Cyanide Leaching Chemistry of Platinum-Group Metals

By P. L. Sibrell, G. B. Atkinson, and L. A. Walters

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ILLUSTRATIONS

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mL	milliliter
cm	centimeter	mM	millimolar
g	gram	(μmol/m^2)/min	micromole per square meter per minute
h	hour	nm	nanometer
in	inch	oz	ounce
K	degree Kelvin	pct	percent
kcal/mol	kilocalorie per mole	ppm	part per million
M	molar, moles per liter	psi	pound (force) per square inch
m^2/g	square meter per gram	rpm	revolution per minute
mg/L	milligram per liter	tr oz	troy ounce
min	minute	tr oz/st	troy ounce per short ton

CYANIDE LEACHING CHEMISTRY OF PLATINUM-GROUP METALS

By P. L. Sibrell,[1] G. B. Atkinson,[2] and L. A. Walters[3]

ABSTRACT

Previous research by the U.S. Bureau of Mines has shown that autoclave cyanide leaching of used automobile exhaust catalysts for recovery of platinum-group metals (PGM) is technically feasible. The purpose of this work was to investigate the chemistry of the dissolution of PGM in cyanide solutions in more detail. Where possible, samples of pure, elemental PGM powders or foils were used instead of automobile exhaust catalysts, because of their greater purity. Ultraviolet spectra revealed that Pt and Pd were solubilized as the square planar tetracyanometallate(II) complexes, while Rh was solubilized as the octahedral hexacyanorhodate(III) complex. This explained the poor recovery of Rh from solution by carbon adsorption, solvent extraction, and ion exchange observed in earlier research, because of the higher anionic charge and size of the octahedral complex. Leaching rate studies showed that the rate of solubilization was greatest for Pd, followed by Pt and Rh. Although the rate of chemical reaction was the controlling step for the dissolution of elemental Pt and Rh samples, the rate of pore diffusion was rate limiting for PGM in catalyst samples.

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INTRODUCTION

The U.S. Bureau of Mines has developed a process for the treatment of spent automobile exhaust catalysts for recovery of the platinum-group metals (PGM) contained therein (1-3).[4] (All references to catalysts in this report should be taken as automobile exhaust catalysts unless otherwise noted.) The process involves leaching at elevated temperatures and pressures with cyanide. The process has been successfully demonstrated on a laboratory scale, and has recently been scaled up to a pilot plant system at the USBM Reno Research Center. However, the basic chemistry of the process has not been investigated in detail up to this point. The purpose of this report is to discuss the chemistry of PGM leaching at elevated temperatures in a cyanide system.

PGM SUPPLY AND DEMAND

It has been estimated that in the western world, 2.2 million tr oz of PGM were used in the manufacture of automobile exhaust catalysts in 1991 (4). This included 1.57 million oz of Pt or 34 pct of total Pt demand, 370,000 oz of Pd or 8 pct of total Pd demand, and 302,000 oz of Rh or 83 pct of total Rh demand. The Stillwater mine in southwestern Montana is the only mine operating in the United States for the primary production of Pt, Pd, and Rh. Most of these metals comes from South Africa and the former Russian republics. Recycling accounts for a small part of the PGM supply in the United States, and much of the catalyst collected in the United States is currently shipped overseas for processing. Development of a simple process to recover the PGM from catalysts would benefit the United States greatly by encouraging domestic recycling of these valuable and strategic metals.

AUTOMOBILE EXHAUST CATALYSTS

Two types of catalytic converters have typically been manufactured for use in automobile exhaust cleaning. In older converters, Pt and Pd were added to catalyze the oxidation of carbon monoxide and unburned hydrocarbons. Newer converters also contain Rh, which catalyzes the reduction of oxides of nitrogen. The older converters are termed two-way or oxidation catalysts, while the newer converters are called three-way catalysts, as three major components of the exhaust gas stream are treated.

Another difference in catalysts is the substrate that the PGM are deposited upon. The monolith type catalyst consists of a ceramic honeycomb structure composed of cordierite, a silicate-based material. A wash coat of high-surface area alumina is applied to the cordierite and impregnated with the PGM. Impregnation of the PGM is done by saturating the catalyst support with an aqueous solution containing the PGM, followed by drying and firing of the catalyst material. The pellet type catalyst, common in early converters, but being used less frequently today, is composed entirely of high-surface area alumina onto which the PGM is impregnated. Catalysts with stainless steel substrates are uncommon currently, but could be used more in the future. In this type of catalyst, the stainless steel substrate is coated with a wash coat of high-surface area alumina and impregnated with PGM. This offers the advantages of greater tolerance to physical abuse and a faster heating rate of the catalyst to operating temperature. Since most emissions of pollutants occur before the catalyst reaches operating temperature, a decrease in the heating time would decrease total emissions dramatically.

Other common additives to catalysts include Ba, rare earth, and transition metal compounds. These additives improve the phase stability of the alumina wash coat and help prevent PGM deactivation, among other things. The exact additions are generally proprietary and vary from one manufacturer to another. From the foregoing, it is evident that there are many possible catalyst formulations, including variable PGM loadings. This leads to a very wide range of catalyst samples available for treatment. In addition, automobile exhaust catalysts are always modified while in service, often by sintering or poisoning of the catalyst.

CURRENT PROCESSING METHODS

There are several alternatives for the processing of automobile exhaust catalysts. However, many of these processes have never been taken beyond laboratory or pilot-plant-scale studies. Hoffmann has reviewed and critiqued several processing methods (5). The main methods currently in use are acid dissolution and plasma melting. Both of these methods have their drawbacks. For the acid dissolution process, waste disposal is a serious concern due to both the waste acid and the large amount of solubilized aluminum. In plasma melting, and indeed in all thermal processing methods, exhaust gas cleaning is a concern, especially with the lead contamination often present in used catalysts. A more selective hydrometallurgical process for catalyst treatment would be beneficial in decreasing waste disposal concerns, while also avoiding the lead emission problem associated with high-temperature processes.

