SIMULTANEOUS RECOVERY OF VALUABLE METALS FROM AUTOMOTIVE CATALYSTS THROUGH HYDROMETALLURGICAL PROCESSING

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ABSTRACT

The continued increase of the automobile production leads to a higher platinum, palladium and rhodium (PGM) demand. Due to the high value of the PGMs the recycle of these metals from automotive catalysts is of special interest. Pyrometallurgical processes, which are only focused on the PGMs, represent the state of the art of automotive catalysts recovery. However, hydrometallurgical recycling processes offer additional recovery of other valuable metals and compounds. The method presented in this paper is based on a combination of hydrochloric acid and hydrogen peroxide to dissolve the valuable metal fraction which can be precipitated afterwards.

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INTRODUCTION

Platinum and the corresponding metals from the PGM group, especially palladium and rhodium are well known as catalytic active materials. They support chemical reactions which are inhibited. This effect is used to decrease the amount of harmful compounds like hydrocarbons, carbon monoxide or nitrogen oxides in automotive exhaust gases. The generation of these toxic substances is based on incomplete combustion, which in turn is caused by non-ideal conditions in the combustion chamber. Catalytic converters minimize the harmful compounds by supporting the following Reactions 1 – 3 (Votsmeier et al., 2009).

$$CO + \frac{1}{2} O_2 \rightarrow CO_2 \quad (1)$$

$$C_nH_m + (n + \frac{1}{4} m) O_2 \rightarrow n\, CO_2 + \frac{1}{2} m\, H_2O \quad (2)$$

$$2\, NO + 2\, CO \rightarrow N_2 + 2\, CO_2 \quad (3)$$

Platinum and palladium are very effective for the oxidation (Reactions 1 and 2), while rhodium supports the decomposition of nitrogen oxides by carbon monoxide (Votsmeier et al., 2009). The classical three way catalyst was a platinum – rhodium combination with a Pt:Rh ratio of 5:1 (Hagelüken et al., 2005). Today the platinum, palladium and rhodium ratio is highly variable and strongly depends on the engine type as well as on the car producer. Diesel engines are operated with a super stoichiometric air addition in comparison to spark ignition systems. Therefore the exhaust gas composition and off gas temperature is different. Based on the high oxygen amount, diesel engines produce less carbon monoxide and hydrocarbons but more nitrogen oxide in contrast to gasoline engines. This leads to various requirements for the catalytic converters.

In the most countries worldwide the emissions of automotive combustion engines are regulated by law. In Europe, this regulation has reached the fifth stage (EURO V) which allows the emission of 1,000 mg/km of CO, 100 mg/km of hydrocarbons and 60 mg/km of nitrogen oxides. To fulfill these requirements every new car has to be equipped with a catalytic converter. Therefore the automotive catalyst represents the major application for platinum, palladium and rhodium. Figure 1 shows the current data of the PGM-demand and overall consumption of these metals for 2011.

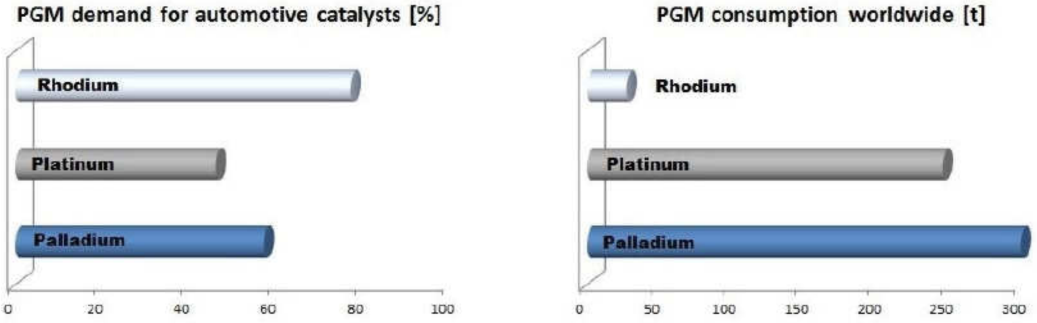


Figure 1 – PGM statistical data 2010 (Loferski, 2011)

Nearly 77 % of rhodium, 57 % of palladium and 46 % of platinum production is used for the automotive catalyst industry (Loferski, 2011). It can be seen that the quantitatively main elements for the car catalysis are palladium and platinum. As these two metals support the same catalytically reactions, a substitution between them is possible. Palladium offers better thermal stability and lower price in contrast to platinum. On the other hand, the sulphur in fuels leads to a deactivation of palladium catalysts. Platinum shows a better resistance against this kind of poisoning. The lower sulphur contents in fuels since the early nineties led to a sharp increase of the palladium consumption (Hagelüken, 2008).

