

Conference Paper

Overview of Technologies for Extraction of Platinum Group Metals from Poor Raw Materials

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Abstract

Currently, about 80% of all industrial chemical reactions are carried out with the help of catalysts or depend on catalytic processes. In this case, catalysts containing platinum group metals (hereinafter - PGM) occupy a special position due to their high catalytic activity and selectivity. A significant part of the net global demand for PGM is for the production of catalysts, accounting for approximately 45% for platinum, 30% for palladium, 92% for rhodium, 35% for ruthenium, and 15% for iridium. The most important condition for the economical use of catalysts containing precious metals is their efficient recycling, which will be discussed further.

Keywords: technology, extraction, platinum group metals, poor raw materials, catalysts

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1. The Use of Catalysts in Various Industries

In fact, taking into account the use of secondary metals, much more PGM is consumed in the production of catalysts than indicated earlier. For example, the demand for platinum is about 30 tons per year, for catalysts used in refineries around the world, is almost entirely provided by recycling. Without recycling, a significant increase in world mining of platinum would have been required. In similar volumes, secondary palladium, used in catalysts of chemical processes, is recovered and recycled; platinum, palladium, rhodium, used autocatalysts. To ensure high recovery of PGM, optimization of technological refining operations and a system for organizing the collection, preparation and delivery of raw materials are needed.

Catalysts used in various industries can be divided into two main groups by the phase state of the catalyst-reaction system: homogeneous catalysis catalysts – when

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the catalyst is dissolved in a reaction medium (in a homogeneous solution) and heterogeneous catalysis catalysts – when the catalyst and the reaction medium are in different phases. The catalyst can be in the form of a homogeneous material (a grid of noble metal) or in the form of beads (tablets, granules, molded particles, powders, etc.). Catalytically active metal, finely dispersed on the carrier surface (Al_2O_3 , SiO_2 , activated carbon).

The applied catalysts used in industrial practice characterize a wide range of types and forms of carriers, the content of precious metals (in mono- and polymetallic form). These properties are important for the choice of processing methods used catalysts with the aim of extracting PGM [1, 2].

2. Methods of Refining Catalyst Based on the Transfer to the Alumina Solution, and the Allocation of Noble Metals with a Solid Insoluble Residue

According to the Czechoslovakian patent, the spent catalysts should be alloyed with caustic soda, and then leached with Al_2O_3 water. Sintering of calcined deactivated catalysts AP-52 and AP-56 with calcined soda at 1200–1250°C and subsequent leaching of the sinter in a solution of NaOH at 90°C makes it possible to obtain concentrates with a platinum content of 14 to 34%. According to another method, it is proposed to leach alumina with 25–40% solution of NaOH at 100–200°C and atmospheric pressure. The solid residue is either further treated with aqua regia with subsequent precipitation of palladium from the solution, or the undissolved platinum is filtered off from the NaOH solution.

In the sulfuric acid treatment of catalysts, after separating the slimes, additional oxides of aluminum are introduced into the solution for the complete utilization of sulfuric acid. The resulting sludge after calcination at 550°C (with a platinum content of 30%) is re-treated with sulfuric acid.

A method for extracting platinum from AP-56 catalyst is known, according to which the sulfatization is carried out at a temperature of up to 300°C. in a muffle furnace at a triple flow rate of concentrated sulfuric acid. The yield of the residue after leaching with water of sulphate sinter is 12.5% with a platinum content of 4.6%. Leaching of sulphate sinter with a 10% solution of sulfuric acid made it possible to reduce the amount of insoluble residue to 6.2% and increase the content of platinum in it to 8.5%.

Given that the spent catalysts consist of 80–90% of aluminum oxide, all of the aforementioned methods require large amounts of liquid reagents to dissolve the alumina.

In addition, during the leaching of aluminum oxide, noble metals also partially pass into the solution, which requires them to be further removed from the solutions.

To obtain pure metals from a complex insoluble residue, it is necessary to use special affinity schemes.

3. Methods for Processing Catalysts Based on Selective Extraction into the Solution or Gas Phase of Noble Metals to Obtain a Solid Residue of Aluminum Oxide

For recycling the catalyst to the destruction of bases used opening processes in solutions and melts, the high temperature and oxidative chlorination roasting to burn off the carrier – carbon. In this case, valuable components are concentrated in a solid residue.

One way to transfer platinum to the gas phase in the form of chlorocarbonyl complexes is to treat the catalysts with a mixture of phosgene, carbon dioxide and carbon tetrachloride for 60 minutes at a temperature of 230–425°C. The amount of gas mixture should be 15–20 times greater than the mass of platinum in the catalysts.

It is also possible to treat the catalysts at 870°C with a gas mixture of nitrosyl chloride and chlorine, obtained by heating 'aqua regia', in order to convert platinum to volatile chloride.

A method for extracting platinum from spent catalysts is known, in which the ground catalyst is mixed with powdered carbon, briquetted, and to remove volatile components from the coal and produce a porous briquette structure, it is processed at a temperature of 800°C. Then the briquettes at 900–950°C are treated with a gas mixture: $C_1_2 + SCl_2$, which allows to extract up to 99% of platinum in the chloride.

In addition to the considered methods, a number of methods have also been developed for the extraction of platinum and palladium from catalysts into a solution.

It is proposed to treat the catalysts with boiling concentrated hydrochloric acid when it is continuously circulated. It is known the way, when to dissolve the palladium, the reduction of the catalyst mass with hydrogen is carried out at 500–600°C, followed by treatment with a solution of nitric acid at 110–115°C. The implementation of these methods involves the production of large quantities of solutions. Because of low temperatures, chemical processes proceed at low rates. The presence of harmful liquids and gases worsens working conditions and requires a number of costly measures

aimed at improving labor protection. Besides, losses of noble metals with solutions are inevitable [3].

