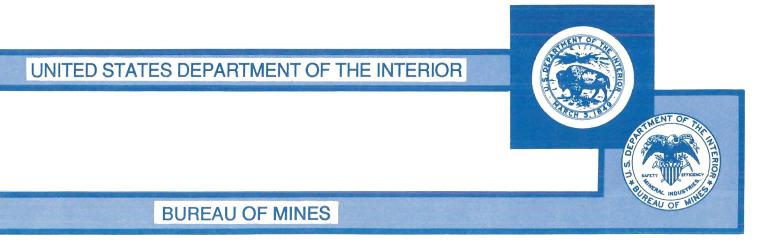


REPORT OF INVESTIGATIONS/1991

PLEASE DO NOT REMOVE FROM LIBRARY

High-Temperature Cyanide Leaching of Platinum-Group Metals From Automobile Catalysts—Laboratory Tests

By D. P. Desmond, G. B. Atkinson, R. J. Kuczynski, and L. A. Walters



U.S. Bureau of Mines

Sy Conto Lesearch Conteg E. Clu L'entger e v Ave. Se Conto, WA - 19207

Law south by Y

ą

Mission: As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally-owned public lands and natural and cultural resources. This includes fostering wise use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also promotes the goals of the Take Pride in America campaign by encouraging stewardship and citizen responsibility for the public lands and promoting citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. Administration.

Report of Investigations 9384

High-Temperature Cyanide Leaching of Platinum-Group Metals From Automobile Catalysts—Laboratory Tests

By D. P. Desmond, G. B. Atkinson, R. J. Kuczynski, and L. A. Walters

UNITED STATES DEPARTMENT OF THE INTERIOR Manuel Lujan, Jr., Secretary

BUREAU OF MINES T S Ary, Director

Library of Congress Cataloging in Publication Data:

-1

ľ

i i

High-temperature cyanide leaching of platinum-group metals from automobile catalysts—laboratory tests / by D.P. Desmond ... [et al.].

p. cm. - (Report of investigations; 9384)

Includes bibliographical references (p. 8).

Supt. of Docs. no.: I 28.23:9384.

1. Platinum group-Metallurgy. 2. Leaching. 3. Cyanide process. 4. Automobiles-Catalytic converters-Recycling. I. Desmond, D. P. (Dennis P.) II. Series: Report of investigations (United States. Bureau of Mines); 9384.

TN23.U43 [TN799.P7] 622 s--dc20 [669'.24] 91-24793 CIP

CONTENTS

| Abstract | | | | | | | | | | | | | | | | | |
|---------------------------|-------|------|------|------|------|------|------|------|-----------|---|------|-------|-----|--|------|------|--|
| Introduction | | | • • • | | | | • • | | | | |
| Sample description | | | | | | | | | | | | | | | | | |
| Equipment and procedure | | | • | | • | | | | | |
| Catalyst leaching | | | • | | • | | | | | |
| Catalyst pretreatment | | | | | • | | | | | |
| Platinum-group metals rec | overy | | | | | | | | | |
| Summary and conclusions | | | | | | | | | | | | | | | | | |
| References | | | | | | | | | | |

ILLUSTRATIONS

| 1. | Effect of temperature on leaching platinum-group metals from virgin monolith automobile catalyst | 4 |
|----|--|---|
| 2. | Effect of temperature on leaching platinum-group metals from used monolith automobile catalyst | 4 |
| 3. | Effect of NaCN concentration on leaching platinum-group metals from virgin monolith automobile | |
| | catalyst | 5 |
| 4. | Effect of NaCN concentration on leaching platinum-group metals from used monolith automobile | |
| | catalyst | 5 |
| | | |

TABLES

| 1. | Amount of platinum-group metals in catalyst samples | 3 |
|----|--|---|
| 2. | Results from leaching used monolith catalyst with 1-pct NaCN solution at 160° C for 1 h | 6 |
| 3. | Effect of temperature for 1 h on removal of platinum-group metals from cyanide leaching solution | 7 |

