

RECOVERY OF PLATINUM GROUP METALS FROM SPENT AUTOMOTIVE CATALYST

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ABSTRACT

A special treatment of platinum group metals (PGMs) leaching from spent automotive catalyst is shown in this paper. Leaching of crushing and grinding automotive catalyst scrap in hydrochloric acid with defined concentration, added nitric acid as oxidant, produced chloride solution of the platinum group metals, while catalyst substrate (Al_2O_3) remained indissoluble. Cementation of the leached platinum group metals from solution was made by powered aluminum with suitable pH values. The precipitate obtained by cementation with Al-powder is mixture of the platinum group metals and surplus aluminum. The surplus aluminum can be removed by selected resolving with hydrochloric acid. The mixture of platinum group metals (Pt, Pd, and Rh) is obtained by this treatment. Separation between platinum group metals was done by well-known chemical processes.

Keywords: platinum group metals (PGMs), catalyst, recycling, leaching

1. INTRODUCTION

Automotive catalysts have been extensively used for reducing the amount of unburned hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NO_x) from the exhaust gas emitted by automobiles. Platinum group metals (PGMs) have been used as catalytic agents because of their heat resistance and special catalytic activity. The content of total PGMs in automotive catalyst is about 0.5 to 2.0 g per kilogram. Autocatalyst essentially comprise a refractory oxide carrier on which two or more precious metals are dispersed in very low concentration. The worldwide demand of PGMs used for autocatalysts has increased with rapid motorization and the enforcement of stringent regulations for exhaust gas. In 2001, 37% of the worldwide demand for platinum, 72% of palladium and 85% of rhodium was for their use as automotive catalysts. In the year 2003, the overall demand of platinum was about 200 metric tons; 5% had to be met from stock in the last years because of lower primary and secondary production. Half of the produced platinum was used for catalysts in the automotive industry. From this, one third is covered by platinum out of secondary metallurgical processes [1,2].

Due to their scarcity and high price, the recovery of PGMs from spent automotive catalyst, generally called catalyst scrap, is a very important. The catalyst scrap generally consists of the surface layer with a high degree of porosity and the catalyst substrate (such as SiO_2 , Al_2O_3 and CeO_2) with honeycomb structure. Ceramic materials were chosen for the initial monolith and they still dominate market. The preferred materials is called cordierite (synthetic cordierite has a composition approximating $2MgO$, $5SiO_2$ and $2Al_2O_3$ and a softening point $>1300^\circ C$). In typical PGMs recovery process, PGMs are extracted from scrap by smelting them with collector metals such as copper or by directly dissolving them in strong acids with the presence of oxidant.

The most commonly used oxidant for leaching of PGMs from autocatalyst are $NaOCl$, $NaClO_3$, H_2O_2 , Cl_2 (gas), HNO_3 , NaF , KF , NH_4F , ... [3-5].

Pyrometallurgical process requires smelting, foundry anodes, electrolysis and processing anode mud in the aim to recovery platinum group metals. The process has long duration and a lot of electrical

energy is spent. On the other hand, hydrometallurgical process is more economical because a sample is directly treated by acid solution and an oxidant or by mixture of acids. By this reason, results of leaching catalyst scrap by hydrochloric acid with added nitric are shown in this paper. The selective leaching of PGMs is obtained by this process and catalytic substrate remains dissolved. The aim is to determine a payable of this process of recovery PGMs from spent automotive catalysts, which are ransom and import in our country. According to experience with platinum and platinum metals in Mining and Metallurgy Institute Bor and by the used of literature, some of preliminary investigation are done. The preliminary investigation has shown that processing of 1 tone of automotive catalyst scrap materializes profit of 20.000 euros.

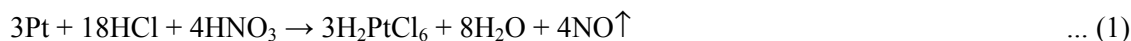
2. EXPERIMENTAL

Spent automotive catalyst was crushed, grinded and sieved. A fraction of -0.295mm with content of 1.6 g/kg PGMs was used for investigation. The 6M HCl with added concentrated nitric acid with continuous mixing was used for leaching. Nitric acid was added very slowly during the entire period of leaching or at 15 minute interval.

The investigation was done in temperature interval 80-95 °C and time duration 1.5-2.0 hours. After leaching, obtained solution of PGMs was separated from base catalyst by filtration. Then, neutralization of surplus acid in the solution was made and cementation of PGMs was done by aluminum-powder. The cemented PGMs were separated from solution and carefully flushed by distill water in the aim to eliminated aluminum-chloride. The residue, which was obtained by cementation, always possess surplus of cemented agent. Because of that, the residue was treated by hydrochloric acid and surplus of aluminum was dissolved and PGMs remain indissoluble.

