Title: RECOVERY OF PLATINUM GROUP METALS FROM PLATINUM GROUP METAL-CONTAINING MATERIALS

Figure 1. Leaching with 15% HCl and Cl₂ gas at 90°C for 5 minutes

Abstract: There is provided a process for extracting platinum group metals from a platinum group metal-containing material, in particular spent automotive catalyst. The process involves roasting said material under oxidative conditions and further roasting said material under reducing conditions, then contacting said roasted material with a chloride leaching solution in the presence of an oxidising agent to produce a leachate solution containing platinum group metals. The platinum group metals may be recovered from the leachate solution by subjecting the leachate solution to conventional recovery techniques, such as electrowinning, solvent extraction, gas-reduction or adsorption, and in particular cementation.
RECOVERY OF PLATINUM GROUP METALS FROM PLATINUM GROUP METAL-CONTAINING MATERIALS

Field
The present invention relates to a process for recovering platinum group metals from platinum group metal-containing materials, in particular to a process for recovering platinum group metals from spent automotive catalysts.

Background
Increasing quantities of scrap automotive catalysts available in the world today represent a major secondary source of platinum group elements (PGE). The metallurgical techniques currently in use for recycling PGE from automotive catalysts include smelting methods which have the advantage that the catalyst does not have to be removed from the container. The few known available hydrometallurgical techniques utilise high temperatures and pressures, or concentrated acids such as aqua regia, and none has found application in large scale commercial practice. Nevertheless, the low levels of impurities associated with the PGE in scrap automotive catalysts suggests that a hydrometallurgical process would be advantageous if a less intensive extraction process could be developed. Such a technique developed for scrap automotive catalysts are likely to be suitable for recovery of platinum group metals from alternative primary and secondary sources.

The present invention seeks to overcome at least some of the aforementioned disadvantages.
Summary

In its broadest aspect, the invention provides a process for recovering platinum group metals from platinum group metal-containing materials. In contrast to prior art processes, the present invention operates under relatively mild conditions at atmospheric pressure.

Accordingly, in a first aspect, the present invention provides a process for extracting platinum group metals from a platinum group metal-containing material comprising contacting the platinum group metal-containing material with a chloride leaching solution in the presence of an oxidising agent to produce a leachate solution containing the platinum group metals.

In a second aspect, the present invention provides a process for recovering platinum group metals from a platinum group metal-containing material comprising the steps of:

a) contacting the platinum group metal-containing material with a chloride leaching solution in the presence of an oxidising agent; and

b) processing a leachate solution resulting from step a) to recover platinum group metals from the leachate solution.

In one embodiment of the invention the step of processing the leachate solution comprises subjecting the leachate solution to electrowinning, cementation, solvent extraction, gas-reduction or adsorption to recover platinum group metals from the leachate solution. In a preferred form of the invention, the leachate solution is subjected to cementation comprising contacting the leachate solution with a metal having a reduction
potential lower than the potential at which reduction of the dissolved platinum group metals in the leachate solution takes place.

In another form of the invention, the process further comprises adding a collector to the leachate solution prior to or during cementation. The collector facilitates agglomeration of platinum group metal precipitates which form during cementation, thus allowing easier separation of the precipitates from the leachate solution.

The processes of the present invention successfully recover significant amounts of platinum group metals from platinum group metal-containing materials. However, the amounts recovered can be further increased by treating the platinum group metal-containing material prior to performing the recovery processes of the present invention. This is particularly the case for spent automotive catalysts where it is thought that hydrocarbon combustion products on the surface of said catalysts provide a barrier between the leach solution and the platinum group metals in the catalyst. The removal of said barrier by subjecting the spent catalysts to a pre-treatment process increases the efficacy of the subsequent recovery processes.

Accordingly, in a further embodiment of the invention, prior to leaching the platinum group metal-containing material, the process comprises roasting the platinum group metal-containing material under oxidative conditions, and subsequently roasting the platinum group metal-containing material under reducing conditions.

