Platinum and Rhodium Recovery from Scrapped Automotive Catalyst by Oxidative Acid Chloride Leaching.

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the Degree of Master of Engineering.


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ABSTRACT

There is a great interest in the treatment of spent autocatalyst because, due to large amounts of PGM used by catalytic converters, the autocatalyst scrap is the largest and constantly growing source of PGM available for recycling. A hydrometallurgical method of PGM extraction from honeycomb type catalyst containing platinum (800 - 1200 ppm) and rhodium (50 - 60 ppm) using HCl-AlCl₃-HNO₃ or HCl-HNO₃ mixtures was studied. Experimental results of the leaches performed in a bench scale tubular reactor with recycled continuous flow of the leaching solution as well as 1000 cc stirred reactor are presented. The results suggest that Cl⁻ single ion activity plays a decisive role in controlling the PGM dissolution. The extent of PGM recovery increased not by increasing HCl concentration to very high levels, but by keeping a relatively low total Cl⁻ level (2.5 M) with a significant proportion present as AlCl₃. Rhodium extraction was always 5-10% lower than platinum, and it appears that increasing the AlCl₃/HCl ratio tends to increase rhodium recovery. High temperature (85-95°C) and an HNO₃ concentration around 3-3.5 M play very important roles in effectiveness of PGM extraction. The presented method of HCl-AlCl₃-HNO₃ tubular reactor leaching supplemented by solvent extraction (Kelex 100) of PGM from pregnant solution appears to be very attractive for small size (5-20 tonnes of catalyst/day) installations.
L'intérêt pour le recyclage des convertisseurs catalytiques est grandissant. Typiquement, ceux-ci ont une teneur de 800 à 1200 ppm de platine et 50 à 60 ppm de rhodium. De plus, une quantité croissante de convertisseurs usés offrent une source de métaux secondaire appréciable pour le recyclage. Les lixivants HCl-AlCl₃-HNO₃ et HCl-HNO₃ furent utilisés pour l'extraction des métaux précieux (MP). Deux procédés d'extraction furent étudiés: le premier, à l'aide d'un réacteur tubulaire fonctionnant en continu, le second un réacteur "batch" de 1000 cc. Les résultats suggèrent que l'activité simple des ions chlorures jouent un rôle déterminant durant le lessivage des MP. Cependant, le recouvrement en MP n'augmenta pas en augmentant la concentration de HCl à teneurs très élevées, mais il augmenta en conservant la concentration totale des chlorures à 2.5 M en présence d'une quantité appréciable de AlCl₃. Généralement, l'extraction du rhodium fut de 5 à 10% inférieure à celle du platine et il semble qu'une augmentation du rapport HNO₃-HCl tend à augmenter la récupération du rhodium. Aussi, la température (85-90°C) ainsi que la concentration de HNO₃ jouent des rôles importants dans l'extraction des MP. Finalement, le procédé présenté semble très adéquat pour une installation pilote (de 5 à 20 tonnes de convertisseur per jour).
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CHAPTER 1: INTRODUCTION

1.1. Introduction

Catalytic converters have been the largest user of Platinum Group Metals (PGM) since the beginning of the 1980’s [1]. In the last ten years, the autocatalyst industry consumed 45-55 tonnes of PGM yearly [2]. The converter, after 4-5 years of operation in a vehicle exhaust system, becomes deactivated and is scrapped. Every year, large quantities of spent catalytic converters have entered scrapyards. Recovery of the PGM from the catalyst has evoked considerable speculation and research interest and the scrapped converters may be viewed as a substantial secondary PGM resource. This is particularly true when we realize that PGM concentrations in the catalyst are, in general, higher than those of the richest ore bodies. However, in 1989 no more than 7 tonnes of PGM derived from scrapped converters were recycled [3]. This indicates that only 15-17% of PGM used in autocoverters is finally recycled. Further expansion of global demand for autocatalyst and high PGM prices raise interest for processing of autocatalyst scrap and demand for improved refining techniques.

1.2. The history of catalytic converters

The concept of catalytic converters as a method to reduce toxicity of vehicle exhaust gases was invented as the answer to automotive emission control standards enacted by California state in the mid 1960’s [4]. Two years later the first autocoverters, containing PGM as a catalyst were introduced. In 1970, the US Senate launched emission standards, similar to California’s in all fifty states of the USA. The resolution, Clean Air Act, mandated a
significant reduction in the level of hydrocarbons and carbon monoxide emitted by automotive exhausts, starting with the 1975 model cars. The converters used in those days were so called "two-way" converters, because they were able to oxidize the two above mentioned species. The two-way converters employed platinum or platinum-palladium alloy as a catalyst. The US emission requirements were followed by Japan, which also introduced similar converters at the same time.

The emission standards were tightened in California in 1977, followed by similar criteria in all the USA in 1983. The new standards lower the permissible levels of hydrocarbons and carbon monoxide, and additionally recommend a maximum level for nitrous oxides. To meet the demands, a new generation of catalysts was designed. The new converters were called three-way, because they were able to eliminate the above mentioned three types of species from exhaust gases. Three-way catalysts contain 1 to 2 g of PGM in the weight ratio Pt/Rh of 10/1, if not lower platinum. The primary reason for adding rhodium is to achieve the reduction of nitric oxide to nitrogen efficiently [5]. Japan followed the US regulations and also introduced a mandatory use of 3-way converters in 1983.

In 1992 autocatalyst will became compulsory in Europe. It will boost actual global demand for autocatalyst by more than 30%. Besides Europe, several other countries also decided to introduce autoconverters [6]. As shown in Table 1, Australia has required autoconverters since 1987, Mexico since 1991, and Brazil is planning to introduce them in 1992. Canada has never introduced official legislation to use catalytic converters, but all auto companies voluntarily adopted US standards and all Canadian vehicles have been equipped with autoconverters since the end of the 1970's.
<table>
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<tr>
<td>USA:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1975</td>
<td>9.3</td>
<td>0.93</td>
<td>1.9</td>
</tr>
<tr>
<td>1983</td>
<td>4.4</td>
<td>0.25</td>
<td>1.2</td>
</tr>
<tr>
<td>1993</td>
<td>2.1</td>
<td>0.25</td>
<td>0.6</td>
</tr>
<tr>
<td>California:</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>1970</td>
<td>5.6</td>
<td>0.25</td>
<td>0.93</td>
</tr>
<tr>
<td>1977</td>
<td>4.4</td>
<td>0.25</td>
<td>0.44</td>
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<tr>
<td>1983</td>
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<td>European Community:</td>
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<td></td>
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<tr>
<td>Over 2 l</td>
<td>1988: 5.3</td>
<td>2.0</td>
<td>0.7</td>
</tr>
<tr>
<td>1.4 - 2 l</td>
<td>1991: 6.2</td>
<td>1.7</td>
<td>-</td>
</tr>
<tr>
<td>Under 1.4 l</td>
<td>1990: 9.3</td>
<td>3.1</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>1992: 3.9</td>
<td>1.1</td>
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<tr>
<td>1993:</td>
<td>2.1</td>
<td>0.25</td>
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*Table 1: Vehicle emission standards in different countries.*
1.3. Catalytic converters, basic definitions.

A catalytic converter is located in an exhaust train of a vehicle, usually less than 1 m behind the engine and in general resembles a muffler in size and shape. The converter is composed of a chromium steel canister and a ceramic catalyst placed inside a steel shell. Figure 1 shows a picture of a dissected converter.

The catalyst is the ceramic portion of the converter containing PGM. Catalysts have three important parts [7]:

1. catalyst support
2. washcoat
3. catalyst material.

1. The catalyst support in the autocatalyst is available in one of two forms: pellets or honeycomb monoliths. Pellets and a monolith are shown in Figure 2. Pellets have a spherical or cylindrical shape usually varying between 2 and 10 mm in diameter. The pellets are composed primarily of γ-alumina. Typically, a pellet charge in a converter weighs about 2 kg. The idea of using pellets in autoconverters was borrowed from catalysts used in the chemical industry [8]. The pellets were initially used by General Motors, but were completely abandoned after a few years, because heat resistance to a pulsating 1000°C gas stream was unsatisfactory.

Monoliths have a continuous honeycomb structure with parallel square channels of an elliptical cross-section. Overall diameter varies from 10 to 14 cm, and
length from 12 to 20 cm. Currently produced three-way honeycombs have 62 channels/cm² and each converter contains two monoliths, with a total weight of about 1.1 kg. The monoliths are composed of a low-thermal expansion magnesium or iron cordierite, which offers very good thermal shock resistance.

2. The washcoat is a very thin γ-alumina layer, which covers the catalyst support. Its main purpose is to produce a high porosity coat (about 200 m²/g) and a suitable surface for the PGM.

3. The catalyst materials in autocatalyst are platinum, palladium and rhodium. These metals are used alone or in combination and are supplemented by base metal promoters which enhance the PGM’s performance. The promoters are nickel, cobalt and cerium. PGM particles are dispersed in the most external layer of the γ-alumina gel. The PGM content of the catalysts has changed several times since 1975. The first two-way converters employed a platinum or platinum-palladium mixture, while currently used three-way converters contain platinum, palladium and rhodium. There were also reports of palladium-only catalyst developed by Ford in 1988 [9], however no data is yet available concerning its use in commercial vehicles.

Three-way converters contain two honeycomb units, which may have different contents of PGM. The honeycomb closest to the engine reduces nitric oxide to nitrogen and contains platinum and rhodium. The second honeycomb contains platinum or a platinum/palladium mixture, and oxidizes carbon monoxide and hydrocarbons.

PGM content varies from 800 to 1500 ppm, as detailed in
Figure 1: Cut away section of honeycomb-type converter.
Figure 2: Samples of the two forms of catalyst ready for leaching: pellets (left) and broken honeycombs (right).
Table 2. Besides PGM, catalysts also contain promoters, usually CeO$_2$ and ZrO$_2$, to enhance the catalytic activity, and NiO to prevent emission of H$_2$S, which can be formed within the catalyst.

1.4. Technology of production of honeycomb catalysts.

To illustrate how PGM and a γ-alumina washcoat is placed onto a catalyst support, the standard technology of honeycomb production is described below [10]. Deposition of γ-alumina and PGM on a honeycomb support requires three immersions in different slurries, interspaced by two baking steps. The process is schematically shown in Figure 3. First, a cordierite support unit is dipped (step 1) in an aqueous slurry, which is composed of Al$_2$O$_3$, boehmite and NiO. Next, the unit is baked (step 2) at 650°C for 1 hour then immersed (step 3) in a solution containing promoters Ce(NO$_3$)$_3$ and ZrO(OH)$_3$. Again the honeycomb is baked (step 4) at 600°C for 5 hours, and finally immersed (step 5) in a solution of Pt(NH$_3$)$_2$(NO)$_3$ and RhCl$_3$ to load Pt and Rh. Concentrations of PGM in this final solution, as well as time of immersion, change with different catalysts for different vehicles.

1.5. Overview of the market.

Substantial demand for catalytic converters began in the middle of the 1970’s, when the USA introduced mandatory use of such devices. Since then, the demand for converters, and the PGM which they contain, has been gradually increasing. The catalytic converter industry has been the biggest consumer of PGM in the last 10 years and in 1989 alone, as shown in Table 3, autocatalyst consumed about 23%
### Table 2: Typical forms and PGM contents of autocatalyst.

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<tr>
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<th>PELLETS</th>
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<td>iron or magnesium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cordierite</td>
</tr>
<tr>
<td>Washcoat</td>
<td>γ-alumina</td>
<td>γ-alumina</td>
</tr>
<tr>
<td>Dimension</td>
<td>2-10 mm in diameter</td>
<td>10-20 cm in diameter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10-20 cm length</td>
</tr>
<tr>
<td>Weight per unit</td>
<td>2 kg</td>
<td>1.2 kg</td>
</tr>
<tr>
<td>Concentration of</td>
<td>Pt 350-850</td>
<td>800-1200</td>
</tr>
<tr>
<td>PGM [ppm]</td>
<td>Pd 150-300</td>
<td>0-300</td>
</tr>
<tr>
<td></td>
<td>Rh 0</td>
<td>0-100</td>
</tr>
</tbody>
</table>
Figure 3: Standard technology of honeycomb-type catalyst production.
**DEMAND**

<table>
<thead>
<tr>
<th></th>
<th>Total Demand [t/y]</th>
<th>Autocatalyst Demand [t/y]</th>
<th>Prices* [$US/oz.]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>108</td>
<td>41.0</td>
<td>520-550</td>
</tr>
<tr>
<td>Palladium</td>
<td>115.3</td>
<td>6.9</td>
<td>100-120</td>
</tr>
<tr>
<td>Rhodium</td>
<td>8.2</td>
<td>6.0</td>
<td>2000-5000</td>
</tr>
<tr>
<td>Total</td>
<td>231.5</td>
<td>53.9</td>
<td>23%</td>
</tr>
</tbody>
</table>

**SUPPLY**

<table>
<thead>
<tr>
<th></th>
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<th></th>
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<th></th>
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<tr>
<td>Pt</td>
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<td>83.2</td>
<td>14</td>
<td>6.0</td>
<td>4.2</td>
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<tr>
<td>Pd</td>
<td>112.5</td>
<td>50.3</td>
<td>55</td>
<td>48.9%</td>
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<tr>
<td>Rh</td>
<td>8.1</td>
<td>6.6</td>
<td>1.2</td>
<td>14.8%</td>
<td>0.3</td>
</tr>
<tr>
<td>Tot.</td>
<td>228.0</td>
<td>140.1</td>
<td>70.2</td>
<td>30.8%</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Table 3: Supply and demand for platinum, palladium and rhodium in the market economy countries in 1989.