3. RESULTS AND DISCUSSION

The PGMs were dissolved by 6M HCl with added HNO₃ and by aqua regia 3HCl (12M):1HNO₃ (16M). Leaching degree of PGMs was 98-99% by the both substance, but in the case of aqua regia was noticed a lager loss of reagent and the reaction was mush tumultuous and with higher content of nitric oxides released:



Dissolving scrap was made in a hot solution at the investigated temperature interval, and there was not noticed significant difference between leaching degree. Suspension boiled over 95°C and it is not recommended to use a higher temperature. Dissolution at room temperature with stirring gives leaching degree lower than 50%. It is determined, that with the same leaching conditions of crushed catalyst (over 1 mm) max leaching degree is 70%.

The investigation was done with the sample of the 2000 g weight in a rich suspension with relation solid:liquid=1:2, with stirring. This is an optimal relation that gives good stirring of suspension with smaller loss chemicals than poor suspension. Also, it was determine that during 90 minutes the most of PGMs were leached, but because of complete leaching it was used leaching time of 120 minutes. After leaching of PGMs, base catalyst as indissoluble part was separated, and from solution the cementation of PGMs was done by aluminum powder by follow reactions:



The pH has to be 2 in the aim to reduce a loss of aluminum. Cemented platinum metals possess surplus of cementation agent (aluminum), which was removed after filtration and washing by dissolving with HCl, according reaction:



During process of removing of surplus aluminum, the platinum metals were not dissolved into hydrochloric acid. They were removed by filtration from solution of aluminum chloride and surplus hydrochloric acid.

After removing of surplus of cementation agent, the mixture of PGMs was obtained. It is so called crude platinum metals with quality of minimum 99%. Then, this mixture of PGMs was treated by some classical chemical processes in the aim to refine (figure 1) and separate on individual metals.

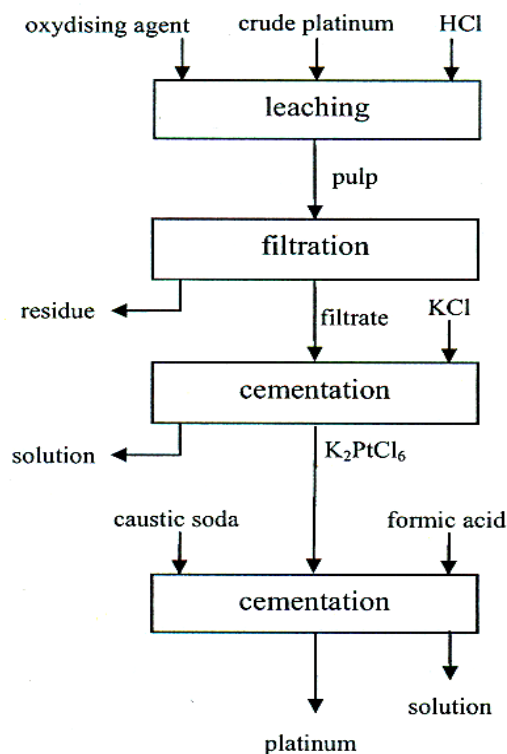


Figure1. Flow chart of the refining process [3]

According to the experimental investigation, it was determined the follow average loss of chemicals per 1 kg spent catalyst:

- 0.9 – 1.2 L HCl (32%)
- 0.45 – 0.6 L H₂O
- 0.3 – 0.4 L HNO₃ (65%)
- 0.3 – 0.5 kg NaOH
- 0.03 – 0.05 kg Al

According to obtained results, the cost of laboratory treatment of 1 tone automotive catalyst is max 2000 euro.

The cost of treatment from crude PGMs to commercial quality catalyst is max 1000 euro per kg PGMs, while purchase cost of spent catalyst is max 40.000 euro per tone (with content PGMs of 1.5-2.5 kg/t).

4. CONCLUSION

It is possible to obtain in average 1.5-2.0 kg PGMs by recovery of 1 tone autocatalyst. It depends of different source materials and their fatigue. Content of impurities in PGMs obtained by shown hydrometallurgical process is max 1%. Significant profit is provided by this process compared with inlay means for supply and treatment of spent autocatalyst. This process could be also used for other raw materials with low content of platinum metals (electronic scrap, catalyst from refinery, and so on).

5. REFERENCES

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