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

CYANIDE LEACHING PROCESS

The cyanide leaching process for spent automobile exhaust catalysts has been described in previous publications (1-3). Early results showed that hydrogen reduction of the catalyst followed by leaching with 5 pct sodium cyanide (NaCN) at 80° C resulted in good PGM recovery from virgin catalysts. However, recoveries from used catalysts were significantly less. Later tests showed that autoclave leaching with cyanide at temperatures above 100° C gave good recovery even from used catalysts. Prereduction with hydrogen was not found to be helpful under these conditions. Another advantage of the higher leach temperature was that fewer base metal impurities were dissolved. A series of tests showed that the optimum leaching temperature was 160° C. Above that temperature Pd recovery

fell off significantly. No gases were introduced into the autoclave, so the pressure at 160° C was entirely due to steam pressure, which is about 90 psi at 160° C. Autoclave leaching was conducted under unstirred conditions. The monolith catalyst was crushed to minus 10 mesh and the pellet catalyst was treated as is, at 1/8 in. in size. While this may seem quite coarse, the PGM are present on the surface of the catalyst, and therefore should be accessible to the leach solution even at these particle sizes. Reagent additions were 1 pct sodium cyanide and $0.1M$ sodium hydroxide. Under these conditions, recoveries of PGM from spent catalysts were usually at least 85 pct Pt and Pd, and 75 pct Rh, and often higher. Since different batches of catalyst showed very wide ranges of PGM content and physical condition, the recovery varied somewhat depending on catalyst type and history.

EXPERIMENTAL

Because of the variable nature of used PGM bearing automobile exhaust catalysts, most leaching tests were conducted on samples of pure elemental Pt, Pd, and Rh. Samples were obtained as powders and foils. The powders are very finely divided and appear black, and are thus called blacks. The blacks were obtained from the Aldrich Chemical Co. and were at least 99.99 pct pure. Metal foil samples were at least 99.9 pct pure. For leaching tests conducted with automobile exhaust catalysts, a sample of monolith three-way catalyst received from Johnson Matthey[5] was used. This material was virgin reject catalyst, meaning that the catalyst was rejected during the manufacturing process and thus never saw service. The catalyst contained about 50 tr oz/st Pt, negligible Pd, and 10 tr oz/st Rh. Other chemicals used in this study were of reagent grade. Reverse osmosis water was used in all experiments.

Autoclave leaching was conducted in a 250-mL teflon fluorocarbon polymer-lined Berghoff autoclave. Typically, 50 g of catalyst was leached with 100 mL of solution containing 1 pct sodium cyanide and $0.1M$ sodium hydroxide for 1 h at 160° C. Owing to the high surface area of the catalyst and the presence of the PGM on the surface of the catalyst, leaching was conducted at fairly coarse particle sizes of minus 10 mesh with no agitation. After the time at temperature had elapsed, the autoclave was cooled, opened, and the pulp filtered and washed. For leaching of PGM black samples, 0.1 g of material was accurately weighed out and leached with 100 mL of solution as with catalysts. Owing to the small amount and fine size of the black samples, these tests were run under agitated conditions using a magnetic stir bar. All solutions were

assayed for PGM content by inductively coupled plasma atomic emission spectroscopy.

Many transition metal complexes show characteristic ultraviolet (UV) spectra due to electronic transitions. Therefore, UV spectroscopy was used to identify the PGM species in solution. Although UV spectra usually are not detailed enough to provide "fingerprint" identification of a certain complex, the technique can be used as confirming evidence based on the previous history of the solution. Ultraviolet spectra were obtained with a Hitachi UV-Visible spectrometer. Optical glass cells with a path length of 1 cm were used.

Leaching rate tests were run using samples of PGM foils and blacks. Foil samples were placed in solution at time zero and removed after a suitable interval had passed. These samples were run under unstirred conditions, due to difficulties in reproducing the agitation level. The leaching rate was calculated from the solution PGM content, the leaching time, and the geometrical area of the sample. Samples of PGM blacks were tested in a similar fashion, except that the particles were fully suspended in the solution by agitation with a stir bar. Intermediate solution samples were taken to get a better indication of the time dependence of the leaching rate. The surface areas of the blacks were measured by the Brunauer, Emmett, and Teller (BET) method, using nitrogen adsorption. The particle-size distributions of the PGM black samples were also measured in a water suspension using a particle-size analyzer based on light-scattering principles.

Some leaching rate tests were run using a rotating disk technique. This technique applied only with Pd and Pt because the dissolution rate of Rh was too low to be measured with this method. In this approach, a disk of metal is implanted into the face of an inert cylinder, which is rotated at a given speed while submerged in the leaching

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solution. Commercially available rotating disks often have Teflon fluorocarbon polymer shrouds. The surface area of the metal is the geometrical area of the highly polished disk. The hydrodynamics governing the rotating disk geometry have been investigated and rigorously solved by Levich (6). The flux of material to the metal surface is proportional to the square root of the disk rotation speed. Other factors include the reactant concentration in solution, its diffusion coefficient, and the solution viscosity. Thus, the level of agitation can be reproduced and quantified by the rotation speed of the disk.

RESULTS AND DISCUSSION

HYDROLYSIS OF CYANIDE

A significant factor that comes into play when high-temperature cyanide leaching is utilized is the loss of cyanide by hydrolysis. The rate of the hydrolysis reaction is negligible at ambient temperatures, but becomes significant above 100° C.

As a cyanide solution is heated, the rate of the following hydrolysis reaction increases rapidly:

$$CN^- + 2H_2O \Rightarrow HCOO^- + NH_3. \qquad (A)$$

Reaction A is pseudofirst order due to the high and essentially constant concentration of water in an aqueous solution. Therefore, the half-life of the cyanide depends on temperature alone. The temperature dependence of the rate of the hydrolysis reaction has been published (7), and from that data, the half-life at various temperatures can be calculated. At 20° C, the hydrolysis reaction is very slow, with a half-life of 3.5 years. At 100° C the half-life is 8.1 h, while at 160° C it is 7 min. In the laboratory autoclave leaching studies, it generally took the autoclave about 1 h to heat to temperature. By that time, 90 pct of the cyanide had been hydrolyzed. There is no advantage in long leach times at 160° C, as the cyanide will have effectively been decreased to less than 1/1,000 of its initial concentration in 10 half-lives (70 min).

These data appear to show that the cyanide may not be effectively utilized in the leaching process due to hydrolysis. It would seem that if cyanide could be added to the autoclave after the operating temperature had been reached, or after a certain time at temperature, PGM leaching may be more complete. Therefore, a method was developed where a concentrated solution of sodium cyanide could be injected into the autoclave while at temperature from a pressurized cylinder. This method was tested on three different catalyst samples and compared with results using the standard leaching procedure. The results showed that an additional 2 to 3 pct PGM extraction was obtained using the injection procedure. Based on the relatively small effects, it does not appear that cyanide depletion is a major limiting factor in the leaching of catalyst samples. However, it may be advantageous to use the injection procedure in another way. By injecting cyanide repeatedly at temperature, multiple stage leaching could be effected without the time and expense of cooling, filtering the pulp, and reheating the autoclave.