* PGM prices in 1990
of total PGM demand, equal to 53.9 t of PGM. This amount includes 41 t of platinum, 6.9 t of palladium and 6 t of rhodium. New converters, once installed, remain in vehicle exhaust systems for 4-5 years (an average vehicle uses 2 converters in its lifetime), and then the used units are scrapped, collected and sent to processors. Theoretically, almost 70% of all PGM used in autocatalyst could be finally recycled [7]. However, the actual PGM recovery from scrapped autocatalyst is much smaller (only 15-20%) due to inefficient collection service and imperfect refining techniques. Nevertheless, recycling provides a significant amount of PGM. In 1989, as shown in Table 3, 8.6 t of PGM was supplied by recycling of autoconverters. This is almost 4% of total PGM supply, or in other words, 16% of PGM currently used to manufacture new converters. Introduction of this equipment in new countries, and the tightening of already existing standards will require more autocatalyst, and consequently more and more of these devices will be scrapped and available for recycling. Financial analysts estimate that the amount of recycled autocatalyst will double over the next five years, and consequently there will be no decline in amount of scrapped autoconverters over the next 20 years [1].

1.6. Recycling of autocatalyst.

The recycling of autocatalyst requires a chain with the following links: dismantler, collector and processor [7]. The dismantler physically removes catalytic converters from vehicles at a garage or at an automobile scrap yard. Later, he sells the entire converters to collectors. The collector separates the catalyst from the steel containers and sells it to a processor. The processor treats the scrapped catalyst to remove, recover and refine the precious metals.
While processing methods confront a variety of technical challenges, described in later chapters, the collecting procedure is also problematic. The most difficult problem is to determine the actual quantity of PGM contained in the catalyst. Catalysts are usually traded at a price which depends on contained PGM value, and its estimation requires precise sampling and analysis methods.

Another problem frequently encountered in recycling of catalyst in North America is inability to find regular sources of scrap autocatalyst. Collector networks established by the Japanese are very efficient, and they collect and send to Japan for processing 65-70% of all catalyst available for recycling from the USA and Canada [3].

1.7. Method of sampling catalyst for PGM analysis.

Autocatalyst is a relatively homogeneous type of scrap. Although there are variations in composition, a well mixed and properly sampled lot will be relatively consistent within the lot. Pellet sampling is easy to perform, and very often a splitter box sampler is used [7]. The splitter box functions by having equally sized and oppositely directed discharge chutes through which the feed material is passed. With every pass, the feed is split into two streams. One of each is alternately used again as the feed stream. After a few passes, a small representative sample is taken.

Honeycomb catalyst is somewhat more difficult to sample because of the irregularity in size and shape, and segregation caused by settling of PGM rich dust. Commonly used mineral processing methods for evaluating monolith, like grab sample and cone and quarter methods can be used
The precision of these methods is ±7%. The ±7% error in PGM concentration in the scrap catalysts can be a highly significant factor, since it is likely to be the source of most commercial disagreements.

1.8. Method of analyzing catalyst.

Chemical analysis of PGM in the ceramic substrate can be done in several ways. Instrumental methods involve analysis by Atomic Absorption [11], Neutron Activation [12] and X-Ray Fluorescence [13]. Each of the analytical methods has its own limitations, however all of them have accuracy ±1-2%. It is not very significant, because when the error in sampling is compared to error in the chemical analysis, it can be seen that the uncertainty is much greater in the former case [7].

1.9. Contaminations.

Various contaminants are picked up from exhaust gases and accumulated on the surface of the catalyst during its usage. Spent catalysts contain contaminants like lead and lead compounds, carbon, soot, base metals, vanadium, phosphorus compounds and also moisture and oil. It is obligatory that lead must be safely removed during processing, and its discharge is difficult and costly.

1.10. Lead and lead compounds.

A small amount of lead is intentionally added to most brands of gasoline and deposited on the catalyst. As a result, the autocatalyst converters can contain as much as
3-10% of lead in various forms [7]. From the processor's viewpoint, lead is the most undesirable and difficult to handle contaminant. Its removal and safe disposal add to the cost of PGM reclamation from scrapped autocatalyst. In the smelting route, because the oxides, sulphide, and chlorides of lead have significant volatility, the process must include provisions for capturing the volatile lead compounds to prevent their emission both into the workplace and the environment. In the hydrometallurgical acid dissolution methods, lead may form soluble complexes which must be removed from the leaching solution to comply with environmental discharge regulations. Therefore, any process suitable for PGM recovery from automotive converters must deal satisfactorily with the lead in the catalyst.

1.1. Oil.

Most scrapped catalysts contain little or no oil because unburned organic materials entering the converter are quickly burned off. Occasionally, a single catalyst unit is oil-soaked because of a malfunctioning engine. Oil contamination is also undesirable from the reprocessing viewpoint. In a hydrometallurgical route, oil can prevent proper acid contact with the ceramic support and can also interfere with solid/liquid separation. In the smelting route, oil contamination will cause localized explosions and flash fires. Oil is not as dangerous a contaminant as lead, and most processes do not use any special treatment to remove it.


Deposits of carbon are not particularly harmful for the
environment, but can significantly alter PGM recoveries during hydrometallurgical treatment. The deposition of carbon or soot in a catalytic converter is a result of engine malfunctioning, such as excessive oil consumption or hard starts in cold weather. The deposits can plug pores and channels in the catalyst structure, making part of the PGM inaccessible to leaching solvents. Some processors suggest calcination of the catalyst at a temperature of 500-600°C before leaching to eliminate the carbonaceous deposits [14]. However, high temperature during the calcination process generates volatile lead compounds, which must be captured, and also converts rhodium to a form which is highly resistant to attack by a chloride leaching solution, risking poor PGM recoveries. Thus, most processors find calcination more trouble than it is worth.

1.13. Other contaminants and factors to be aware of during catalyst processing.

A variety of other contaminants may be present. They include base metals, vanadium, and phosphorus compounds. The processor must be aware of their potential presence both during processing and in the resultant effluent streams.

Another problem to be aware of is that melting of the cordierite into an irregular glassy mass, which is caused by an engine malfunction, is observed quite frequently and perhaps 10-20% of all scrapped catalyst material is partially damaged [7]. This disfiguration can significantly decrease PGM recovery by leaching methods.
CHAPTER 2: PREVIOUS WORK

2.1. Hydrometallurgical methods.

Intensive research studies on PGM recoveries from spent autocatalyst have resulted in development of several methods of PGM extraction. Some of the processes have found industrial applications in plants operating in Japan and North America. Generally, recovery methods employ hydrometallurgical or pyrometallurgical steps.

The hydrometallurgical methods of PGM recovery from spent catalysts can be classified into two different groups:

1. Support dissolution techniques, which involve dissolution of the catalyst support (\(\gamma\)-alumina) in nonoxidizing acidic or basic solutions leaving the PGM undisturbed.

2. Solution extraction methods, which involve dissolution of PGM in an oxidizing acidic medium. These methods aim to minimize dissolution of the catalysts' support.

The support dissolution techniques require dissolution of the entire catalyst support, and so are ineffective for honeycomb-type catalyst, which consists of acid-resistant cordierite. Since honeycombs now completely dominate the catalyst market, further study should focus on PGM dissolution from catalyst support methods rather than the support dissolution techniques. PGM in general are very resistant to acid dissolution, and only a very strong hydrochloric acid solution is able to slowly dissolve them under non-oxidizing conditions. However, the presence of a
suitable oxidant strongly promotes dissolution. Based on this observation, almost all process chemistry of PGM involves the use of chlorides plus oxidant, and chloride leaching is well suited to noble metal recovery from spent autocatalyst [15].

2.2. Oxidants.

Standard reduction potentials of commonly used oxidants are as follows [16]:

\[
\begin{align*}
\text{ClO}_3^- + 6 \text{H}^+ + 6 \text{e}^- & \rightarrow \text{Cl}^- + 3 \text{H}_2\text{O} & E^0 &= 1.45 \text{ V} \\
\text{HOCI} + \text{H}^+ + 2 \text{e}^- & \rightarrow \text{Cl}^- + \text{H}_2\text{O} & E^0 &= 1.49 \text{ V} \\
\text{Cl}_2(\text{gas}) + 2 \text{e}^- & \rightarrow 2 \text{Cl}^- & E^0 &= 1.35 \text{ V} \\
\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- & \rightarrow 2 \text{H}_2\text{O} & E^0 &= 1.77 \text{ V} \\
\text{BrO}_3^- + 6 \text{H}^+ + 6 \text{e}^- & \rightarrow \text{Br}^- + 3 \text{H}_2\text{O} & E^0 &= 1.44 \text{ V} \\
\text{NO}_3^- + 4 \text{H}^+ + 3 \text{e}^- & \rightarrow \text{NO} + 2 \text{H}_2\text{O} & E^0 &= 0.96 \text{ V}
\end{align*}
\]

Aqua regia oxidation of PGM is discussed in a subsequent chapter, the role played by NO$_3^-$ being shown in simplified form by reaction (6). All of the above oxidants are able to oxidize PGM and theoretically can be used for PGM recovery from spent autocatalyst. Previous studies suggested that some of these oxidants provided much better oxidation kinetics than others. Bradford and Baldwin studied catalyst leaching in mixtures of HCl with different oxidants. They investigated HNO$_3$, Cl$_2$(gas), NaOCl, NaClO$_3$, HOCI, NaBrO$_3$, and H$_2$O$_2$, and reported that the rate of PGM dissolution is much faster when HNO$_3$ or Cl$_2$(gas) is used [17]. The results were confirmed by D’Aniello, who found a much faster rate of PGM dissolution in HCl-HNO$_3$ compared to other
oxidizing agents [15]. Bonucci and Parker compared leaches with HNO₃ and Cl₂(g) and found that HNO₃ was a slightly more aggressive oxidant than Cl₂(g) [18]. The effectiveness of HCl-HNO₃ leachant was confirmed in tests done by Bautista [19]. Mishra reported on the use of more than one oxidant at the same time [20].

The above experimental data provide good evidence that HNO₃ and Cl₂(g) are much more efficient oxidants than other oxidizing agents, and use of one of them in catalyst treatment is the most desirable.

2.3. Problems with excessive alumina dissolution.

Many PGM extraction methods aim to minimize dissolution of the alumina catalyst support. The ideal process should be able to extract all PGM from the spent catalyst leaving the alumina support unattacked. Unfortunately, γ-alumina dissolves easily in strong HCl solution under oxidizing conditions, and its presence in the pregnant leaching solution has a negative impact on the economy of the process, where excessive amounts of acids and other reagents are required [21].

To minimize this dissolution, Bonucci and Parker suggested converting γ-alumina to α-alumina [18]. α-alumina is a refractory compound only slightly soluble in both acidic and alkaline aqueous solutions. γ-alumina undergoes a phase transformation to α-alumina at a temperature of approximately 1200°C, and a simple heating of the catalyst can greatly reduce reagent requirements during PGM dissolution. The authors recommended preheating of the catalyst at about 1500°C for 2 hours. However, this heat
treatment affects the reactivity of PGM, and requires a difficult and expensive capture of volatile compounds of lead contained in spent catalyst to prevent their emission to the environment.

Lakshmanan and Ryder suggested a pretreatment reduction of catalyst by sodium borohydride at 95°C for 1 hour [22]. This pretreatment enhances PGM ability to react rapidly with leaching solutions, and allows use of less concentrated leachants, so also permitting reduced alumina dissolution.

Letowski and Distin proposed to suppress alumina dissolution by using leaching mixture containing AlCl₃, in partial replacement of HCl [23]. A mixture composed of 2.46M HCl / 0.96M AlCl₃ / 1.46M HNO₃ reduced alumina dissolution to 12% of the total initial weight of pellets, leaving platinum and palladium recovery unaffected at over 95%.

The above method seems to be the most attractive for further study, because additional pretreatment steps are not required. Fortunately, the problem with alumina dissolution is much less critical in the case of honeycombs, because they are composed of 85% refractory, acid-resistant cordierite. So in the worst case, only 15% of the entire catalyst is dissolved.

2.4. Leaching reactors.

In general, leaching techniques include use of a stirred reactor, a fluidized bed column reactor or a static bed column reactor. The fluidized bed column reactor was studied and recommended by Bautista, who suggested that the residence time could be reduced to 70% of that in a static
bed reactor [19]. However the fluidized bed column required finely grounded material, and so the grinding and solid/liquid separation steps caused the fluidized bed techniques more trouble than it is worth for the autocatalyst processing. For coarse fractions, as applicable to our case where coarse, broken honeycombs or unground pellets are involved, a static bed reactor is suitable. Some proposed industrial applications envisage batch type reactors, stirred by boiling action with additional air sparging, for catalyst leaching [18] [25]. However a great advantage of column leaching is it allows production of pregnant solution more concentrated in PGM than is obtainable by leaching in a stirred reactor and two pilot plants commissioned in Canada in the 1980’s found it more appropriate to use static bed column leaching reactors, which involved upward flow of solution through uncrushed pellets or coarsely crushed honeycombs in a static externally heated column [22] [24].

2.5. Rate of PGM dissolution.

A knowledge of leaching kinetics helps to determine leach retention time. Tyson and Bautista found that the rate of platinum and palladium dissolution into a relatively weak HCl-HNO₃ solution (3.65 M HCl and 0.35 M HNO₃) started at relatively high values and then dropped off very quickly over a period of time [25]. They empirically determined a kinetic expression for the experimental data, and found a logarithmic equation to fit the changes with time of the PGM concentration in the leaching solution.