In a third aspect, the invention provides a method of treating a platinum group metal-containing material to
facilitate subsequent recovery of platinum group metals from said material, comprising the steps of:

a) roasting the platinum group metal-containing material under oxidative conditions; and

b) further roasting the platinum group metal-containing material from step a) under reducing conditions.

In a further aspect, the invention provides a method of recovering a platinum group metal from a spent automotive catalyst comprising the steps of:

a) roasting the spent automotive catalyst under oxidative conditions;

b) further roasting the roasted spent automotive catalyst from step a) under reducing conditions;

c) contacting the roasted spent automotive catalyst from step b) with a chloride leaching solution in the presence of an oxidising agent; and

d) processing a leachate solution resulting from step c) to recover the platinum group metals from the leachate solution.

In one embodiment of the invention, roasting under oxidative conditions comprises heating the platinum group metal-containing material in air at 500 °C for 2 h.

In another embodiment, roasting under reducing conditions comprises heating the platinum group metal-containing material in a gas mixture comprising about 5% H₂ and about 95% N₂ at 500 °C for 2 h.

Description of the Figures Accompanying the Description

Figure 1 is a graphical representation of percentage extraction of platinum group metals from spent automotive catalyst resulting from an extraction process in
accordance with one embodiment of the present invention;
and
Figure 2 is a graphical representation of percentage recovery of platinum group metals from leachate solutions containing platinum group metals in accordance with another embodiment of the present invention.

Detailed Description of Preferred Embodiment

The present invention is useful for recovering platinum group metals (PGM) from platinum group metal-containing materials. The platinum group metals are selected from a group consisting of platinum, palladium, rhodium, rhenium, osmium, iridium, technetium, ruthenium and mixtures thereof. The processes of the present invention are particularly suitable for recovery of platinum, palladium and rhodium from spent automotive catalysts.

Primary source platinum group metal-containing materials include, but are not limited to, (PGM) ores which can be in the oxide, sulphide, mixed, and other forms, and (PGM) concentrates. Platinum group metals are also often associated with Cu and/or Ni ore deposits. Concentrates, tailings, leach residues and by-products of mining processes of such ores may also be considered as primary source platinum group metal-containing materials.

Secondary source platinum group metal-containing materials include, but are not limited to, scrap electrical and electronic components, scrap printed circuit boards, and other e-waste, spent industrial catalysts such as used in petroleum refining, and in particular spent automotive catalysts.
Generally, the concentration of PGM in the platinum group metal-containing material may be up to about 0.2% w/w Pt, up to about 0.35% w/w Pd, and up to 0.02% w/w Rh.

Prior to performing the processes of the present invention, the platinum group metal-containing materials are usually reduced in size to increase the metallurgical efficiency of the recovery processes of the present invention. Typically, the platinum group metal-containing materials are comminuted to P80 < 2 mm. Conventional crushing, grinding, and milling equipment as will be known to those skilled in the art may be used to comminute the platinum group metal-containing material.

Dissolution of platinum group metals from the platinum group metal-containing material into aqueous solution may be achieved by preparing a slurry (about 20% w/v to about 30% w/v) of the comminuted platinum group metal-containing material in the chloride leaching solution, in the presence of an oxidising agent (e.g. either sparging the slurry with a gaseous oxidising agent, such as chlorine gas, or adding a solid oxidising agent or solution of the oxidising agent to the slurry).

Dissolution of the platinum group metals is governed by the following half-reactions:

\[
\begin{align*}
Pt + 4Cl^- & \rightarrow PtCl_4^{2-} + 2e^- \\
PtCl_4^{2-} + 2Cl^- & \rightarrow PtCl_6^{3-} + 2e^- \\
Pd + 4Cl^- & \rightarrow PdCl_4^{2-} + 2e^- \\
Rh + 6Cl^- & \rightarrow RhCl_6^{3-} + 3e^- \\
Cl_2 + 2e^- & \rightarrow 2Cl^- 
\end{align*}
\]

In one embodiment of the invention the chloride leaching solution comprises about 10-20% w/w hydrochloric acid and one or more chloride salts. The purpose of the chloride
salt is to raise the activity of chloride ions in solution. Suitable chloride salts include, but are not limited to, metal chloride salts, in particular trivalent metal chlorides, such as AlCl$_3$, FeCl$_3$, CrCl$_3$, and lanthanide chloride salts. Preferably the chloride leaching solution comprises about 10-20% w/w hydrochloric acid and up to 1 M AlCl$_3$. Even more preferably the chloride leaching solution comprises about 15% w/w hydrochloric acid and about 0.33 M AlCl$_3$.

