DETERMINATION OF LEACHING PARAMETERS FOR THE RECOVERY OF PLATINUM GROUP METALS FROM SECONDARY MATERIALS

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Abstract: The leaching parameters for the recovery of platinum group metals were investigated with potentiostatic measurements using wire electrodes. The dissolution rates of Pt, Pd and Rh were measured in concentrated NaCl solution. The parameters inspected were the temperature, redox potential and chloride content. Measurements were done at temperatures 25–94 °C using four different NaCl concentrations, 62.5–250 g/l. Measurements were done at potentials of 950–1250 mV vs. SCE for Pt and Rh and 380–470 mV vs. SCE for Pd. Although higher temperature, potential and chloride content generally increased the dissolution rate, the effect was found to be nonlinear and slightly different for different metals. Based on the results, strongly oxidizing conditions are needed for the leaching process in order to achieve reasonable dissolution rates.

Keywords: platinum dissolution, palladium dissolution, rhodium dissolution, chloride concentration

Introduction

Platinum group metals (PGMs) are exploited for many purposes. They are nearly irreplaceable in catalysing reactions. Catalytic converters used for exhaust gas cleaning are one of the most important applications of PGMs. As the requirements for emission levels have become tighter, the demand for the metals has increased. The regulations requiring exhaust gas cleaning have become more stringent in the developing countries, which probably will lead to an even further increase in demand. At the same time, the supply and the number of suppliers of primary PGMs is very low in comparison with many other metals. The main producers are located in South Africa and Russia, which has meant that high amounts of these metals have had to be imported to Europe. The life cycle of the products where PGMs are used is usually relatively short. Therefore an increasing amount of the PGMs is in the scrapped e-waste, catalytic converters etc. The utilization of these secondary sources appears very
attractive, as the concentration of PGMs in secondary material can be in the range of g/kg of scrap material while the concentration in the ores is less than 10 g/Mg (Cawthorn, 1999; Faisal et al., 2008).

The recovery of PGMs from the secondary material has been attempted by several different methods (Marinho et al., 2010), including for example dissolving them in strong acids (Harjanto et al., 2006; Jimenez de Aberasturi et al., 2011), metal vapour treatment (Kayanuma et al., 2004) and carbochlorination (Kim et al., 2000). The hydrometallurgical treatment has appeared to be the most economical alternative. The valuable elements are leached using proper solvent and then recovered from the solution. It has been claimed that aqueous chloride solutions are the only cost-effective medium in which all the PGM can be brought into solution and concentrated (Cleare et al., 1979; Grant, 1989). In general the dissolution of PGM is based on high oxidation potential and effective complexing ions in the solution (Mahmoud, 2003). Some authors have proposed the use of HCl with an oxidant, which appears to be a functioning alternative (Barakat et al., 2006; Harjanto et al., 2006).

The low PGM concentrations become an issue if the whole matrix of the catalytic converter is fed into the leaching process. An attempt to separate the phase containing the PGM particles has been proposed by Liu et al. (2012). They have shown that the PGMs can be separated from the matrix by heating and quenching the catalysts. The separation of extracted PGMs has been attempted by several methods, including solvent extraction (Lee et al., 2010), ion exchange (Shen et al., 2010a; Shen et al., 2010b), chromatographic separation methods (Kokate and Kuchekar, 2010) and molecular recognition methods (Izatt et al., 2012).

The objective of this study was to determine the suitable parameters for preliminary laboratory-scale leaching experiments to recover PGMs from catalytic converter scrap. The parameters considered were the influence of temperature, redox potential and chloride concentration. Metals studied in this research were platinum, palladium and rhodium. The leaching process is planned to work under atmospheric pressure using NaCl solutions. The dissolution behavior of PGMs has to be precisely known in order to determine suitable oxidizing agents and optimal conditions. The dissolution rates were measured using potentiostatic measurements.

Materials and Methods

Measurements were conducted using wire electrodes fabricated by mounting the metal wire in glass tubes with epoxy so that only the tip of the wire reacted in the measurements. Wire electrodes were fabricated from platinum (Alfa Aesar Standard grade thermocouple), palladium (Alfa Aesar 99.99%) and rhodium (Alfa Aesar 99.8%). Approximately 20 mm of metal wire was soldered to a copper wire. The diameter of rhodium wire was 0.25 mm while the diameter of palladium was 0.5 mm and platinum 0.508 mm.
Electrochemical measurements were conducted in a three-electrode cell, where a Luggin capillary and solution bridge connected the cell to the reference electrode. The reference electrode used in the experiments was saturated calomel electrode (SCE), type Radiometer REF 401, which was separated from test solution by a KCl salt bridge. The counter electrode used in the experiments was platinum wire.