An additional complication of the hydrolysis of cyanide is that the products of the reaction, ammonia and formate, may react with PGM in solution. Ammonia can act as a ligand for transition metals, and formate may react to form carbonyl complexes, or possibly react as a reductant for the PGM. This increases the number of possible PGM species dramatically. Since the chemistry of the PGM depends on the species present, it was therefore necessary that the PGM species be identified and characterized.

CHARACTERIZATION OF PGM SPECIES

One of the major questions concerning the leaching of PGM in a cyanide system is the speciation of the PGM in solution. The most promising experimental approach for identification of the PGM species was UV spectroscopy. This is because many transition metal complexes show characteristic UV spectra due to electronic transitions. Sharpe has written a treatise on the cyanide complexes of transition metals (8). The most common complexes that would be expected under the conditions used in the catalyst leaching process would be tetracyanoplatinate(II), $[Pt(CN)_4]^{2-}$, tetracyanopalladate(II), $[Pd(CN)_4]^{2-}$, and hexacyanorhodate(III), $[Rh(CN)_6]^{3-}$. The Pt and Pd complexes have square planar geometries, while the Rh complex is octahedral. The potassium salts of these cyanide complexes were obtained for use as standards in the UV analysis. Solutions of the PGM complexes were also generated by leaching samples of pure, elemental Pt, Pd, and Rh blacks under identical conditions as the catalyst samples, to form the same species in solution. The spectra of the leach solution from the blacks were then compared with the spectra from a solution containing the PGM standards.

For the Pt and Pd species, the results were fairly clear-cut. The spectra of the Pt species is shown in figure 1. It can be seen that the two spectra are very similar, thus demonstrating that the relevant Pt species is indeed tetracyanoplatinate(II). The UV spectra of the Pd species is shown in figure 2. As with Pt, the match with the standard is good, confirming the presence of the tetracyanopalladate(II) species. The wavelengths of the peak
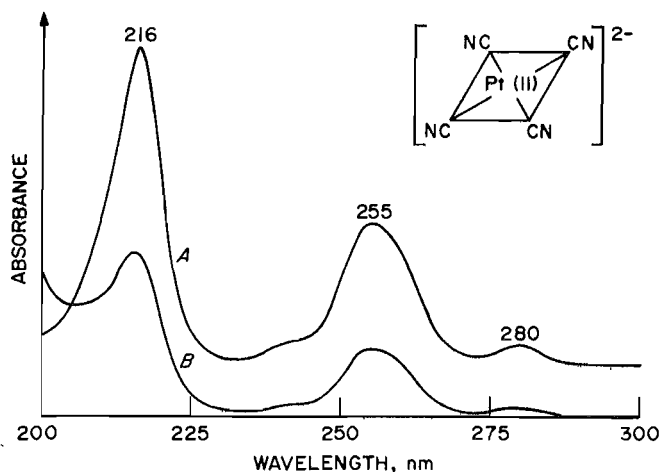
Figure 1.—Ultraviolet spectra of tetracyanoplatinate(II). Pt concentration is 0.03 mM. A, Complex derived from $K_2Pt(CN)_4 \cdot 3H_2O$; B, complex derived from autoclave leach of Pt black.
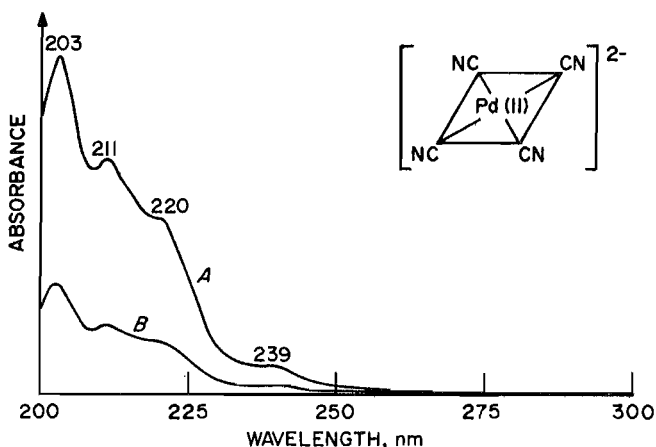

Figure 2.—Ultraviolet spectra of tetracyanopalladate(II). Pd concentration is 0.03 mM. A, Complex derived from $K_2Pd(CN)_4 \cdot 3H_2O$; B, complex derived from autoclave leach of Pd black.

maxima also correspond with those given by Sharpe for both Pt and Pd (8).

For the Rh complex, the situation was different. The spectra for the Rh black leach solution and the hexacyanorhodate(III) standard are shown in figure 3. The spectra are not as distinctive as those of the Pt and Pd complexes. Although the spectra appeared to be similar, the evidence was not conclusive that the Rh was indeed in this form. Therefore, additional samples of Rh complexes were examined. These included the ammonia complex, $[Rh(NH_3)_5Cl]Cl_2$, the nitrite complex $K_3Rh(NO_2)_6$, the acetate complex $[Rh(CH_3COO)_2]_2$, and the chloride complex $RhCl_3 \cdot xH_2O$. Each of these compounds gave UV spectra with distinctive peaks that did not agree with the leach solution spectra. Mixed ligand complexes were also prepared by reaction of the chloro salt with ammonia,
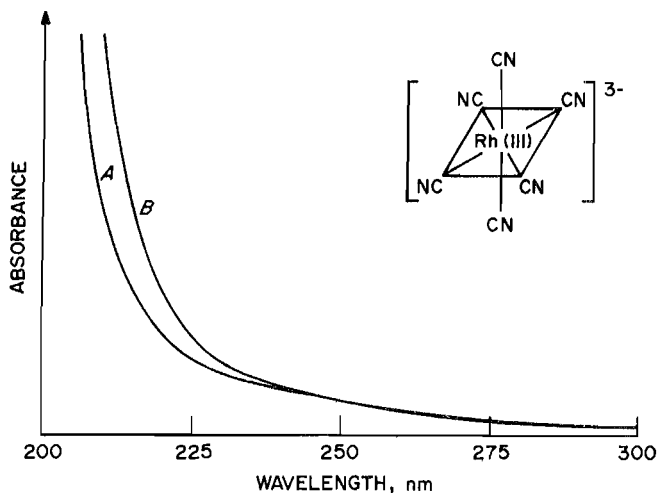

Figure 3.—Ultraviolet spectra of hexacyanorhodate(III). Rh concentration is 0.1 mM. A, Complex derived from $K_3Rh(CN)_6$; B, complex derived from autoclave leach of Rh black.

sodium nitrite, and sodium cyanide in various combinations in water. However, none of the UV spectra of any of these compounds matched that of the Rh leach solution. The hexacyano complex was still the closest match, despite its ill defined spectrum.