Extraction data obtained by Letowski and Distin also suggested that, for a highly concentrated solution,
dissolution of most of the PGM took place during the first hour of leaching [23]. The authors reported the extraction of 60% of total PGM during the first 40 minutes of the leaches. To obtain better leaching efficiency, use of a multistage leaching system was suggested.

2.6. Industrial applications.

Several hydrometallurgical flowsheets have been tested and four of them are discussed below. The methods include:
1. Catalyst substrate dissolution by a sulphuric acid digestion [26].
2. PGM extraction from catalyst support by leaching in dilute sulphuric acid first, and then in HCl [26].
3. PGM extraction from catalyst support by chloride leaching: CRO-Redox process [22].
4. PGM extraction from catalyst support by HCl-AlCl₃-HNO₃ leaching [27].
Process 1 is a catalyst substrate dissolution method, while Processes 2, 3, 4 are PGM dissolution-from-catalyst-support methods.

2.7. Process 1: Catalyst substrate dissolution by a sulphuric acid digestion.

The support dissolution techniques were widely used for treatment of spent catalyst from the petrochemical industry and an equivalent method was developed for autocatalyst treatment. In this method, catalyst support (γ-alumina) dissolution in sulphuric acid was followed by dissolution of remaining solids, which contain platinum and palladium, in HCl. This process was based on solubility of γ-alumina in
sulphuric acid, and was designed to treat pellet type catalyst. Its suitability for cordierite substrate catalyst (honeycombs) is questionable. The process is shown in Figure 4, and its steps are discussed below.

Pellets are removed from their steel canisters and ground (step 1) in a rod or ball mill to <200 mesh. To prevent lead dust emissions, wet grinding is performed. Next the pellets are dissolved in sulphuric acid (step 2). To keep pH between 5 and 7, an excess of catalyst is added. After filtration (step 3), the filtrate, which contains small amounts of PGM, is sent to PGM recovery (steps 11 and 12), while the residue is fumed (step 4) with concentrated sulphuric acid. Next the solution is cooled, diluted with H₂O and filtered (step 5). After filtration, the filtrate (sulphuric acid) is recycled to the catalyst dissolution (step 2), while remaining solids (small amounts) are combined with residues from cementation (step 11), and leached with HCl/Cl₂ (step 6). After leaching, the solution is filtered (step 7), and residue (very small amounts) is sent either to calcination or pyrosulphate fusion for recovery of any traces of remaining PGM. The filtrate is treated with sulphur dioxide and tellurium, which is used as a collector, to precipitate (step 8) PGM and other base metal contaminants. The reduced solution is filtered hot (step 9) to keep lead chloride in solution. Next, the solution is cooled, which allows lead chloride to crystallize, and after decantation and PbCl₂ removal HCl is recycled to PGM dissolution (step 6). Small amounts of PGM dissolved in sulphuric acid during catalyst dissolution (step 2) are precipitated from the leaching solution (together with lead and other contaminants) by cementation (step 11) with aluminum in the presence of tellurium as a collector. Again, the solution is filtered (step 12). The
Figure 4: Flowsheet of Process 1 - Catalyst substrate dissolution by a sulphuric acid digestion.
filtrate (aluminum sulphate) is evaporated to produce alum for use in water treatment plants, while the solids are combined with those from fuming digestion (step 4) and sent to HCl/Cl₂(gas) leaching (step 6).

D'Aniello evaluated this method and concluded that amounts of reagents required were too large to be economically feasible for the sparsely loaded automotive catalysts [15]. Additionally, this method can be used only for pellet type catalysts, consisting of γ-alumina, which are becoming obsolete.

2.8. Process 2: PGM extraction from honeycombs by sulphuric acid, and subsequent HCl leaches.

This process is used for treatment of honeycombs. The chemical concept of this method is almost the same as is used in the previously described method for pellets treatment (Process 1) and includes a sulphuric acid leach to remove γ-alumina washcoat, followed by an HCl leach to dissolve PGM remaining on cordierite substrate. The leaches leave cordierite unattacked. The process is shown in Figure 5, and its’ steps are discussed below.

Honeycombs are decanned and crushed (step 1) to approximately 4×2×2cm pieces to ensure complete penetration of the catalyst by leaching solutions. Next, dilute sulphuric acid leaching (step 2) is performed to dissolve γ-alumina washcoat. This step is performed in a batch type vessel, at boiling temperature, where agitation is provided by the boiling action, and air sparging. Some PGM are dissolved by sulphuric leaching, which is followed by decantation and washing (step 3) steps. The remaining PGM is
Figure 5: Flowsheet of Process 2 - PGM extraction from honeycombs by sulphuric acid, and subsequent HCl leaches.
dissolved during hydrochloric acid leaching (step 4) in HCl/Cl₂ or HCl/HNO₃ solution. Following decantation, the washes of step 5 provide nearly quantitative recovery of the solubilized PGM. Filtrate from step 3 is transferred to cementation, where PGM precipitate by cementation with aluminum in the presence of tellurium (step 11). Optionally, hydrogen sulphide is used for the precipitation. The slurry is filtered, step 12, the filtrate, aluminum sulphate, being transferred to alum production, while the residue is co-mixed with PGM from step 7. Catalyst residue from step 5 is discharged to waste disposal, while the filtrate is treated with sulphur dioxide, using tellurium as a collector to precipitate PGM, step 6. The slurry is filtered hot, step 7, to prevent crystallization of lead chloride, then the filtrate is cooled, the lead chloride allowed to crystallize, step 13, and, after decantation, the HCl is recycled to the PGM dissolution, step 4. This recycle eliminates a potential source of PGM losses. Freshly precipitated PGM from step 7 co-mixed with solids from aluminum cementation, step 12, readily redissolve in chlorinated HCl, step 8. The volume of the solution is kept as small as possible, because a high concentration of PGM in solution is beneficial. The last steps include tellurium solvent extraction, step 9, and stripping step 10. Tellurium is recovered from PGM solution by solvent extraction with tri-n butyl phosphate (TBP), step 9. Some coextraction of the PGM may occur, depending on the strength of the HCl, but none are lost, since the tellurium is recycled to the PGM precipitation, step 6. The raffinate from step 9 contains the PGM at high concentration in a hydrochloric acid solution, ideal for purification and recovery. Finally, the TBP is stripped of tellurium, step 10, with concentrated HCl.
This method requires much less reagents than the previously described Process 1, but disadvantages include poor rhodium recovery and water balance problems.

2.9. Process 3: PGM extraction from catalyst support by chloride leaching: CRO-Redox process.

This process includes extensive pre-treatment steps, followed by chloride leaching and PGM solvent extraction. The process was first designed to treat pellets, but later its usability was expanded for honeycombs. The method is shown in Figure 6, and its steps are discussed below.

Catalyst is removed from the steel canisters. Honeycombs are crushed to approximately 4×2×2cm pieces, while pellets are treated unground. The catalyst is washed with detergent, rinsed, step 1, and calcined for 1 hour at 600°C, step 2. Next, catalyst is treated with sodium borohydride, step 3, to reduce PGM oxides. The reduction is carried out in a column reactor at 95°C and for 1 hour. Subsequent chloride leaching, step 4, employs a hydrochloric acid - chloride salts mixture. The leach is performed at 85°C for 6 hours in a column reactor under upflow conditions. After decantation, step 5, solids are rejected, while the filtrate is cooled. The cooling allows crystallization of lead chloride (step 6), and its later separation by decantation, step 7. To separate PGM from leach liquor, solvent extraction with Kelex 100 is performed, step 8. The aqueous phase is recycled to chloride leaching, step 4. This recycling prevents potential PGM losses. Next, a selective stripping, step 9, and precipitation, step 10, is used to separate PGM. The method includes 4 extraction stages, 3 stripping stages for palladium, and 4 extraction stages, 6 stripping stages for
**Figure 6:** Flowsheet of Process 3 - PGM extraction from catalyst support by chloride leaching: CRO-Redox process.
platinum. Extractant, Kelex 100, and stripping agent are regenerated and recycled.

This method allows good PGM recovery, but the excessive pretreatment is a disadvantage. A pilot plant using this process to treat 5 tonnes/day of catalyst has been commissioned by Platinum Lake Technology in Rexdale, Ontario.

2.10. Process 4: PGM extraction from catalyst support by HCl-AlCl₃-HNO₃ leaching.

This process is applicable to PGM recovery from pellets as well as honeycombs. The treatment is based on a selective extraction of PGM, leaving the γ-alumina washcoat as much unattacked as possible. The method employs a HCl-AlCl₃-HNO₃ leach, which extracts PGM with good efficiency, and does not dissolve the entire alumina washcoat. The process is shown in Figure 7, and its' steps are discussed below.

The charge of unground pellets or crushed honeycombs (to approximately 4×2×2 cm pieces) is leached in a teflon-lined, steel tubular reactor, step 1. The leach is performed at 85-95°C for 1 hour in HCl-AlCl₃-HNO₃ solution. Gases emerging during the leach are absorbed, step 11, and HCl/HNO₃ solution formed during this absorption is recycled to the leaching step 1. Leach (step 1) is followed by two washing steps, first in AlCl₃ solution, step 12, and then in water, step 13. During the washes, an additional amount of PGM is recovered. The washes and leaches are performed in the same column. After final decantation, step 13, pellet residue is dissolved in sulphuric acid, step 14 and transferred to alum production, while honeycombs residue is
**Figure 7:** Flowsheet of Process 4 - PGM extraction from catalyst support by HCl-AlCl₃-HNO₃ leaching.
rejected. Essentially, during leaching step 1, complete removal of impurities is achievable, leaving a purified residue that is suitable for conversion to alum. Pregnant solution from step 2 is allowed to cool, and PbCl₂ is crystallized. Next, the solution is filtered and PbCl₂ is removed, step 3. A system of PGM recovery from the leaching solution consists of neutralization, by NaOH, step 4, so removing impurity metal hydroxides, step 5, sorption and reduction-to-metal on an anion exchange resin, Amborane 345 (step 6), and then cementation with aluminum, step 7. Excessively high resin consumption was experienced and the step was replaced by PGM precipitation directly from non-neutralized leach solution by hydrogen reduction. PGM concentrates from filtration steps 6 and 7 are sent to further refining, while the filtrate is treated to allow AlCl₃ crystallization, step 8, and filtration, step 9. The filtrate is recycled to leaching step 1, while residue (AlCl₃·6H₂O) is readily decomposed to HCl and alumina at over 200°C, step 10. The HCl(\textsubscript{g}) generated during the decomposition is absorbed in the spent leach solution, step 11, and recycled to the leaching stage.

This method can be used for both types of catalyst, pellets and honeycombs. The process requires much less reagents than the previously described methods, and although rhodium recoveries were never studied, the method seems to be very efficient. A pilot plant was built and operated in Boucherville, Quebec in the mid 1980's. In the future, the process will require a more economically feasible system of PGM recovery from pregnant solution, most likely a solvent extraction method.

2.11. Pyrometallurgical processes.
In general, pyrometallurgical practice to recover PGM from a solid source, where the PGM are in a highly dispersed form, is to melt the solid material with flux components and then contact the molten slug containing PGM with a molten metal pool, commonly referred to as a collector metal, into which the PGM dissolve and accumulate. Iron, copper, nickel, lead-copper, and nickel mattes are used as collector media [28]. Subsequently, the PGM containing collector metal is treated to extract the PGM. Almost 60% of collected scrapped autocatalyst is treated in copper or nickel primary smelters, and an additional 10% is processed by another pyrometallurgical process, plasma arc smelting.

2.12. Process 5: Primary Copper or Nickel Smelters.

Primary copper or nickel smelters process the bulk of spent autocatalyst. A major advantage of the method is the absence of capital costs and minimal operating costs.

Smelter treatment includes crushing, grinding and mixing of autocatalyst with the required fluxes prior to being combined with copper or nickel concentrates [25]. Depending on the type of smelting process employed, and the concentrate composition, additional silica or lime may be required. Copper or nickel matte is a very good collector of PGM and during smelting, the PGM report, virtually completely, in the copper or nickel matte. Only very small changes in flux additions are required by this process, incremental energy requirements are insignificant, and there is almost no additional labour costs in either smelting or refining. Additionally, lead emissions are not a problem since all smelters are already equipped to deal with it. A major disadvantage is that a considerably longer processing time than for other methods is required. Also some large
primary smelters may find processing of autocatalyst more trouble than is worthwhile, because collecting, sampling and settlement assays associated with purchasing catalyst cause a lot of problems.


Plasma fusion relies on extremely high temperatures to melt alumina and cordierite. These high temperatures are generated by a very intensive heat flux produced by DC transferred plasma arc, and may exceed 2000°C. The process is shown in Figure 8, and its' steps are discussed below [29].