The oxidising agent may be chlorine gas, a hypochlorite salt, or a chlorite salt.

Chlorine gas may be present under atmospheric pressure or a slight over pressure of between about 1 and 2 atm.

In another embodiment, contacting the platinum group metal-containing material with the chloride leaching solution described above takes place in the presence of a slight overpressure of chlorine gas of between 1 and 2 atm.

In a preferred embodiment, the process comprises contacting the platinum group metal-containing material with about 10-20% w/w hydrochloric acid and up to 1 M AlCl$_3$ in the presence of chlorine gas at a temperature up to boiling point and for a period of up to about 120 minutes. In a preferred embodiment, the process is performed at a temperature in a range of about 55 °C to about 90 °C.

The leaching conditions of the process are relatively mild, and the leaching process may be performed at a temperature up to boiling point and for period less than 120 minutes. In a preferred embodiment, the process is performed at a temperature in a range of about 50 °C to
about 75 °C. The dissolution kinetics of Pd under these conditions is faster than the dissolution kinetics of Pt or Rh, and maximum extraction of >90% may be achieved for Pd at around five minutes reaction time.

The process described above successfully extracts >95% Pt, >95% Pd, and >90% Rh which compares well with other extraction processes which use much more rigorous conditions, for example high pressure, high temperature, and prolonged reaction times.

The resulting leachate solution containing dissolved platinum group metals may be separated from the leach residue by filtering. The solid leach residues may be washed with dilute hydrochloric acid followed by water to remove any residual leachate solution, and the washings may be subsequently combined with the leachate solution.

The leachate solution may be readily recycled for use as the chloride leaching solution, following acid make-up, in order to increase the tenor of platinum group metals in the leachate solution.

Preferably, recovery of platinum group metals from the leachate solution may be achieved by cementation, otherwise known as electroless reduction. It will be appreciated, however, the leachate solution may be subjected to conventional recovery techniques as will be known to the person skilled in the art, such as electrowinning, solvent extraction, gas-reduction or adsorption, and so forth to recover platinum group metals from the leachate solution.

The leachate solution may be subjected to cementation by contacting the leachate solution with a metal having a reduction potential lower than the potential at which
reduction of the dissolved platinum group metals in the leachate solution takes place. Illustrative examples of such metals include Al, Cu, Fe and Ti.

The preferred metal is Al as achievable recovery of platinum group metals from the leachate solution are substantially 99%, according to a reaction such as:

\[ 4\text{Al} + 3\text{PtCl}_6^{2-} \rightarrow 3\text{Pt} + 4\text{Al}^{3+} + 18\text{Cl}^- \]  

The preferable form of Al is one that has a large surface area to volume ratio, such as Al strips and foil.

Additionally, a collector may also be added to the leachate solution prior to or during cementation. The collector is selected to co-reduce with the platinum group metals and encourage agglomeration of the resulting mixed precipitate of platinum group metals.

Suitable collectors include Pb(II), Cu(II), TeO₂, Fe or Zn powder. TeO₂ conveniently selectively reacts with the platinum group metal ions and can be recycled. Fe is also useful in that any residual Fe powder can be readily separated by magnetic separation means and recycled.

Pb(II) is a particularly convenient reagent for instances where the platinum group metal-containing material is spent automotive catalyst because Pb(II) is already present in most spent automotive catalysts.

It will be appreciated that platinum group metal-containing materials from secondary sources, particularly spent automotive catalysts, may be contaminated with hydrocarbonaceous or carbonaceous materials which provide a barrier to ready dissolution of the platinum group metals therein by the chloride leaching solution.
For instance, the extraction of spent automotive catalysts using the process described above affords about 85% Pt, 94% Pd, and about 72% Rh, under conditions which result in >99% extraction of all three PGE from virgin catalysts.