Page

| UN | IT OF MEASURE ABBREVIATIO | NS USED | IN THIS REPORT |
|-------|---------------------------|----------|-----------------------------|
| °C | degree Celsius | pct | percent |
| g | gram | ppm | part per million |
| h | hour | psig | pound per square inch gauge |
| lb/st | pound per short ton | tr oz | troy ounce |
| mg/L | milligram per liter | tr oz/st | troy ounce per short ton |
| mL | milliliter | \$/L | dollar per liter |
| mm | millimeter | \$/lb | dollar per pound |
| Ν | normal | \$/st | dollar per short ton |
| | | | |

Ì

ł

HIGH-TEMPERATURE CYANIDE LEACHING OF PLATINUM-GROUP METALS FROM AUTOMOBILE CATALYSTS—LABORATORY TESTS

By D. P. Desmond,¹ G. B. Atkinson,² R. J. Kuczynski,³ and L. A. Walters⁴

ABSTRACT

The U.S. Bureau of Mines investigated leaching automobile catalysts with sodium cyanide (NaCN) solutions at high temperatures to recover platinum-group metals (PGM). The feed was virgin monolith rejects, used monolith, and used pellet catalysts. Leaching with a 5-pct NaCN solution for 1 h at 160° C dissolved over 97 pct of the PGM in the virgin monolith, over 85 pct of the PGM in the used monolith, and over 90 pct of the PGM in the used pellet catalyst. Over 99.8 pct of the dissolved PGM was recovered as a precipitate by heating the solution to 250° C for 1 h in an autoclave. The cyanide complexes were decomposed, and free cyanide was destroyed.

¹Chemical engineer (now with TBI-Bailey Controls, Carson City, NV).
²Supervisory chemist.
³Chemical engineer.
⁴Supervisory physical scientist.
Reno Research Center, U.S. Bureau of Mines, Reno, NV.

ģ

The primary use of Pt and Rh in North America is in the production of automobile catalysts. In 1989, the amount of platinum-group metals (PGM) used in automobile catalysts, as a percentage of total Western World demand for each metal, was 37 pct for Pt, 6 pct for Pd, and 79 pct for Rh (approximately 1.3 million tr oz of Pt, 200,000 tr oz of Pd, and 260,000 tr oz of Rh) (1).⁵ Recovery of PGM from scrap catalysts has been expanding steadily over the past years because of high PGM prices and the increasing number of States requiring scrap yards to remove converters from cars before they are crushed or shredded.

A large percentage of the catalytic converters collected in the United States are decanned, and the catalyst supports are shipped to Japan and Europe for processing. Improved technology for recovering PGM from catalytic converters would benefit the United States by encouraging domestic recycling of critical and strategic PGM.

Both pyrometallurgical and hydrometallurgical processes are currently used to recover PGM from automobile catalysts. Hoffman (2) published a review of current technology for recovering PGM from automobile catalysts. This review describes six processes: substrate dissolution for pellet processing, insoluble substrate for monolith processing, dry chlorination, plasma fusion, Cu collection, and charging crushed catalysts to Cu smelters. Excluding the indirect method of PGM recovery by charging to Cu smelters, estimated recoveries for the other processes ranged from 80 to 94 pct for Pt, from 80 to 96 pct for Pd, and from 65 to 90 pct for Rh. Problems exist with each method. The acid systems are complex and corrosive, and generate large volumes of liquid waste. The melting systems have high electrical energy consumption and major lead emission control problems, and produce a low-grade alloy concentrate. Higher recoveries would be beneficial.