Catalyst is decanned, charged to a plasma reactor, step 1, and fused with iron or iron oxide. To reduce the melting point of the feed, especially when cordierite is present, lime is added to the charge. The reactor requires a highly effective gas collection system, step 7, for control of lead fume emission. The fused charge is transferred to a settler where slag and metal phases are allowed to separate, step 2. Because of the low PGM content of the catalyst, an excellent separation is required to ensure good metal recovery. Fortunately, the large density difference between the slag and metal phases gives a good separation. Next, the slag is discarded, while the metal phase, composed of an iron alloy, is atomized, step 3, to provide an extended surface for rapid leaching. To dissolve the iron alloy and leave behind a PGM residue, sulphuric acid leaching is used, step 4. The leach slurry is filtered, step 5, leaving behind a PGM concentrate. The filtrate must be neutralized, step 6 prior to discharge. This neutralization is both costly and difficult.
Figure 8: Flowsheet of Process 6 - PGM recovery by plasma fusion technique.
A great advantage of the method is rapid throughput and easily disposable slag. Disadvantages of the process are costly lead collection systems for the plasma reactor, difficult neutralization, step 6, of discharged solution, difficult fusion and separation, step 2, when cordierite from honeycombs is processed, and high energy cost. Also low (65-75%) rhodium recovery is frequently reported. Despite many disadvantages, the plasma fusion process is operated by Multi-Metco, the successor of Texas Gulf Corp. in Anniston, Alabama as a full scale industrial installation.


Several other routes for PGM recovery have been developed, but none of them have been tested, even on a pilot plant scale. The most important two methods include:

1. Copper collection process [20], where ground catalyst is fused with copper carbonate or copper oxide.

2. Dry chlorination process [20], where crushed honeycombs or uncrushed pellets are treated by chlorine gas at 600-700°C. PGM are converted into chlorocomplexes, which are separated and later reduced by carbon monoxide to the elemental form.

2.15. Chemistry of aqua regia.

Results of previous research show that HCl-HNO₃ mixture, commonly known as aqua regia is a much more efficient leachant of PGM from scrap autocatalyst than other
examined agents. In the next sections, results of previous work with aqua regia are discussed in more detail.

Despite the fact that aqua regia has been known and used for centuries, a composition of the mixture was never defined. In 1916, Hoke and Moore reported that chemists and chemical textbooks described aqua regia as a mixture of HCl and HNO₃ but did not specify the acids ratio [30]. Some other sources defined aqua regia as three parts of HCl and one part of HNO₃ taken as ordinary concentrated commercial acids [31] [32] [33]. In those days, the molality of concentrated HCl was the same as now, equal to 10.1 M, but HNO₃ was only 11.1 M (~16 M today). The acid ratio and molalities roughly corresponded to a widely accepted assumption that HCl and HNO₃ reacted in the ratio 3HCl/1HNO₃.

Nowadays handbooks define aqua regia as a mixture of 1 part of concentrated HCl and 3 parts of concentrated HNO₃, or 1 part of concentrated HCl, 3 parts of concentrated HNO₃, and 1 part of water [16]. The above definition is imprecise, and also does not mean the same as in 1916, because while molality of concentrated HCl has remained unchanged since 1916, the term "concentrated HNO₃," now means ~16 M acid.

2.16. Spontaneous decomposition of aqua regia.

When concentrated HCl and HNO₃ are mixed together and heated slightly, an instantaneous and very energetic reaction takes place associated with a formation of brown-red fumes. In 1916, Briner showed that the brown-red colour medium, which emerged at a boundary between HCl and HNO₃ was nitrosyl chloride (NOCl) [33]. Based on this observation, he
proposed a reaction for spontaneous decomposition of aqua regia, as follow [34]:

\[ 3 \text{HCl} + \text{HNO}_3 \rightleftharpoons \text{NOCl} + \text{Cl}_2 + 2 \text{H}_2\text{O} \]  \hspace{1cm} (7)

Later, Oishi measured the specific conductivity of diluted HCl-HNO\textsubscript{3} mixtures and found, at least for diluted acids ranging from 0.1 to 0.9 M, that the equilibrium of the HCl-HNO\textsubscript{3}-H\textsubscript{2}O system could not be expressed by reaction (7), because the equilibrium constant (K) of this reaction changes dramatically with acid concentrations [35]. He suggested the following reaction as more representative of the decomposition of aqua regia:

\[ 2 \text{HCl} + \text{HNO}_3 \rightleftharpoons \text{HNO}_2 + \text{Cl}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (8)

Additionally, the following side reaction was assumed:

\[ \text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCl} + \text{HClO} \]  \hspace{1cm} (9)

For reaction (8), an estimate of \( K = 90 \) at 30°C and for diluted aqua-regia was made.

Reaction (7) is widely accepted for concentrated aqua regia. However, laboratory measurements were never done, and the reaction was questioned by Fleury's theoretical assumption, which postulated that nitroxy1 chloride produced in reaction (7) immediately reacts with water [36]:

\[ \text{NOCl} + 2 \text{H}_2\text{O} \rightleftharpoons \text{HNO}_3 + 3\text{HCl} \]  \hspace{1cm} (10)

Thus, similarly to diluted aqua regia, the total reaction for concentrated aqua regia would then be better described by reaction (8) instead of (7).

A different mechanism of the decomposition reaction was proposed by Walcott, who studied the oxidation potential of aqua-regia [37]. He suggested that NOCl was produced first, but it immediately decomposed in aqueous solutions creating nascent chlorine:
\[
\text{NOCl} \rightleftharpoons \text{NO} + \text{Cl}^-
\] (11)

Because very few specific data about aqua regia are available, the reaction of decomposition requires further study. It seems possible that all of reactions (7), (8) and (11) take place simultaneously in the mixture.

2.17. Basic chemistry of platinum and rhodium.

Platinum and rhodium are two of six closely related Platinum Group Metals - elements of Group VIIIb. They are frequently referred to as noble metals, which generally means that they are unattacked by corrosive environments under all but the harshest conditions. Nobility can be divided into its theoretical and practical aspects [38]. The theoretical nobility depends on thermodynamic stability of an element in the presence of water and is graphically described by Eh-pH diagrams. The practical nobility considers additional areas of resistance to oxidation in which the metal is thermodynamically unstable and forms insoluble oxidation products. These products form a passivating film preventing or drastically slowing further reaction. Both platinum and rhodium are on the top of the list of thermodynamically noble metals. In the case of rhodium, any species formed are completely passivating and in practical terms, rhodium is the most noble metal.

The extremely high nobility of platinum and rhodium necessarily requires a high temperature and a very fine grinding to increase the rate at which the metals are dissolved in aqueous media. Elevated temperatures also improve the solubilities of potentially passivating species and for example, at room temperature rhodium dissolves very
slowly in concentrated sulphuric acid, while at 300°C the metal is attacked quickly [39].

Grinding of metals is even more important than high temperatures. Rhodium sheets or ingots do not dissolve in aqua regia at all. However, rhodium will dissolve surprisingly quickly in aqua regia if present at low levels in a platinum–rhodium alloy [38]. A likely explanation for this phenomenon is that solution of the platinum leaves rhodium in a finely divided state, which increases the surface area of the metal available for attack. In our case of autocatalyst, rhodium is present as very fine particles, which can dissolve quite rapidly.

2.18. Redox reactions in aqua regia.

Common oxidation states for platinum are II and IV and for rhodium are I and III. For dissolution of platinum and rhodium, the standard potentials in aqueous chloride solutions are as follows [16]:

\[
\begin{align*}
\text{Pt} + 4 \text{Cl}^- & \rightarrow \text{PtCl}_4^{2-} + 2 \text{e}^- & E^0 &= -0.73 \text{ V} & (12) \\
\text{PtCl}_4^{2-} + 2 \text{Cl}^- & \rightarrow \text{PtCl}_6^{2-} + 2 \text{e}^- & E^0 &= -0.74 \text{ V} & (13) \\
\text{Rh} + 6 \text{Cl}^- & \rightarrow \text{RhCl}_6^{3-} + 3 \text{e}^- & E^0 &= -0.44 \text{ V} & (14)
\end{align*}
\]

The oxidation reactions (12) and (14) are also dissolution reactions, while reaction (13) is a redox reaction in solution.

Since, as was discussed in a previous section, the chemistry of aqua regia is not fully understood, it is difficult to determine redox reactions which take place in the solution and their standard potentials. Reduction reactions of nitric acid are as follow [16]:
It has also been suggested that the oxidation potential of aqua regia is determined by nascent chlorine formation described by reaction (11) [37], and also, some authors proposed an occurrence of Cl₂ reduction in the solution [21]:

$$\text{Cl}_2(g) + 2e^- \rightarrow \text{Cl}^- \quad E^0 = 1.358 \text{V.} \quad (18)$$

### 2.19. PGM oxidation in aqua regia.

Two different types of reaction representing the dissolution of PGM from automotive catalysts into aqua regia have been used. Hoffman proposed that chlorine generated by aqua regia reacted with platinum and rhodium as follows [21]:

$$\text{Pt} + 2 \text{HCl} + 2 \text{Cl}_2 \rightarrow \text{H}_2\text{PtCl}_6 \quad (19)$$

$$2 \text{Rh} + 6 \text{HCl} + 3 \text{Cl}_2 \rightarrow 2 \text{H}_3\text{RhCl}_6 \quad (20)$$

Letowski and Distin represented the platinum reaction by [23]:

$$3 \text{Pt} + 4 \text{HNO}_3 + 18 \text{HCl} \rightarrow 3 \text{H}_2\text{PtCl}_6 + 4 \text{NO} + 8 \text{H}_2\text{O} \quad (21)$$

By analogy, the equivalent reaction for rhodium would be:

$$\text{Rh} + 6 \text{HCl} + \text{HNO}_3 \rightarrow \text{H}_3\text{RhCl}_6 + \text{NO} + 2 \text{H}_2\text{O} \quad (22)$$

Depending on which decomposition reaction of aqua regia is assumed, the PGM dissolution reactions can be represented in different ways.
2.20. PGM extraction from pregnant solution by Solvent Extraction methods.

In chloride solutions, platinum and rhodium form complexes, for which thermodynamic and kinetic properties are shown in Table 4. The rhodium chlorocomplex, RhCl₆⁻³, is thermodynamically and kinetically unstable, and can easily be hydrolized. In aqueous solution, platinum forms a very stable PtCl₆⁻² ion, which however, can also be relatively easily hydrolized in the presence of Pt⁺² [38]. Nevertheless, for high chloride concentration, the degree of hydrolysis is low and platinum and rhodium occur as PtCl₆⁻² and RhCl₆⁻³.

Some previous works suggested PGM reduction in the pregnant solution by a reduction-to-metal on an anion exchange resin and then cementation with aluminum [23], hydrogen reduction [27] or PGM cementation on a mixture of aluminum and tellurium dioxide [21]. Recent developments in solvent extraction proved that the method is presently considered the most suitable and powerful separation technique for PGM. Commercially available alkylated 8-hydroxyquinoline derivatives Kelex 100 and Lix 26 are used by PGM refineries to extract PGM from chloride acidic solutions [54] [55]. The processes involve the coextraction of PGM from a feed liquor, followed by differential stripping and may be adopted for use in spent autocatalyst treatment [22].
Complex stability in aqueous solution:

\[ \text{MCl}_x + \text{H}_2\text{O} \rightleftharpoons \text{MCl}_{x-1}\text{H}_2\text{O}^{+1} \]

<table>
<thead>
<tr>
<th></th>
<th>$K$ [m$^{-1}$]</th>
<th>$k$ [sec$^{-1}$]</th>
<th>$t_{\mu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{PtCl}_4^{-2}$</td>
<td>$1.3 \times 10^2$</td>
<td>$3.9 \times 10^{-5}$</td>
<td>4.9 hrs</td>
</tr>
<tr>
<td>$\text{PtCl}_6^{-2}$</td>
<td>$5.6 \times 10^3$</td>
<td>Inert</td>
<td>Inert</td>
</tr>
<tr>
<td>$\text{RhCl}_6^{-3}$</td>
<td>1.7</td>
<td>$1.8 \times 10^{-3}$</td>
<td>6.4 min</td>
</tr>
</tbody>
</table>

Table 4: Aquation of platinum and rhodium chlorocomplexes.
CHAPTER 3  EXPERIMENTAL AND ANALYSIS.

3.1. Preparation of catalyst for leaching.

Catalyst used in the experiments were removed from several 1986-1988 Ford Tempo converters. Each converter had two honeycomb units, which had different ratios of PGM. Only the honeycombs from the front parts of the converters were used for experimentation. Detailed PGM contents of catalyst are shown in Table 5.

The monoliths were 15 cm in length and had elliptical cross-sections 12 cm in diameter. After removal from steel cans, they were manually chopped to obtain 4×2×2cm pieces. Some catalyst was further ground by a laboratory ball mill to the size range of 60 to 120 mesh. The ground portion was used for performing tests of the effect of grinding on PGM recoveries and for analysis of the raw catalyst.

3.2. Leaching experiments.

Leaching tests were performed in a 1000 cc kettle and in a tubular, 65 cm high glass reactor. The kettle was used for most of the tests, because it was much easier to operate than the column. Column tests were performed to study usability of a column type reactor in a large scale installation.

3.3. Leaching Setup 1.

The setup is showed in Figure 9. It consisted of a 1000 cc PYREX leaching kettle, which was placed in a water bath.
<table>
<thead>
<tr>
<th>Metal</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum</td>
<td>800 - 1050 [ppm]</td>
</tr>
<tr>
<td>Palladium</td>
<td>0</td>
</tr>
<tr>
<td>Rhodium</td>
<td>50 - 60 [ppm]</td>
</tr>
<tr>
<td>Aluminum</td>
<td>6.5 - 9 [%]</td>
</tr>
<tr>
<td>Lead</td>
<td>1.2 - 2.0 [%]</td>
</tr>
<tr>
<td>Iron</td>
<td>0.7 - 0.9 [%]</td>
</tr>
</tbody>
</table>

*Table 5: PGM and other metals contents of autocatalyst used in the experiments.*
The bath was equipped with a Haake E-52 water heater and circulator to keep the leaching system at constant temperature (±0.5°C). The leaching kettle was fitted with a PYREX glass top with one centrally-located and three circumferentially-located ports. The cap was held in place by a peripheral clamp. Solids in solution within the kettle were kept mixed by the use of a variable speed electric stirrer. The glass impeller was driven through the centrally-located outlet. A 400 mm high PYREX glass reflux condenser cooled by circulating water was held in one of the outlets to minimize evaporation losses from the leach solution. Other ports were used to accommodate an electrode and a 0-110°C thermometer. The combination pH Fisher electrode type 13-620-272 was connected to a Fisher Scientific Accumet pH-meter type 910 and was used to monitor the pH of the solution. The port which accommodated the thermometer was also used as the charging point.