The present invention additionally provides a method of treating a platinum group metal-containing material to remove said hydrocarbonaceous or carbonaceous contaminants from the platinum group metal-containing material and facilitate subsequent processing of said material to recover platinum group metals from said material.

Broadly, the method involves the steps of:

a) roasting the platinum group metal-containing material under oxidative conditions; and

b) further roasting the platinum group metal-containing material from step a) under reducing conditions.

Preferably, roasting the platinum group metal-containing material under oxidative conditions comprises heating the platinum group metal-containing material in air at 500 °C for 2 h.

Preferably, roasting the platinum group metal-containing material under reducing conditions comprises heating the platinum group metal-containing material in a gas mixture comprising about 5% H₂ and about 95% N₂ at 500 °C for 2 h.

The invention will be illustrated in greater detail with reference to the following examples.

Examples

Feed materials
Platinum group metals from virgin and spent automotive catalysts were recovered according to the processes of the present invention.

The automotive catalysts were of the monolith type, consisting of Pt, Pd and Rh, dispersed onto a layer of alumina and cerium oxide deposited over a refractory ceramic cellular honeycomb base structure, such as a silico-aluminate (e.g. cordierite).

The virgin and spent automotive catalysts were respectively crushed and milled to $P80 < 2\, \text{mm}$, mixed well and split into identical sample portions of 20 or 30 g with a sample splitter.

There were significant variations in the platinum group metal content and condition of the virgin and spent automotive catalysts. The platinum group metal composition of virgin and spent catalyst is shown in Tables 1 and 2, respectively.

**Table 1. Platinum group metal composition of virgin catalysts**

<table>
<thead>
<tr>
<th>Virgin No</th>
<th>Pt</th>
<th>Pd</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/t</td>
<td>g/t</td>
<td>g/t</td>
</tr>
<tr>
<td>1</td>
<td>240.0</td>
<td>96.1</td>
<td>63.6</td>
</tr>
<tr>
<td>2</td>
<td>267.0</td>
<td>--</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>177.0</td>
<td>59.0</td>
<td>46.4</td>
</tr>
<tr>
<td>4</td>
<td>156.0</td>
<td>43.0</td>
<td>38.4</td>
</tr>
<tr>
<td>5</td>
<td>175.0</td>
<td>64.0</td>
<td>38.0</td>
</tr>
<tr>
<td>6</td>
<td>214.0</td>
<td>925.0</td>
<td>107.0</td>
</tr>
<tr>
<td>7</td>
<td>230.0</td>
<td>75.0</td>
<td>45.0</td>
</tr>
<tr>
<td>8</td>
<td>314.0</td>
<td>949.0</td>
<td>42.1</td>
</tr>
<tr>
<td>9</td>
<td>270.0</td>
<td>85.0</td>
<td>64.0</td>
</tr>
<tr>
<td>10</td>
<td>201.0</td>
<td>639.0</td>
<td>48.0</td>
</tr>
</tbody>
</table>
Pre-treatment

Some samples of the spent automotive catalysts were subjected to a pre-treatment to remove hydrocarbonaceous and carbonaceous residues therefrom. The pre-treatment of spent automotive catalysts involved oxidative roasting followed by reductive roasting.

The oxidative roasting of crushed spent catalysts was conducted at a temperature of 500 °C in air for 2 h, followed by reductive roasting at the same temperature in a gas mixture containing 5% H₂ and 95% N₂, for a further 2 h.

