after each autoclave treatment and repulp wash. Typically, 1 h was required to filter the slurry after autoclaving and up to 2 h was required to filter the slurry after repulp wash to produce a filter cake with a moisture content between 20 and 25 pct. This increase in time was due to the generation of fines from the degradation of the gamma-alumina washcoat.

Results in table 5 show that a NaOH pretreatment did not improve the leaching of PGM from used pellet catalyst. When compared with standard conditions, no real change in the amount of PGM dissolved was observed, and the results were similar to those obtained when a 0.1*N* NaOH and 1-pct NaCN leach solution was used. The NaOH-pretreated pellets filtered poorly and required additional time. The pellet residues after autoclave leaching required 1 h of filtering to produce a filter cake with about a 25-pct moisture content. The residues after repulp washing required from 4 to 6 h of filtering to produce a filter cake with a 25-pct moisture content.

EFFECT OF OTHER PRETREATMENT METHODS ON AMOUNT OF PGM LEACHED

Grinding to a smaller particle size is a common technique to improve leaching. Although this is true for solid materials where smaller particle size significantly increases surface area, it is not necessarily true for automobile catalyst. The surface area for used catalyst was typically 4 m^2/g. Decreasing the particle size from minus 8 mesh to minus 65 mesh would theoretically increase the surface area of the catalyst material by less than 0.01 pct, an insignificant increase for the cost required. To test this, a sample of used monolith was crushed to minus 65 mesh and processed in the PDU. Results were similar to those obtained from processing minus 8-mesh material. This indicated that additional size reduction of the monolith material was not significantly beneficial.

EFFECT OF REPETITIVE AUTOCLAVE LEACHING AND REPULP WASHING ON AMOUNT OF PGM LEACHED

Changes to the PDU flowsheet were made in an attempt to increase the amount of PGM leached. Analysis of used monolith residues indicated that in some instances more than 6 tr oz/st of PGM remained after PDU processing. Repetitive autoclave treatments were at first ruled out as a method for increasing PGM extractions because of the added cost involved. However, with increasing PGM prices, especially for Rh, the use of additional autoclave treatments became more attractive. It was thought that the cost of repetitive leaching treatments could be outweighed by the value of the additional amount of PGM leached. Results obtained after reprocessing used monolith material showed that additional PGM were extracted. This indicated that the maximum amount of extractable PGM was not yet reached.

To determine how much more PGM could be extracted, a 2,000-g sample of used Chicago monolith material was treated in the PDU autoclave six times. The first autoclave leach solution contained 0.1*N* NaOH and 1 pct NaCN at a pH of 13, and the remaining five leach solutions contained 1 pct NaCN at pH of 11. The leach solutions were not recirculated, and the catalyst was not repulp washed. Following autoclaving, the slurry was filtered and displacement washed with water, and solid samples were removed for analysis. All autoclave leaching was conducted at 160° C for 1 h, and the extractions were based on residue analysis and compared with the head analysis.

Figure 3 is a bar graph of the cumulative percent of PGM removed versus the number of autoclave leaches. The maximum amount of extractable PGM appeared to be obtained after the fifth autoclave leach. The amount of Pt leached increased from 78 pct after the first autoclave leach to 92 pct after the fifth autoclave leach. The amount of Pd leached increased from 62 pct after the first autoclave leach to 85 pct after the fifth autoclave leach. The amount of Rh leached increased from 77 pct after the first autoclave leach to 93 pct after the fifth autoclave leach. Table 6 shows dollar values of the PGM contained in a 2,000-lb sample of used Chicago monolith catalyst and dissolved after repetitive leaches. Using estimated dollar values of $500/tr oz Pt, $120/tr oz Pd, and $4,500/tr oz Rh, a maximum of 92 pct of the PGM dollar value available was removed after the fifth autoclave leach.

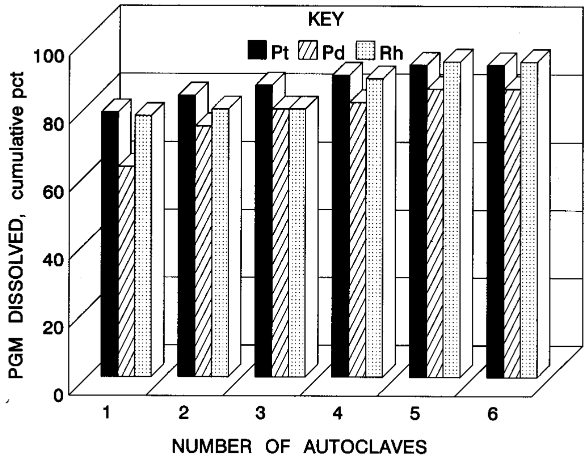

Figure 3.—Cumulative percent PGM extracted by repetitive autoclave leaching.