The concentration of the platinum group metals in the earth crust is really low and consequently, the price of these metals is quite high. Furthermore they are used for financial investments and speculative trading, which is an additional reason for their high cost. These reasons lead to an unstable market price which causes difficulties in managing PGM sources. Beside the rarity of platinum group metals, the geographical location of resources is located only in some specific areas of the earth. South Africa represents the main platinum supplier with a production volume of 77 % of the global demand. In case of palladium, the most important producers are Russia (42 %) and South Africa (41 %) (Loferski, 2011; van Gelder and Kammeraat, 2008). The principal consumers North America, Europe and China cannot supply their own demands. Therefore the recycling of PGM containing materials is of particular interest for these countries. Figure 2 shows the demand and supply of these metals by country.

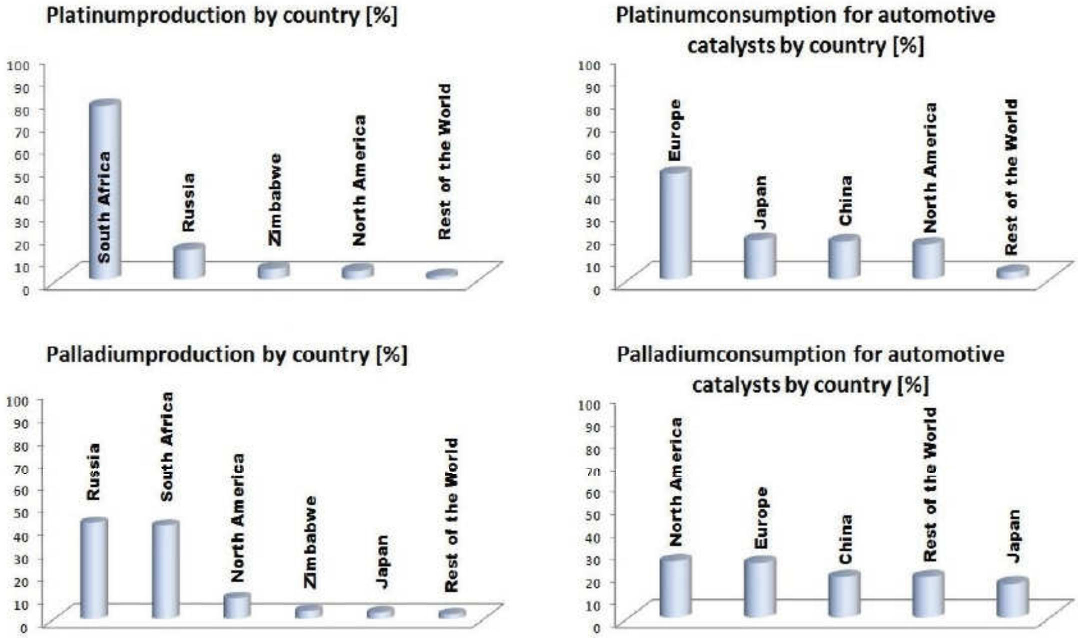


Figure 2 – Consumption and production of palladium and platinum (Loferski, 2011)

It can be seen, that the European car manufacturers prefer platinum as catalytically active component, while in the rest of the world palladium represents the main element for automotive off-gas catalysis. Furthermore the geographical imbalance in production and consumption is shown. Only North America is able to supply a significant amount of their PGM-demand.

The increasing demand in the automotive industry and the limited lifetime of the catalytic converters make the efficient PGM recycling a key goal for this industry. It is estimated that the platinum group metal content of the existing vehicles worldwide is approximately 2,300 tons (Hagelüken, 2008). This value corresponds to the 6-fold value of the global primary production of PGMs. Therefore increase in car production in the industrialized nations goes hand in hand with enrichment of precious metal secondary sources.

The above mentioned facts highlight the importance of PGM recycling, especially for the industrialized countries. According to Hagelüken (2008) and Benson (2000) the current recycling technologies exhibit recycling rates of more than 95%. The state of the art process is the melting of the whole catalytic material and collecting the precious metal fraction in a copper bath. By further refining steps the pure platinum group metals can be recovered. Beside the pyrometallurgical process several hydrometallurgical methods are also available. The aim is to separate the valuable fraction by leaching.

Previously, these recycling technologies were rarely used, but especially new materials in modern catalysts can lead to a regain in importance. One of these elements is cerium, which is not as expensive as platinum group metals, but due to its relatively high concentration the recycling of this compound could be interesting. Therefore this work presents a hydrometallurgical method to recover the valuable metals from spent automotive catalyst simultaneously, with a special focus on high PGM yields.

CHARACTERIZATION OF AUTOMOTIVE CATALYSTS

Most of cars use typical three way catalyst to decrease the harmful exhaust gas compounds. The main component is the so called honeycomb substrate, which is covered with the PGM containing washcoat. A wire mesh packing in combination with the steel shell protects the catalyst against external damage. Figure 3 shows the principle design of an automotive catalytic converter.

