Extraction of Pd and Pt from dead catalysts using the leaching reagents

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Abstract
We studied the possibility of using electrochemical methods for the extraction of metals from dead catalysts, based on the example of the platinum-group metals. Leaching of palladium and platinum was carried out in a solution with sodium hydroxide applying sulphur - graphite electrode, which served as a source of formation of leaching reagents (sodium thiocompounds). The reactions of the formation of leaching reagents and transfer of metals into the solution were performed simultaneously in the volume of a reaction vessel.

One of the reasons complicating extraction of useful metals from fulfilled catalysts of petrochemical processes, their coke up. At research of the fulfilled catalysts it is shown that carbon completely closes the catalyst that interferes with effective dissolution of metals. It is established that the preliminary washing of the fulfilled catalyst organic solvent allows to increase significantly efficiency of leaching from 25 to 52%. At increase in concentration of solution of alkali from 0,1 M to 2,0 M extraction of platinum (Pt) from the fulfilled catalyst on the basis of Al_2O_3 increases from 12,8 to 24,4%.

Keywords: PLATINUM, PALLADIUM, ELECTRO-LEACHING, ELECTRODE, COMBINED ELECTROCHEMICAL REACTION

Introduction

Recently it has become economically more advantageous to use a secondary raw materials for the purpose of extraction of useful materials to further use it. In particular, wastes of electrical industry, radio and appliances are secondary sources of precious metals. There are technologies and methods of processing such wastes, but due to a number of problems they are not widely used.

For organization of plants for processing and recycling of secondary raw materials municipal and state support is needed, as well as the creation and modernization of technologies for waste utilization, in order to increase the economic benefits of the process.

Among the industrial wastes spent catalysts are essential, the scale of production of which is increasing with the increase of number of refineries and refinery products. Volumes of processing of spent catalysts increase annually in a few dozen times. Spent catalysts are sources for precious metals, of rare earth metals of the platinum group and others [1-4]. Modern technology requires an increasing amount of precious metals. Currently, production of precious metals declined sharply and does not provide requirements, so is essential to use every opportunity to mobilize the resources of these metals, and therefore, the role of the secondary metallurgy of precious metals is increased. Furthermore, the extraction Au, Ag, Pt and Pd, contained in the waste profitable than from ores [5-10].

Objective

To develop a framework for the creation of innovative electrochemical leaching of precious metals from man-made and recycled materials. Extracting metals from secondary raw materials is the most important part of the problem of recurrent use of resources. Importance of processing of secondary metals is continuously growing, as the continuously growing need for modern equipment and instruments for various applications - from industrial equipment and military equipment to household electrical appliances and personal electronics. Therefore, in the world there is a constant development and improvement of extracting technology of metals from various types of secondary sources of metal, which in its chemical and mineral composition also continuously complicated. As the object of investigation waste hydrogenation catalysts based on alumina and coal is used: Pt / Al_2O_3, Pd / Al_2O_3, Pd /C.

Chemical composition of the investigated catalysts is shown in Table 1.

Table 1. Chemical composition of the investigated spent catalysts

Catalysts	Content of metals, %						
	Pt	Pd	Fe	Co	Ni	Cu	Mo
Pt/Al_2O_3	5,1	-	0,46	0,23	-	0,06	0,07
Pd/Al_2O_3	-	5,95	0,35	0,65	0,31	3,34	0,64
Pd/C	-	5,2	0,23	-	0,01	0,02	0,09