Reduced Rh Species

During autoclave leaching of Rh black, it was observed that, immediately after leaching, the solution had a yellow color, but this color disappeared by the following day. The yellow color could be made to reappear if the solution was reheated in the autoclave to 160° C. Further investigation showed that the yellow color was enhanced by leaching under an inert He atmosphere, rather than air, as in the usual procedure. However, this increase in color was not accompanied by an increase in Rh recovery to solution. The yellow complex was also shown to be air-sensitive: the yellow color could be maintained by placing solution fresh out of the autoclave into an air-tight bottle. The solution was analyzed by UV spectroscopy, and the resulting spectra are shown in figure 4. Since the solution was exposed to air while the spectra were being recorded, the yellow color faded with time, which is apparent in the figure. Also associated with the complex was a pair of bands in the UV region of the spectra, at 324 and 366 nm, with a much higher absorbance than the band at 425 nm that was responsible for the yellow color. This distinctive doublet in the UV region, combined with the air sensitivity of the complex, enabled its identification as tetracyanorhodate(I), $[Rh(CN)_4]^{3-}$. Sharpe gives the wavelengths of the maxima in the $[Rh(CN)_4]^{3-}$ spectrum as 322 and 365 nm (8).
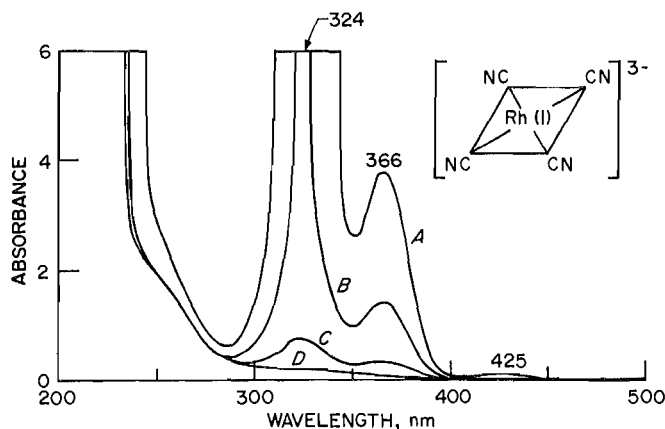
Figure 4.—Ultraviolet spectra of tetracyanorhodate(I). Rh concentration is 3 m*M*. *A*, Fresh solution; *B*, 30 min elapsed time; *C*, 60 min elapsed time; *D*, 90 min elapsed time. (The maximum absorbance that the instrument was capable of measuring was 6.)

Additional tests were conducted to ascertain the conditions necessary for the formation of the Rh(I) complex. A sample of leach solution that had previously been shown to contain the Rh(I) complex, but from which the yellow color had faded, was boiled to drive off ammonia, then reheated in the autoclave to 160° C. The Rh(I) complex was observed when the autoclave was cooled and opened, indicating that ammonia was not required for the formation of the Rh(I) complex. Another sample of the same leach solution was treated with hydrogen peroxide, to oxidize the formate to carbonate. After heating in the autoclave to 160° C for 1 h, the autoclave was cooled and opened. No Rh(I) was observed. Sodium formate was added back to this solution, which was then reheated in the autoclave. The Rh(I) complex was again present when the autoclave was opened. These results show that the presence of formate results in the formation of the Rh(I) complex. This was later confirmed by heating a solution of potassium hexacyanorhodate(III), $K_3Rh(CN)_6$, both in the absence and in the presence of formate. The Rh(I) complex was formed only when formate had been added. In cyanide leaching at elevated temperatures, formate will always be present due to hydrolysis of the cyanide.

A review of the literature regarding the Rh(I) complex showed that the complex can react to form a pentacyanohydridorhodate(III) complex (*9*), as follows:

$$[Rh(CN)_4]^{3-} + CN^- + H_2O \Rightarrow [RhH(CN)_5]^{3-} + OH^-. \quad (B)$$
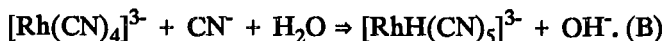
One possible mechanism for Rh(I) formation is as an intermediate in the oxidation of elemental Rh to Rh(III). In the presence of free cyanide, the hydride would be formed, which may be oxidized to hexacyanorhodate(III). In the later stages of leaching, when the free cyanide

concentration was low, the Rh(I) complex would accumulate, with no way to convert to the higher oxidation state. However, this mechanism does not require the presence of formate, and therefore does not seem to be supported by the experimental results. A more likely mechanism for the formation of the Rh(I) complex is by reduction of hexacyanorhodate(III) by the formate to give the hydride complex. This in turn reacts in a manner termed reductive elimination, the reverse of reaction (B), to form the Rh(I) complex. Thus, in Rh black leach solutions, each of these three species may be present. This also would explain why Rh extraction was not increased when the Rh(I) complex was observed, since it was formed from species already in solution.

One possible consequence of the formation of the Rh(I) complex is reprecipitation of some of the Rh, by the following disproportionation reaction:

$$3[Rh(CN)_4]^{3-} \Rightarrow [Rh(CN)_6]^{3-} + 2Rh + 6CN^-. \quad (C)$$
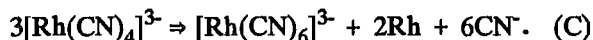
If this was the case, the Rh concentration would be expected to first increase with time as the Rh was solubilized, and then to decrease as the Rh(I) complex was formed and disproportionation took place. Therefore, an additional group of autoclave leaching tests was performed concerning the effect of time at temperature for leaching of the Rh black. Leaching tests were done with no holding time at temperature and 30 min at temperature, for comparison with the standard 60 min leaching time at temperature. Surprisingly, it was found that essentially all of the leaching took place by the time the solution reached the target temperature of 160° C. Extraction of the Rh from Rh black was about 30 pct for all three cases. There was no evidence of the yellow Rh(I) complex after 0 min at 160° C, but the complex was present after 30 and 60 min at temperature. Since the Rh concentration in solution did not decrease when the Rh(I) complex was formed, no significant disproportionation must have taken place.

The Rh(I) complex has so far not been observed in the leaching of automobile exhaust catalysts. This is a marked contrast to the leaching behavior of the elemental Rh samples. Often, catalyst leach solutions are brown tinted and could be masking the yellow color of the complex. However, even when leaching virgin catalyst, where the leaching solution was colorless, the Rh(I) complex was not observed. A leach solution generated from catalyst was reheated separately to 160° C in an autoclave. Interestingly, under those conditions, the solution had a yellow color, demonstrating the presence of the Rh(I) complex. It is possible that in the presence of the catalyst, the Rh(I) species are reoxidized as they are formed.