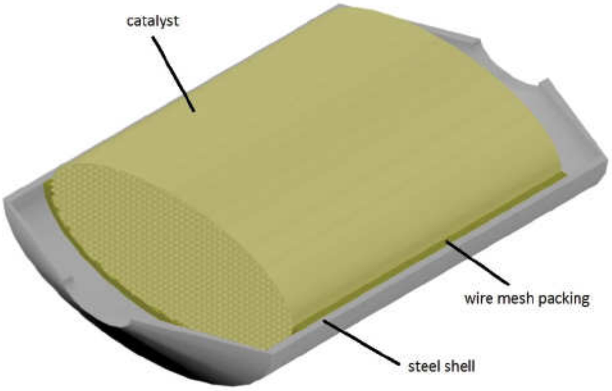
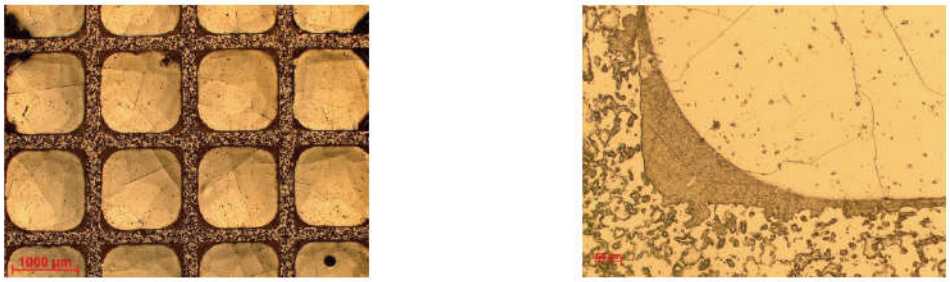


Figure 3 – Design of an automotive catalytic converter

The geometry of the catalyst can vary widely and depends on the vehicle manufacturer. The most common designs have a circular or elliptical cross section. For the recycling the steel shell and the wire mesh packing are removed and recycled separately. Finally only the ceramic monolith remains for the recovery process. According to South Africa (2012) the average PGM content of a catalytic converter is around 4 – 5 g, but this value strongly depends on the car type. The typical amount ranges from 1 g for microcars up to 15 g for heavy and powerful vehicles. Therefore spent automotive catalysts represent a quite valuable PGM source. For the extraction of one gram from primary sources, 350 – 900 kg of ore has to be handled (South Africa, 2012). In contrast the recycling of catalytic converters processes only 1 – 3 kg of ceramic material to recover one gram of platinum group metal.

The catalytically active substances are embedded in the washcoat. This material is made of aluminium oxide which meets the requirements of heat resistance and high specific surface. Typical surface areas for alumina carriers are according to Votsmeier (2009) 50 – 250 m²/g. To improve the characteristics of the catalyst some dope compounds can be added. A quite common additive is cerium oxide. Based on the ability to act as reducing and oxidizing agent, Ce^{IV} and Ce^{III} can be used as an oxygen buffer to ensure constant O_2 concentrations (Votsmeier et al., 2009). Kaspar (2003) reports about several further effects of cerium oxide, such as better noble metal dispersion or improved thermal stability of the alumina support. The maximum stabilization of alumina could be achieved at CeO_2-levels of 5 %. Another well-known dope is barium oxide, which is very often added to stabilize the alumina surface area (Kaspar et al., 2003). Therefore automotive catalysts can contain high additive amounts, which justify the extraction of these materials.

The washcoat is deposited on the monolith. There are two main materials for the monolith, whereby in the field of automotive catalysts the ceramic carrier has established against the metallic. In principle the ceramic designs are mainly consisting of a mixture of aluminum, magnesium and silicon oxide. The typical material is cordierite (2 $Al_2O_3 \cdot 2\ MgO \cdot 5\ SiO_2$), which offers a number of advantageous characteristics for the application in automotive catalysts. These have high melting point, high mechanical strength and a very low thermal expansion coefficient, which guarantees a perfect thermal shock resistance (Votsmeier et al., 2009). Figure 4 shows the cross-section of a catalyst with the typical honeycomb structure. The inner part represents the monolith while the dark areas show the washcoat. Thickness measurements of the different phases revealed 200 µm for the monolith and 12 µm (edge) up to 130 µm (corner) for the washcoat.



cross section

cross section detailed

Figure 4 – Light microscope image of a catalyst

Table 1 and 2 are showing the chemical composition of two different automotive catalysts from two European car brands. The catalyst presented in Table 1 was assembled in a Renault 19 driven by a gasoline engine.