Table 6.—Dollar value of PGM contained in 2,000 lb of Chicago monolith catalyst and dissolved after repetitive leaches[1]

Sample	Pt	Pd	Rh	Total	Dollar value, pct
Head[2]	$11,700	$996	$6,750	$19,446	100
Autoclave leach:					
1st	9,126	618	5,197	14,941	77
2d	9,711	737	5,333	15,781	81
3d	10,062	787	5,333	16,182	83
4th	10,413	807	5,940	17,160	88
5th	10,764	847	6,278	17,889	92
6th	10,764	847	6,278	17,889	92

[1] PGM dollar values: Pt, $500/tr oz; Pd, $120/tr oz; Rh, $4,500/tr oz.

[2] Head analysis: 23.4 tr oz/st Pt, 8.3 tr oz/st Pd, 1.5 tr oz/st Rh.

Further testing of repetitive autoclave leaching in combination with repulp washing was continued by making two distinct modifications to the PDU flowsheet shown in figure 1.

Because of a shortage of used Chicago monolith material, the used composite monolith material was tested. Earlier testing indicated that this material yielded results similar to those obtained with used Chicago monolith. Figure 4 is the modified PDU flowsheet with three autoclave treatments and an intermediate repulp wash between each autoclave. Figure 5 is the modified PDU flowsheet with three autoclave treatments followed by three repulp washes. For these tests, the first autoclave leach solution was 0.1*N* NaOH and 1 pct NaCN and the remaining leach solutions were 1 pct NaCN. The remainder of the tests followed the standard conditions outlined earlier. Results in table 7 show that there was no significant difference between the results obtained with and without the intermediate repulp wash. The amount of PGM leached from the used monolith composite sample using either modified PDU flowsheet was about 91 pct Pt, 80 pct Pd, and 90 pct Rh.

Table 7.—Leaching used monolith composite material in process development unit with 1-pct NaCN solution at 160° C for 1 h

	Pt	Pd	Rh
Head . . . . tr oz/st . .	27.4	5.3	2.6
0.1*N* NaOH primary leach solution. Repulp wash after each of three autoclave treatments:			
Residue . . . . tr oz/st . .	2.69	1.16	0.32
PGM dissolved . . . . pct . .	90	78	88
1.0*N* NaOH primary leach solution. Three autoclave treatments followed by three repulp washes:			
Residue . . . . tr oz/st . .	2.40	1.08	0.29
PGM dissolved . . . . pct . .	91	80	89

RECOVERY OF PGM FROM PREGNANT LEACH SOLUTIONS

Bench-scale testing indicated that the best method for PGM recovery from pregnant leaching solutions was thermal hydrolysis (*5*). More than 99.8 pct of the PGM was removed from the solution by this method. Results in table 8 show that heating a pregnant solution generated from the treatment of virgin oxidation catalyst in an autoclave at 250° C for 1 h decreased the concentration of PGM to less than 0.5 mg/L. The total cyanide concentration decreased to less than 0.2 mg/L. Heating the pregnant leach solutions from used catalysts to 250° C did not always precipitate 99 pct of the PGM. Increasing the treatment temperature to 275° C for 1 h resulted in precipitation of greater than 99.8 pct of the PGM from all solutions tested. When the PGM concentration of the solution analyzed less than 0.5 mg/L, the total cyanide concentration in solution was always less than 0.2 mg/L. Destruction of the cyanide to this concentration should allow for safe discharge of the solution from a cyanide standpoint, providing other allowable standards are met. The final solid concentrate recovered was a fine black powder of agglomerated particles of less than 1 μm in size. This fine black powder usually contained more than 70 pct metallic PGM.

Table 8.—Effect of temperature on precipitation of PGM from virgin monolith cyanide leaching solutions

Temperature, °C	Reactor pressure, psig	PGM in solution, mg/L		
		Pt	Pd	Rh
Head	NAp	145	42	14
200	210	146	1.4	12
225	350	102	.4	5.4
250	600	.2	<.1	<.1
275	900	.4	<.1	<.1

NAp Not applicable.