Ramifications of PGM Species Geometry

The identification of the Pt and Pd species as square planar cyanide complexes, and the Rh as an octahedral cyanide complex, helps explain some of the experimental results observed in earlier phases of this work. For example, it was found that recovery of the PGM from solution was difficult. Activated carbons were found to adsorb both Pt and Pd to some extent, but not to high enough loadings to effect a significant concentration factor after elution. In addition, it was found that Rh was not extracted by the activated carbon. This can now be explained on the basis of the speciation of the PGM complexes. Activated carbon is routinely used for gold adsorption, where the gold is in the form of the dicyanoaurate(I) ion, $[Au(CN)_2]^-$. This ion is linear with a single negative charge. Research has shown that although neutral and singly charged anions are easily adsorbed by activated carbon, doubly and triply charged anions are adsorbed much less readily (*10*). For example, adsorption of copper onto activated carbon can be minimized by the addition of cyanide, which converts the predominant copper cyanide complex from $[Cu(CN)_2]^-$ to $[Cu(CN)_3]^{2-}$ or $[Cu(CN)_4]^{3-}$. This results in an increase in anionic charge, which inhibits adsorption significantly. Similar effects must therefore be occurring with the doubly charged Pt and Pd complexes, and especially with the triply charged Rh complex. This explanation is probably applicable also to the solvent extraction and ion exchange results observed earlier in this project, where PGM extractions, especially Rh, were not complete. Sharpe has documented similar results for solvent extraction of metal cyanide complexes with a quaternary amine in methyl isobutyl ketone (*8*, pp. 237, 270, 275, 277, 289, 294). Complexes with a single negative charge were extracted, while doubly and triply charged anionic complexes were not.

An alternative approach to PGM recovery that was found to give complete recovery of PGM from solution was thermal decomposition. In this process, the solution was heated to 275° C in an autoclave for several hours. This was found to give complete removal of PGM from solution, with the added benefit that the total cyanide concentration was decreased to less than 0.2 ppm.

Another consequence of the bulkier size of the Rh complex is that its rate of diffusion is slower. This may be especially important when diffusion through the pores of catalyst samples is involved. Much of the catalyst pore area is associated with micropores, which may be only slightly larger than the Rh complex. This is one possible explanation for the experimental observation that the percentage of Rh leached from catalyst samples was always less than that of Pt or Pd. The pores in the catalyst had to be big enough for the Rh complex to diffuse in

during the impregnation process, but it is also possible that thermal cycling may have resulted in a reduction of pore diameter for the catalyst samples. This is supported by the experimental observation that the surface areas of used catalysts were usually about one third of the area of equivalent virgin catalysts. Thus, the Rh would be trapped in the pores, with no way of removal, except by opening of the pores by ultrafine grinding. This was supported by the results from a series of releaching tests on a monolith catalyst sample. These tests showed that a 5-pct improvement in recovery could be obtained by pulverization to less than 400 mesh. However, this would not be practical on a commercial basis, due to subsequent significant problems with liquid-solid separation.

An alternative explanation for the lower recovery of Rh from catalysts is that the rate of the chemical dissolution reaction at the metal surface is slow, which is shown to be the case later in this report. However, once formed in solution, the complex still must diffuse through the pores to reach the bulk solution. Typically, one of these processes is much slower than the other and acts as a bottleneck, thus controlling the rate of the overall process. In hopes of generating more data that could be useful in this analysis, a leaching rate test was run to determine the relative dissolution rates of the PGM from a catalyst sample. The test was conducted using the Johnson Matthey virgin reject automobile catalyst. Intermediate samples were taken using a pressurized sample cylinder at 30 min intervals once the autoclave reached operating temperature. The results showed that some leaching had already taken place by the time the autoclave reached 160° C: Pt extraction was 33 pct and Rh extraction 17 pct. After 30 min at temperature, Pt and Rh extractions were 77 and 58 pct, and after 60 min, 86 and 67 pct, respectively. The cyanide concentration had fallen to 10 pct of the original concentration by the time operating temperature had been reached, and was less than 1 pct after 30 min at temperature. The fact that the concentrations of both Rh and Pt increased steadily even when the cyanide concentration had decreased to negligible levels indicates that the pore diffusion step takes time, and could, therefore, be the controlling step. This topic will be discussed again in this report after more information on the PGM leaching rates has been presented.

OPTIMIZATION OF CYANIDE LEACHING PROCESS

Under the typical autoclave leaching conditions used in earlier studies ($0.1M$ NaOH, 1 pct NaCN in solution, 160° C for 1 h) approximately 80 to 90 pct of the Pt, Pd, and Rh were recovered from spent automobile exhaust catalysts. Further research was done at this point to see

if any improvements in PGM recovery could be obtained by varying the leaching parameters. However, the spent catalysts were not an ideal sample for leaching studies, due to their highly variable impurity contents and physical conditions. Many additional leaching tests were therefore performed with high purity samples of Pt, Pd, and Rh black to increase recovery of the PGM.

When the blacks were leached under the standard conditions, Pt and Rh dissolution were much lower than was observed with catalysts. This was probably due to differences in the sizes of the PGM particles in the samples. The rate of a leaching reaction is dependant on the surface area of the sample, which is inversely related to particle size for a given mass of solid material. For the catalyst samples, the PGM are present in clusters of atoms that are distributed over the high-surface area of the alumina washcoat. The diameter of metallic Pt, Pd, or Rh atoms are all about the same, at 0.3 nm (11). This is a much finer scale than the blacks, finely divided as they are. The blacks have surface areas of 30 to 50 m^2/g, which for nonporous solids, gives particle sizes on the order of 10 nm. However, it is likely that the primary particles of the black aggregate into larger clumps, especially when contacted with solution.

Typical extractions from PGM blacks after the standard autoclave leach were 90 pct for Pd, 20 pct for Pt, and 30 pct for Rh. Despite the lower extractions than were observed with catalysts, a process that improved dissolution with the blacks also might apply to catalyst samples. The effect of oxygen addition to the autoclave was the first variable tested. It is likely that oxygen is necessary for the cathodic half reaction (the reduction of oxygen to water), which is paired with the anodic PGM dissolution half reaction. This has been shown to be the case for dissolution of Au and Cu in alkaline cyanide solutions (12, pp. 172-179). Therefore, an increase in oxygen concentration should increase the rate of reaction. However, passivation, through formation of a protective oxide coating on the metal surface, also may occur at higher oxygen potentials. This would decrease the rate of the dissolution reaction. Treatment of samples of PGM black with oxygen overpressure had little effect on Pd dissolution, enhanced Pt dissolution to 60 pct, but completely suppressed Rh dissolution. However, these results did not carry over to catalyst leaching, where application of oxygen overpressure inhibited both Pt and Rh. (No Pd was present in the catalyst sample.) The oxygen must therefore be passivating the Rh surface in these tests.