This setup was used to conduct tests at up to 85°C. Aqueous solutions used for the tests were prepared from concentrated hydrochloric and nitric acids and AlCl₃·6H₂O. Fresh solutions were prepared shortly before experiments. In some cases, recycled mixtures were employed. The water bath was heated up to the required temperature by the thermostat, the kettle was filled with 235 ml of HCl-H₂O or HCl-AlCl₃-H₂O mixture and left for 15-20 minutes to allow the solution to warm up. Then, 65 ml of HNO₃ and 35g of fragmented catalyst were added, and the first sample of solution (10 ml) was immediately taken. Slurry stirring was kept at a constant rate of 120 rpm for all experiments. During the test, samples of 10 ml of leachant were taken every hour, using a 5 ml pipette. In addition to solution analysis, solid analyses, which are much more accurate, were done. In this case, 2 pieces of catalyst were removed every hour and
Figure 9: Schematic diagram of the equipment used for the stirred reactor leaching of spent catalyst at 60-85°C (Setup 1).
analyzed. Also every hour, a small portion of HNO	extsubscript{3} (10-15 ml) was added to compensate for the loss of oxidant during the leach. After 3 or 4 hours, pieces of catalyst were removed from the solution, final samples were taken, and the catalyst pieces were subjected to further treatment. Some tests were done with a finely ground catalyst. In these cases, filtration was performed to obtain solid-liquid separation. At the end of a test, the pieces of catalyst were removed from the liquid and a sample of the final leach solution was taken. All samples were then retained for subsequent analysis.

3.4. Leaching Setup 2.

Setup 2 was essentially the system described above, modified to carry tests over 90°C. The system is shown in Figure 10. It consisted of the same 1000 cc PYREX reactor with the four-ports top, used in Setup 1. The same variable speed electric stirrer, the condenser, the electrode and 0-150°C thermometer were also used. The kettle was placed inside a heating jacket. The temperature was regulated by a variable transformer, which controlled current delivered to the heating jacket. The jacket allowed tests to be run at up to 110°C with ±2°C accuracy. In some of the tests performed at the boiling points, the stirrer was removed, because the slurries were agitated by the boiling action. The leaching procedure was exactly the same as described above.

3.5. Leaching Setup 3.

Setup 3 was used to examine leaching in a column type reactor. The system consisted essentially of a glass column
Figure 10: Schematic diagram of the equipment used for the stirred reactor leaching of spent catalyst at 90-108°C (Setup 2).
shown in Figures 11 and 12. The column comprised two sections: a leaching section and a preheating section. The leaching section was 65 cm high and 5.1 cm in diameter and the preheating section was 70 cm high and 5.1 cm in diameter. Both sections were constructed with Corning glass elements and connected through their bottoms by a teflon tube, which had 1.5 mm inside diameter. Both sections were heated by electric heating tapes and insulated with fibreglass. The temperature was controlled by variable voltage transformers, which allowed leaching tests up to 97°C with ±2°C accuracy. The complete installation was 160 cm high, and did not fit into a standard laboratory fume hood. To prevent the escape of fumes to the environment, the system was sealed and all fume outlets from the column were directed into the fume hood by plastic tubes. The installation had 3 ports for thermometers, located at various positions, as shown in Figure 11. The total volume of the column was 2600 cc. To maintain constant flow of solution, 3800 cc of a leachant was used during each experiment.

Before the leaching, catalysts were manually crushed to obtain -4×2×2 cm pieces and placed inside the leaching section of the column. Column tests required 380 to 420 g of crushed honeycombs. A freshly prepared mixture of HCl-H₂O or HCl-AlCl₃-H₂O was warmed up to the required temperature and HNO₃ was added. Next, thus 4500 cc of hot leaching solution was passed through a 3000 cc storage tank 50 cm above the column and slowly poured into the column. The feed was leached by a continuous flow of leaching solution passed upwards through the static bed of catalyst. The leaching solution, which left the storage tank above the column, flowed by gravity through the heating section of the column, where the liquid warmed up, and then upwards through the
Figure 11: Schematic diagram of the equipment used for the column leaching of spent catalyst (Setup 3).
Figure 12: General view of the column used for leaching of spent catalyst (Setup 3).
leaching section. A teflon tube, 1.5 mm in inside diameter, connected the warming and leaching sections of the column, and helped to maintain a slow, 3 l/hour, flow of leaching solution. The pregnant solution, which passed the catalyst bed was collected into a 2000 cc conical flask and manually transferred to the storage tank above the column for recirculation. The leaching tests were 4 hours long and, if the solution flow rate was kept at 3 l/h, the leachant recirculated 3 times during each experiment. Every hour, a 10 ml sample of the leaching solution was taken and later analyzed. Every 0.5 hour, a 35 ml portion of HNO₃ was added to compensate for loss of oxidant during the leach. After 4 hours of leaching by HCl-HNO₃ or HCl-AlCl₃-HNO₃ mixture, a 1 h washing by AlCl₃ solution followed by water was carried out in the column. The washing periods coincided with cooling of the catalyst bed. After the wash, the column was drained, the catalyst removed and analyzed.

3.6. Analysis of PGM.

Quantitative analysis of PGM on the ceramic substrate can be done in several ways, including chemical or instrumental techniques. To control production of autocatalyst several new chemical methods, aimed particularly to analyze honeycombs, were developed. The chemical methods give highly accurate and precise results but are tedious, and, what is more important, require a highly skilled operator [13] [41].

More rapid instrumental methods of PGM analysis include Atomic Absorption [41] [11], Neutron Activation [12], and X-ray Fluorescence [13], as well as recently developed-for-honeycombs Analytical Electron Microscopy [42] and Electron
Probe Microanalysis [43]. Atomic Absorption Spectrometry coupled with the heated graphite furnace and Neutron Activation techniques were used to determinate PGM in our samples. All liquid samples were analyzed by Atomic Absorption Spectrometry at McGill University, while all solid samples were sent to Becquerel Laboratories Inc., Mississauga, Ontario and analyzed by the Neutron Activation technique.

The instrumentation for Atomic Absorption analysis involved a Perkin-Elmer Model 403 spectrometer with deuterium background correction, an HGA-2100 and a temperature ramp programmer. Light sources were a platinum hollow cathode lamp operated at 12 mA and a rhodium hollow cathode lamp operated at 14 mA. Palladium was not detected in the catalyst in the initial analyses, and was not monitored. The platinum resonance line at 265.9 nm and rhodium resonance line at 343.5 nm were used. Injected samples were brought from room temperature to 240°C in 21 sec., maintained at 240°C for 2 sec., then heated to 1850°C over 25 sec., and held at 1850°C for another 20 sec., prior to atomization at 2700°C for 10 sec. A continuous flow of argon was maintained in the furnace at all times. Samples were analyzed as they were taken, without any conditioning. The extremely complex matrix of leaching solution was very difficult to calibrate and finally analysis from Becquerel Lab. helped to determine standards. Simultaneous presence of platinum and rhodium in the solution significantly increased the platinum absorbtion signal and decreased the rhodium absorbtion signal. These interferences between platinum and rhodium caused at least 10% error in analysis. To obtain more accurate results, all important samples were analyzed by the Neutron Activation technique at Becquerel Lab. Additionally, aluminum was monitored by Atomic Absorption with an acceptable accuracy ±3%.
CHAPTER 4: RESULTS AND DISCUSSION

4.1. Preliminary tests.

The experimental part of the study was designed to examine PGM recoveries, especially rhodium, under different leaching conditions. The results of previous work show several variables to be very important in getting high PGM extractions. Temperature, length of leaching, Cl⁻ and AlCl₃ concentration in a leaching solution were found to be the critical variables.

Before systematic tests began, preliminary work was carried out to answer the following questions:
- effect of grinding the catalyst
- effect of HNO₃ concentration.

As shown in one of the following sections, catalyst grinding does not increase PGM recoveries from honeycombs. Breakage of honeycomb catalyst into ~4×2×2cm pieces gave a suitable leach feed. These fragments are easier to handle in both laboratory tests and industrial operation than finely ground material.

In most cases, an HNO₃ concentration of 3.5 M was chosen, this choice being based on tests described in a subsequent section. An initial addition of 3.5 M HNO₃ was sufficient to prevent a shortage of oxidant being a limitation on PGM extraction into solutions containing up to 8 M HCl.

Most tests were done in a 1000 cc reactor, but some were later repeated using a bench scale column. Reactor tests were done over a full range of different leaching
conditions, while a small number of column tests were carried out to compare the performance of stirred reactor and static bed systems.

For tests which were carried out in a 1000 cc kettle, described in Setup 1 and Setup 2 in Chapter 3, feeds were made up of 35 g of honeycomb catalyst crushed to ~4×2×2 cm pieces and leached in 300 ml of acidic solutions. Column tests required 380 to 420 g of crushed honeycombs leached in 3800 cc of circulating solutions.

4.2. Effect of temperature.

Previous work with pellet catalyst shows temperature to be the most important variable [23]. It is desirable to leach at as low a temperature as possible, however according to this earlier publication, chloride leaching at low temperature did not result in good PGM recovery, and the process should be carried out at a minimum temperature between 80-100°C. In initial tests, using solutions of compositions typical of those found suitable for pellets, a feeling for the general leachability of honeycomb was obtained by leaching at various temperatures for a nominal time of 3 hours. Here detailed kinetics are not followed and final extractions, based on residue analyses, were obtained. The tests were performed in the range 30°C to 106-108°C, giving results presented in Figures 13 to 16. Figures 13 and 14 refer to tests carried in HCl-HNO₃, while Figures 15 and 16 refer to those with HCl-AlCl₃-HNO₃ solutions.

Figure 13 shows the effect of temperature on 3 hour extractions with 4.1M HCl and 3.5M HNO₃. At 30°C, only 27% of platinum and 17% of rhodium were extracted, but the
Figure 13: Catalyst leaching in stirred reactor using 4.1M HCl / 3.5M HNO₃ for 3 hours.
recoveries rapidly increased with a rise in temperature. A significant increase can be observed up to 95°C. The results suggest that a minimum of 80°C would be required for relatively high extraction within a reasonable leach time. It can be observed that rhodium extraction is less than that of platinum, a pattern followed in all further tests.

Results of HCl-HNO₃ leaching into a higher initial acid concentration are presented in Figure 14. Comparison of Figures 13 and 14 shows the effect of increasing HCl to 8 M. This approaches maximum practicable level above which corrosion problems and HCl vapour losses become unacceptable in strongly heated solutions. PGM recoveries were from 8% to 15% higher than in 4.1M HCl (Figure 13) at all corresponding temperatures. Although some improvement is obtained at the low temperature end of the range studied, again 80°C is a minimum temperature below which detailed study is not justified. The recoveries quickly increased between 30°C and 85°C and remained almost unchanged at higher temperatures, approaching commercially acceptable levels of 93% of platinum and 83% of rhodium at 95°C. HCl-HNO₃ leaching, though effective has a few disadvantages: the conditions are severely corrosive, while large HCl vapour losses are generated, the capture of which would require efficient gas absorption equipment.

One way to lower Cl⁻ losses, as vapour, and improve leaching selectivity, at least with pellets, is to replace part of HCl with AlCl₃. In Figure 15, total molality of Cl⁻ (3.84M) has been reduced below levels of Figures 13 and 14, and part of Cl⁻ is in the form of AlCl₃ (0.54M Cl⁻ present as 0.18M AlCl₃). Despite relatively low total Cl⁻, significant improvement in extractions is observed, especially at 30°C where recoveries are over 10% better than for HCl-HNO₃.
Figure 14: Catalyst leaching in stirred reactor using 8.0M HCl / 3.5M HNO₃ for 3 hours.
Figure 15: Catalyst leaching in stirred reactor using 3.3M HCl / 0.18M AlCl₃ / 3.5M HNO₃ for 3 hours.
solution. PGM extractions very quickly increase with an increase of temperature, and are from 5% to 8% better than for HCl-HNO₃ solutions (Figures 13 and 14), however higher temperatures are still necessary to achieve good recoveries. A temperature of 90°C was considered to be the approximate optimum for leaching, because recoveries are only 2-3% lower than at the boiling point of 107°C.

Finally, the apparent effectiveness of AlCl₃ was examined further in Figure 16, where total Cl⁻ is further decreased to 2.53M, but AlCl₃ is increased to 0.29M. Again, a noticeable improvement in extractions over those in Figures 12 and 13 are observed, which appears to be attributable to AlCl₃. Recoveries at 106°C are extremely high: 98% of platinum and 88% of rhodium, and 2.0% and 3% respectively higher than for 80°C. However, recoveries drop rapidly at temperatures below 80°C, so that further work was restricted to the 80°C to boiling point range.