Leaching

Table 2. Platinum group metal composition of spent catalysts

<table>
<thead>
<tr>
<th>Used No.</th>
<th>Pt</th>
<th>Pd</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/ft</td>
<td>g/ft</td>
<td>g/ft</td>
</tr>
<tr>
<td>1</td>
<td>342.4</td>
<td>1241.0</td>
<td>38.7</td>
</tr>
<tr>
<td>2</td>
<td>292.0</td>
<td>1070.0</td>
<td>90.4</td>
</tr>
<tr>
<td>3</td>
<td>1050.0</td>
<td>0.5</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>1275.0</td>
<td>0.3</td>
<td>119.0</td>
</tr>
<tr>
<td>5</td>
<td>224.0</td>
<td>712.0</td>
<td>49.5</td>
</tr>
<tr>
<td>6</td>
<td>434.3</td>
<td>31.7</td>
<td>70.9</td>
</tr>
<tr>
<td>7</td>
<td>339.5</td>
<td>3.5</td>
<td>56.3</td>
</tr>
<tr>
<td>8</td>
<td>10.2</td>
<td>1.0</td>
<td>2.1</td>
</tr>
<tr>
<td>9</td>
<td>57.7</td>
<td>6.3</td>
<td>12.9</td>
</tr>
<tr>
<td>10</td>
<td>338.0</td>
<td>1.8</td>
<td>38.0</td>
</tr>
<tr>
<td>11</td>
<td>598.0</td>
<td>2290.0</td>
<td>87.0</td>
</tr>
<tr>
<td>12</td>
<td>165.0</td>
<td>666.0</td>
<td>33.3</td>
</tr>
<tr>
<td>13</td>
<td>149.0</td>
<td>465.0</td>
<td>44.5</td>
</tr>
<tr>
<td>14</td>
<td>600.0</td>
<td>6.0</td>
<td>42.0</td>
</tr>
<tr>
<td>15</td>
<td>850.5</td>
<td>51.3</td>
<td>93.4</td>
</tr>
<tr>
<td>16</td>
<td>85.0</td>
<td>10.1</td>
<td>26.1</td>
</tr>
</tbody>
</table>
Platinum group metals from several samples of virgin catalyst, spent catalyst, and pre-treated spent catalyst were then extracted by stirring 30 g samples of said catalysts with 300 mL of 5-20% w/w HCl and 0.33 M AlCl₃ solution in the presence of chlorine gas at 70-90 °C for 5-90 minutes in a batch stirred reactor (BSR).

The solid leach residues are then removed by filtration and stirred with 300 mL of an acid wash solution (5-20% w/w HCl) at 70-90 °C for 5-60 minutes in the batch stirred reactor, followed by a second filtration. The solid residues are then stirred again with 300 mL of deionised water at 70-90 °C for 5-30 minutes in the batch stirred reactor, followed by a third filtration.

The results of these tests under varying conditions are shown in Table 3.

The test with untreated feed confirmed earlier observations regarding the positive effect of the pre-treatment process of the present invention.
Tests for recovery of platinum group metals from pregnant leach liquor resulting from the above processes were conducted using a leachate solution which contained 77.8 mg/L Pt, 5.74 mg/L Pd and 10.7 mg/L Rh, and a leachate solution which contained 72.7 mg/L Pt, 6.33 mg/L Pd and 8.62 mg/L Rh. The test conditions are provided in Table 4.
The extent of precipitation was calculated based on the composition of the feed and final solutions assuming that no volume change occurred during the treatment.

The recovery of PGE by addition of aluminium metal into the leach solution was expected to take place as a result of reduction to the metallic form either on the surface of the aluminium metal or as powder in the solution (i.e. cementation). The initial test was conducted by placing some aluminium foil inside a beaker containing 25 mL of the leach solution at room temperature. This resulted in complete recovery of all three PGE from the leach solution, with partial dissolution of aluminium foil.

A further series of tests were conducted in order to establish the optimum conditions for aluminium reduction. The source of Al (rod or foil), the amount of Al, the reduction kinetics, the effect of initial temperature and the effect of agitation were evaluated in this series as shown in Table 4.

The results are illustrated in Figure 2.

Clearly better results were achieved by the use of Al foil (T1) as compared with Al rod (T2) as could be expected from the higher surface area of the former. The results show that the recovery of the PGE increases with the amount of Al added to the leach solution up to about 5% w/w but a decrease is observed at higher amounts. The viscosity of the solution following addition of 7% w/v Al to the leach liquor was also significantly increased which resulted in very slow filtration. Moreover, it was
observed that at the higher additions of Al, significant amounts of fine precipitated solids passed through the filtration medium (glass-fibre filter paper) and reported to the filtrate. This explains the lower apparent recoveries in tests T7 and T6.