As part of its mission to help ensure a domestic supply of strategic and critical minerals, the U.S. Bureau of Mines is investigating the use of cyanide solutions to dissolve PGM for recovery. Using sodium cyanide (NaCN) offers

potential advantages over both acid and melting systems, such as low corrosion, decreased energy requirements, less complicated unit operations, and selectivity for PGM. Cyanide solutions were tested, with limited success, in treating oxidized PGM ores from the Republic of South Africa (3). Previous Bureau research (4) investigated leaching virgin monolith catalysts with cyanide solutions to establish baseline leaching parameters. In that research, two types of monolith were tested: an oxidation type containing Pt and Pd, and a three-way type containing Pt and Rh. The monolith biscuits were crushed to minus 12 plus 30 mesh. To obtain consistently high PGM recovery, it was necessary to have the PGM in elemental form before leaching; therefore, the catalyst samples were roasted in air for 1 h at 550° C, then reduced in flowing H₂ for 1 h at 550° C. Rate experiments were conducted to evaluate the effect of NaCN concentrations, promoter concentrations, leaching temperatures, solution pH's, and catalyst pretreatment methods. The best conditions determined for leaching virgin catalysts were 5 pct NaCN, 1 pct promoter, natural pH of 11.8, and catalyst pretreatment by oxidation and reduction. The highest leaching temperature investigated was 80° C. Under these conditions, more than 95 pct of the PGM were extracted. The best conditions determined for processing virgin catalysts were used to treat used catalysts. Less than 75 pct of the PGM were extracted from used catalysts at 80° C.

This report describes further research with cyanide leaching conducted at higher temperatures. Initial tests at higher temperatures showed that adding the promoter had no benefit; therefore, the promoter was removed from the system. Although higher temperatures increased cyanide consumption, the added cost of the reagent may be offset by improved extraction of the valuable PGM. Several methods were tested for recovering PGM from the cyanide leaching solution, including cementation, C adsorption, ion resins, electrowinning, and thermal decomposition of the cyanide complexes.

SAMPLE DESCRIPTION

Three types of automobile catalyst were tested: virgin monolith, used monolith, and used pellet. The virgin monolith was a reject from a manufacturer's production line and was a mixture of three-way and oxidation-type monolith catalysts. Used catalysts were obtained from a commercial decanner and consisted of grab samples from several lots to obtain a representative sample. Oxidation catalysts are made with Pt and Pd; three-way catalysts contain Rh in addition to Pt or Pd. There is no standard catalyst formulation, and both types of catalyst can contain other metals and compounds. Metals are added to promote the catalytic reactions, and compounds are added

⁵Italic numbers in parentheses refer to items in the list of references at the end of this report.

to stabilize the gamma-alumina wash coat. Table 1 shows the amount of PGM in the virgin and used catalyst samples.

Table 1.—Amount of platinum-group metals in catalyst samples, troy ounces per short ton

| Catalyst type | Pt | Pd | Rh |
|------------------|------|-----|-----|
| Virgin monolith | 55.0 | 8.5 | 3.0 |
| Used monolith | 24.0 | 8.4 | 1.5 |
| Used pellet | 8.9 | 3.2 | .1 |

Monolith catalysts consist of a honeycomb structure of cordierite coated with gamma-alumina and impregnated with PGM. The cordierite base provides support, while the gamma-alumina provides the large surface area necessary for good catalyst operation. Pellet catalysts were approximately 3-mm-diam by 4-mm-long cylinders of gamma-alumina impregnated with PGM. The monolith catalysts were crushed in stages to minus 12 mesh. Crushing eliminated the large pores in the monolith structure, which trap air bubbles during leaching and solution during washing. Pellet catalysts were not crushed.

During its useful life, an automobile catalyst undergoes many chemical and physical changes caused by impurities and extreme temperature cycles. The major contaminants are Pb from tetraethyl Pb used as a gasoline additive, and C from inefficient engine operation. The used monolith sample contained 0.85 pct Pb and 0.63 pct C, and the used pellet sample contained 1.1 pct Pb and 1.1 pct C. Sulfur contamination was also present in the used catalysts, primarily as sulfates, and ranged between 0.03 and 0.15 pct S. Some used catalyst samples tested had been operated at temperatures high enough to melt the ceramic support. Reaction of PGM with impurities, such as Pb and sulfate, could form compounds that are refractory to cyanide solutions. High-temperature excursions, as evidenced by melted ceramic, caused sintering, which decreased the surface area and masked the PGM. Sintering would prevent the cyanide solution from dissolving PGM by limiting solution to solid contact. All of these problems would decrease leaching of PGM from used catalysts compared with virgin catalysts.