DISPOSAL OF WASTE RESIDUES

The solid residues from some PDU tests were tested using the EP Tox Test, WET, and TCLP. Results in table 9 show the virgin catalyst residue passed the EP Tox Test and WET for all elements but failed the TCLP for Ba. The virgin catalyst residues contained 0.36 pct Ba and failed the 100-mg/L TCLP Ba standard by producing a leach solution containing 360 mg/L Ba. Tests were conducted in which sulfate in the form of sodium sulfate (Na_2SO_4) was added to the residue in sufficient concentrations to combine with the Ba and form highly insoluble barium sulfate ($BaSO_4$). Addition of a stoichiometric ratio of 1.5:1 sulfate to Ba, or 15 lb Na_2SO_4 per short ton of catalyst residue, yielded a TCLP leach solution of about 1 mg/L Ba. Because sulfate was already in the used catalyst, the residues passed the TCLP for Ba without sulfate addition. Used catalyst residues passed the EP Tox Test for all elements but failed the WET and TCLP for Pb. The 5-mg/L Pb standard for both tests was not met.

Table 9.—Results of EP Tox Test, WET, and TCLP on catalyst samples before and after process development unit processing

Sample	EP Tox Test[1]	WET[2]	TCLP[3]
VIRGIN 3-WAY MONOLITH			
Head:			
Pass . .	Cd,Ni,Pb,Zn	Cd,Ni,Pb,Zn	Ag,As,Cd,Cr,Hg,Pb,Se
Fail . . .	Ba	Ba	Ba
Residue:			
Pass . .	Ba,Cd,Ni,Pb,Zn	Ba,Cd,Ni,Pb,Zn	Ag,As,Cd,Cr,Hg,Pb,Se
Fail . . .	None	None	Ba

Sample	EP Tox Test[1]	WET[2]	TCLP[3]
USED PELLET, CHICAGO MONOLITH, AND MONOLITH COMPOSITE			
Head:			
Pass . .	Ba,Cd,Ni,Zn	Ba,Cd,Ni,Zn	Ag,As,Ba,Cd,Cr,Hg,Se
Fail . . .	Pb	Pb	Pb
Residue:			
Pass . .	Ba,Cd,Ni,Pb,Zn	Ba,Cd,Ni,Zn	Ag,As,Ba,Cd,Cr,Hg,Se
Fail . . .	None	Pb	Pb

[1] EPA Extraction Procedure Toxicity Test.
[2] State of California Waste Extraction Test.
[3] EPA Toxicity Characteristic Leaching Procedure.

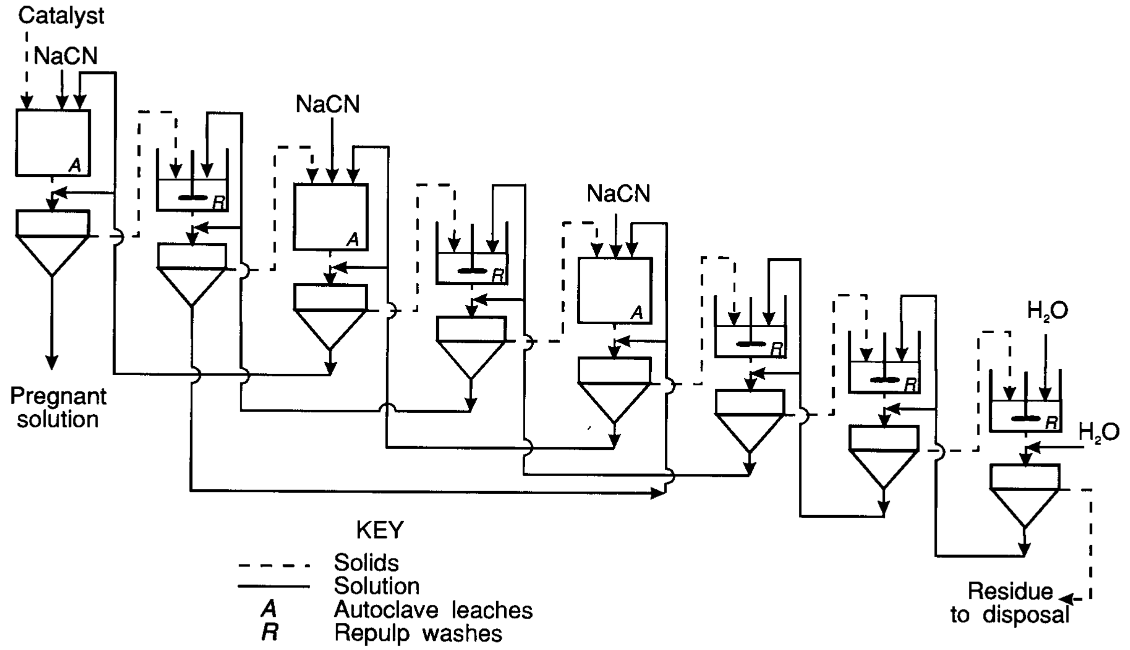

Figure 4.—Modified process development unit flowsheet with repetitive autoclave and intermediate repulp wash.