The initial tests performed at various temperatures provide two general conclusions:

1. Temperature plays a very important role in effectiveness of PGM extraction. Even leaching in optimally composed solutions must be at not less than 80-85°C to approach commercially acceptable levels of PGM extraction. A detailed study at below 80°C leaching temperature is not justified.

2. It appears that better results can be obtained, not by increasing HCl concentration to very high levels, but by keeping a relatively low total Cl⁻ level with a significant proportion present as AlCl₃.
4.3. Leaching kinetics.

The next step was a more detailed investigation of leaching kinetics at 80°C and higher, taking a representative selection of solution compositions. First, Figure 17, all Cl⁻ was present as HCl at close to the maximum realistic level 8.0M. Here extractions are based on solution samples taken during the leach. A fast leaching rate at the beginning of the process allows recovery of 55% of platinum and 41% of rhodium within the first hour of the process. Extractions during further leaching significantly slow down and essentially stop after 4 hours, at which rhodium recovery is especially low at around 75%.

The temperature was then increased to 106°C, Figure 18. As might be expected, major increases in both extraction rates and final recoveries are obtained. We can reduce retention time to 2.5 hours and get 85% rhodium and 95% platinum recoveries. However boiling concentrated HCl produces very severe corrosion conditions and HCl vapour losses, which are tolerable in small laboratory tests, but are less readily controlled on a large industrial scale.

Initial experiments indicated that the HCl-AlCl₃-HNO₃ system is easier to work with than HCl-HNO₃, at equivalent Cl⁻ levels, while the presence of AlCl₃ promotes Rh extraction. Since the AlCl₃ content of the solution may be more critical than a high Cl⁻ with HCl, the total Cl⁻ was then lowered below 8M, and some AlCl₃ was introduced. The benefit of AlCl₃, even at low total Cl⁻ and low concentration of HCl can be seen, at 80°C, by comparing Figures 17 and 19. Four hour leaches, at 80°C, with 8M HCl (Figure 17) give 88% of platinum recovery and 73% of rhodium, while 93.6% of platinum and 79.2% of rhodium are extracted at the same
Figure 16: Catalyst leaching in stirred reactor using 1.66M HCl / 0.29M AlCl₃ / 3.5M HNO₃ for 3 hours.
Figure 17: Catalyst leaching in stirred reactor using 8.0M HCl / 3.5M HNO₃ at 80°C.
Figure 18: Catalyst leaching in stirred reactor using 8.0M HCl / 3.5M HNO₃ at 106°C.
temperature and time of leaching with only 1.66M HCl, but with 0.29 M AlCl₃ addition (Figure 19). Similar conclusions can be made from the equivalent comparison, made at 106-107°C (boiling point) leaches. Four hour leaches with 8M HCl give, as demonstrated in Figure 18, 95% platinum and 85% rhodium recoveries, while 1.66M HCl / 0.29M AlCl₃ leaches give 97% and 88% extractions respectively (Figure 20).

Since it is not possible to increase temperature beyond 106-108°C without going to autoclave operations, two further tests (Figures 21 and 22) were carried out at higher total Cl⁻ levels than applicable to Figure 20. An increase in Cl⁻ through extra HCl addition from 1.66 M (Figure 20) to 3.30 M (Figure 21) makes little difference to leaching response. Finally the importance of AlCl₃ in promoting rhodium dissolution is again demonstrated by comparing Figures 21 and 22 in which the AlCl₃ level is changed under otherwise the same conditions. Leaching with the higher AlCl₃ level gives slightly higher recoveries than leaching with the lower AlCl₃ level. For example, after 4 hour leaching in 0.29M AlCl₃ (Figure 21), 95% of platinum and 89% of rhodium were extracted, while leaching with 0.18M AlCl₃, give 95% and 83% respectively under otherwise the same conditions (Figure 22).

Three main conclusions can be drawn from results obtained from the above series of kinetic experiments:

1) Three hour leaching is sufficient at the boiling point (106-108°C).
2) Rhodium extraction is always lower than platinum. This effect has also been demonstrated by other workers (e.g. Hoffman [21]).
3) Importance of AlCl₃ is again confirmed.
Figure 19: Catalyst leaching in stirred reactor using 1.66M HCl / 0.29M AlCl₃ / 3.5M HNO₃ at 80°C.
Figure 20: Catalyst leaching in stirred reactor using 1.66M HCl / 0.29M AlCl₃ / 3.5M HNO₃ at 107°C.
Figure 21: Catalyst leaching in stirred reactor using 3.3M HCl / 0.29M AlCl₃ / 3.5M HNO₃ at 108°C.
Figure 22: Catalyst leaching in stirred reactor using 3.3M HCl / 0.18M AlCl₃ / 3.5M HNO₃ at 108°C.
4.4. Effect of solution composition.

The next step was a systematic study of effects of solution composition. Here results based on 3 hour leaches at the boiling point (106-108°C) are compared. Figure 23 shows recoveries from leaches with constant HNO₃ (3.5M), no AlCl₃, and different levels of HCl. Maximum extractions, observed at the high HCl concentration end, are 95% of platinum and 82% of rhodium. While platinum extraction at 95% is reasonable, rhodium recovery at 82% is less than desirable. It is important to note that, while recoveries rise quickly between 1M and up to 8M HCl, only negligible improvement beyond this last concentration can be observed.

As can be seen in Figure 24, introduction of a small, 0.18M, amount of AlCl₃, gives dramatic improvement in recoveries, especially at low (1-2 M) HCl levels. For example, at only 1.66M HCl, platinum recovery is 96% and rhodium 83%. Also seen is the unexpected result that further HCl addition above 2M HCl does not improve recoveries, but in fact, slight decreases are observed.

The effectiveness of AlCl₃ is confirmed in Figure 25, where AlCl₃ addition has been increased from 0.18M (Figure 24) to 0.29M (Figure 25). The general pattern of results in Figure 25 is similar to that of Figure 24, and dramatic improvement in recoveries is seen at low HCl levels. Maximum platinum extractions remain almost the same (96.5%) as in Figure 24, but rhodium extractions have slightly increased, with a maximum of about 88% at 3M HCl. It seems probable that with AlCl₃ addition above 0.29 M, the trend to better recoveries would continue, but it was difficult to prepare more concentrated AlCl₃ solutions by the method used of
Figure 23: Catalyst leaching in stirred reactor using various HCl concentrations with 3.5M HNO₃ at 106°C and for 3 hours.
**Figure 24:** Catalyst leaching in stirred reactor using various HCl concentrations with 0.18 AlCl₃, 3.5M HNO₃ at 106°C and for 3 hours.
Figure 25: Catalyst leaching in stirred reactor using various HCl concentrations with 0.29 AlCl₃, 3.5M HNO₃ at 107°C and for 3 hours.
dissolving hydrated AlCl₃ (AlCl₃·6H₂O), because it gives a very viscous solution above 0.3-0.4 M concentration.

Figures 26 and 27 rearrange the results of Figures 23-25, in such a way as to show the effects of Cl⁻ source and concentrations for platinum (Figure 26) and rhodium (Figure 27) recoveries. The effectiveness of relatively low Cl⁻ levels, as AlCl₃, especially at low HCl concentration, is readily seen.

The above tests, performed in solutions with various HCl and AlCl₃ contents, provide two general conclusions:

1. For leaching in HCl-AlCl₃-HNO₃, it appears that increasing AlCl₃ concentration tends to increase rhodium recovery, while that of platinum remains unchanged.

2. Leaching in HCl-AlCl₃-HNO₃ does not require highly concentrated solutions, because relatively low AlCl₃ and HCl levels assure good PGM extractions.

4.5. Concentration of HNO₃.

Although platinum and rhodium dissolve in aqua regia through formation of chloride complexes, these metals are resistant to dissolution in HCl alone, because the formation of the chlorides requires an oxidizing agent, which is in this case, HNO₃. The precise mechanism of HCl/HNO₃ leaching/oxidation is not well established, but most previous workers, as discussed more in Chapter 3, believe that HCl and HNO₃, react together in the ratio 3 HCl/ 1 HNO₃ or 2 HCl/ 1 HNO₃ to generate an oxidizing leachant. The
Figure 26: Effect of chloride source and concentration on platinum recovery using 3 hours stirred reactor leaches at 106-107°C and 3.5M HNO₃.
Figure 27: Effect of chloride source and concentration on rhodium recovery using 3 hours stirred reactor leaches at 106-107 °C and 3.5M HNO₃.
Figure 28: Effect of HNO₃ concentration on leaching into 8M HCl at 106°C for 3 hours.
effect of HNO₃ on its own is to oxidize the metals through reactions evolving NO and NO₂. It may also be assumed that HNO₃ not only generates a strong oxidation potential in HCl-HNO₃ mixtures, but also controls ionic activities by contribution to the overall dissolved H⁺ concentration. To evaluate the importance of HNO₃, tests were conducted in the 0 M to 4.3 M range in both HCl - HNO₃ and HCl-AlCl₃-HNO₃ mixtures.

Figure 28 shows the effect of HNO₃ on PGM extraction into 8.0 M HCl. Leaching without HNO₃ allows recovery of 60.4% of platinum and 50.1% of rhodium. Results suggest a minimum of 1 M HNO₃ would be required for significant extraction, while further increases in molality give gradually increasing recoveries.

Other tests, for which results are presented in Figure 29, were done in HCl-AlCl₃-HNO₃ solution. At zero HNO₃ concentration, the results show up to 25% lower extractions than for HCl-HNO₃ (Figure 28) and it appears that about 1.6 M is a minimum concentration below which recoveries quickly decrease. Again, a further increase (over 1.6 M) of the HNO₃ molality gives substantially improved extractions.

It should be noted that there is significant extraction at zero HNO₃, but this may not be a true PGM dissolution process. Here, HCl, on its own, may be dissolving the alumina coat releasing tiny particles of PGM into the solution. This apparent extraction may result from the recoveries of Figures 27 and 28 being based on residue analyses.

The above tests produce two overall conclusions:
1. Leaching without HNO$_3$ or in small concentrations of HNO$_3$ is ineffective.

2. Despite the fact that recoveries are significant in leaches containing about 1.6M HNO$_3$, a further increase in this acid concentration (up to 3-4 M) would give an extra 10% rise in extractions. At more than 4 M HNO$_3$, in a boiling solution, corrosion and toxicity problems become severe. Thus 3.5M HNO$_3$ was chosen as the standard for experiments described in the previous and following sections.

4.6. Effect of grinding.

Grinding is a frequently employed operation in ore treatment processes, and is used to liberate locked particles of the desired mineral from the ore body to increase final recoveries. In the case of artificially produced catalyst, liberation of PGM particles by grinding may be not necessary, because they are exclusively dispersed in the surface of the catalyst substrate. Previous work done with pellets not only does not recommend grinding of catalyst, but even strongly advises against it [23]. PGM were not locked inside the pellets, but dispersed in their outermost surface, which is easily reached by the leaching solution. Grinding of pellets not only did not increase PGM recoveries, but, in fact, added a new problem, i.e. an increased amount of Al$_2$O$_3$ dissolved during leaches. In the case of pellets, one of the main goals of the recovery process was to minimize the amount of dissolved aluminum in the leaching solution to avoid an extra cost of chemicals used for solution treatment.
Figure 29: Effect of HNO₃ concentration on leaching into 1.66M HCl and 0.29M AlCl₃, at 106°C for 3 hours.
The above considerations are less applicable to honeycombs, because the structures of pellets and honeycombs are very different. Honeycomb catalyst has narrow internal channels difficult to penetrate by the leaching solution, and this suggests that, to increase PGM recoveries, honeycombs, unlike pellets, may require grinding to expose PGM trapped inside the channels. Excessive Al₂O₃ dissolution is not a problem, because honeycombs are mostly made of acid resistant cordierite.

A few leaches were done to study the effect of grinding of honeycombs on PGM extraction. The tests were 4 hours long, and carried out using a 1000 cc reactor at -106°C in HCl-HNO₃ or HCl-AlCl₃-HNO₃ solutions. Catalyst was separated into three parts and ground into three different sizes:

1. 4×2×2cm pieces
2. 2×2×1mm pieces
3. < 60 mesh

Results of leaches are shown in Tables 6 and 7. The results indicate that there is almost no difference in extraction of PGM between ground (< 60 mesh or 2×2×1mm pieces) and unground (4×2×2cm pieces) catalyst. In all tests, recoveries are 94% for platinum and 85% for rhodium if leaches are performed in HCl-HNO₃ (8.0M/3.5M) solutions, or 95% and 87% for leaches in HCl-AlCl₃-HNO₃ (3.3M/0.29M/3.5M). The main conclusion from this set of tests is that leaching solution has, in fact, no trouble penetrating catalyst channels.

4.7. Column leaching.

In column leaching, scrap catalyst is leached as a static bed in a tubular reactor, through which an upward
The flow of leachant is passed. This system has the following advantages over other types of reactors:

1. It gives solutions more concentrated in platinum and rhodium than obtainable using a stirred reactor due to a high solid/liquid ratio acquired by circulation of as small an amount of leachant as possible.

2. A solid/liquid separation step is avoided.

Since it has been previously shown that fine grinding is not required for honeycombs, a column vessel can be used for leaching of this type of catalyst. In the present work, most tests for optimizing leachant composition and temperature were carried out using a stirred reactor system, as described above, because when a relatively large number of experiments under different conditions is required, this latter method is more convenient to operate than column leaching. A few column tests, which used leaching solutions approximating those of optimum composition determined earlier in reactor tests, allowed leaching kinetics in the column to be compared with results found previously with the reactor. Since the most desirable equipment to use on an industrial scale is a tubular type reactor, the test carried out in a laboratory scale column allow direct scaling up, because the leaching procedure is the same in both cases: continuously flowing solution passes through a static-bed of crushed catalysts. The column tests were done at 80-82°C and 94-97°C, instead of the boiling point (106-108°C), because bubbles generated at the boiling temperature perturb the smooth unbroken flow of solution. In each test, 380-420 g catalyst, broken into 4×2×2 cm pieces, was leached in a 3-4 l/hour upward flow of circulating leachant.

Similarly to reactor tests, the first experiment,
<table>
<thead>
<tr>
<th>Form of catalyst</th>
<th>% Pt leached</th>
<th>% Rh leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>4×2×2cm pieces</td>
<td>94.2</td>
<td>85.1</td>
</tr>
<tr>
<td>2×2×1mm pieces</td>
<td>94.5</td>
<td>84.9</td>
</tr>
<tr>
<td>&lt;60 mesh</td>
<td>94.1</td>
<td>85.1</td>
</tr>
</tbody>
</table>

Table 6: Effect of grinding catalyst on platinum and rhodium recovery using stirred reactor leaches at 106°C, 8.0M HCl / 3.5 M HNO₃, for 4 hours.
<table>
<thead>
<tr>
<th>Form of catalyst</th>
<th>% Pt leached</th>
<th>% Rh leached</th>
</tr>
</thead>
<tbody>
<tr>
<td>4x2x2cm pieces</td>
<td>95.2</td>
<td>87.0</td>
</tr>
<tr>
<td>2x2x1mm pieces</td>
<td>94.7</td>
<td>87.2</td>
</tr>
<tr>
<td>&lt;60 mesh</td>
<td>95.1</td>
<td>86.7</td>
</tr>
</tbody>
</table>

Table 7: Effect of grinding catalyst on platinum and rhodium recovery using stirred reactor leaches at 108°C, 3.3M HCl / 0.29 M AlCl₃ / 3.5M HNO₃, for 4 hours.
Figure 30, was performed at 80°C, with all Cl\textsuperscript{-} as HCl at close to the maximum realistic level (8.0M). Results are based on analysis of solution samples taken during the leach. By comparing stirred reactor and column results for the same conditions of solution composition and temperature (Figure 31) it can be seen that both platinum and rhodium extraction curves are virtually independent of reactor type, a conclusion that holds in all cases where tests using the two different systems were carried out under comparable conditions. It is surprising that, despite the arbitrary choice of stirring rate or solution flow rate, reaction kinetics are so insensitive to reactor configuration. The conclusion must be that reaction rates are controlled by the interfacial dissolution reactions rather than by mass transfer effects.

As might be expected based on the results of reactor leaches, major increases in both extraction rates and final recoveries are obtained when the temperature is increased from 80°C to 96°C, Figure 32. Here, at least 4 hours is required to assure high recoveries, these being 93% for platinum and 85% for rhodium.

On account of the results obtained during reactor tests, special attention was paid to HCl-AlCl\textsubscript{3}-HNO\textsubscript{3} leaches, because there is no doubt that AlCl\textsubscript{3} addition to a leaching solution not only makes the system easier to work with, but also produces higher recoveries. The benefit of AlCl\textsubscript{3} addition, similar to that observed from reactor tests, can be seen by comparing Figures 29 and 32, which apply to about 80°C. Figure 33 shows results of leaching in HCl-AlCl\textsubscript{3}-HNO\textsubscript{3} at much lower total chloride (2.53M) than for Figure 30, where 8 M total chloride, all as HCl, applies. The results confirm previous findings that PGM recoveries are better in
Figure 30: Catalyst leaching in column using 8.0M HCl / 3.5M HNO₃ at 80-82°C.
Figure 31: Catalyst leaching in column using 8.0M HCl / 3.5M HNO₃ at 94-97°C.
Figure 32: Catalyst leaching in column using 1.66M HCl / 0.29M AlCl₃ / 3.5M HNO₃ at 80-82°C.
Figure 33: Catalyst leaching in column using 1.66M HCl / 0.29M AlCl₃ / 3.5M HNO₃ at 94–97°C.
Figure 34: Catalyst leaching in column using 3.3M HCl / 0.18M AlCl₃ / 3.5M HNO₃ at 80-82°C.
the relatively low chloride system, where part of the chloride is supplied as AlCl₃.

A similar comparison can also be made between Figures 32 and 34. Leaching conditions were similar to tests from Figures 30 and 33, but temperature was increased to 94-97°C. Again, much lower total chlorides, Figure 34, where part of the chloride is as AlCl₃, gives better recoveries than leaches in 8M chloride, all as HCl (Figure 32). Also, with an increase of temperature from 80-82°C (Figures 30 and 33) to 94-97°C (Figures 32 and 34), a major increase in recoveries is observed. Figure 34 represents the best results obtained for column leaching experiments, similar to Figure 20 for the stirred reactor tests, the leachant composition being the same for both cases. After 4 hours leaching (Figure 34) extractions are 96% for platinum and 85% for rhodium. Retention time can be reduced to 2.5-3.0 hours at which 82-83% of rhodium and 94-95% of platinum can still be extracted.

Two further tests were carried out at higher total Cl⁻ through an extra HCl addition from 1.66M (Figures 33 and 34) to 3.30M (Figures 35 and 36). Concurrently, the AlCl₃ addition was decreased from 0.29 M to 0.18 M. Despite the increase in total Cl⁻, extractions tend to be slightly lowered, presumably on account of the decreased AlCl₃ content.

The main conclusions of the column experiments are:

1) Importance of AlCl₃ is again confirmed.

2) The best PGM extractions, of 95% for platinum and
85% for rhodium, where obtained using 1.66M HCl and 0.29M AlCl₃ at 94-96°C. Although improved extractions would be expected at 106-107°C, it was impractical to operate the tubular reactor with a boiling solution.

3) For the particular agitation conditions (stirred reactor) and flow rates (tubular reactor) used, recoveries and extraction rates obtained by the two contacting methods studied are similar for equivalent conditions of solution composition and temperature.

4.8. Penetration of catalyst by leaching solution.

Platinum and rhodium are dispersed in the outermost layer of honeycomb catalyst, and inside very narrow (0.5-1 mm in diameter) parallel channels. The shape of the catalyst may make it difficult for leaching solution to penetrate the channels, depending on their orientation relative to the solution flow direction. The assumption was made that, if pieces of catalyst were placed in such a way that their channels would be parallel to a stream of leaching solution, then the solution would have less trouble in penetrating the catalyst, and this could result in better extraction of PGM. Two column tests were done to study this presumption. In one case, pieces of catalyst were placed parallel, and in the other, horizontally to the leaching stream. Results are shown in Table 3. Surprisingly, 4 hour leaching tests did not produce any difference in PGM recoveries from catalyst placed in these two different ways.

4.9. Washing.
Figure 35: Catalyst leaching in column using 3.3M HCl / 0.18M AlCl₃ / 3.5M HNO₃ at 94-97°C.
Figure 36: Effect of reactor type on leaching into 8.0M HCl / 3.5M HNO₃ at 80-82°C for 3 hours.
Table 8: Effect of the catalyst position in the column ("vertical" or "horizontal") on platinum and rhodium recovery using leaches at 80°C, 8.0M HCl / 3.5M HNO₃, and for 3 hours.
Previous work showed that PGM extraction from pellets by column leaching could be increased by up to 8%, if a leach is followed by an efficient washing of the leached bed [23]. These authors suggested 1 hour washing at high temperature (90°C) by a low acid aluminum chloride solution, followed by 2 hour washing in water as the catalyst bed cooled to room temperature. This earlier study was done for pellets, and when we repeated the washing procedure for honeycomb catalyst, a much smaller increase in recoveries was obtained.

Figure 37a shows results for a 3 hour column leach in 8M HCl / 3.5M HNO₃ at about 95°C. A subsequent "hot wash" in AlCl₃ solution (Figure 37b) gave additional extraction of only 1.2% of platinum and 0.8% of rhodium. A further 1 hour of leaching (4 hours total - Figure 37c) under the conditions of the original 3 hours leaching recovered an extra 1-2% of platinum and rhodium. However, a dramatic improvement in PGM recoveries can be obtained by washing the leach residue in a water jet (Figure 37d). A likely explanation of this last phenomenon is that small quantities of alumina remain on leached catalyst surfaces, and this residual layer retains significant amounts of PGM's. After leaching in HCl/HNO₃, the remaining alumina has the consistency of wet paint, and can easily be washed off using a water jet. The simple agitation of leached catalyst with wash water was ineffective, since significant physical force is required to detach the residual alumina coating. This washing method (Figure 37d) recovered an extra 5.8% of platinum and 18.5% of rhodium giving almost 98% total recoveries of each metal.

The procedures described above for Figure 37 were repeated for an initial leach in HCl-AlCl₃-HNO₃ (Figure 38a-
Figure 37: Effect of washing following leaching into 8.0M HCl / 3.5M HNO₃ at 94-97°C.
Figure 38: Effect of washing following leaching into 1.66M HCl / 0.29M AlCl₃ / 3.5M HNO₃ at 94-97°C.
d) Here, the improvements shown by Figures 38b-d are less marked than in the equivalent experiments of Figure 37. This is because the initial leach (Figure 38a) gave higher recoveries than in Figure 37a. Also the alumina remaining on the leach residue is strongly adherent after a low acid AlCl₃ leach and is more difficult to remove by a water jet.

The practical operation of a water jet would require a specially designed vessel in which a minimum amount of water is used to give a low volume sludge which could be releached. It is probable that minor (1-3\%) amounts of PGM will remain trapped within internal channels of the catalyst and will not readily be recovered.

The above tests produced the following overall conclusions:

1. Aluminum chloride and water washing, used previously for pellets, produces only a small increase in recoveries when honeycombs are treated.

2. Jet washing dramatically improves PGM recoveries (up to 98\%) following a "high" acid (8 M HCl) leach, but this technique is less effective for a "low" acid leach with AlCl₃ (1.66M HCl and 0.29M AlCl₃).

4.10. Estimation of Cl⁻ activity.

Results shown in Figures 26 and 27 indicate, particularly at low HCl concentration, that platinum and rhodium recoveries are dramatically improved when part of HCl leachant is replaced by AlCl₃. The chemistry of PGM dissolution suggests that Cl⁻ ion activity (aCl⁻) plays a
decisive role to control the PGM dissolution.

The activity \( \alpha \) of a completely dissociated electrolyte
\[
C_\alpha A_\beta \rightleftharpoons \nu_+ C_\alpha^{2+} + \nu^- A_\beta^{2-}
\]
is defined as the product of single ion activities \( \alpha_+ \) or \( \alpha_- \)
or a mean activity \( \alpha_\pm \):
\[
\alpha = \alpha_+ \alpha_- = \alpha_\pm
\]

The overall activity \( \alpha \) of a pure solution, which contain only one cation-anion pair is measurable, and much of the experimental data expressed as the mean activity coefficient \( \gamma_\pm \) of strong electrolytes at various concentrations in aqueous solutions, are available in the standard references [44]. The Debye-Hückel equation applies to these data below ionic strength \( I_m \) 0.01, while several other equations apply to higher concentrations [45].

Several experimental data for mean activity coefficient \( \gamma_\pm \) in mixed electrolytes containing more than one cation-anion pair (eg. HCl/AlCl\(_3\)) are also available [46] [47]. To calculate the coefficients in other mixtures, a simple empirical method proposed by Meissner and co-workers is used [48] [49] [50].

Unlike the overall activity \( \alpha \), the single ion activity \( \alpha_+ \) is impossible to measure and its estimation is based on an ionic hydration theory formulated by Robinson and Stokes [51]. By using this theoretical approach, Bates and co-workers developed a method to calculate single ion activities \( \alpha_+ \) in unassociated chlorides [52]. Later, Jansz extended the method to estimate the single ion activities \( \alpha_+ \) for mixed solutions [53]. He developed equations for a solution containing both a
Figure 39: HCl mean activity ($a_{\text{HCl}}$) in HCl-3.5M HNO$_3$ and HCl-0.29M AlCl$_3$-3.5M HNO$_3$ in different HCl concentrations and at 100°C.
univalent and a bivalent chloride. The estimation method for a more complex mixture, containing more than two species, and especially a non-chloride one, is not yet developed.

4.11. Estimation of HCl mean activity coefficients.

To estimate mean activity coefficients ($\gamma_{HCl}$) in HCl-HNO$_3$ and HCl-AlCl$_3$-HNO$_3$ solutions a method proposed by Kusik and Meissner is used [50]. The calculations are shown in Appendix 1 and the final result of the calculations, HCl mean activities in HCl-HNO$_3$ and HCl-AlCl$_3$-HNO$_3$ mixtures are shown in Figure 39. It can be seen that for corresponding HCl concentrations, addition of AlCl$_3$ raises the HCl activities in the mixtures.

Although a quantitative estimation of Cl$^-$ single ion activity ($a_{Cl^-}$) in a complex solution is not yet available, two facts can help to approximate activity values:

1. Cl$^-$ single ion activity coefficient ($\gamma_{Cl^-}$) in our mixtures may be considerably lower than the mean HCl activity coefficient ($\gamma_{HCl}$). Several reports showed that H$^+$ single ion activity coefficient ($\gamma_{H^+}$) considerably exceeds Cl$^-$ activity coefficient ($\gamma_{Cl^-}$) in pure HCl or in mixed HCl-chloride solutions. In mixtures up to 6 M HCl, the Cl$^-$ activity coefficient ($\gamma_{Cl^-}$) remained relatively stable and equals 0.7 - 0.9 [53].