EQUIPMENT AND PROCEDURE

The primary reagent used to dissolve PGM was reagent-grade NaCN. The use of cyanide requires that trained personnel be employed and safety precautions be observed. The pH of solutions must be maintained above 11 to retard formation of poisonous hydrocyanic gas (HCN). Good hygiene must be practiced to prevent contact of cyanide with the skin (5). Leaching tests were conducted in a 250-mL autoclave lined with Teflon⁶ fluorocarbon polymer. Twenty-gram samples of catalyst were leached with 100 mL of solution both with and without agitation for 1 h at different temperatures. Solids and liquids were separated after leaching by vacuum filtration with a Buchner funnel. The residue was displacement washed with 400 mL of water.

PGM extraction was calculated using analysis of the PGM content of the leaching solution and leach residue. The calculated head was always within 10 pct and usually within 5 pct of an independent head analysis. The discrepancy in the mass balance is due to the sample's inhomogeneity and difficulties in analyzing the low PGM concentrations. Solutions were analyzed with a sequential inductively coupled plasma (ICP) spectrometer. Amounts of PGM in solid samples were determined by fire assaying the solids, dissolving the doré bead, and analyzing the solution by sequential ICP (6).

Cementation, C adsorption, and ion resin were tested for ability to recover PGM by placing 100 mL of pregnant leaching solution in a beaker with excess recovery reagent and stirring. Vacuum filtration with a Buchner funnel was used to separate the solids and liquids. Solution analyses were used to calculate recoveries. Tests to evaluate recovery of PGM by electrowinning were conducted in a 100-mL cell containing a porous graphite cathode and a stainless steel anode. High agitation was achieved by pumping. The solution was periodically sampled, and comparison with the feed solution was used to calculate the recovery. Recovery by thermal decomposition was tested by placing pregnant solution in an autoclave and heating to temperatures between 200° and 275° C with no agitation. The residue was collected on filter paper but was present in too small a quantity to analyze accurately. Solution analyses for PGM both before and after thermal treatment were used to calculate recoveries.

⁶Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.

The effect of leaching automobile catalysts with a NaCN solution at temperatures greater than 80° C was tested. Twenty-gram samples of virgin monolith were leached at temperatures between 100° and 200° C with 100 mL of a 5-pct NaCN solution for 1 h. The 5-pct NaCN solution supplied 5 g of NaCN, which ensured cyanide in excess of the less than 0.05 g of NaCN required to complex the PGM. Experiments conducted at 80° C had shown no further leaching after 1 h (4). Therefore, 1-h retention at temperature was considered acceptable to ensure maximum leaching. Tests were conducted with and without agitation. After the first series of tests, no change in results was noticed with or without agitation. Therefore, agitation was discontinued and all reported results are for tests without agitation. Tests required approximately 2 h to reach temperature and 2 h to cool sufficiently for filtering. Figure 1 shows the results from individual tests on leaching virgin monolith at temperatures between 100° and 200° C. Best leaching results were obtained at 160° C; at this temperature over 97 pct Pt and Pd and 90 pct Rh were dissolved from virgin catalyst. Above 160° C the amount of Pd in solution quickly decreased and only 8 pct was solubilized at 175° C. Extraction of Pt and Rh decreased more slowly than Pd above 160° C, indicating that the Pt- and Rh-cyanide complexes are more stable than the Pd-cyanide complexes at higher temperatures. The concentration of free cyanide

decreased from 26,500 to 50 ppm after 1 h at 160° C because of thermal hydrolysis of free cyanide at high temperatures.