Table 4. Experimental conditions for aluminium reduction tests

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Added Al</th>
<th>Vol of liquor</th>
<th>L/S ratio</th>
<th>Res. time</th>
<th>Start temp.</th>
<th>Liquor Stir level</th>
<th>Lead acetate</th>
<th>Filtration paper</th>
<th>Concentration after treatment</th>
<th>Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g</td>
<td>ml</td>
<td>%wv</td>
<td>min</td>
<td>°C</td>
<td></td>
<td></td>
<td></td>
<td>Pt (%)</td>
<td>Pg (%)</td>
</tr>
<tr>
<td>T1</td>
<td>1.05</td>
<td>50</td>
<td>3.7</td>
<td>2</td>
<td>20</td>
<td>62 hand stir none</td>
<td>GxF1</td>
<td></td>
<td>7.140 0.845 1.260</td>
<td>90.82 85.78 68.22</td>
</tr>
<tr>
<td>T2</td>
<td>1.05</td>
<td>50</td>
<td>3.7</td>
<td>2</td>
<td>20</td>
<td>62 hand stir none</td>
<td>GxF1</td>
<td></td>
<td>32.00 0.970 5.990</td>
<td>56.87 83.10 44.02</td>
</tr>
<tr>
<td>T3</td>
<td>0.12</td>
<td>10</td>
<td>1.0</td>
<td>2</td>
<td>20</td>
<td>62 hand stir none</td>
<td>GxF1</td>
<td></td>
<td>55.300 2.230 6.710</td>
<td>29.92 61.15 37.29</td>
</tr>
<tr>
<td>T4</td>
<td>0.1</td>
<td>10</td>
<td>1.0</td>
<td>2</td>
<td>20</td>
<td>62 hand stir none</td>
<td>GxF1</td>
<td></td>
<td>69.800 3.810 8.680</td>
<td>10.26 33.62 18.86</td>
</tr>
<tr>
<td>T5</td>
<td>0.3</td>
<td>10</td>
<td>3.0</td>
<td>2</td>
<td>20</td>
<td>62 hand stir none</td>
<td>GxF1</td>
<td></td>
<td>24.200 4.650 1.950</td>
<td>68.89 91.90 61.76</td>
</tr>
<tr>
<td>T6</td>
<td>0.5</td>
<td>10</td>
<td>5.0</td>
<td>2</td>
<td>20</td>
<td>62 hand stir none</td>
<td>GxF1</td>
<td></td>
<td>7.720 1.170 6.100</td>
<td>90.06 79.62 63.06</td>
</tr>
<tr>
<td>T7</td>
<td>0.5</td>
<td>10</td>
<td>5.0</td>
<td>2</td>
<td>20</td>
<td>62 hand stir none</td>
<td>GxF1</td>
<td></td>
<td>4.240 0.825 1.010</td>
<td>94.55 85.63 90.96</td>
</tr>
<tr>
<td>T8</td>
<td>0.7</td>
<td>10</td>
<td>7.0</td>
<td>2</td>
<td>30</td>
<td>62 hand stir none</td>
<td>GxF1</td>
<td></td>
<td>16.600 1.420 3.060</td>
<td>79.66 75.26 71.40</td>
</tr>
<tr>
<td>T9</td>
<td>0.5</td>
<td>10</td>
<td>5.0</td>
<td>2</td>
<td>20</td>
<td>62 hand stir none</td>
<td>GxF1</td>
<td></td>
<td>1.930 0.455 0.670</td>
<td>97.52 92.07 93.74</td>
</tr>
<tr>
<td>T10</td>
<td>0.5</td>
<td>10</td>
<td>5.0</td>
<td>4</td>
<td>20</td>
<td>62 hand stir none</td>
<td>GxF2</td>
<td></td>
<td>1.260 0.305 0.365</td>
<td>98.35 94.69 96.59</td>
</tr>
<tr>
<td>T11</td>
<td>0.5</td>
<td>10</td>
<td>5.0</td>
<td>6</td>
<td>20</td>
<td>62 hand stir none</td>
<td>GxF2</td>
<td></td>
<td>1.980 0.385 0.490</td>
<td>97.46 93.29 96.42</td>
</tr>
<tr>
<td>T12</td>
<td>0.5</td>
<td>10</td>
<td>5.0</td>
<td>6</td>
<td>20</td>
<td>62 hand stir none</td>
<td>GxF2</td>
<td></td>
<td>0.870 0.310 0.275</td>
<td>98.88 94.60 97.43</td>
</tr>
<tr>
<td>T13</td>
<td>0.5</td>
<td>10</td>
<td>5.0</td>
<td>2</td>
<td>25</td>
<td>74 level 8 0.1 M+GxF2</td>
<td>0.020 0.020 0.033</td>
<td>99.97 99.21 99.57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T14</td>
<td>0.5</td>
<td>10</td>
<td>5.0</td>
<td>2</td>
<td>35</td>
<td>74 level 5 0.1 M+GxF2</td>
<td>0.254 0.070 0.026</td>
<td>98.95 98.89 99.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T15</td>
<td>0.5</td>
<td>10</td>
<td>5.0</td>
<td>2</td>
<td>45</td>
<td>74 level 5 0.1 M+GxF2</td>
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It was possible to improve the solid liquid separation somewhat by the use of double layer filter paper as shown by the results for tests T9 to T12. Further improvement was achieved by the addition of lead acetate to the feed solution and the use Millipore glass plus double glass fibre paper. Lead acetate is reported in the literature to act as a collector for PGE and increases the particle size of the precipitated PGE solids. In this way it was possible to increase the recovery of all three PGE to better than 99%.
It was also observed that the reduction of the PGE by Al is rapid and there is no benefit in increasing the contact time beyond 2 minutes (see T9 to T12).