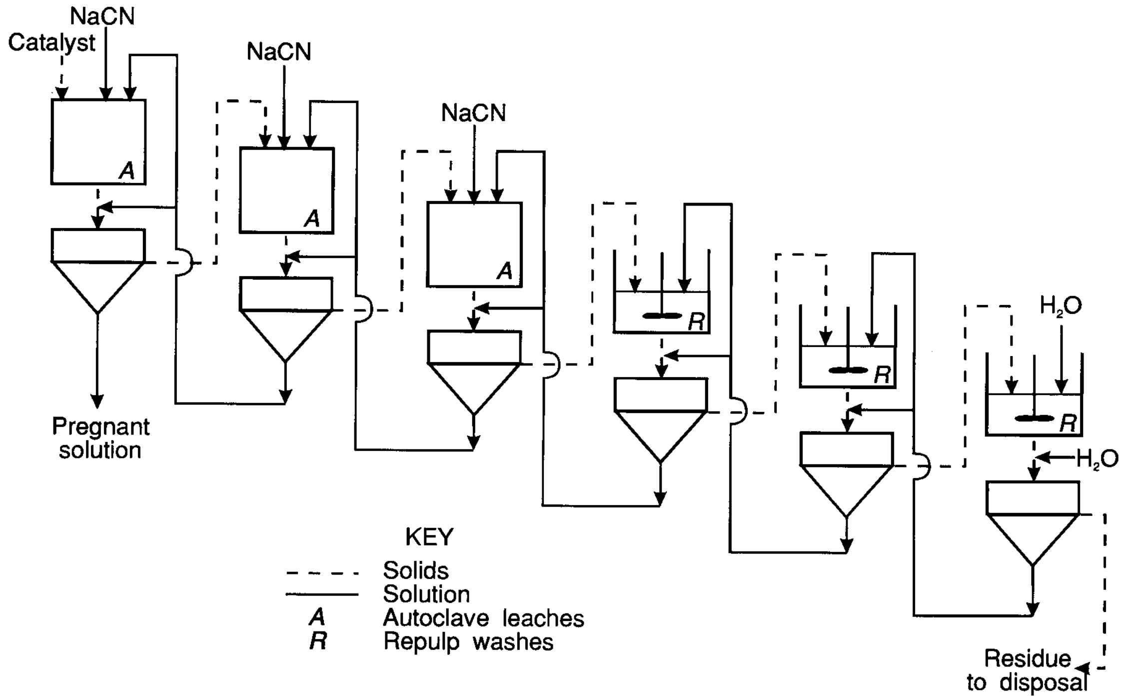

Figure 5.—Modified process development unit flowsheet with repetitive autoclave and repulp wash.

CONCLUSIONS

The Bureau operated on a batch basis a 2,000-g (4.4-lb) per day PDU for recovering PGM from automobile catalysts. More than 95 pct of the PGM was dissolved from virgin monolith and more than 90 pct from used pellet catalysts by using a two-stage autoclave leach at 160° C for 1 h with a 0.1*N* 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 in an autoclave at 160° C for 1 h with a 0.1*N* NaOH and 1-pct NaCN solution. NaCN consumption was 40 lb/st of catalyst for each autoclave leach. NaOH requirements were 16 lb/st of catalyst. The differences between the results from leaching virgin and used monolith catalyst 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 autoclave leaching to improve PGM extraction was not effective. For example, preleaching the catalyst material with 1.0*N* NaOH solution decreased the amount of PGM leached. Crushing catalyst material to minus 65 mesh did not increase PGM recovery.

Thermal hydrolysis of the cyanide complexes was used for recovering PGM from pregnant leach solutions. More than 99.8 pct of the PGM contained in the solutions was removed. A precipitate analyzing more than 70 pct metallic PGM was recovered. Pregnant solutions from virgin and used catalyst were hydrolyzed 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 EP Tox Test and WET for all elements and failed the TCLP for Ba. The addition of 15 lb Na_2SO_4 per short ton of virgin catalyst residue stabilized Ba so that the residue passed the TCLP. The used catalyst residue passed the EP Tox Test and failed both the WET and TCLP for Pb.

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