The relationship between metal-cyanide complexes, free cyanide, and temperature can be explained using Pd as an example. As initially prepared, the leach solution contained a significant excess of cyanide, but the rate of soluble Pd-cyanide complex formation was slow. As the temperature was increased, the rate of Pd-cyanide formation increased but free cvanide was being destroyed. At 160° C, the rate of Pd-cyanide formation was maximized versus cyanide destruction. Above 160° C, in addition to free-cvanide destruction, the rate of Pd-cvanide complex destruction is significant. This resulted in loss of Pd from the solution and destruction of the liberated cyanide. These factors combined to create a balance between Pd-cyanide in the solution and thermal destruction of the Pd-cyanide complex and free cyanide after 1 h at about 160° C.

Figure 2 shows results of tests of 20-g samples of used monolith leached with 100 mL of 5-pct NaCN solution for 1 h at temperatures between 100° and 200° C. The curves show behavior similar to that shown in leaching virgin monolith, but the amount of PGM leached was less. Best results were obtained by leaching at 160° C; recoveries of Pt, Pd, and Rh were 88, 80, and 75 pct, respectively. Based on the results from leaching monolith catalysts, 20 g

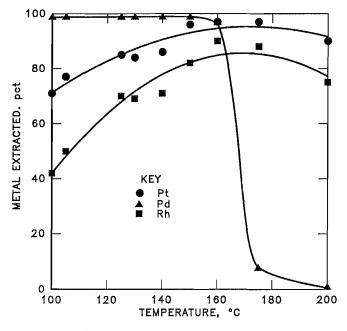


Figure 1.—Effect of temperature on leaching platinum-group metals from virgin monolith automobile catalyst (5 pct NaCN, 1 h, 5:1 solution-to-solid ratio).

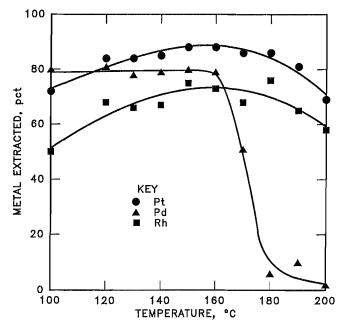


Figure 2.—Effect of temperature on leaching platinum-group metals from used monolith automobile catalyst (5 pct NaCN, 1 h, 5:1 solution-to-solid ratio).

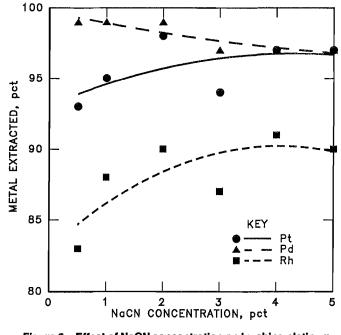


Figure 3.—Effect of NaCN concentration on leaching platinumgroup metals from virgin monolith automobile catalyst (160° C, 1 h, 5:1 solution-to-solid ratio).

of used pellets was leached for 1 h at 160° C with 100 mL of 5-pct NaCN solution. Tests consistently produced leaching extractions for Pt, Pd, and Rh of 95, 95, and 90 pct, respectively.

Tests were conducted to determine the effect of NaCN concentration on leaching virgin and used monolith catalysts. Twenty-gram samples of catalyst were leached for 1 h at 160° C with solutions having NaCN concentrations between 0.5 and 5 pct. Figure 3 shows the

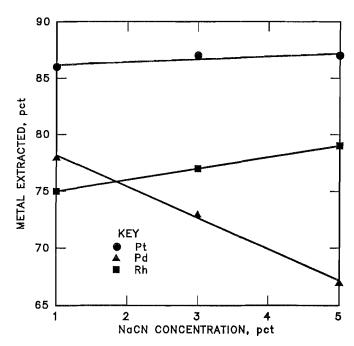


Figure 4.—Effect of NaCN concentration on leaching platinumgroup metals from used monolith automobile catalyst (160° C, 1 h, 5:1 solution-to-solid ratio).

percentage of PGM leached from virgin monolith, and figure 4 shows the percentage leached from used monolith at different NaCN concentrations. These results indicate that comparable results are obtained from leaching virgin and used monolith with solutions having NaCN concentrations between 1 and 5 pct. NaCN concentrations below 1 pct tended to decrease the percentage of PGM in solution. Selection of NaOH concentration would be a tradeoff between reagent cost and product extraction.