Table 1 – Composition of a Renault 19 catalyst in weight%

Pt	Pd	Rh	Al	Si	Mg	Ce	Ba	Ca	C	S
0.097	<0.001	0.008	23.000	15.600	5.500	0.610	0.500	0.120	0.096	0.040

The chemical analysis of an Opel Vectra catalyst powered by a diesel engine is shown in table 2. The analyses were carried out by wet chemical analysis of a certified laboratory according to the standards of DIN EN ISO.

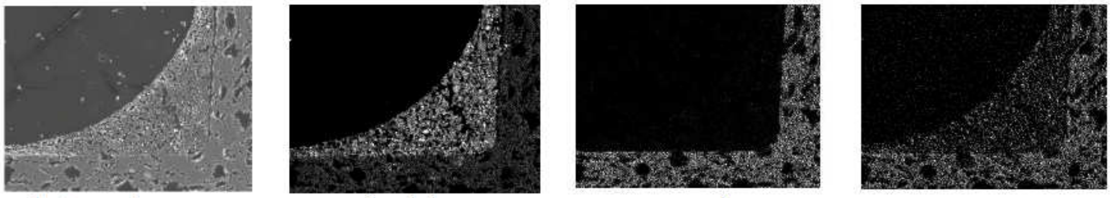
Table 2 – Chemical composition of an Opel Vectra in weight%

Pt	Pd	Rh	Al	Si	Mg	Ce	Ba	Ca
0.110	<0.001	0.024	16.200	9.000	6.100	2.500	0.490	0.650

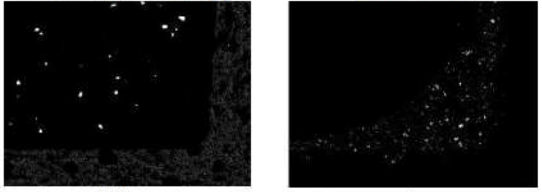
It can be seen that mainly platinum, the characteristic catalytically active component, is used in Europe. The platinum content of these materials are nearly the same, but the diesel catalyst additionally contains a significant rhodium amount, with the typical platinum rhodium ratio of 5:1.

Aluminium, as carrier material in the washcoat and in the monolith, is the quantitative main component. As Cordierite is used as monolith material, the silicon and magnesium concentrations are also quite high. In the case of the above catalysts cerium and barium in form of oxides are also added. While the barium amount is nearly the same, the cerium content varies. As the diesel catalyst is relatively new in comparison to the gasoline catalyst, it has to fulfil stricter emission standards, which can be guaranteed by dope materials. Further reasons for different valuable metal contents are the vehicle size, level of motorization, social prestige, etc. The included carbon and sulphur are representing unwanted impurities. Depending on the driving behaviour (e.g. short distances in the city), particulate matter, which contains carbon as well as sulphur, could be disposed on the catalyst. Especially diesel engines in combination with low engine temperatures (short driving distances) are sensitive for such emissions. The residues are removed if the temperature in the off gas system raises (long distances), therefore the carbon- and sulphur amount is usually very low.

Figure 5 represents the elemental distribution of the investigated gasoline catalyst. It can be seen that the monolith is made of aluminium, silicon and magnesium oxides. The main elements of the washcoat are aluminium, cerium and oxygen. Based on the rather low PGM content and the very small particle size, they are not visible with the used scanning electron microscope (Figure 5). For the observation of the very small PGM particles, the Electron Probe Micro Analysis (EPMA) would represent a better suitable method.



electron microscopy aluminium magnesium oxygen



silicon cerium

Figure 5 – Scanning electron microscope mapping

EXPERIMENTAL

The principle of the recycling technique is to leach the valuable metal fraction selectively and retain the ceramic parts as residue. A similar procedure was used by Konetschnik (2007). The platinum group metals can be leached as chloro-complexes. Their formation requires special conditions, regarding pH value and potential. This context is shown in Pourbaix diagrams, which can be seen in Figures 6 – 8. These diagrams are calculated with HSC Chemistry 6.1.

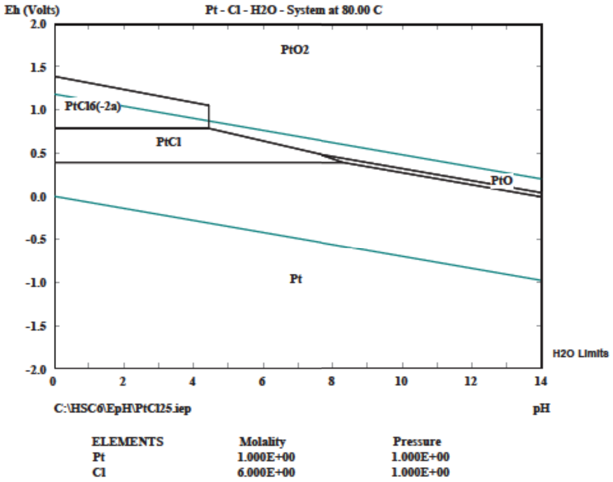


Figure 6 – Pourbaix diagram for platinum

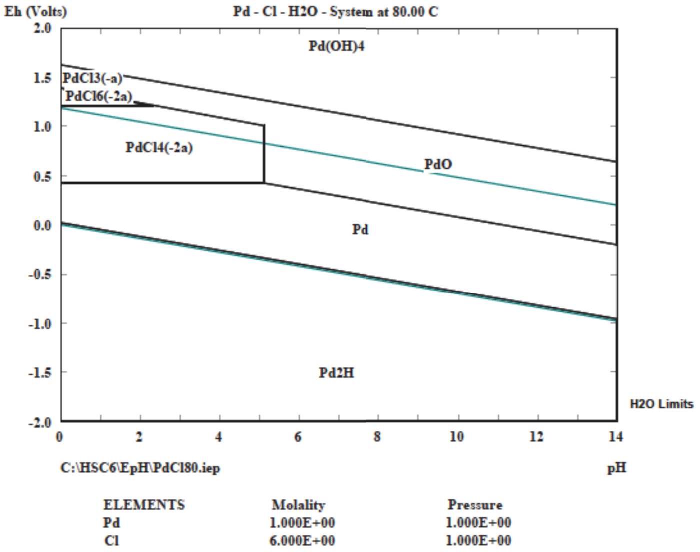


Figure 7 – Pourbaix diagram for palladium

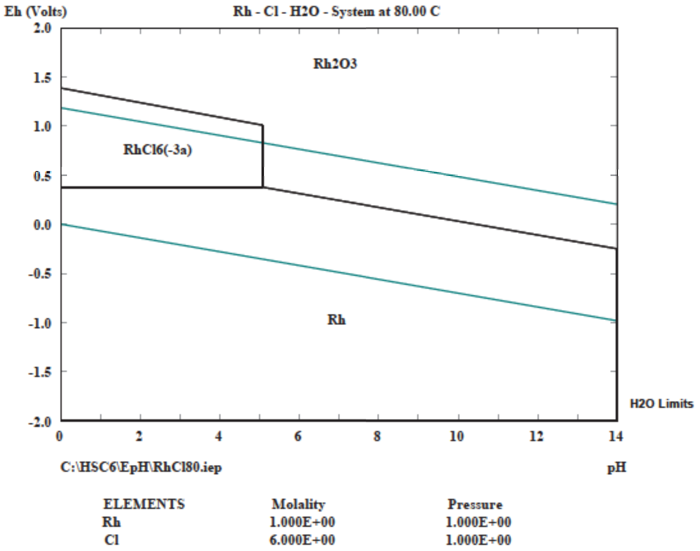


Figure 8 – Pourbaix diagram for rhodium

It can be seen, that high hydrogen ion concentrations in addition to high potentials are required for dissolution of PGMs. Therefore hydrochloric acid and hydrogen peroxide are added. The hydrochloric acid provides the pH value as well as chlorine ions for the complex formation. With an addition of hydrogen peroxide the necessary potential can be generated. The leaching of the PGM-fraction is described by the following reactions 4 – 7:

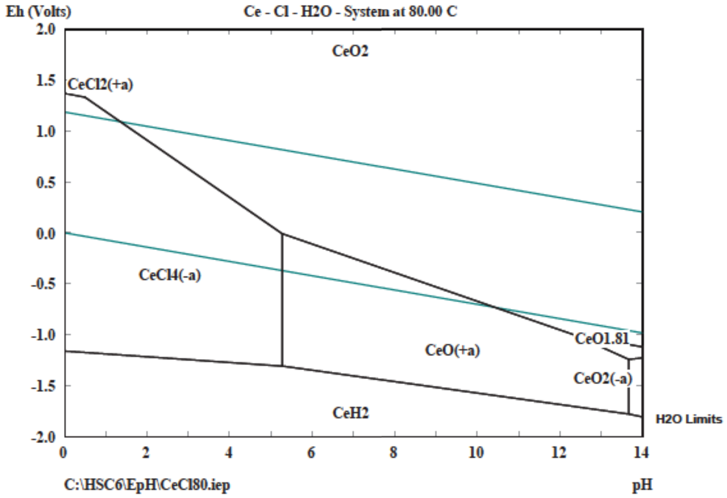
$$\mathrm{Pt(s)} + 8\,\mathrm{H}^{+} + 4\,\mathrm{O}^{-} + 6\,\mathrm{Cl}^{-} \rightarrow [\mathrm{PtCl}_6]^{2-} + 4\,\mathrm{H_2O(l)} \tag{4}$$

$$\mathrm{Pd(s)} + 4\,\mathrm{H}^{+} + 2\,\mathrm{O}^{-} + 4\,\mathrm{Cl}^{-} \rightarrow [\mathrm{PdCl}_4]^{2-} + 2\,\mathrm{H_2O(l)} \tag{5}$$

$$2\ \mathrm{Rh(s)} + 12\ \mathrm{H}^{+} + 6\ \mathrm{O}^{-} + 12\ \mathrm{Cl}^{-} \rightarrow 2\ [\mathrm{RhCl}_6]^{3-} + 6\ \mathrm{H_2O(l)} \qquad (6)$$

$$\mathrm{H_2O_2} + 2\ \mathrm{H}^{+} + 2\ \mathrm{e}^{-} \leftrightarrow 2\ \mathrm{H_2O} \qquad [E^0 = 1.77\ \mathrm{V}] \qquad (7)$$

In addition to the PGM leaching, the present conditions cause the dissolving of cerium oxides. Therefore this leaching method is suited for a simultaneous metal recovery. Figure 9 shows the Pourbaix diagram for cerium. As the PGM leaching needs high potentials, the hydrogen ion concentration should be high enough to avoid the stability zone of CeO_2.



ELEMENTS	Molality	Pressure
Ce	3.800E-01	1.000E+00
Cl	1.371E+01	1.000E+00

Figure 9 – Pourbaix diagram for cerium

The process layout for the simultaneous recovery of the platinum group metals and cerium oxide is illustrated in Figure 10. At the beginning of the process, the ground catalytic material is charged in the leaching agent. The solution is heated up to 80 °C and hydrogen peroxide is added. The presence of carbon and sulphur lead to the formation of carbon and sulphur dioxide. As this reaction consumes oxygen, the hydrogen peroxide addition has to be increased if high carbon and sulphur contents are present. After a defined time the sludge is filtrated and a yellow-gold solution can be gained. The filtercake includes the nondissolvable oxides. Although according to equilibrium conditions parts of ceramic material especially alumina are leached. This leads to hydrogen ion consumptions, which has to be balanced in the solution regeneration. Equation 8 shows the alumina dissolving as well as the hydrogen ion depletions.

$$\mathrm{Al_2O_3} + 6\ \mathrm{H}^{+} \rightarrow 2\ \mathrm{Al}^{+} + 3\ \mathrm{H_2O} \qquad (8)$$

The pregnant solution is further processed in the cementation step. In principle, the cementation is the replacement of a dissolved noble metal by a less noble metal. In fact the leaching of a non-noble metal leads to the precipitation of the most precious metal. The idea is to recycle the solution, therefore all impurities have to be removed. Otherwise they will be concentrated and affect the leaching process. Aluminum represents a possible cementation agent, because it is very ignoble and based on the partial leaching of ceramic material aluminum has to be removed anyway. The corresponding reactions 9 – 11 illustrate the cementation reactions.

$$2\ \mathrm{Al(s)} + \mathrm{H_2PtCl_6(aq)} \rightarrow \mathrm{Pt(s)} + 2\ \mathrm{Al}^{3+} + 6\ \mathrm{Cl}^{-} + \mathrm{H_2(g)} \qquad (9)$$

$$4\,Al(s) + 3\,H_2PdCl_4(aq) \rightarrow 3\,Pd(s) + 4\,Al^{3+} + 12\,Cl^- + 3\,H_2(g) \tag{10}$$

$$2\,Al(s) + H_3RhCl_6(aq) \rightarrow Rh(s) + 2\,Al^{3+} + 6\,Cl^- + 1.5\,H_2(g) \tag{11}$$

It can be seen that the cementation leads to hydrogen formation. The aluminum should have an optimal grain size, because too fine particles lead to extreme hydrogen formation without precipitation of the PGM fraction. Based on the huge electrochemical potential difference between aluminum and hydrogen, the reaction could get out of control if the cementation agent is too fine. On the other hand, coarse particles increase the required time. After filtering, a crude PGM fraction with some impurities remains. This residue has to be treated to recover pure platinum group metals.

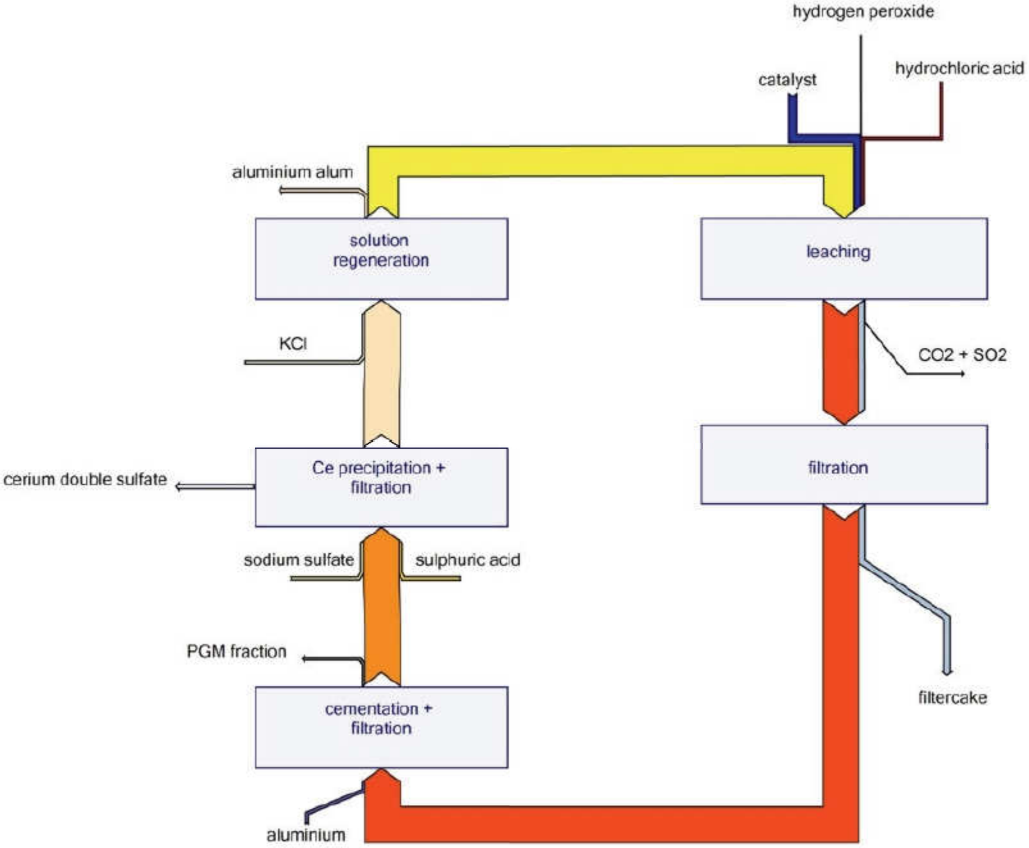
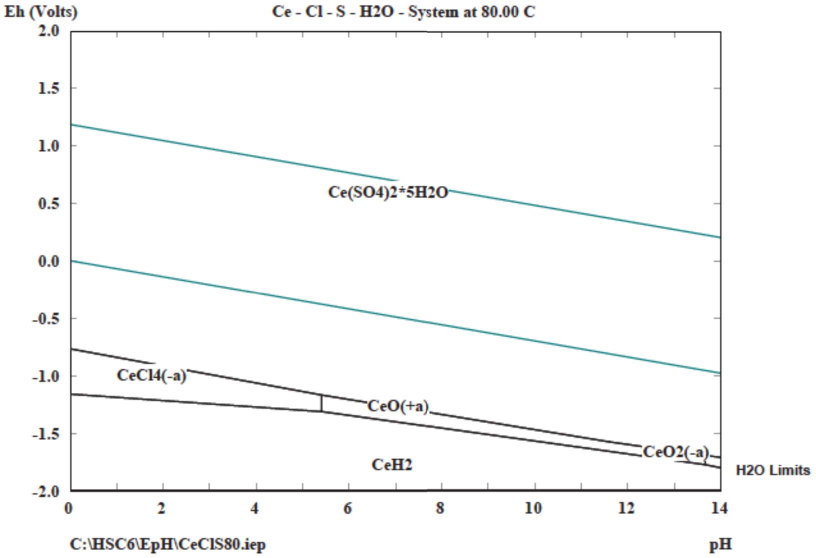


Figure 10 – Process layout

The next step is to recover additional valuable metals like cerium. Cerium sulphate is known as hardly soluble compound, as shown in the following Pourbaix diagram (Figure 11).



ELEMENTS	Molality	Pressure
Ce	3.800E-01	1.000E+00
Cl	1.600E+01	1.000E+00
S	9.000E-01	1.000E+00

Figure 11 – Pourbaix diagram of the system Ce-Cl-S

The idea is to precipitate cerium as disulphate, therefore sodium or potassium sulphate can be used. Additionally some sulphate ions are necessary, which can be seen in the reactions 12 and 13.

$$Na_2SO_4 + Ce^{3+} + SO_4^{2-} \rightarrow NaCe(SO_4)_2 + Na^+ \qquad (12)$$

$$K_2SO_4 + Ce^{3+} + SO_4^{2-} \rightarrow KCe(SO_4)_2 + K^+ \qquad (13)$$

As shown in Figure 11, it should be theoretical possible to precipitate cerium sulphate also only with sulphuric acid (reaction 14).

$$Ce^{4+} + 2\ SO_4^{2-} \rightarrow Ce(SO_4)_2 \qquad (14)$$

The liquid solid separation is carried out by filtration. The double sulphate can be further treated to recover pure ceria. This can be done by thermal processing.

The last step is the removal of impurities from the leach liquor. As mentioned before aluminum represents the main impurity. A very elegant method to remove this element is by precipitation as aluminum-alum. This also represents a double sulphate, similar to the cerium precipitation. Equation 15 shows the removal by potassium chloride.

$$Al^{3+} + 2\ SO_4^{2-} + KCl(aq) \rightarrow KAl(SO_4)_2(s) + Cl^- \qquad (14)$$

The advantage of this method is the generation of a marketable product. After the cleaning of the solution and adding the consumed hydrogen ions, it can be reused for the next leaching step. A further benefit of the closed circle is that there are no metal losses to effluents. Additionally the wastewater amount is also minimized.

EXPERIMENTAL RESULTS

The aim of the first experimental investigations is the verification of the process design to extract the valuable metals with satisfying recovery rates. Figure 12 represents the leaching efficiency at 80 °C, with hydrochloric acid and hydrogen peroxide. Furthermore the influence of sulphuric acid addition is studied.

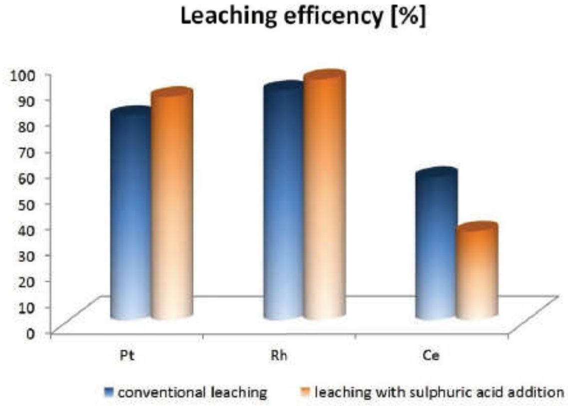


Figure 12 – Leaching efficiencies

The PGM leaching rates in Figure 12 are about 79 and 86 % for platinum as well as 89 and 93 % for rhodium. The addition of sulphuric acid leads to higher precious metal dissolution, while the cerium amount in the solution is lower. These effects are based on the influence of the sulphuric acid on the potential and pH-value. Furthermore the SO_4^{2-}-ions build the hardly soluble cerium sulphate, which leads to lower cerium leaching. The focus of the whole process lies on the leaching step, because the solution is circulated in a closed cycle so that no PGM losses occur.

Further experiments with diverse precipitation agents were carried out to identify possible methods to recover cerium. A common technique is the treatment with sodium sulphate to generate an insoluble sodium cerium double sulphate. Additionally some further trials with potassium sulphate, sulphuric acid, ammonia and sodium hydroxide were carried out in order to study the cerium recovery. Figure 13 shows the cerium content of different precipitation products, which derive from the addition of the corresponding compound. Especially sodium and potassium sulphates are suitable for this treatment, as the gained concentrate includes up to 30 % cerium. The precipitation via ammonia and sodium hydroxide is caused by a raise of the pH value. Based on the high hydrogen ion concentration, the required neutralization agent amount is quite high. Furthermore the last step, the acid balance, causes more effort.

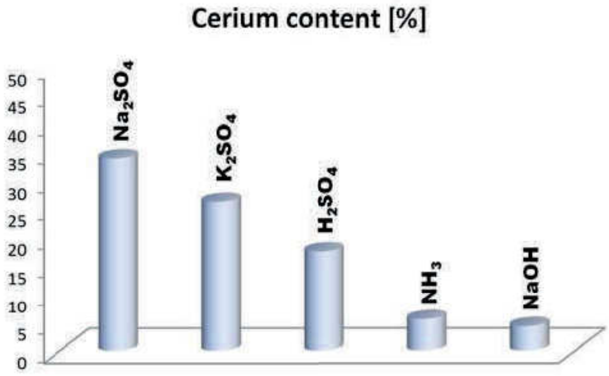


Figure 13 – Cerium content of various precipitation products

CONCLUSION

The recycling of platinum group metals from spent automotive catalysts is increasingly gaining importance. As a result of this research work, high recovery rates for PGMs are possible. Based on steadily stricter off gas emission limits, new materials are applied in catalytic converters. Therefore other valuable compounds are available in spent automotive catalysts. One of them is cerium, which is a rare earth metal with relatively high prices. Due to the ignoble character of cerium, the supplementary recovery in pyrometallurgical recycling methods is not possible. Therefore the present work represents a process, which offers the simultaneous recovery of the PGMs and the rare earth metal. The experiments show the principle functionality of the proposed process. As economically feasible recycling of platinum requires recovery rates above 90 %, more tests for improving the leaching parameters are necessary. The cerium precipitation trials demonstrated that sodium and potassium sulphates are potential extraction reagents. The benefits of these compounds are the high cerium amount in the precipitate and a minimal effect on the circulated solution. The aim of the subsequent experiments is the recovery rate improvement to develop an industrial applicable process.

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