Optimization of filtration process management in hydrometallurgy

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Abstract. In the process of processing deactivated catalysts, there are problems that arise at each of the stages: in the process of filtration, carburizing and obtaining a concentrate of platinum (palladium) for transfer to refining. When considering these problems, we come to the conclusion that the purity of mother liquors affects the quality and time of catalyst processing, as well as the production of a concentrate with no impurities. The authors proposed to improve the quality of catalyst processing control at the filtration stage after the filter press to install a suspension slip control device and control automation for sampling and stopping the filter press. Such a change will improve the quality of the resulting concentrate during processing of the deactivated catalyst.

1. Introduction
Catalysts containing platinum metals, rhenium, vanadium, molybdenum or Nickel based on A1₂O₃ (based on aluminum oxide), silica gel or carbon carrier are widely used in the chemical (synthesis of nitrogen-containing compounds) and petrochemical (hydrogenation and dehydrogenation processes) industries, are used in devices for afterburning exhaust gases by car and some other areas [1]. The content of palladium in various brands of catalysts varies from 0.4 to 5.0%, and the concentration of platinum, ruthenium and rhenium ranges from 0.1-0.5%. Given the significant amounts of deactivated catalysts produced, they should be considered as the most important secondary raw materials for the production of platinum metals, rhenium, vanadium, molybdenum and Nickel. During operation, the catalysts are deactivated as a result of carburization or being exposed to catalytic poisons (compounds of sulfur, arsenic, etc.). In some cases, the poisoning of the catalysts is reversible and they can be activated, high-temperature regeneration is carried out. In other cases, the poisoning is irreversible and the catalysts must be recycled to extract valuable components.

A large number of hydro- and pyrometallurgical methods have been developed for processing deactivated (palladium, platinum) catalysts. Existing methods of processing catalysts can be divided into two large groups: a - with the destruction of the base, b - without the destruction of the base. For processing group a catalysts (with the destruction of the base), the processes of opening in solutions and melts, high-temperature chlorination and oxidative firing for burning out the carbon carrier are used. In this case, valuable components are concentrated in the solid residue. When processing group b catalysts, methods based on the selective chemical dissolution of platinum metals and rhenium or the method of
concentrating valuable components in reservoir metals are used (A1, Pl, N1, Cu, Pb, ...) with subsequent separation by the method of liqution or cupellation.

There are also methods of full opening of catalysts, when both valuable components and the base material pass into the solution or melt. As a rule, at the first stage of processing, oxidative roasting is used to remove organic impurities and change the modification of the carrier (y- A1₂O₃-α- A1₂O₃). Examples of processing spent and deactivated catalysts of various types are discussed below. Consider the process of processing a carbon-based deactivated palladium catalyst. The main stages of the process are oxidative roasting, leaching, electrolysis, filtration.

Oxidative firing is carried out in hearth or tunnel furnaces at a temperature of 400-600°C. The degree of carbon burnout is 90-95%. The concentration of palladium (platinum) in the stub increases to 3-10%. Increasing the firing temperature to 800-1000°C increases the speed of the process, but at the same time begins to emit toxic carbon monoxide. The resulting stub is leached 6 mol / l with a solution of hydrochloric acid in the presence of an oxidizer-chlorine gas [2]. The process is carried out at a temperature of 70-80°C. The total recovery of palladium (platinum) in the solution at the stages of leaching, filtration and washing, taking into account the turnover, reaches 99%.

2. Solution electrolysis process
The process of electrolysis of a solution containing palladium (plates) is carried out in two stages. At the first stage, a polished titanium sheet cathode and a graphite anode are used. At the cathode, powdered palladium (platinum) is leached, and at the anode, chlorine gas is sent to the leaching stage of the stub. The recovery of palladium (platinum) at the first stage of electrolysis is 92-94%. Further isolation of palladium (platinum) on a titanium cathode from a low-concentration electrolyte becomes unprofitable due to the low current output. Therefore, the depleted electrolyte is sent to the leaching stage or to the second stage of electrolysis, where a three-dimensional electrode with a highly developed surface is used as the cathode (graphite granules are part of the initial catalyst) [3]. Pellets with deposited palladium (platinum) are returned to the first stage. The use of a three-dimensional electrode reduces the probability of hydrogen release and increases the recovery of palladium (taking into account the turnover of granules) to 98.5-99.0%. If necessary, electrolysis can be replaced by the process of cementation of palladium (platinum) on aluminum or zinc. It should be remembered that in this case, the solution after cementation can not be returned to the recycle, as it is contaminated with metal ions-cementator. When processing waste from catalysts that are supported by aluminum oxide, the process flow chart should be selected in accordance with the conditions under which it was used. If the temperature at which it was operated or regenerated did not exceed 900°C, the carrier remains in the original soluble modification (y- A1₂O₃).