The starting temperature, in the range 20 to 55 °C, had no effect on the extent of precipitation which is not surprising considering the rapid heating that occurs upon addition of the Al foil to the solutions. The temperature was monitored in test T14 and showed a rapid increase from 35 °C to about 101 °C, followed by cooling to about 65 °C after a few minutes. The heating is accompanied by vigorous frothing of the solution due to vigorous hydrogen evolution which provides sufficient agitation.

Based on these results, optimal conditions for precipitation involves addition of lead acetate to the solution at room temperature with the addition of Al foil (5% w/v) for a period of 2 minutes, followed by filtration of the slurry using a fine filtration medium (porosity 45 μm or lower).
CLAIMS:

1. A process for extracting platinum group metals from a platinum group metal-containing material comprising contacting the platinum group metal-containing material with a chloride leaching solution in the presence of an oxidising agent to produce a leachate solution containing the platinum group metals.

2. A process for extracting platinum group metals from a secondary source platinum group metal-containing material comprising contacting the secondary source platinum group metal-containing material with a chloride leaching solution in the presence of an oxidising agent to produce a leachate solution containing the platinum group metals.

3. The process according to claim 1 or claim 2, wherein the chloride leaching solution comprises about 10 - 20 w/w% hydrochloric acid and one or more chloride salts.

4. The process according to claim 3, wherein the one or more chloride salts is a trivalent metal chloride.

5. The process according to claim 4, wherein the trivalent metal chloride is selected from a group comprising AlCl₃, FeCl₃, CrCl₃, or lanthanide chloride salts.

6. The process according to claim 5, wherein the chloride leaching solution comprises about 10-20 w/w% hydrochloric acid and up to 1M AlCl₃.

7. The process according to claim 6, wherein the chloride leaching solution comprises about 15 w/w% hydrochloric acid and about 0.33M AlCl₃.
8. The process according to any one of the preceding claims, wherein the oxidising agent comprises chlorine gas, a hypochlorite salt, or a chlorite salt.

9. The process according to claim 8, wherein contacting said platinum group metal-containing material with the chloride leaching solution takes place in the presence of an overpressure of chlorine gas.