2. According to the hydration theory [51], cations with high hydration numbers slightly increase anions activities. It can be expected that the very significant hydration number of Al$^{3+}$, equals 31-33,
raises the Cl⁻ activity.

Considering the above suggestions, roughly estimated single chloride ion activity in HCl-0.29M AlCl₃-3.5M HNO₃ is shown in Figure 40. The phenomenon observed in our tests (Figure 26 and 27), that PGM recoveries in 1M HCl-0.29M AlCl₃-3.5M HNO₃ solution are higher than in 6M HCl-3.5M HNO₃ can be explained by higher Cl⁻ activity in the former solution as shown in Figure 40.


Finally, a process for PGM recovery from spent honeycombs is proposed. The process includes crushing, HCl/AlCl₃/HNO₃ leaching, solvent extraction, as well as lead chloride removal and absorption of gases evolved during the leaching step. The schematic flowsheet is shown in Figure 41. The treatment is based on a selective extraction of PGM, leaving the γ-alumina washcoat as much unattacked as possible.

Honeycombs are removed from steel canisters and crushed, step 1, to approximately 4×2×2cm pieces to ensure complete penetration of the catalyst by leaching solutions. The catalyst charge is leached in a tubular teflon-lined steel reactor, step 2. The leach is performed at 95°C for 2.5 hour in slowly circulated 1.66M HCl-0.29M AlCl₃-3.5M HNO₃ solution. Gases emerging during the leach are absorbed, step 10, and HCl/HNO₃ solution formed during this absorption is recycled to the leaching step 2. After the leach, leachant is decantated, step 3, solids remain in the column and are washed by AlCl₃-H₂O mixture, step 11. Then, the solids are discharged to waste disposal, while the filtrate is
Figure 40: Estimated chloride single ion activity ($a_{Cl}$) for HCl-0.29M AlCl$_3$-3.5M HNO$_3$ and HCl-3.5M HNO$_3$ in different HCl concentrations and at 100°C.
**Figure 41:** Proposed flowsheet of PGM recovery from spent autocatalyst by an aluminum chloride leach process.
transferred back to the absorption step 10. Pregnant solution from step 3 is allowed to cool and PbCl₂ is crystallized, step 4. Next, the solution is decanted, step 5, and PbCl₂ removed. To separate PGM from leach liquor, solvent extraction with Kelex 100 or Lix 26 is performed, step 6. Aqueous phase is recycled to chloride leaching step 2. The recycling prevents potential PGM losses. A stripping step, step 7 and precipitation, step 8, are used to separate PGM from impurities. Finally, the slurry is filtered, step 9, and PGM concentrate transferred for further treatment. Extractant and stripping agent are recycled.
CHAPTER 5: CONCLUSIONS

5.1. Contribution to original knowledge.

The following should be considered contributions to original knowledge:

1. Detailed research study on rhodium recovery from spent autocatalyst by HCl/AlCl₃/HNO₃ and HCl/HNO₃ leaches.

2. Optimization of HCl/AlCl₃/HNO₃ leaching of spent autocatalyst. The optimization includes:
   - Cl⁻ concentration and AlCl₃/HCl ratio in the leachant
   - temperature of the process
   - HNO₃ concentration in leaching solution
   - retention time of leaching
   - grinding of the feed.

3. Comparative study on different types of leaching reactors (stirred and tubular) used in this process.

5.2. Conclusions.

I. Fast extraction of platinum and rhodium from spent honeycomb-type catalyst with HCl/AlCl₃/HNO₃ or HCl/HNO₃ solutions has been obtained. The results show the following advantages of HCl/AlCl₃/HNO₃ over HCl/HNO₃ leaching.

1. Unlike HCl/HNO₃, the HCl/AlCl₃/HNO₃ leaching
The leaching process does not require highly concentrated solutions, because relatively low AlCl₃ and HCl levels assure good PGM extractions.

2. The HCl/AlCl₃/HNO₃ system is much easier to work with, because of less fumes and less corrosive medium than HCl-HNO₃ at equivalent Cl⁻ levels.

II. Experimental data allowed definition of optimum conditions of the HCl/AlCl₃/HNO₃ leaching process.

1. The PGM extraction should be performed at a low level of HCl, but a relatively high AlCl₃/HCl ratio. Increasing AlCl₃ concentration tends to increase rhodium recovery, while that of platinum remains unchanged. The highest recoveries were obtained for 1.66M HCl-0.29M AlCl₃-3.5M HNO₃.

2. Temperature was found to be one of the most important variables and leaching performed at less than 80°C is ineffective. 90-95°C is recommended to keep retention time relatively short, around 2.5 hours.

3. Leaching without oxidant (in this case HNO₃) or in small concentrations of the oxidant results in weak PGM extraction. To obtain good recoveries, the initial concentration of HNO₃ should be maintained at not less than 3M.

4. A jet washing step significantly improves PGM recoveries, but this is difficult to perform effectively.
III. Recoveries and extraction rates obtained by the two contacting methods studied, stirred and tubular reactors, are similar for equivalent conditions of solution composition and temperature. This suggests the use of a tubular type reactor, which gives solutions more concentrated in platinum and rhodium and avoids a solid/liquid separation step. A possibility of higher PGM recoveries by using a finely ground feed, a potential advantage of stirred reactor leaching, was not demonstrated in the case of honeycomb-type catalyst. The results showed that grinding is not necessary, and breaking honeycombs into 4x2x2cm pieces assures good penetration of catalyst channels by leachants. This means that, in this case, a batch type reactor has no advantage over the column type vessel.

The transfer of experimental data from a lab-scale column to a small industrial installation is acceptable from an engineering point of view, because both reactors are operating under similar conditions.

IV. The results suggest that Cl– single ion activity plays a decisive role to control PGM dissolution. The very good performance of HCl/AlCl3/HNO3 can be explained by the high hydration number of Al3+ which raises the Cl– activity.

V. The presented method is effective and inexpensive, and can be very attractive and highly competitive as compared to actually operating pyrometallurgical methods. A considerable advantage of this method is the
possibility of building and operating a small (5-20 tonnes of catalyst/day) and inexpensive installation.
Appendix 1. Estimation of HCl mean activity coefficients by Meissner method.

To estimate HCl mean activity coefficients ($\gamma_{\text{HCl}}$) in HCl-HNO$_3$ and HCl-AlCl$_3$-HNO$_3$ solutions a method proposed by Kusik and Meissner is used [50]. The method is based on calculation of a reduced activity coefficient ($\Gamma^o$) in different ionic strengths ($I_m$). A single cation-anion pair is characterized by value $q^o$ defined by Meissner [49] at 25°C for over 200 different salts. At temperature other than 25°C, the $q_i$ value is calculated from the empirical equation [50]:

$$\frac{q_i - q^o(25)}{(t - 25)} = -0.005 \cdot q^o(25) + 0.0085$$

(25)

By using the above equation the values of $q_{100}$ for pure HCl, HNO$_3$, and AlCl$_3$ were calculated and are shown below:

<table>
<thead>
<tr>
<th></th>
<th>$q_{25}$</th>
<th>$q_{100}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>6.69</td>
<td>5.34</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>3.66</td>
<td>2.92</td>
</tr>
<tr>
<td>AlCl$_3$</td>
<td>1.92</td>
<td>1.79</td>
</tr>
</tbody>
</table>

When $\Gamma^o$ is plotted against the $I_m$, a family of curves for different $q$ values is obtained. The curves were published by Meissner [49] [50] and three of them representing HCl, AlCl$_3$, and HNO$_3$ at 100°C are shown in Figure 42. Using this graph $\Gamma^o$ of pure HCl, AlCl$_3$, and HNO$_3$ is determined at 100°C and in different ionic strengths.
Figure 42: Reduced activity coefficients for HCl, HNO₃, AlCl₃, vs. the total ionic strength at 100°C.
For a mixture of more than 2 ions, the reduced activity coefficient of the cation-anion pair \( \Gamma^n \) is estimated by using \( \Gamma^o \) of various cation-anion pairs, which can be formed within the solution. The \( \Gamma^o \) of the cation-anion pairs must be determined at total ionic strength of the solution. Meissner proposed a general equation to calculate \( \Gamma^n \) for a solution of any number of ions. For any specific electrolyte identified by cation numbered \( i \) and anion \( j \):

\[
\log \Gamma_{ij} = \frac{Z_i}{Z_i + Z_j} \cdot \left( \frac{V_{ij} I_j \log \Gamma^o_{ij} + V_{ij} I_j \log \Gamma^o_{ij} + \cdots}{I_T} \right) \\
+ \frac{Z_j}{Z_i + Z_j} \cdot \left( \frac{V_{ij} I_i \log \Gamma^o_{ij} + V_{ij} I_i \log \Gamma^o_{ij} + \cdots}{I_T} \right)
\]

(26)

Thus, for a mixture of two salts, Equation 27 is true and for a mixture of three salts, Equation 28 holds.

\[
\log \Gamma_{12} = \frac{Z_1}{Z_1 + Z_2} \cdot \left( \frac{V_{12} I_2 \log \Gamma^o_{12} + V_{14} I_4 \log \Gamma^o_{14}}{I_T} \right)
+ \frac{Z_2}{Z_1 + Z_2} \cdot \left( \frac{V_{21} I_1 \log \Gamma^o_{21} + V_{23} I_3 \log \Gamma^o_{23}}{I_T} \right)
\]

(27)

\[
\log \Gamma_{13} = \frac{Z_1}{Z_1 + Z_2} \cdot \left( \frac{V_{12} I_2 \log \Gamma^o_{12} + V_{14} I_4 \log \Gamma^o_{14} + V_{14} I_4 \log \Gamma^o_{14} + V_{16} I_6 \log \Gamma^o_{16}}{I_T} \right)
+ \frac{Z_2}{Z_1 + Z_2} \cdot \left( \frac{V_{21} I_1 \log \Gamma^o_{21} + V_{23} I_3 \log \Gamma^o_{23} + V_{25} I_5 \log \Gamma^o_{25}}{I_T} \right)
\]

(28)

Where

\( \Gamma^o_{ij} \) - the reduced activity coefficient of a cation-
anion pair in a solution contains only 1 pair of ions.
\[ \Gamma_{\text{a}} = \gamma_{\pm(0)}^{1/(2\alpha \beta)} \]  
(29)

\[ \gamma_{\pm(0)} \] - electrolyte mean ionic activity coefficient.

\[ \Gamma_{\text{i}} \] - the reduced activity coefficient of ij salt in a mixture of three or more ions. For HCl:
\[ \Gamma_{\text{i}} = \gamma_{\pm(0)} \]  
(30)

\[ Z \] - absolute number of unit charges on the ion, indicated by the subscript. (\( Z_{\text{H}^+} = 1, Z_{\text{Cl}^-} = 1, Z_{\text{NO}_3^-} = 1, Z_{\text{Al}^{3+}} = 3 \)).

\[ I_i \] - ionic strengths of ions indicated by the subscript:
\[ I_i = 0.5 \cdot m_i \cdot Z_i^2 \]  
(31)

\[ I_{\text{Total}} \] - total ionic strengths of solution
\[ I_{\text{Total}} = I_1^+ + I_2^+ + I_3^+ \ldots \]  
(32)

\[ V_i \] - weighting factor defined as follow:
\[ V_i = 0.5 \cdot (Z_i^+ + Z_i^-)^2 / (Z_i^+ \cdot Z_i^-) \]  
(33)

\[ a_{\text{HCl}} \] - HCl activity calculated as follow:
\[ a_{\text{HCl}} = \gamma_{\text{HCl}m_0} \cdot m_{\text{HCl}} \]  
(34)

For HCl - HNO₃ mixtures composed of 3.5M HNO₃ and HCl concentration varying from 1M to 8M, calculations are shown in Table 9, and for HCl - AlCl₃ - HNO₃ mixtures composed of 3.5M HNO₃, 0.29M AlCl₃ and HCl concentration varying from 1M to 8M, calculations are shown in Table 10.
<table>
<thead>
<tr>
<th>m_{HCl}</th>
<th>I_{H^+}</th>
<th>I_{Cl^-}</th>
<th>I_{NO_3^-}</th>
<th>I_{\text{Total}}</th>
<th>I_{HCl}^o</th>
<th>I_{HNO_3}^o</th>
<th>\Gamma_{HCl}</th>
<th>\Gamma_{HNO_3}</th>
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**Table 9:** Calculation of HCl mean activity coefficients ($\gamma_{HCl}^{\text{geo}}$) in HCl–HNO₃ solution by Meissner method.
<table>
<thead>
<tr>
<th>( m_{\text{HCl}} )</th>
<th>( I_{\text{H}^+} )</th>
<th>( I_{\text{Cl}^-} )</th>
<th>( I_{\text{Al}^{+3}} )</th>
<th>( I_{\text{NO}_3^-} )</th>
<th>( I_{\text{Total}} )</th>
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</table>

<table>
<thead>
<tr>
<th>( m_{\text{HCl}} )</th>
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<th>( \Gamma_{\text{HNO}_3} )</th>
<th>( \Gamma_{\text{AlCl}_3} )</th>
<th>( \Gamma_{\text{HCl}} )</th>
<th>( a_{\text{HCl}} )</th>
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</table>

**Table 10:** Calculation of HCl mean activity coefficients \((\gamma_{\text{HCl}(\text{aq})})\) in HCl-AlCl\(_3\)-HNO\(_3\) solution by Meissner method.
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