CATALYST PRETREATMENT

Several pretreatment methods were tested to enhance leaching of PGM from used catalysts. Carbon contamination was considered a potential problem because C might adsorb cyanide complexes. This would be similar to problems with premature Au removal from solution encountered with C in Au ores in which Au extractions are decreased during cyanidation by adsorption of cyanide complexes. Carbon was removed from used catalysts by heating at 550° C in air for 1 h. Analyses showed that C concentration generally decreased to less than 0.1 pct. Cyanide leaching of samples both with and without heat treatment in air gave similar extractions of PGM. This showed that C contamination was not responsible for decreases in PGM extraction. Results from leaching tests conducted on virgin catalysts at 80° C showed that extractions were enhanced if the PGM were in elemental form. Used catalyst samples were roasted in air at 550° C for 1 h, followed by treatment in H_2 atmosphere at 550° C for 1 h. This pretreatment did not enhance the extraction of PGM from used catalysts during high-temperature leaches.

Chemical and physical changes during the catalyst life, such as formation of chemical compounds and sintering of the metals and gamma-alumina wash coat, cause masking of the PGM. To expose more PGM to the NaCN leaching solutions, samples of used catalyst were pretreated by leaching with 1.25N NaOH solution at 80° C for 1 h to decrease Pb contamination and dissolve a portion of the gamma-alumina wash coat. The NaOH solution did not dissolve PGM. Approximately 30 pct of the Pb and less than 2 pct of the alumina dissolved. Twenty-gram samples of used monolith treated with NaOH were leached in an autoclave with 100 mL of a 5-pct NaCN solution at 160° C for 1 h. Values obtained by averaging the results of five tests conducted under the same NaOH pretreatment and NaCN leaching conditions showed the amounts of PGM leached were 89 pct Pt, 82 pct Pd, and 80 pct Rh. These results are slightly better than the 88, 80, and 75 pct Pt, Pd, and Rh, respectively, leached from untreated used monolith. Pretreatment with 2.5N NaOH was also tested. No improvement was observed in extraction of PGM compared with pretreatment at 1.25N, but more alumina was dissolved, which could cause processing problems.

A lower solution-to-solid ratio would help decrease cyanide requirements. Because stoichiometric requirements accounted for less than 5 pct of the cyanide, most cyanide that did not form stable metal-cyanide complexes was destroyed during processing at 160° C. Figure 3 shows the importance of having a NaCN concentration above 1 pct. Although the 0.5-pct NaCN solution was strong enough to provide excess stoichiometric cyanide requirement, it appears the cyanide was not available at high temperatures. By decreasing the solution-to-solid ratio, a strong cyanide solution can be provided while decreasing the cyanide consumption per pound of catalyst processed. Table 2 shows the results from leaching used monolith catalyst both with and without NaOH pretreatment with a 1-pct NaCN solution at 160° C for 1 h at different solution-to-solid ratios. The best results were obtained with a 2:1 solution-to-solid ratio on a sample pretreated with 1.25N NaOH. The results from this experiment compare favorably with those obtained for a catalyst pretreated with 1.25N NaOH and leached with a 5:1 solution-to-solid ratio. By decreasing the NaCN concentration from 5 to 1 pct and decreasing the solution-to-solid ratio from 5:1 to 2:1, the amount of NaCN required for each autoclave leach decreases from 500 lb/st of catalyst to 40 lb/st of catalyst. At the 1990 price of \$1/lb for NaCN, this represents a savings of \$460/st of used catalyst treated for each autoclave leach. Decreasing NaCN concentration from 5 to 1 pct had no noticeable effect on leaching used catalyst.