The effect of cyanide addition was also tested using Rh black. Owing to hydrolysis, much of the cyanide had been consumed by the time the autoclave reached temperature, but PGM leaching also took place during this period, as shown earlier. A tripling of the cyanide concentration to 3 pct gave no improvement in Rh extraction. This can be

discussed in terms of the rate of hydrolysis at 160° C, where the half-life of cyanide is 7 min. Tripling of the cyanide addition would give between one and two half lives additional leaching time, or 7 to 14 min. This additional time appears to have had a negligible effect on Rh recovery. A slightly different methodology was used in the next test: the Rh addition was cut to one third of the usual amount. Extraction was again 30 pct, although the solution concentration was one third the usual. This indicates that the controlling factor in the leaching rate must be the surface area of the Rh, rather than the concentration of reactants in solution.

Other reagents, either alone or in combination with cyanide, have also been tested in an attempt to enhance Rh dissolution from the black. It was hoped that this also could be applied to catalyst leaching, if successful. The hydrolysis of cyanide leads to the formation of ammonia and formate species, as discussed earlier. Since it is well known that PGM can be dissolved to some extent by ammonia, additional leaching tests were run using, not cyanide, but its degradation products, formate and ammonia, both separately and in combination. No extraction of PGM was observed, either from catalysts or from PGM blacks. The addition of either ammonia or formate to the standard cyanide leach had no beneficial effect. Application of reducing agents, such as sodium borohydride, H_2, or CO also did not improve PGM recovery. The addition of a complexing agent to the standard cyanide leach, such as nitrite or ethylene diaminetetraacetic acid (EDTA), had no beneficial effect. Oxidants would be expected to increase the dissolution rate, unless passivation of the metal surface took place. This appears to be the case with oxygen, but as an additional check, hydrogen peroxide was added to a standard cyanide leach of Rh black. Rhodium extraction was not affected in this case, although it is possible that the peroxide was decomposed by the finely divided Rh black. An increase in sodium hydroxide addition resulted in only a marginal increase in Rh recovery. In summary, none of the variables tested resulted in improved PGM recovery from elemental samples, and it is likely that this is also true for PGM in catalysts.

LEACHING RATE STUDIES

The rate of dissolution of the PGM was the next factor to be investigated. From catalyst leaching tests, it appeared that Pt and Pd were more easily leached than Rh. However, more quantitative data in this area would be desirable. Also, the rates of dissolution processes are often controlled by the rate of a single step, or "bottleneck," of the process. For a material that does not form a porous reaction layer, the steps are mass transfer of the reactants to the surface, chemical reaction at the metal surface, and mass transfer of the products away from the

surface. If the rate-limiting step of the dissolution process can be identified, it may be possible to increase the dissolution rate by increasing the rate of the limiting step.

PGM Foil Samples

Initially, rate studies were conducted using metal foil samples of Pt, Pd, and Rh. These studies were run under the usual conditions used for treatment of catalysts, with 0.1M NaOH, 1 pct NaCN in solution, at 160° C for 1 h. There was no agitation in these tests, as it would be difficult to reproduce the agitation level from test to test because of factors such as the orientation of the foil sample. The surface areas of the foils were taken as their geometrical areas. The exposed surface areas of these samples were of course much less than catalyst samples, but for Pd and Pt, enough metal was dissolved so that a weight loss could be detected, and as a more accurate measure, the solution could be analyzed for PGM content. Owing to hydrolysis of cyanide, and to leaching during the heatup period, absolute leaching rates could not be calculated from these data. However, this procedure gives a reasonable duplication of the leaching procedure used for catalysts and can at least show differences between the PGM. Based on the area of the foil samples and the solution analysis, Pd leached 20 times faster than Pt. For Rh, no measurable weight loss occurred and no Rh was detected in solution after the leach test. Therefore, only an upper limit can be assigned to the leaching rate of Rh based on the detection limit of Rh in solution. This limiting rate was less than one fifth of the Pt leaching rate, and the actual rate was probably less than that. As a general result, leaching at 160° C with no agitation dissolved Pd at a rate 20 times faster than the Pt, which in turn was at least five times faster than Rh.

Additional rate tests were performed at lower temperatures with Pd foils. This was possible with Pd due to its relatively rapid rate of dissolution. Greater sensitivity was obtained by increasing the contact time of the test, up to 24 h at ambient temperatures. A leaching rate of 26 (μmol/m^2)/min was found for Pd at 15° C. Leaching rates were also measured at 50° C, and at 80° C, and were found to be 79 and 103 (μmol/m^2)/min, respectively.

The temperature dependance of a dissolution process can often be evaluated to find the rate determining step of the process. This is because chemical reaction rates generally show much higher sensitivity to temperature than diffusion rates. Therefore, if the rate of dissolution shows a high activation energy or a high sensitivity to temperature, then the process is probably controlled by the rate of the chemical reaction at the surface of the metal. On the other hand, if the activation energy is low, then the rate-limiting step of the process is probably diffusion of

reactants or products to or from the surface of the metal. Wadsworth has set out some numerical values for these rate controlling regimes, and gives less than 5 kcal/mol activation energies for diffusion controlled processes, and 10 to 25 kcal/mol for chemical reaction controlled processes (12, p. 135).

The procedure to determine the activation energy is to plot the natural log of the reaction rate as a function of the reciprocal of the absolute temperature. This kind of plot is termed an Arrhenius plot. The data for dissolution of Pd from foils at 15° to 80° C was analyzed in this way, and the Arrhenius plot is shown in figure 5. An activation energy of 4 kcal/mol was obtained from the plot. This indicated a diffusion controlled mechanism according to the guidelines presented above.