Measurements were conducted at five different temperatures: 25, 40, 60, 80 and 94 °C. The test solutions used were 62.5, 90, 125 and 250 g/l NaCl solutions. Solutions were prepared from distilled water. The volume of the solution in the measurements was 175 ml. The solution was stirred with a magnetic stirrer using a stirring rate of about 500 rpm before the experiments and about 350 rpm during the experiments. The relatively high stirring rate during the experiments was used in order to prevent the bubbles from adhering to the surface of the working electrode. Experiments were conducted in oxygen-free environment. Before the beginning of each measurement oxygen (air) in the cell was removed by using nitrogen purging (purity >99.99%). Purging was conducted through a sintered disk with a constant flow rate one hour before and during the experiments. Nitrogen flow was reduced during the experiments to prevent the bubbles from affecting the results.

Polarization curve measurements were conducted from –50 to 750 mV vs. rest potential for Pd and –50 to 1500 mV for Pt and Rh. Sweep rate was 50 mV/min. The potentiostatic measurements were conducted at potentials of 380, 410, 440 and 470 mV vs. SCE for Pd and at 950, 1050, 1150 and 1250 mV vs. SCE for Pt and Rh. The current density was measured as a function of time in potentiostatic measurements. The initial current density of the dissolution reaction was determined by extrapolating the current density determined during the first few seconds of the measurement back to the start of the experiment. As the dissolution starts, reaction products are formed and the current density changes as a function of time.

### Results and Discussion

At first, a series of potentiodynamic polarization curve measurements were conducted to understand the overall dissolution behavior of the metals. Based on the curves (example shown in Fig. 1), the dissolution rate of Pt and Rh is significantly higher when they are polarized to over 1000 mV vs. SCE, and Pd when it is polarized to over 400 mV vs. SCE. The current density was found to increase rapidly when these potentials are exceeded.

Based on the potentiostatic measurement series, higher temperature, potential and chloride content generally increased the dissolution rate although the effect was nonlinear and slightly different for different metals. Fig. 2 shows the dissolution rates of palladium at 470mV vs. SCE as a function of temperature and chloride content. At potential of 1250 mV vs. SCE and with the highest chloride content, the dissolution rate of Pt can exceed 1000 µm/h, and Rh 100 µm/h. However, these potentials are so high that some of the measured current density might be caused by the gas evolution
reactions. At the highest tested potential for palladium, 470 mV vs. SCE, a dissolution rate of over 700 µm/h was reached.

Fig. 1. Polarization curves of platinum, palladium and rhodium measured in 250 g/l NaCl solution at 25 °C.

**The effect of temperature**

Fig. 2. Dissolution rate of palladium (470 mV vs. SCE) as a function of temperature and chloride content.
The temperature was found to increase the dissolution rate significantly. The effect was found to be different for different metals. The effect was exponential with the measured potentials, as shown in Fig. 3. Therefore the use of temperatures near the water boiling point seems reasonable for the leaching process. However, the effect might be different when an oxidant is used as some of the oxidants degrade at high temperatures.

![Fig. 3. Temperature dependence of dissolution rates](image)

**The effect of redox potential**

The effect of redox potential on the dissolution rate appeared to be exponential with the measured potentials, as shown in Fig. 4. The Tafel coefficient for Pd dissolution was 52 mV/decade, which indicates dissolution with a two-electron mechanism. The Tafel coefficient for Pt dissolution was 123 mV/decade, which is in accordance with the one-electron dissolution mechanism. For Rh the value was 284 mV/decade, which cannot be explained by a pure charge transfer. The high value can be explained by the formation of an oxide layer, but this could not be verified. The Rh dissolution reaction follows most likely more complicated reaction mechanism than Pt and Pd. Llopis (1965) has proposed the dissolution to follow a multistep mechanism, where halide ions are first specifically adsorbed on the surface and then dissolved in the second step.