Table 2.—Results from leaching used monolith catalyst with 1-pct NaCN solution at 160° C for 1 h

| Catalyst | Solution- | Pct leached | | | | | | |
|--------------|-----------|-------------|-------------|----|--|--|--|--|
| pretreatment | to-solid | Pt | Pd | Rh | | | | |
| | ratio | | | | | | | |
| None | 5:1 | 88 | 80 | 75 | | | | |
| 1.25N NaOH | 5:1 | 89 | 82 | 80 | | | | |
| None | 2:1 | 84 | 75 ' | 71 | | | | |
| 1.25N NaOH | 2:1 | 88 | 82 | 86 | | | | |
| None | 1:1 | 85 | 76 | 79 | | | | |
| 1.25N NaOH | 1:1 | 79 | 78 | 62 | | | | |

PLATINUM-GROUP METALS RECOVERY

Methods were tested to recover the PGM from the pregnant leach solutions. When evaluating PGM recovery methods, the concentration of PGM in pregnant leaching solution must be considered. A typical pregnant leaching solution might contain 500 ppm of PGM with a potential value of \$10/L. Economic considerations make it desirable that recovery of a PGM concentrate for shipment to a refiner be both fast and complete. Methods tested included cementation, carbon adsorption, ion resins, electrowinning, and thermal decomposition of the cyanide complexes.

Cementation tests were conducted with powdered Zn (Merrilite) or Al. One-hundred-milliliter samples of catalyst leach solution containing 550 ppm Pt, 100 ppm Rh, and 50 ppm of free cyanide were treated with five Al or Zn additions of 1, 1, 2, 4, and 8 g each, made at 1-h intervals. Solution samples were taken after 1 h and before each addition. Tests were conducted at 30°, 45°, and 60° C. The best results obtained were 50-pct removal of Pt and 10-pct removal of Rh with Zn powder at 60° C. Al powder was not effective for removing Pt or Rh.

Because of very poor removal of PGM, no further tests with cementation were conducted.

Loading PGM on activated C was evaluated as a possible recovery method because of its wide use in the gold industry. Samples of leaching solution were contacted with activated C for 1 h in a stirred beaker using 10 times the recommended amount of C. More than 99 pct of the Pt and Pd was removed from solution, but less than 15 pct of the Rh was removed for all types of C tested. Contacting activated C with solutions containing high concentrations of PGM resulted in maximum loadings of 70 tr oz PGM per short ton of C. Testing of activated C was discontinued because of the incomplete removal of Rh and the relatively low loading of PGM.

Ion exchange and ion reduction resins were screened for ability to recover PGM. Each type of resin was added in stages to 100 mL of pregnant leaching solution; the final addition resulted in an excess of at least 30 times the theoretical requirement. Solution analyses showed that after 24 h of contact, the best reduction resin removed 95 pct of the Pt and 50 pct of the Rh. The best ion exchange resin gave better results: it removed 99 pct of the Pt and 80 pct of the Rh. Resins rapidly removed PGM from solution, but incomplete removal was a drawback and resin testing was terminated.

Electrolysis was tested for ability to recover PGM directly from leaching solutions, since the concentrations of PGM in solution are relatively high. Electrolysis removed PGM from solution, but deposition rates steadily decreased as the concentration of PGM decreased, and many metal impurities were codeposited. After several days of electrolysis, current efficiency of less than 1 pct was calculated and only 50 pct of the PGM was removed. Because of the long time requirement and low amount of PGM removed, electrolysis was not selected as the recovery method.