When implementing methods for the selective extraction of platinum and palladium in the gas phase, hazardous chemical agents such as chlorine, phosgene, hydrogen chloride, etc., are involved in production. The high reactivity of these gases at high temperatures, the lack of inert structural materials, the large consumption of gases due to the interaction with them of the basis of catalysts (Al_2O_3), the complexity of ensuring labor protection – all this is a serious obstacle to the implementation of these processes.

4. Pyrometallurgical Methods for the Recovery of Precious Metals from Spent Catalysts Based on Aluminum Oxide

Pyrometallurgical methods can be divided, in turn, into two groups:

- melting with and without chemical interaction, namely melting to slags or an alloy with a metal-collector;
- solid phase halogenation (more often – chlorination, less often – fluorination) of spent catalysts with various halogenating reagents.

The latter method can be carried out both for the purpose of transferring noble metal chlorides to the sublimate and capturing valuable components in the gas phase, and for extracting platinum metals by leaching the previously prochlorinated material (combination of pyro- and hydrometallurgical methods).

The first group of pyrometallurgical methods involves melting catalysts in electric furnaces at high temperatures (over 2000°C). The material is melted, molten alumina is removed from the upper part of the melt, and the melt containing the PGM is removed from the lower part. In order to increase the recovery of valuable components, the catalysts are subjected to calcination before melting at temperatures between 500 and 600°C .

The British Petroleum Co P (UK) company for the separation of PGM from a graphite base (containing barium or cesium) proposes to conduct the process in an electric arc furnace in two stages: oxidation (in a stream of oxygen or air) at a temperature of 723 – 823 K and reduction (hydrogen) at 473 – 523 K. At the same time, the extraction of PGM into the residue is 95%. Subsequent treatment with hydrochloric acid increases the recovery to 97.6%. The purity of the product is 95% by weight.

The process of electric arc melting is well known and does not need a detailed description. In the case of plasma melting, the recovery of PGM is markedly increased. This technology is similar to electric arc furnaces, but it has the following advantages:

1. plasma heating is a 'clean technology', there is no contamination of the melt by products of combustion/interaction of graphite electrodes;
2. much less burnt part of the melt (metal) part;
3. good sealing of the furnace allows creating a protective controlled atmosphere (due to the plasma-forming gas), which leads to low oxidation of the smelting products;
4. more uniform and volumetric distribution of heat in the furnace zone;
5. the plasma furnace does not require (as opposed to an electric arc furnace) constant and continuous regulation of the arc length, because there is a certain constant arc length that depends on the current strength and at which the optimal and efficient heat transfer to the melt bath is carried out;
6. lower power consumption with the same melting parameters (mass of processed raw materials, processing time, working volume of the furnace);
7. higher heat output with smaller dimensions.

The improvement of the design makes it possible to increase the recovery of PGM to 99% (instead of 95% in traditional furnaces) and heavy non-ferrous metals from a variety of catalysts and successfully separate them from the non-metallic base. Additional extraction of metals is achieved by keeping the slag that is separated from the metal in the storage tank at a certain temperature [4].

Plasma-arc melting (up to 2273K, without flux) is well known for processing auto-catalysts, however, attention is drawn to the preferred processing of the γ -phase of aluminum oxide, since it is possible to efficiently separate the metal phase from the slag. In addition, in the presence of a small amount of carbon, silicon is partially reduced from the base, and the resulting iron silicides serve as a collector. Alloys of iron contribute to the increase in the surface of the product, which shortens the duration of the subsequent leaching process with sulfuric acid (the process can be carried out simultaneously with neutralization). However, it must be kept in mind that iron alloys with a high silicon content do not dissolve in acids, which makes processing of the concentrate difficult. The obtained product can be used for charging the furnace.

The collection of copper and nickel is studied in sufficient detail. Given the undoubted merits of these processes, it is worth noting significant shortcomings: the need to involve in the production of technological schemes for the processing of non-ferrous metals; significant losses of metal with slags; a decrease in the quality of the metal-collector due to harmful impurities; large costs of neutralization.

The method developed in the USA, the charge additive includes, in addition to copper (copper oxide) and flux, reducing agent (coal). The melt blowing is carried out by air (partial oxidation of copper) or oxidants are introduced-nitrate or copper oxide.

Catalyst melting is widely used at temperatures over 1100°C with using fluxes (CaO, cryolite) and metal-collector. As a collector it is used copper, lead, aluminum, iron, nickel or cobalt. Upon contact of the formed slag with the metal-collector, noble metals transfer to the metal-collector. Slag is drained, granulated, crushed and re-melted to recover precious metals. As the flux can be used not only CaO, CaF₂, but sodium fluoride. An obligatory condition for the deep separation of oxide and dispersed metal phases in the smelting process is sufficient fluidity of melts, which is achieved by the addition of fluxes and overheating of the melt. As fluxes, inexpensive, low-toxic substances having low volatility and chemically non-interacting in melts with noble metals should be used. In addition, the consumption of fluxes should be small in order to avoid a large increase in the volume of the melted material. At the same time, the working temperature of the melt should not exceed 1500–1550°C [5].

5. Summary

Technologies of extraction of platinum group metals from catalysts of various origins were considered. The advantages and disadvantages of methods used in industry are considered. The problems of efficient recycling of these metals are important. To ensure high recovery of PGM from secondary waste, optimization of technological refining operations and systems for organizing the collection and preparation of raw materials are necessary. All this requires intensification of scientific research in this field.

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