The potential range where the dissolution of Pd starts is relatively low and, hence, there are a variety of possible oxidizers to be used in the actual leaching process. For the leaching of platinum and rhodium the choice of an oxidizer is much more critical, as relatively high potential is needed for economic operation. Barakat et al. (2006)
have proposed the use of hydrogen peroxide as an oxidant, which appears to be a suitable alternative. The effect of different oxidants has to be further experimented in order to define the best alternative.

![Graph showing the effect of redox potential on the dissolution rates](image)

**Fig. 4.** The effect of redox potential on the dissolution rates

**The effect of chloride content**

The chloride content increased the dissolution rate relatively linearly, as can be seen from Fig. 5. The higher concentration provided much higher dissolution rates. The optimum concentration for a leaching process appears to be near the NaCl solubility limit.

The reaction order of the dissolution reaction with respect to chloride ion can be calculated from equation 1:

\[
n = \frac{\log(rate)}{\log([\text{Cl}^-])}
\]  

where \( n \) is reaction order, \([\text{Cl}^-]\) is chloride concentration and \( rate \) is the determined dissolution rate.
In Fig. 6 are shown the logarithms of dissolution rate of Pt, Pd and Rh as a function of the logarithm of chloride concentration. Based on the results, two chloride ions take part in the dissolution reaction of one platinum or palladium atom. This is in accordance with the dissolution mechanism proposed by Llopis (1969), who proposed that PdCl$_2^-$ is formed in the primary process and it subsequently reacts with water. Pd and Pt are usually present in the +2 or +4 oxidation states (Cotton, 1997). Unlike Pt and Pd, Rh is usually present in the +3 oxidation state (Benguerel et al., 1996; Cotton, 1997). The results support the mechanism of three chloride ions taking part in the dissolution reaction of Rh. All of the metals are also known to form hexachloro-complexes MeCl$_6^{2-}$ (Cotton, 1997).

**Activation energy**

The mechanism limiting the reaction rate can be defined by determining the activation energies. These were defined using the Arrhenius law. The activation energies determined from the potentiostatic measurements using steady state current densities are shown in Table 1. Activation energies showed no change with respect to chloride content or potential in the potential range of rapid dissolution. Based on the activation energies shown, it is very likely that the reaction rates are controlled by charge transfer (Peters, 1973). Llopis (1969) has given a value of 84 kJ/mol for the activation energy of Pt in HCl solution. Similarly Baghalha et al. (2009) determined the activation energy of dissolution of Pt in aqua regia to be 72.1 kJ/mol. Although both having a higher value, this also indicates the reaction to be controlled by the electron transfer step.
Fig. 6. Logarithm of dissolution rate (Pt 94°C 1150 mV, Pd 94°C 470 mV and Rh 25°C 1250 mV vs. SCE) vs. logarithm of chloride concentration.

Table 1. Activation energies determined at the potential range of rapid dissolution with all measured chloride concentrations.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Activation energy [kJ]</th>
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<tbody>
<tr>
<td>Platinum</td>
<td>59 ± 1</td>
</tr>
<tr>
<td>Palladium</td>
<td>68 ± 1</td>
</tr>
<tr>
<td>Rhodium</td>
<td>61 ± 1</td>
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</tbody>
</table>

**Conclusions**

The results show that strongly oxidizing conditions are needed to achieve reasonable leaching rates of Pt, Pd and Rh in NaCl solutions. The dissolution of Pt and Rh can be assumed to take place at high potential where chlorine and/or oxygen evolution can also occur during the electrochemical testing. Pd dissolves at lower potential than these gas evolution reactions. Pd could be dissolved using chlorine or hydrogen peroxide as an oxidant. A suitable concentration of hydrogen peroxide could provide necessary redox potential also for the leaching of Pt and Rh. The choice of the optimum oxidant requires testing of redox-potential of different possible alternatives before the actual leaching experiments.

The results showed that higher chloride concentration increased the dissolution rate significantly, and therefore highly concentrated chloride solutions should be used in the leaching process. The chloride concentration should be optimized near the NaCl
solubility limit when establishing the leaching process. Increasing temperature increased the dissolution rates. The higher temperature naturally increases the energy cost, so the most economic conditions have to be defined for the actual leaching process. The optimum leaching conditions might also depend on the oxidant used, as some of the oxidants degrade at high temperatures.

According to determined activation energies and similar studies found in the literature, it is suggested that the dissolution processes of the examined platinum group metals in chloride solutions are controlled by the electron transfer step.

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References