In the scheme, the first stage provides for the dissolution of A1₂O₃. If the catalyst was operated or regenerated at a temperature above 900°C, then u-A1203 passes into the chemically stable form α-A1₂O₃-corundum. In this case, use the flow diagram in figure 1.

Stage 2 is based on selective dissolution of palladium (platinum). We'll look at both options below. According to the first variant (figure 1), the spent catalyst granules are dissolved in an enameled reactor with a stirrer at a temperature of 90-95°C. With a solution of hydrochloric acid in the presence of an oxidizer hydrogen peroxide or chlorine:

\[
Pd + 4HCl + 2H₂O₂ = PdCl₄ + 4H₂O, \quad A12O₃ + 6HCl = 2A1C₁₃ + 3H₂O
\]

As a result, 92 to 95% of the carrier mass - A1₂O₃ and palladium (platinum) - passes into the solution. If the residue from the dissolution after washing contains more than 2-3% of the original palladium (platinum), it is returned to the dissolution stage. Palladium is isolated from the solution by cementation. Aluminum sheets are used for this purpose. The Ratio Pd:A1= 1:8 compared to the stoichiometric quantity.

An excess of aluminum is necessary, since in addition to the main cementation reaction, aluminum reacts with hydrochloric acid (A1 + HCl = A1C₁₃ + H₂) [4]. Palladium (platinum) concentrate containing from 25 to 50% Pd (Pt) is sent for refining, and the solution, after cementation containing
aluminum chloride and excess hydrochloric acid, is neutralized with aluminum hydroxide or aluminum metal waste and subjected to evaporation to reduce the volume by 2-3 times. This product is used in organic synthesis plants. According to the second option, the spent palladium (platinum) catalyst is calcined at a temperature of 950°C to burn out organic impurities that accumulate during its operation and cause difficulties at the leaching and filtration stages. In addition, the carrier is almost completely converted to the form $\alpha-Al_2O_3$, insoluble in hydrochloric acid. The product is treated with a solution of hydrochloric acid (6 mol/l) at a solid ratio after calcination:liquid = 1:4 and a temperature of 70°C for the conversion of palladium (platinum) into solution. The process is carried out with intensive stirring for 3-4 hours, periodically adding an oxidizer, potassium persulfate (or hydrogen peroxide). Extraction of palladium (platinum) into the solution, taking into account wash water, is 98.0-98.7%. The solubility of $Al_2O_3$ does not exceed 10-12%. Palladium (platinum) is isolated from the solution by cementation, according to the technology described above. Platinum is extracted from the solution by cementation on aluminum sheets. The use of electrolysis to extract platinum from dilute solutions is limited due to the low current output.

![Figure 1. Process flow diagram for catalyst operation above 900°C.](image)

In the considered examples of processing deactivated catalysts containing palladium or platinum, hydrometallurgical methods are usually used. The latter are characterized by multi-stages, the formation of large volumes of acidic or alkaline solutions, and so on. In addition, when extracting platinum metals by cementation on metallic aluminum in both acidic and alkaline solutions, a high consumption of the cementator metal is observed [5].

3. Recycling process of deactivated catalysts
In the process of processing deactivated catalysts, there are problems that arise at each stage: during filtration, cementation and obtaining platinum (palladium) concentrate for transfer to refining.

When filtering technological pulps, there are 3 main mechanisms of its flow: mesh filtration, filtration with clogging of the filter partition, and filtration with the formation of sediment on the surface of the filter partition [6]. When filtering process pulps, there may be cases when either all the listed mechanisms occur simultaneously, or some of them are absent. In the industry, various mechanisms are
combined and combined to ensure efficient operation of filters with maximum performance [7, 8]. For example, when filtering with the formation of sediment on the surface of the filter partition, it is very effective to have some thin layer of it formed using the grid filtration mechanism. With this approach, at the very beginning of the process, small particles will be trapped in this thin layer, and not in the depth of the filter partition, which significantly impairs the filtration rate. Another example is filtration with clogging of the pores of the filter partition. At the beginning of the process, the particles are not retained on the surface, but inside the partition, thereby reducing the size of the partition pores. This will continue until the mechanisms caused by the formation of sediment on the surface of the filter partition start to work, gradually increasing the filtration efficiency. The vast majority of particles are delayed by a number of forces and mechanisms, such as gravity deposition, the influence of diffusion and inertia forces, as well as by electrostatic forces and intermolecular interaction forces [9].

Let’s look at each problem in turn and the possible solutions that follow from it.

4. Problems of the process of processing deactivated catalysts and ways to solve them

The behavior of the filtration process is influenced by the characteristics of both the solid and liquid phases of the pulp. These characteristics can be used to determine the entire variety of existing suspensions. All characteristics can be divided into three categories: basic properties, the state of the liquid-solid system, and macroscopic parameters.