Rotating Disk Experiments

Further tests regarding the mechanism of PGM dissolution were run using rotating disk samples. This technique applied only with Pd and Pt, as the dissolution rate of Rh was too low to be measurable with this technique. As discussed in the experimental section, the flux of material to a rotating disk is proportional to the square root of the disk rotation speed, ω (6). Information regarding the mechanism of dissolution can be extracted from the experimentally observed relationship between the disk rotation speed and the rate of dissolution. If the rate of reaction is controlled by transport of reactants to the disk, then the reaction rate will be proportional to the square root of the rotational speed of the disk. However, if the rate is controlled by the rate of chemical reaction at the metal surface (and the flux of reactant is greater than this
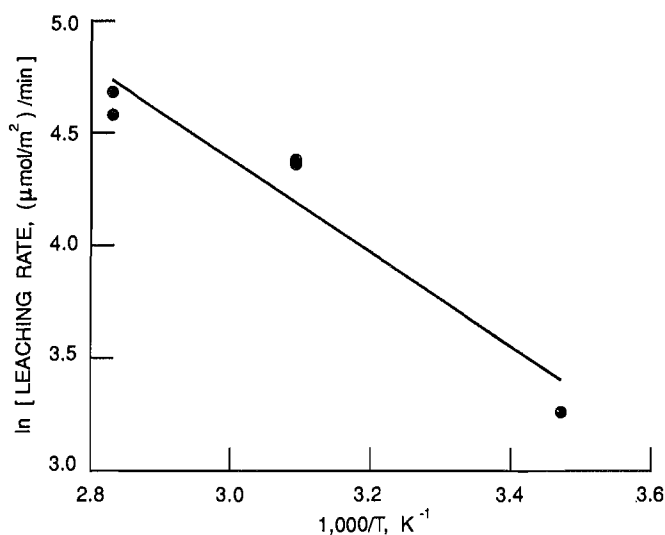
Figure 5.—Arrhenius plot for dissolution of Pd foils in 0.1M NaOH, 1 pct NaCN, at 15°, 50°, and 80° C.

rate), then the rate will be independent of the disk ro-
tational speed. The data is commonly plotted as the dis-
solution rate versus the square root of the rotational speed
ω. What is often observed is a linear relationship, which
levels out above a certain speed, where the mechanism
changes from mass transfer to chemical reaction control.

This was observed for a Pd disk in a solution of 1 pct
NaCN and $0.1M$ NaOH at 25° C, as shown in figure 6.
The critical rotational speed in this case was 950 rpm, with
mass transfer control below that speed, and chemical reac-
tion control above that speed. The reaction rate where
the mechanism changed over was 700 $(\mu mol/m^2)/min$.
This is therefore the maximum leaching rate for Pd at
25° C in this solution. The leaching rate of the Pd disk
where no stirring took place was 31 $(\mu mol/m^2)/min$, less
than one tenth of the chemical reaction rate. This agrees
well with the rate obtained by leaching of Pd foil at 15° C,
26 $(\mu mol/m^2)/min$. The maximum reaction rate under
well-stirred conditions at 25° C was much faster than that
measured for Pd foil under unstirred conditions at the
much higher temperature of 160° C.

The rotating disk experiment was repeated with a Pt
disk. However, even after 24 h at stirring speeds up to
1,000 rpm, less than 1 mg/L Pt was detected in 25 mL of
solution. The Pt dissolution rate could be increased by
heating; however, it was not possible to use the rotating
disk system at elevated temperatures due to the difference
in thermal expansion between the metal and the inert
shroud. Still, the fact that the Pt concentrations were
much less than those observed for Pd indicates that Pt
dissolution must be controlled by chemical reaction, not
mass transfer, since the mass transfer conditions were
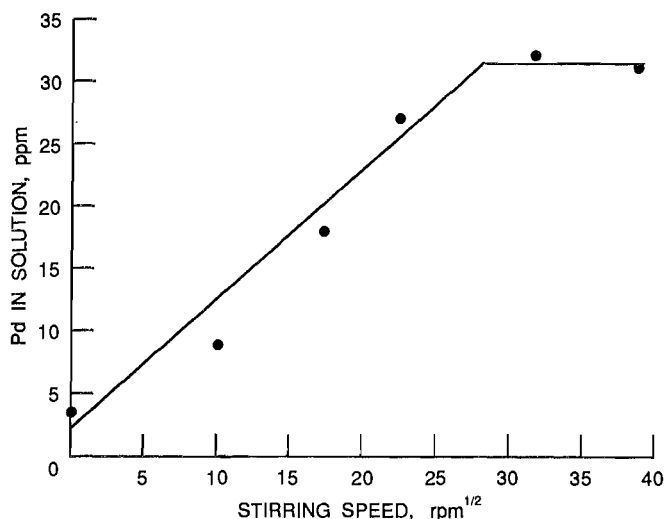identical in the two test series.

PGM Black Samples

Powdered PGM black samples have much higher sur-
face areas than foil samples; therefore, the amount of
PGM solubilized per unit time is much higher. Thus, the
use of PGM black samples might give the greater sen-
sitivity that is needed to measure the dissolution rates of
the Pt and Rh. For this reason, the investigation turned to
the use of PGM blacks. Sampling from a pressurized
autoclave is difficult, so these tests were performed under
atmospheric pressure, at 25°, 50°, and 80° C. The leach
slurries were well stirred, with the PGM blacks in com-
plete suspension. Solution samples were taken at selected
intervals during these tests, giving the extent of dissolution
as a function of time. The rate of dissolution of Pt, Pd,
and Rh at 25° C is shown in figure 7. It is immediately
apparent that the same order has been followed as with
the foil samples, with Pd being solubilized most rapidly,
followed by Pt and Rh. Leaching rates were calculated
based on solution assays taken early in the test, at less
than 10 pct extraction, to minimize the effect of the
decrease in surface area caused by leaching. The surface
areas of the blacks were based on experimentally deter-
mined BET surface areas. At 25° C, the calculated leach-
ing rates of the PGM were 0.82 $(\mu mol/m^2)/min$ for Pd,
0.10 $(\mu mol/m^2)/min$ for Pt, and 0.0018 $(\mu mol/m^2)/min$
for Rh. The Pd leaching rate does not agree with the
rates obtained from the Pd foil and rotating disk studies,
especially considering that the blacks were leached in an
agitated system. The variable most subject to error in
PGM black leaching tests was the surface area of the
blacks, upon which calculation of the leaching rate de-
pended. The surface areas of the blacks were measured