10. The process according to claim 9, wherein the overpressure of chlorine gas is about 1 atm to about 2 atm.

11. The process according to any one of the preceding claims, wherein the process comprises contacting said platinum group metal-containing material with a chloride leaching solution in the presence of an oxidising agent at a temperature up to boiling point.

12. The process according to claim 11, wherein the process is performed at a temperature in a range of about 55 °C to about 90 °C.

13. The process according to any one of the preceding claims, wherein the process comprises contacting said platinum group metal-containing material with a chloride leaching solution in the presence of an oxidising agent for a period up to about 120 minutes.

14. The process according to any one of the preceding claims wherein the leachate solution may be recycled for use as the chloride leaching solution.

15. The process according to any one of the preceding claims further comprising processing the leachate solution to recover platinum group metals.
16. The process according to claim 15, wherein processing the leachate solutions to recover platinum group metals comprises subjecting the leachate solution to electrowinning, cementation, solvent extraction, gas-reduction or adsorption to recover platinum group metals from the leachate solution.

17. The process according to claim 16, wherein subjecting the leachate solution to cementation comprises contacting the leachate solution with a metal having a reduction potential lower than the potential at which reduction of the dissolved platinum groups metals in the leachate solution takes place.

18. The process according to claim 17, wherein said metal for cementation comprises Al, Ti, or Fe.

19. The process according to claim 17 or claim 18, wherein subjecting the leachate solution to cementation further comprises adding a collector to the leachate solution prior to or during cementation.

20. The process according to claim 19, wherein the collector comprises Pb(II), Cu(II), TeO₂, Fe powder or Zn powder.

21. The process according to any one of the preceding claims, wherein prior to contacting said platinum group metal-containing material with a chloride leaching solution, the process comprises roasting the platinum group metal-containing material under oxidative conditions, and subsequently roasting the platinum group metal-containing material under reducing conditions.

22. The process according to claim 21, wherein roasting said platinum group metal-containing material under
oxidative conditions comprises heating the platinum group metal-containing material in air at 500 °C.

23. The process according to claim 21 or claim 22, wherein subsequently roasting said platinum group metal-containing material under reducing conditions comprises heating said platinum group metal-containing material in a gas mixture comprising about 5% H₂ and about 95% N₂ at 500 °C.

24. A process for recovering platinum group metals from a platinum group metal-containing material comprising processing a leachate solution produced from a process according to any one of the preceding claims to recover platinum group metals from the leachate solution.

25. A method of recovering a platinum group metal from a spent automotive catalyst comprising the steps of:

a) roasting the spent automotive catalyst under oxidative conditions;

b) further roasting the roasted spent automotive catalyst from step a) under reducing conditions;

c) contacting the roasted spent automotive catalyst from step b) with a chloride leaching solution in the presence of an oxidising agent to produce a leachate solution containing platinum group metals; and

d) processing the leachate solution to recover the platinum group metals.
Figure 1. Leaching with 15% HCl and Cl₂ gas at 90°C for 5 minutes

Figure 2. PGE recovery by reduction with Al
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.  
C22B 3/10 (2006.0) C22B 11/00 (2006.0)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WIPO, EPDOC: C22B 3/00, C22B 3/04, C22B 3/06/-, C22B 7/00/-, C03B 7/00, B01 J3 38/48, C22B 3/20, C22B 3/22/-, C22B 3/26, C22B 3/44/-, C22B 1/02/- & Keywords (PLATINUM, GROUP, NOBLE, PGM, PT, PD, RH, RE, OS, IR, TC, RU, ORE, CATALYST, WASTE, LEACH, CHLORIDE, OXIDISING) and like terms

ESPACENET, USPTO, GOOGLE PATENTS & Keywords (EXTRACTION, CHLORIDE, LEACH, SOLUTION, OXIDIZING, PLATINUM, GROUP, LEACHATE, RECOVERY, PGM) and like terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C

Date of the actual completion of the international search 27 June 2011

Date of mailing of the international search report 04 JUL 2011

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Form PCT/ISA/2 10 (second sheet) (July 2009)
This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX