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RECYCLING OF PLATINUM GROUP METALS FROM AUTOMOTIVE CATALYSTS BY AN ACIDIC LEACHING PROCESS

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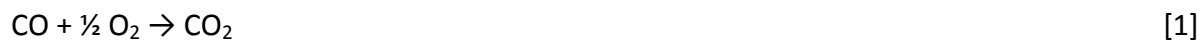
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Abstract

The platinum group metals (PGMs) palladium, platinum, and rhodium represent the key materials for automotive exhaust gas treatment. Since there are currently no adequate alternatives, the importance of these metals for the automotive industry is steadily rising. The high value of PGMs in spent catalysts justifies their recycling. The state-of-the-art technology is to melt the ceramic carrier and collect the precious fraction in a liquid metal bath. As the feed material has quite high melting points, huge amounts of energy are required for this process. Hydrometallurgical treatments of the spent catalysts offer the possibility to recycle the PGMs with less energy and time demands. Moreover, automotive catalysts contain further valuable materials to improve the exhaust gas treatment. These compounds, like cerium oxide, cannot be recovered in pyrometallurgical processes. This paper deals with a special process that uses hydrometallurgical principles to recycle the valuable metal fraction from spent automotive catalytic converters. Hydrochloric acid in combination with hydrogen peroxide is used as leaching agent. This combination selectively dissolves the PGMs and the cerium, which can be recovered in separate steps. As the leaching solution is regenerated and reused, wastewater generation is minimized. Furthermore, the process residues constitute potential byproducts.

Introduction

The combustion of organic fuels leads to the formation of harmful compounds such as carbon monoxide, hydrocarbons, and nitrogen oxides. Their amounts in automotive exhaust gas, which are legislated by law, can be decreased by fitting catalytic converters to the exhaust gas system. Platinum, palladium, and rhodium are the essential constituents of automotive catalysts. These metals decrease the activation barrier for the following reactions 1 – 3¹:



The high price of these metals led to intensive research activities to substitute them. Nowadays no cheaper materials are available that offer similar properties for these kinds of catalytic reactions. Based on the facts that every new car has to be equipped with a catalytic converter and the number of car registrations is steadily increasing, the demand for platinum group metals (PGMs), particularly platinum, will grow continuously. Taking into account that one catalytic converter contains approximately from 1 g up to 15 g of PGMs, it could be easily supposed that this field represents the main application for palladium, platinum and rhodium². Figure 1 shows the general consumption of PGMs, together with the demand for automotive catalyst applications.

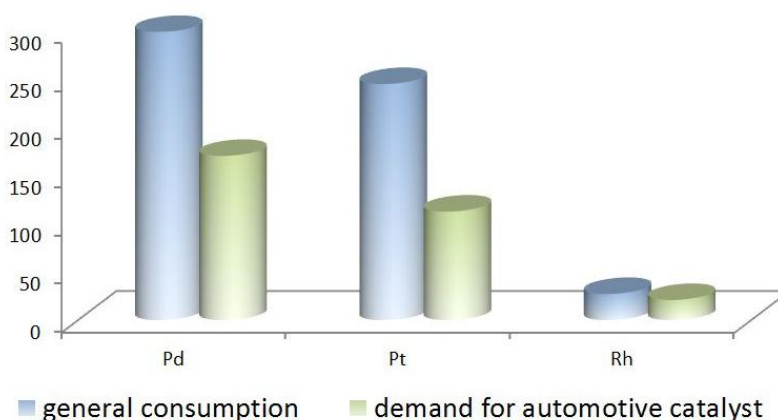


Figure 1-PGM demand³

To cater for the rising demand and to avoid negative environmental impacts, the recycling of automotive catalysts is indispensable. Furthermore, the spent catalytic converters, containing an average of approximately 4 g PGMs, represent a high-grade raw material in comparison to primary sources². Another fundamental motivation for PGM recycling is the limited raw material availability. The primary sources are strongly geographically limited and often displaced from the main consumers. Figure 2 shows the main producers of platinum and palladium as well as the main consumers. It can be seen that Europe constitutes the highest platinum demand, while nearly the whole of production is situated in South Africa. A similar situation can be seen for palladium; the main producers are again South Africa, and Russia. In contrast to platinum, the consumption of palladium is fairly evenly distributed between the major industrial powers³.

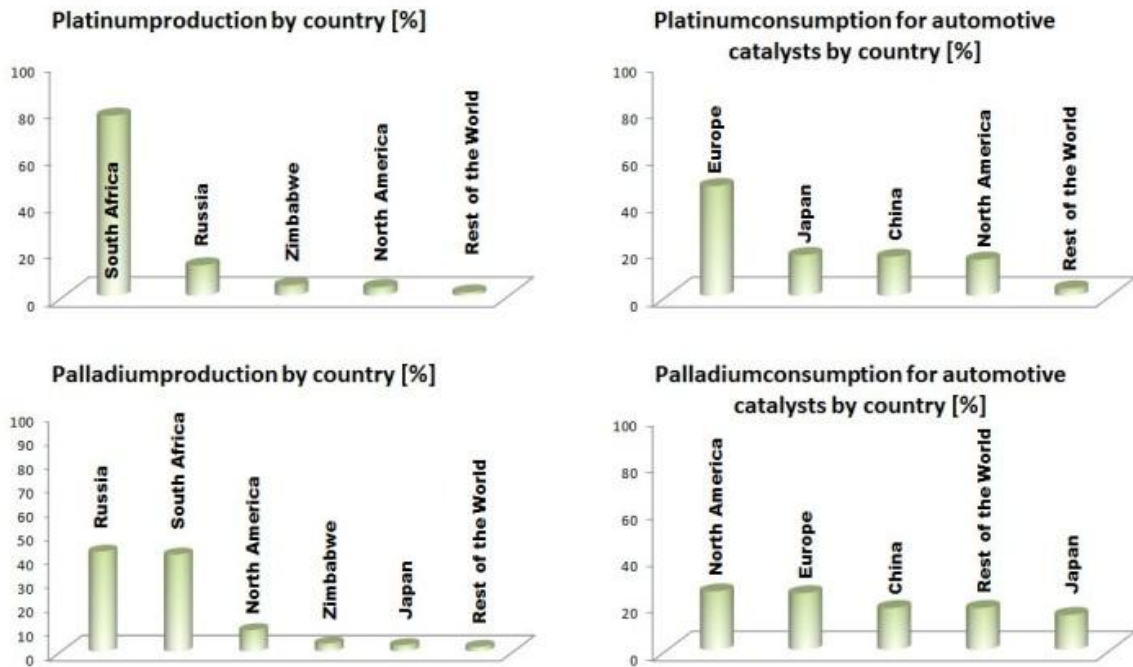


Figure 2-Palladium and platinum producers and consumers³

This discrepancy between production and consumption leads to a high level of recycling activity in the consuming countries.

Recycling of spent automotive catalysts

The recycling of PGM-bearing catalytic converters can be carried out through hydrometallurgical or pyrometallurgical processes.

Pyrometallurgical methods

Today the recycling of spent catalysts is carried out mainly by pyrometallurgical processes. The principle of these methods is to generate a liquid slag that is formed by the ceramic part of the catalyst and to collect the precious metal fraction in a metal bath. The typical ceramic material for automotive catalysts consists of a silicon-aluminium-magnesium oxide called cordierite. Melting of this material requires high temperatures and the addition of fluxes. The operating temperature of common processes is between 1500°C and 1900°C. Such high temperatures can be generated by plasma, electric slag, or electric arc heating³⁻⁵.

The PGMs, owing to their high specific density, fall through the slag into the metal bath. The most frequently used material for the metal bath is copper, but iron, lead, and nickel can also be used. Another significant mechanism for separating the PGMs from the slag is the collection of PGM particles by collector-metal drops⁶. High turbulence and increased area of the metal-slag interface lead to an increased recovery of the precious metals from the slag. The recovery of very small particles in particular is improved by this principle. Owing to their high melting points (e.g. rhodium: 1966°C), the PGMs are not always liquid during this process. Also in this case the collector metal droplets improve the recovery rates. Benson⁶ mentioned that the plasma torch system, which is used in the Johnson Matthey process, is particularly suitable to support droplet formation. The PGM-enriched copper is further processed by electrowinning, where the precious metals are concentrated in the sludge. This step can also be done by electrorefining but the time required is longer. The separation of the individual elements from the electrolysis residue is carried out by several hydrometallurgical techniques, including solvent extraction, precipitation, and ion exchange^{4, 5}.

The slag generated from the melting stage can be further processed in a lead shaft furnace. This facility recovers entrained PGMs as speiss, which is returned to the first melting step. Benson⁶ and Hagelüken⁵ report recovery rates of more than 95 per cent for platinum and palladium, and 85 per cent for rhodium. The high recovery rates are the main advantage of pyrometallurgical recycling.

Hydrometallurgical methods

These methods, which are rarely applied to recycle PGMs, use various leaching agents to dissolve specific fractions. The most common technique is the leaching of the individual PGMs. As these metals show a very noble character, their resistance to dissolution is quite high. Consequently, strong acids in combination with oxidants are required in the leaching process. These conditions lead to the formation of soluble PGM complexes. Hydrochloric acid is a common complexing agent, while nitric acid (HNO₃), chlorine, or hydrogen peroxide (H₂O₂) can act as oxidant^{7, 8}. The combination of hydrochloric acid and nitric acid, called *aqua regia*, is the most common leaching agent for precious metals, but not all of the PGMs can be dissolved with it. After the extraction step, the pregnant solution is separated and can be treated by different principles. One option is direct cementation with a less noble metal. An alternative is solvent extraction, which concentrates the solution and allows the separation of platinum, palladium, and rhodium. The adsorption of the PGMs on an ion exchange column presents another option to recover the noble metals⁹.

An alternative approach is to leach the ceramic material with sodium hydroxide or hot sulphuric acid under pressure. Platinum, palladium, and rhodium are not soluble under these conditions and remain as solids. Separation can be carried out by simple filtrations. This method offers the

advantage of winning rhenium through ion exchange from the solution. Moreover, the crude PGM fraction can be recovered without any further treatment, such as cementation or precipitation. However, owing to the large quantities of wastewater generated and relatively low PGM yields, this process is quite unsuitable for the recycling of automotive catalysts⁴.

A very novel technique is the recycling of PGMs through biosorption. The noble metals are bonded by biomaterials including algae, bacteria, and fungi, and desorbed by various eluants. The medium used depends strongly on the biosorbent, and can be NaOH, NaCN, HCl etc¹⁰. Nilanjana¹⁰ reports satisfactory metal recoveries at the laboratory scale, but the scaling up to industrial size requires further research.

This route offers a faster metal recovery and lower fixed capital costs. Moreover, modern automotive catalysts contain additives, such as cerium. The hydrometallurgical processes are able to simultaneously recover these metals, whereas they are lost in pyrometallurgical recycling. Another advantage of the hydrometallurgical route is the lower energy consumption; pyrometallurgical processing requires high temperatures to melt the raw material. The disadvantages are the lower overall metal yields at the industrial scale and a complex wastewater handling in comparison to pyrometallurgical recycling.

Experimental

The aim of this study is to design a recycling process for spent automotive catalyst that allows the reusing of the leach liquor. In addition, other valuable compounds should be recycled simultaneously. The experiments carried out are aimed at evaluating if the designed process is able to fulfill these requirements in general.

Materials

The used PGM-containing catalytic converters originated from a local scrap dealer that collects and processes accident-damaged vehicles and scrap cars. One of the processed converters can be seen in Figure 3.



Figure 3-Spent catalytic converter

The conventional catalytic converter includes three main parts. These are the PGM-containing monolith, the outer steel shell which protects the monolith against external mechanical destruction, and the fibre blanket, which acts as a buffer between the steel shell and monolith. The monolith can be easily removed by slicing the steel shell. To guarantee a homogenous sample and to fulfill process requirements, the ceramic material was crushed. The experiments were carried out with two different catalytic converters originating from various vehicle brands. Figure 4 shows the grain size distribution of the prepared sample 1. The distribution of sample 2 is almost identical to sample 1.

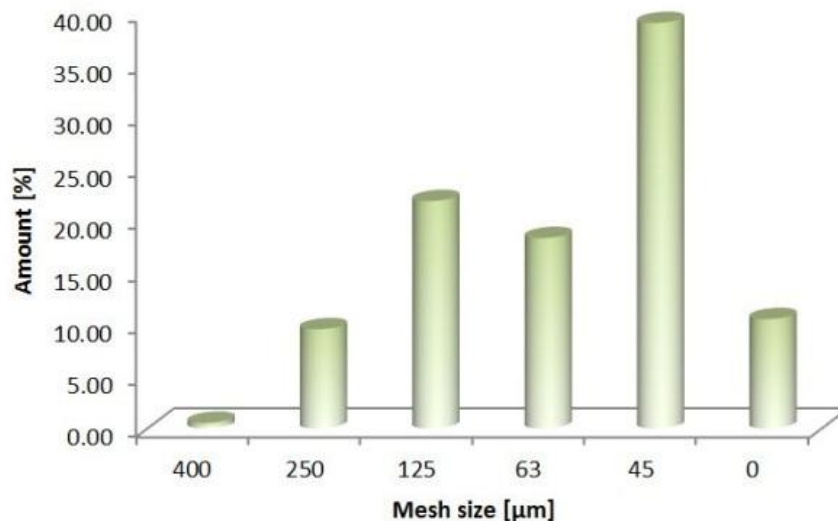


Figure 4-Grain size of the feed material

According to Benson⁶, the particle size of PGMs in the washcoat is estimated to be between 1 – 20 µm. Therefore with decreasing grain size, higher leaching efficiencies are expected. The main fraction of the feed material is below 63 µm, which represents a satisfactory value compared to the grinding effort. Apart from improved the leaching rate, grinding is necessary to allow uniform sampling of the monolith. In general, the amount PGM varies between different catalyst types. Comminution is therefore necessary to generate a homogenous feed material.

The chemical composition of the catalytic materials was determined by ICP-OES and infrared absorption. The results are shown in Table I.

Table I – Catalyst composition in weight per cent

Sample	Pt	Pd	Rh	Al	Si	Mg	Ce	Ba	Ca	C	S
1	0.097	<0.001	0.008	23.000	15.600	5.500	0.610	0.500	0.120	0.096	0.040
2	0.110	<0.001	0.024	16.200	9.000	6.100	2.500	0.490	0.650		

It can be seen that the catalytically active component is a combination of platinum and rhodium. These two elements are typical for the European automotive catalyst industry. Therefore, as mentioned in the Introduction, Europe shows the highest platinum consumption. Sample 2 represents the typical platinum-rhodium ratio of 5:1⁴. Sample 1 originates from an

older car; the valuable metal content is therefore slightly lower as a consequence of less strict emission standards. The quantitative main fraction is represented by the carrier material, which is made out of silicon-aluminium-magnesium oxide. These oxides possess the optimal characteristics to fulfill the required characteristics to carry the washcoat¹¹. The washcoat builds the surface on the monolith and includes the catalytically active component as well as additives. A quite common dope for automotive catalysts is cerium oxide. This compound has several positive effects during the treatment of the exhaust gases, and is used in concentrations of up to 5 per cent¹¹. Sample 2 contains 2.5 per cent Ce. Barium oxide is another dope for catalytic converters, as it acts as a thermal stabilizer of the alumina carrier¹¹. The total barium content of approximately 0.5 per cent is too low to justify an economical recycling. Further constituents of spent automotive catalysts are carbon and sulphur. These elements are the result of unburned fuel particles. Their formation depends strongly on the operating mode of the vehicle. Particularly during the warming up period of the engine, a lot of unburned carbon and sulphur is deposited on the catalyst. These impurities can be easily noticed by a dark coloring of the white monolith, as shown in Figure 5.



Figure 5-Carbon-contaminated monolith

As the used samples exhibited a bright color, the carbon content had to be very low. The chemical analysis confirmed this suspicion, as the carbon and sulphur contents are less than 0.1 per cent. Catalysts with significant contaminations, like the example in Figure 5, have to be thermal treated to lower the amount of carbon.

Figure 6 represents the element distribution of sample 2. It can be seen that the monolith is made of aluminium, silicon, and magnesium oxides. The quantitative main elements of the washcoat which covers the monolith are aluminium, cerium, and oxygen.

Owing to the rather low content and the very small particle size of the PGMs, it is not possible to view them with the scanning electron microscope. Electron probe micro-analysis would represent a more suitable tool for the observation of the very fine PGM particles.

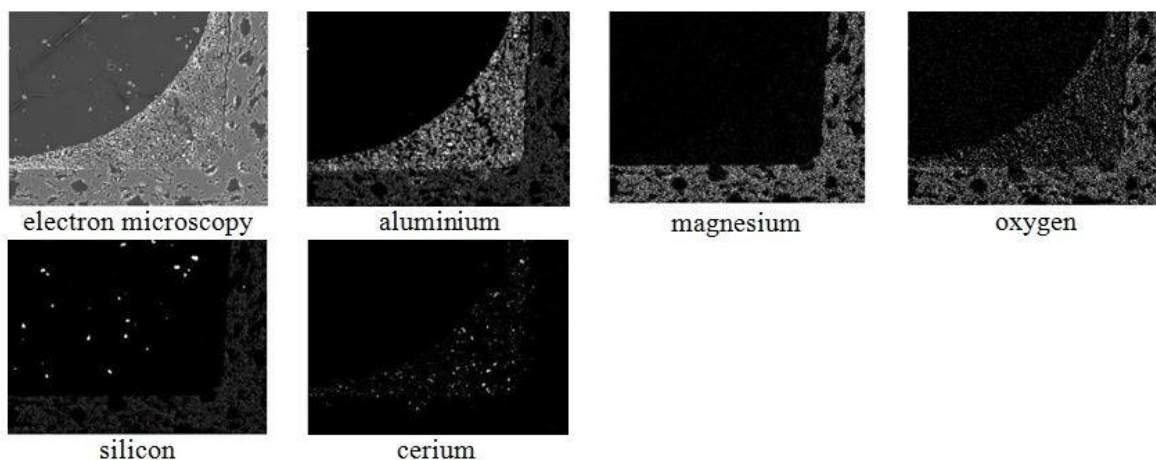


Figure 6-Element distribution of the used catalyst

Experimental procedure

The PGM recycling experiments are based on the selectively leaching and precipitating of the valuable metal fraction. Furthermore, the leaching liquor is regenerated after the precipitation and can be re-used. The following sections illustrate the particular steps in detail. After each step the solution was analysed to calculate the recovery efficiencies.

Leaching

The procedure used in this study leaches the PGMs as well as cerium, while the other materials remain as residue. A common soluble form of the platinum group metals is the combination with chlorine to form chloro-complexes. Their formation requires specific conditions regarding pH value and redox potential. The Pourbaix diagrams (Figure 7), which were calculated using HSC Chemistry 6.1, show the area of solubility for platinum, palladium, rhodium, and cerium.

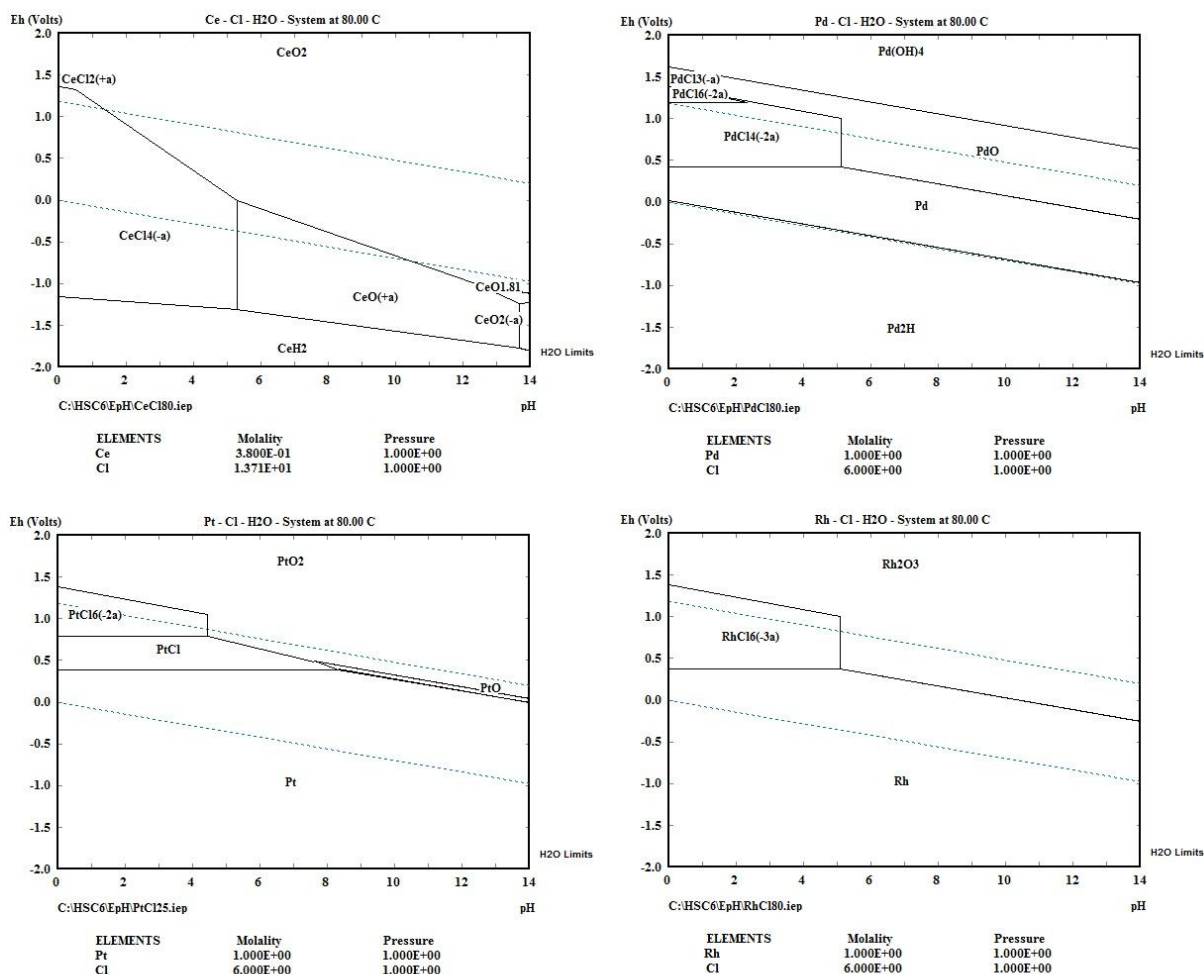
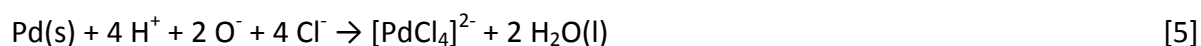
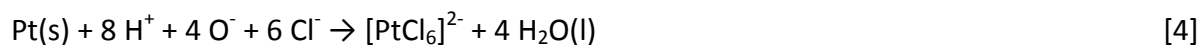
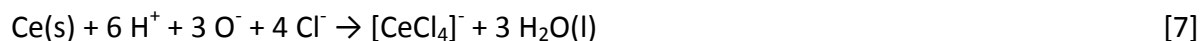
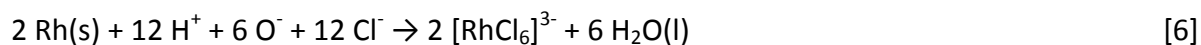


Figure 7-Pourbaix diagrams of the valuable metal-Cl system

It can be seen, that high hydrogen ion concentrations, in addition to adequate redox-potentials, promote the dissolution of the valuable metal fraction. Hydrochloric acid and hydrogen peroxide are therefore added. The hydrochloric acid provides the required pH value as well as chlorine ions for complex formation. With an addition of hydrogen peroxide, the required potential can be generated. The leaching of the valuable metal fraction is described by the reactions in Equations 4 – 7:





According to equilibrium conditions, parts of the ceramic material, especially alumina, the quantitative main component, are also leached. This leads to the consumption of hydrogen ions, which has to be balanced at the solution regeneration step. Equation 8 represents the dissolution of alumina as well as the hydrogen ion depletion.

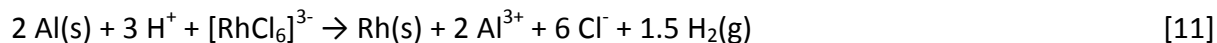
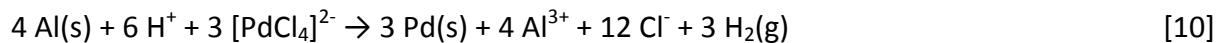
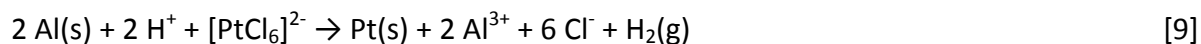


In the first experiments, sulphuric acid was used to compensate for the hydrogen consumption. The PGMs cannot be leached by sulphuric acid, consequently there is no direct influence on the leaching process. However, the addition increases the redox potential and leads to an impact at the leaching step. As the presence of sulphate ions can result in cerium sulphate formation, the addition of sulphuric acid can cause problems in the recycling of cerium. If the catalyst contains carbon and sulphur, CO₂ and SO₂ can be generated in the presence of strong oxidants like H₂O₂. As this leads to consumption of hydrogen peroxide, these ingredients should be removed by a thermal pretreatment if they are present in significant amounts. The presence of carbon and sulphur can be deduced by intense bubble formation during the leaching process.

The experiments were carried out with 150 g of catalyst and 570 ml of synthetic solution. To enhance the leaching conditions, the temperature was raised to 80°C. The addition of the hydrogen peroxide was made very slowly to avoid extreme bubble formation.

Cementation of the PGM fraction

In principle, cementation is the replacement of a dissolved noble metal by a less noble metal. The dissolution of the non-noble metal causes the precipitation of the most precious metal. As the idea is to recycle the solution, all impurities have to be removed, otherwise they will be concentrated and affect the leaching process. Aluminium represents a suitable cementation agent, owing to its non-noble character. Furthermore, the partial leaching of the ceramic material requires the removal of aluminium any case. Equations 9-11 illustrate the cementation reactions.



In addition to the crude PGM cementate, hydrogen is generated by the cementation reactions. Based on the huge electrochemical potential difference between aluminium and hydrogen, as well as the low hydrogen overvoltage, the reaction could get out of control if the cementation agent is too fine. On the other hand, coarse particles increase the cementation time. The aluminium should therefore have an optimal grain size to guarantee optimal cementation conditions. As the electrochemical potential of cerium is below that of aluminium, the dissolved cerium is unaffected by the cementation and can be recovered in a separate process.

The cementation step was carried out with a hyperstoichiometric amount of aluminium at a temperature of 60°C. The raised temperature improves the reaction kinetics and leads to a lower treatment time, but the temperature should not be too high for optimal cementation rates.

Cerium precipitation

As mentioned previously, the electrochemical potential of cerium is quite low, therefore the winning by cementation is fairly difficult. A common technique for recovering cerium from solutions is to precipitate it as sulphate. Figure 8 presents the stability area of cerium sulphate in relation to redox potential and pH-value. This diagram shows that the cerium sulphate is extremely insoluble in the presence of sulphur.

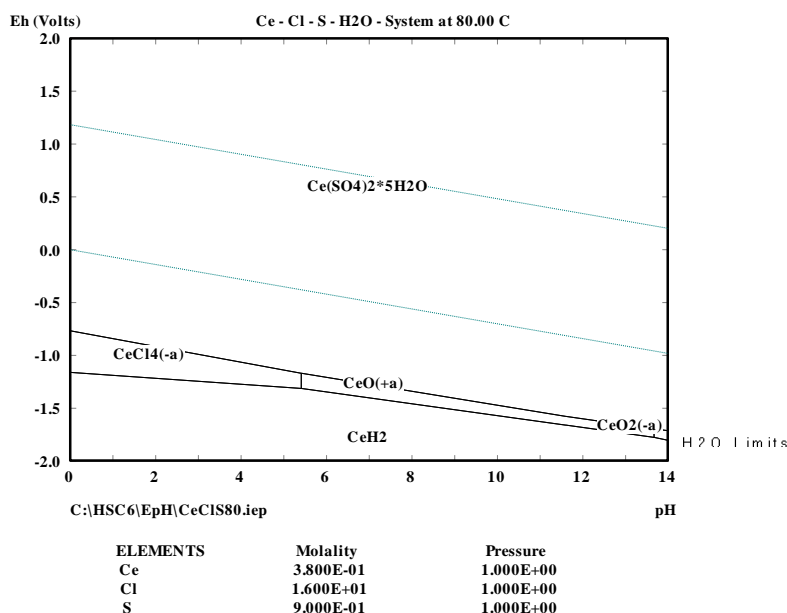


Figure 8-Pourbaix diagram of the Ce-Cl-S system

According to Figure 8 the addition of sulphate ions should lead to the formation of insoluble cerium double sulphate. Potassium and sodium sulphate are common precipitation agents, and thermodynamic calculations showed that they are suitable for recovering cerium. Theoretically, the precipitation process proceeds according to the reactions in Equations 12 and 13.



As these equations show, precipitation requires a further sulphate source beside potassium or sodium sulphate. Therefore sulphuric acid represents an optimal carrier, as its addition is accompanied by an increase in the hydrogen ion concentration, which balances the hydrogen consumption of the cementation step.

Solution regeneration

As the solution is circulated the impurities have to be removed, otherwise some elements will be enriched in the leach liquor and can influence the individual process steps. The main impurity is aluminium, which is partially dissolved in the first step. One method to remove this element is by precipitation as potassium alum according to Equation 14.



Subsequent to the precipitation, an adequate amount of acid has to be added to compensate several depletions. After this step the solution is ready for the next leaching procedure. In principle, there is no limitation in respect of solution regeneration.

Process flow sheet

Figure 9 depicts the entire process flow sheet. The first step is the leaching of the spent catalyst, which yields the pregnant solution. Beside the PGM-enriched solution, carbon dioxide and sulphur dioxide may be generated, depending on the amount of contamination in the feed material. Another by-product is the filter cake, which contains the oxidic fraction of the catalyst. The separation is carried out by settling and subsequent filtration. This leads to a mixture of silicon, aluminium, and magnesium oxides with a low impurity content. After separating the pregnant solution the cementation process is carried out. This procedure yields the crude PGM fraction, which has to be further treated to separate the precious metals. The next process is the precipitation of cerium double sulphate, which can be carried out by adding sodium sulphate and sulphuric acid to the cerium-enriched solution. After the discharge of cerium, the crude solution remains and can be re-used. If the main impurity aluminium reaches a critical value, the solution has to be cleaned by adding potassium chloride.

Another important task of the regeneration step is the balancing of the acid concentration, which yields the re-usable solution.

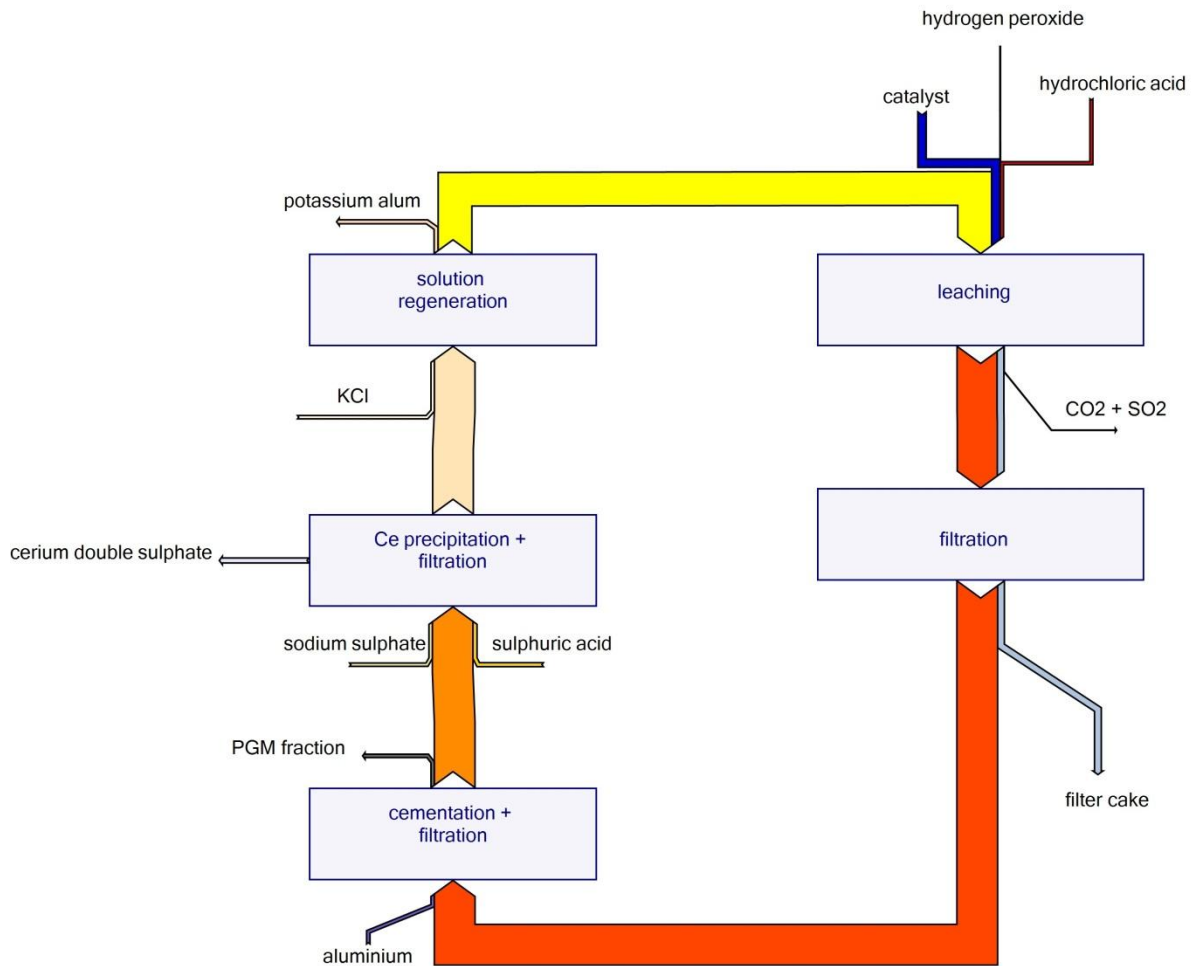


Figure 9-Process flow sheet

Results

The aim of the first experimental investigations was to verify if the process design is able to extract the valuable metals. The solution was analysed by ICP-MS after every process step.

Leaching

The leaching efficiencies for the valuable materials are shown in Figure 10. It can be seen that almost 91 per cent of platinum and nearly 70 per cent of rhodium were leached. In addition to the PGMs, approximately 91 per cent of the cerium was leached under conventional conditions (without sulphuric acid). The addition of sulphuric acid decreases the leaching rate to 26 per cent. As supposed, the presence of SO_4^{2-} ions leads to the formation of barely-soluble cerium sulphate, which results in lower leaching efficiencies for cerium. In general the values are quite good, taking into account that the experiments were only the first tentative trials. Furthermore, these figures represent only the average values, and the maximum leaching efficiencies were accordingly higher.

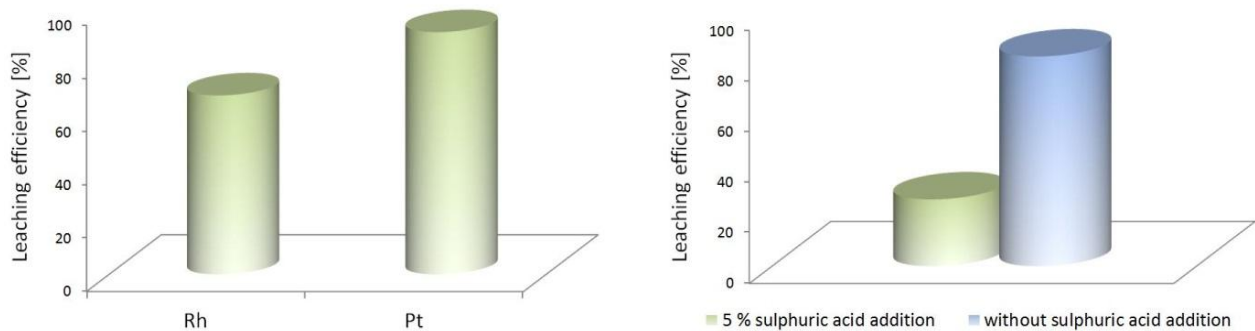


Figure 10-Leaching efficiencies

The main focus of the whole process lies in the leaching step, because the solution is circulated in a closed cycle so that no PGM losses apply.

Cementation

Cementation is carried out by adding aluminium chips at a defined temperature. Figure 11 represents the PGM recovery rate as a function of the aluminium addition. As mentioned previously, the cementation of one mole of platinum/rhodium requires two moles of aluminium, therefore the stoichiometric amount of aluminium was 27 mg.

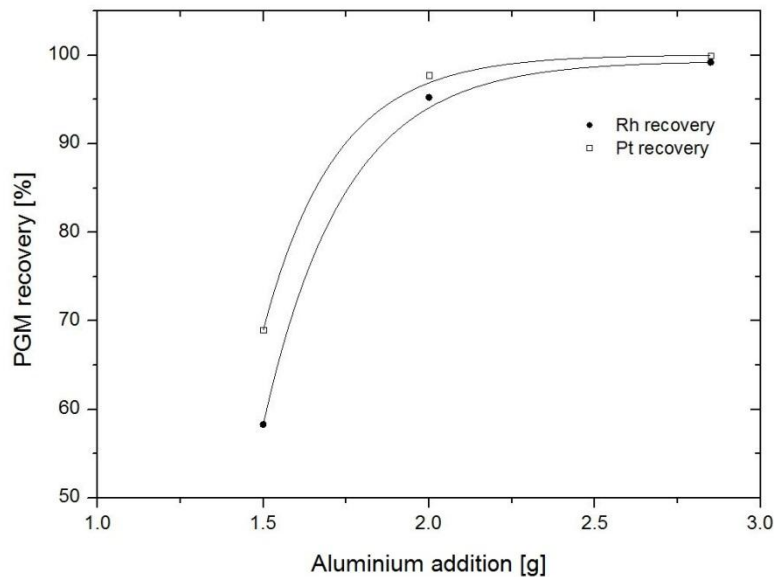


Figure 11-PGM cementation recovery rate

The minimum aluminium addition has to be a hundredfold of the stoichiometric requirement in order to obtain satisfying PGM cementation results. These high amounts of cementation agent are based on the large potential difference with respect to hydrogen, as well as the low hydrogen overvoltage of aluminium. These characteristics lead to a high rate of hydrogen formation during the cementation, which results in a high aluminium consumption.

Cerium precipitation

Further experiments with various precipitation agents were carried out to identify possible methods to recover the rare earth metal cerium. A common technique is the treatment with sodium sulphate to generate an insoluble sodium-cerium double sulphate. Additionally, some further tentative trials with potassium sulphate were carried out. Figure 12 represents the cerium recovery as a function of several parameters. It can be seen that in general, the recovery rates increase with higher additions of precipitation agent. Basically, sodium sulphate results in higher cerium yields in comparison to potassium sulphate. As it can be seen in Figure 12, more than twice the amount of potassium sulphate is necessary to obtain the same efficiency as precipitation with sodium sulphate.

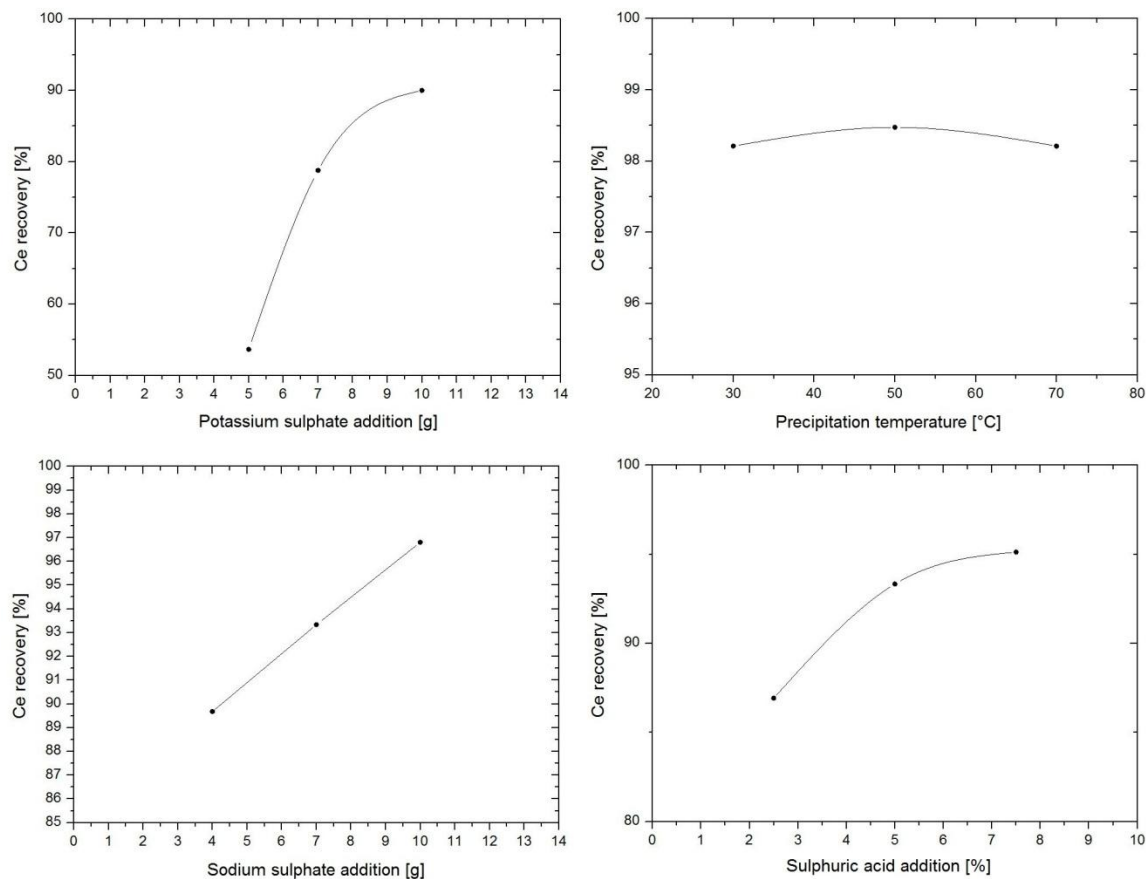


Figure 12-Cerium recovery rates

A further parameter is the sulphuric acid addition, which is responsible for providing enough SO_4^{2-} ions. As with the other precipitation agents, an increase in the sulphuric acid addition leads to higher cerium recovery rates. The temperature represents another process parameter, but as can be seen in Figure 12, the influence of temperature is not very pronounced. Nevertheless, the optimum temperature is 50°C, although 30°C also results in good recovery rates.

Conclusions

The recycling of platinum group metals from spent automotive catalysts is becoming increasingly important. The state-of-the-art technique for the recycling of spent automotive catalyst is pyrometallurgical processing. As the melting point of this secondary raw material requires high temperatures, the energy consumption is high. Additionally, the pyrometallurgical processing is accompanied by long processing times, which cause high in-stock capital.

Based on increasingly stricter off-gas emission limits, new materials are applied in catalytic converters. Therefore other valuable constituents are also available in spent automotive catalysts. One of these is cerium, which is a rare earth metal with limited availability. Due to the non-noble character of cerium, its recovery in pyrometallurgical recycling processes is problematic. Since energy costs are steadily rising and stricter exhaust regulations require higher additions of doping metal, alternatives should be considered. Based on these facts, the present work presents a process flow sheet that offers the potential for lower energy consumptions, decreased processing time, and the simultaneous recovery of the rare earth metal cerium. Another characteristic of this hydrometallurgical recycling process is the minimized amount of wastewater as a result of the solution recirculation. The process in general is designed to generate only marketable byproducts. Therefore the filter cake of the leaching step could constitute a raw material for the refractory industry, and the alum from the solution regeneration step for the paper production. The experimental work demonstrated the basic functionality of the process, with high overall recovery rates of up to 90 per cent for platinum, 65 per cent for rhodium, and 86 per cent for cerium. As the trials in this study were only preliminary experiments, there is a lot of potential for improvement leading to higher recovery rates.

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Bachelor course of metallurgy from 2005 to 2010 at the University of Leoben. Graduated from University of Leoben in 2011 with a Master of Science Degree in nonferrous and ferrous metallurgy. Since 2011 research associate at the Christian Doppler Laboratory for Optimization and Biomass Utilization in Heavy Metal Recycling / Chair of Nonferrous Metallurgy. The research focusses lie at the recycling of PGM containing spent catalysts as well as the recycling of complex residues from the lead and copper industry