Figure 6.—Rotating disk dissolution of Pd in $0.1M$ NaOH, 1 pct NaCN at 25° C.
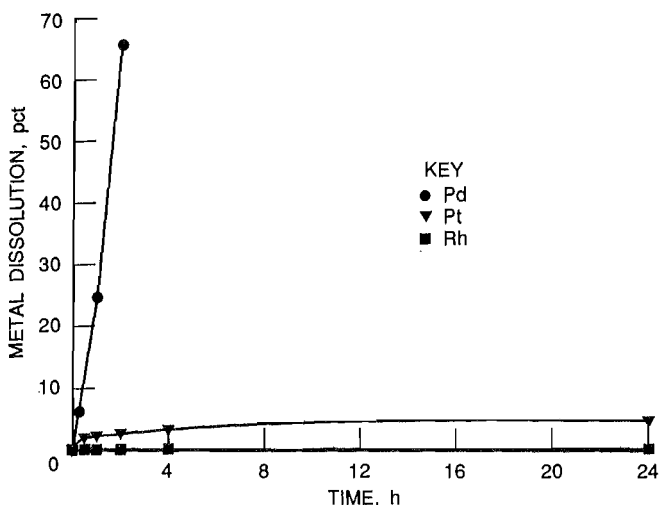

Figure 7.—Rate of dissolution of Pt, Pd, and Rh blacks at 25° C, in $0.1M$ NaOH, 1 pct NaCN.

by the BET method using nitrogen adsorption, which is an accepted technique, but the determination was carried out under dry conditions. It may be that the particles aggregated when added to solution, especially at the high ionic strength and elevated temperatures of some of these tests. In fact, some aggregation was observed during the the experiments, especially at elevated temperatures. This would lead to a decrease in available surface area, and rates calculated based on the BET surface area would therefore be less than the actual rate. The particle-size analyses of the PGM blacks were also checked using a particle-size analyzer based on light-scattering principles. These measurements were performed in a water suspension. Under these conditions, the size distributions of the blacks were much coarser than would be calculated from the BET surface area. However, the particle-size distributions also changed with time, indicating time-dependent aggregation behavior. Without a precise measurement of the powder surface area, absolute leaching rates cannot be calculated. Thus, it appears that it will not be possible to determine the absolute leaching rates of the Pt and Rh from these data.

Application to Catalyst Leaching

From the experimental results discussed above, it appears that diffusion is the rate-limiting step for elemental Pd samples, but chemical reaction is limiting for Pt and Rh. However, the situation is more complicated for catalyst leaching, since the catalysts are not pure samples of PGM. Therefore, catalyst leaching behavior may be different. For example, it was found that, in the autoclave leaching of Pt, Pd, and Rh black samples, no further extraction took place after the autoclave reached operating temperature. This was in contrast to the catalyst samples, where significant leaching of the PGM contained in the catalyst took place while at temperature. The main difference between the elemental PGM samples and the

catalyst samples is that the PGM in the catalysts are widely dispersed on a porous matrix, but the elemental PGM are immediately accessible in a pure state. Thus, the rate of pore diffusion, which is a possible rate-limiting step for the catalysts, is not a factor for the elemental samples. In addition, because of the fine size and small amount used in leaching, the blacks were usually leached under agitated conditions. However, agitation leaching of catalysts was not found to be beneficial, probably since the PGM are located within the pore structure, and thus not immediately accessible to the solution. Possible rate-limiting steps for the dissolution of PGM from catalysts are therefore either the rate of pore diffusion, or the rate of the chemical reaction at the surface of the metal.

The data from catalyst leaching tests published earlier (3) were analyzed for the dependence of the leaching rate on the temperature. The resulting activation energies ranged from 1 to 6 kcal/mol, suggesting diffusion control. These leaching tests were conducted at temperatures of 25° to 80° C. However, since diffusion rates are generally less temperature sensitive than chemical reaction rates, diffusion is likely to still be rate controlling at 160° C. Additional support for the pore diffusion mechanism can be found in the results from the leaching rate test conducted with the Johnson Matthey catalyst. In this case, Pt and Rh were still appearing in solution long after the cyanide had been depleted. Based on the relative sizes and shapes of the PGM complexes, Pt and Pd should be leached at roughly the same rate, while Rh would be slower, due to the greater size of the octahedral complex. This is also consistent with catalyst leaching data.

The rate of pore diffusion cannot be increased by mechanical means, that is by stirring, but can be increased by an increase in temperature. However, the cyanide complexes, especially Pd, begin to precipitate above 160° C. Therefore, it appears that it will not be possible to increase the dissolution rate for the catalyst samples above that observed at 160° C.

CONCLUSIONS

Unlike ambient temperature cyanide leaching processes, those at elevated temperatures show rapid loss of cyanide due to hydrolysis to ammonia and formate. The half-life of cyanide at 160° C is about 7 min, therefore, there is little point in leaching for extended periods at elevated temperatures.

For Pt and Pd dissolution in cyanide solutions, the relevant cyanide complexes were identified as square planar tetracyanoplatinate(II) and tetracyanopalladate(II) species. This was proven by their distinctive UV spectra. For Rh, the geometry of the cyanide complex was found to be octahedral, as the hexacyanorhodate(III), rather than

the square planar geometry seen for Pt and Pd. Although the UV spectra for the Rh cyanide complexes were much less distinctive, the match was evident. This difference in geometry and charge density is the most probable explanation for the behavior of the PGM in various solution treatment steps such as carbon adsorption, solvent extraction, and ion exchange, where Rh extraction was observed to be much less than extraction of Pt or Pd.

Under certain conditions, a reduced form of Rh is also produced during cyanide leaching, as tetracyanorhodate(I). This species has a distinctive yellow color and UV spectra. The species is evidently formed by the reducing action of

formate on the hexacyanorhodate(III) species and therefore does not result in increased extraction of Rh from solid samples. The Rh(I) complex is not formed in the presence of automobile exhaust catalysts, possibly due to the oxidizing nature of these materials.

The rate of dissolution of elemental PGM samples was measured by three different techniques. These were metal foil leaching, metal powder leaching, and rotating disk leaching. For the metal foil samples at 160° C, the rate of solubilization was greatest for Pd, followed by Pt and Rh. The ratios of the leaching rates were 20 to 1.0 to less than 0.2 for the Pd, Pt, and Rh, respectively. From the temperature dependence of Pd dissolution from foil samples, it was determined that the rate-limiting step was due to mass transfer considerations. This was confirmed by rotating disk tests using a Pd disk. Since the leaching rate from a Pt disk was much less than that of Pd under identical conditions, the Pt dissolution process must be controlled by the rate of the chemical reaction at the metal surface. Leaching tests using PGM blacks confirmed that the rate of solubilization increased in the order Rh, Pt, and Pd, but due to uncertainties in the surface areas of the samples, absolute leaching rates could not be calculated.

The rate of pore diffusion appears to be the limiting step for PGM dissolution from catalyst samples. Diffusion rates can be increased by an increase in temperature, but the stability of the Pd cyanide complex sets the upper temperature limit at 160° C.

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