Basic properties can be measured independently of other system parameters and include: physical properties of the solid and liquid phases, particle size and particle size distribution, particle shape, and surface properties of the particles. Characteristics that evaluate the state of the liquid-solid system depend on the main properties and include: difference, concentration, homogeneity, and degree of particle dispersion. Finally, macroscopic parameters are usually defined to determine whether a particular separation method can be performed. These parameters may include: the permeability or resistivity of the sediment, the particle deposition rate, etc. [10].

After the leaching process, the deactivated catalyst is dissolved, and its components (Pt or Pd) pass from the solid state to the liquid state to form a suspension in the solution, which must be filtered out at the next stage. When the suspension is filtered, a solid precipitate is formed at the exit of the filter press (which is used for recycling) and a solution containing noble metals-Pt or Pd. The purity of the mother liquor affects the entire course of the further process.

The next step is cementation of the solution containing Pt or Pd. The presence of a suspension in the mother liquor can increase the consumption of reagents during cementation and increase the time of the process itself, since the goal of cementation is the maximum possible transfer of Pt or Pd from the liquid state to the solid state, i.e., obtaining a concentrate [11]. The cementation process is continued by filtration, in which the liquid phase is separated from the solid phase and, accordingly, the concentrate is obtained. The resulting suspension in the masterbatch can react with chemical reagents during the cementation process, which can, in turn, adversely affect the filtration process, resulting in a low-quality concentrate. The process diagram is shown in figure 2 below.

Having considered the problems of processing the deactivated catalyst, we can come to the following conclusion [12]. The frequency of masterbatch solutions affects the quality and processing time of the catalyst and the preparation of a concentrate with no impurities (table 1).

| Table 1. Below shows data for ideal conditions. |
|------------------------------------------------|
| **loading, quantity, pc** | **Loading weight, kg** | **Volume of solutions, l, V** | **Average content Pt (Pd), mg / dm³, C** | **Pt (Pd) concentrate yield (including 35% wet) kg, M** |
|-----------------------------------------------|------------------------|-------------------------------|------------------------------------------|------------------------------------------------------|
| Uploading to a single device                  | 1                      | 200                           | 1000                                     | 180                                                   | 0.243                                               |
| Per shift                                     | 5                      | 1000                          | 5000                                     | 180                                                   | 1.215                                               |
| For days                                      | 10                     | 2000                          | 1000                                     | 180                                                   | 2.43                                                |
| Per month (30 days)                           | 300                    | 60000                         | 300000                                   | 180                                                   | 72,9                                                |
\[ M = \left( V \times \frac{C}{1000000} \right) + 35\% \]

Next, we will consider the process under real conditions, in which the suspension slips at the stage of filtration of solutions after the deactivated catalyst is dissolved. The volume of the suspension can vary from 150 mg / dm\(^3\) to 100,000 mg / dm\(^3\).

The calculations for the minimum and maximum overshoot are shown in table 2 below.

![Figure 2. The modified process flow.](image)

**Table 2. Calculations for minimum and maximum slip.**

| Loading, quantity | Uploading to a single device | Per shift | For days | Per month (30 days) |
|-------------------|----------------------------|-----------|----------|---------------------|
| Volume of solutions, l, V | 1 | 5 | 10 | 300 |
| Average content Pt (Pd), mg / dm\(^3\), C | 180 | 180 | 180 | 180 |
| The particle suspension a minimum mg/dm\(^3\), Pmin | 150 | 150 | 150 | 150 |
| The breakthrough of suspended solids max mg/dm\(^3\), Pmax | 1000000 | 1000000 | 1000000 | 1000000 |

\[ M_{\text{min}} = \left( V \times \left( C + P_{\text{min}} \right) /1000000 \right) + 35\% \]
\[ M_{\text{max}} = \left( V \times \left( C + P_{\text{max}} \right) /1000000 \right) + 35\% \]

Analyzing the data from tables 1 and 2, we come to the conclusion that even with minimal suspension slip, the yield of Pt (Pd) concentrate increases by more than 80%, by weight, but not by the amount of precious metal. The frequency of the concentrate decreases and at the same time the amount of reagent...
increases during cementation of masterbatch solutions from 2 to 10 times or more, if we take the parameter of the maximum slip of Pmax.

5. Conclusions
To improve the quality of control of the process of processing the catalyst at the filtration stage (after dissolution), after the filter press, install a device for monitoring the suspension slip and control automation, for sampling and stopping the filter press. Methods and devices that enable automatic rapid monitoring of sedimentation and electrokinetic parameters of the suspension are given in [13]. Based on these indicators, the control system can evaluate the progress of the coagulation process and manage this process based on the coagulation assessment.

At the first stage, the control system can be limited to a single reaction-switching off the filter press with a signal to the operator, who is required to take a sample of the solution. Next, the condition of the filter elements of the filter press is analyzed and replaced, partially or completely. After carrying out maintenance work, the filtration process resumes. A change in the process of processing the deactivated catalyst will fully improve the quality of the resulting concentrate (Pt or Pd).

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