Thermal decomposition of cyanide complexes was also tested as a recovery method. Figures 1 and 2 show that, at higher temperatures, the amount of metal in solution decreased from a maximum at 160° C, suggesting that the metal-cyanide complexes formed at lower temperatures were unstable at higher temperatures and decomposed to precipitate the metal from solution. Tests were conducted in which the pregnant leaching solution was reheated in a pressure vessel to even higher temperatures to remove PGM from solution. Table 3 shows the results of tests in which pregnant leaching solutions from virgin catalysts were heated to temperatures above 200° C for 1 h. More than 99.8 pct of the PGM was removed by heating the solution to 250° C or higher for 1 h. Additional tests

showed that Pt was the most difficult of the PGM to remove from solution, indicating that Pt-cyanide is more thermally stable than Pd-cyanide and Rh-cyanide. Another important benefit of thermal decomposition for PGM recovery is the almost complete destruction of total cyanide during thermal treatment. Cyanide determinations on solutions after all PGM were removed to less than 1 ppm showed that total cyanide concentrations were less than 0.2 ppm. Although the solution is safe for disposal from a cyanide and heavy-metal standpoint, the total amount of dissolved solids, primarily Na₂CO₃, and pH are too high for recycling or dumping into the sewer. The precipitated product was a fine black powder containing mostly metallic PGM. PGM with a potential value of \$15,000 can be recovered from each ton of catalyst using less than \$100 in reagents, primarily NaCN.

| Table 3Effect of temperature for 1 h on |
|---|
| removal of platinum-group metals from |
| cyanide leaching solution |

| Temp, | Reactor | Partial analysis, mg/l | | | | | | | | |
|-------|-------------------|------------------------|-----|-----|--|--|--|--|--|--|
| ۰C | pressure, psig | 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 | | | | | | |
| MAn | Alat applica | ha Lo | | | | | | | | |

NAp Not applicable.

SUMMARY AND CONCLUSIONS

Extraction of PGM from automobile catalysts by leaching with NaCN solutions at high temperatures in an autoclave was tested. Leaching virgin auto catalyst with a 5-pct NaCN solution at 160° C for 1 h at a solution-tosolid ratio of 5:1 removed over 97 pct of the PGM. Leaching used catalyst under the same conditions dissolved 85 pct of the PGM from the monolith-type and over 90 pct of the PGM from the pellet-type catalyst. No negative effect was found from leaching without agitation. The decrease in leachability shown between virgin and used monolith catalyst was due to contamination by exhaust byproducts and physical alteration of the catalyst substrate impeding good solution-to-solid contact. Preleaching used monolith with 1.25N NaOH produced an average 3-pct improvement in overall leaching results. However, a \pm 5-pct mass balance accuracy makes determination of absolute effectiveness difficult. Experiments showed that decreasing NaCN concentration to 1 pct and solution-to-solid ratio to 2:1 produced similar recoveries and decreased NaCN requirements for each autoclave leach from 500 to 40 lb per ton of catalyst.

The best method tested for recovering PGM from the leaching solution was thermal decomposition of all cyanide complexes. Over 99.8 pct of the PGM contained in the solutions was recovered as a precipitate by treating the solutions at 250° C for 1 h while decreasing the total cyanide concentration to less than 0.2 ppm.

1. Coombes, J. S. Platinum 1989. Johnson Matthey, London, 1990, 64 pp.

2. Hoffmann, J. E. Recovering Platinum-Group Metals From Auto Catalysts. J. Met., v. 40, No. 6, 1988, pp. 40-44.

3. Dawson, M. F. Testwork on Samples of Oxidized Ore From the Potgietersrust Prospect. Mintek, Randburg, South Africa, No. M59D, 1982, 26 pp.

4. Atkinson, G. B., D. P. Desmond, R. J. Kuczynski, and L. A. Walters. Recovery of PGM From Virgin Automotive Catalyst by

Cyanide Leaching. Paper in Platinum Group Metals and the Quality of Life (Proc. Int. Precious Met. Inst., Las Vegas, NV, Jan. 29-31, 1989), Int. Precious Met. Inst., 1989, pp. 109-118.

5. Sax, N. I. Dangerous Properties of Industrial Materials. Van Nostrand Reinhold, 5th ed., 1979, 1118 pp.

6. Barry, W. L. Bureau of Mines Practice in Fire Assaying. BuMines OFR 130-82, 1982, 18 pp.