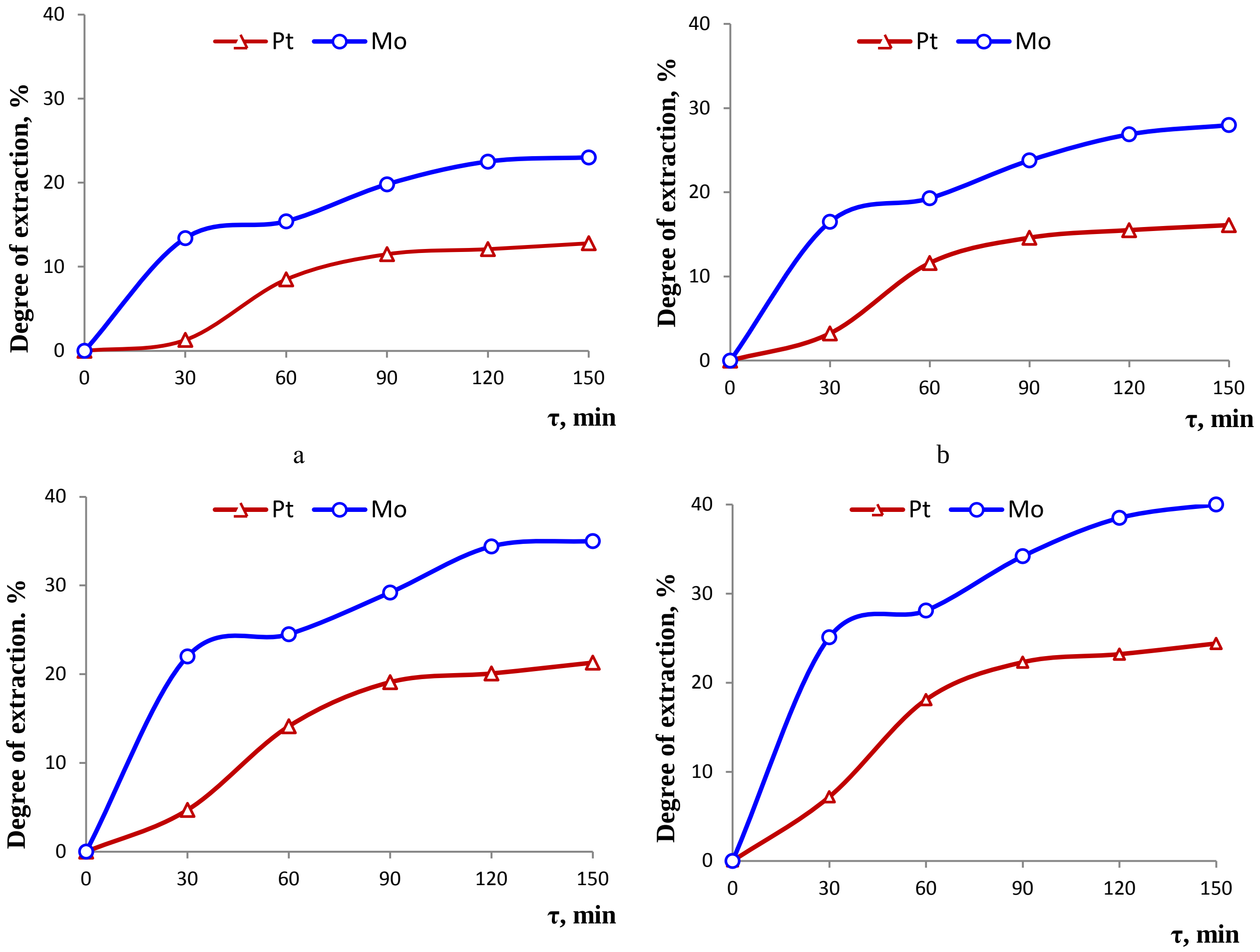
Methodology

Investigated the effect of process parameters of electroleaching on extraction of metals from spent catalysts was carried out in the presence of carbon disulfide electrode at a current density i = 150 A / m^2, with stirring of 480 rpm for 2.5 hours. The volume of sodium hydroxide solution with a concentration of 0.1 -2.0 M is 250 mL, at temperature 25 °C, 5 g of the catalyst. Investigated leaching platinum, palladium, and comparative analysis of the behavior - metal impurities from a molybdenum oxide catalysts on alumina and carbon carriers.

Results

As can be seen from Figure 1 (a), platinum extraction from the spent alumina catalyst is low and extraction increases with increasing concentration of alkali in solution. With the increase of the concentration of the alkali solution from 0.1 M to 2.0 M extraction of platinum (Pt) from spent catalyst Al_2O_3 increases from 12.8 to 24.4%. Extraction of the platinum to the solution increases with the increase of leaching time and reaches a peak after two and half hours. The sequence of increasing of the yield of metal extraction in the solution gives reason to believe that the dissolution process follows the certain mechanism that does not change during leaching.

Recovery of palladium is significantly lower than recovery of platinum, but palladium extraction increases faster at first 30 minutes than the dissolution of platinum. Also extraction of molybdenum takes place, which is 2% higher than the recovery of palladium. Extraction of palladium (Pd) from the spent catalyst in a solution of Al_2O_3 increases with increasing alkali concentration from 5.4 to 8.25%.



a

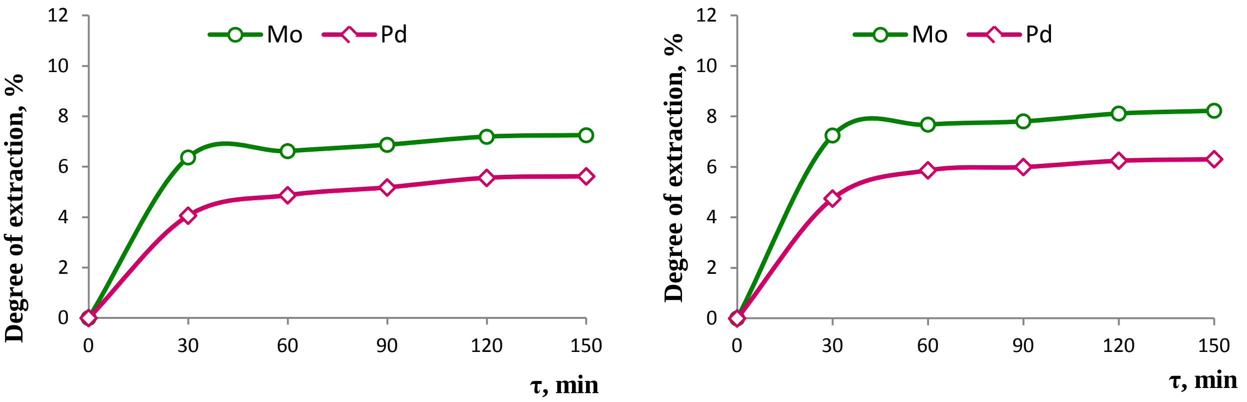
b

c

d

Figure 1. Dependence of degree of extraction of platinum and molybdenum from waste catalysts Pt/Al_2O_3 from concentration NaOH: a – 0,1 M; b – 0,5 M; c – 1,0 M; d – 2,0 M (i– 150 A/m^2, t– 25 °C)

Unlike platinum molybdenum yield in solution exceeds the yield of platinum by about 10%. In this case, after 30 minutes of leaching observed a small area, which may indicate a change in the chemical reaction process of dissolution of molybdenum. Recovery of palladium from spent catalyst in a solution of alumina also increases with increasing concentration of alkali (Figure 2).



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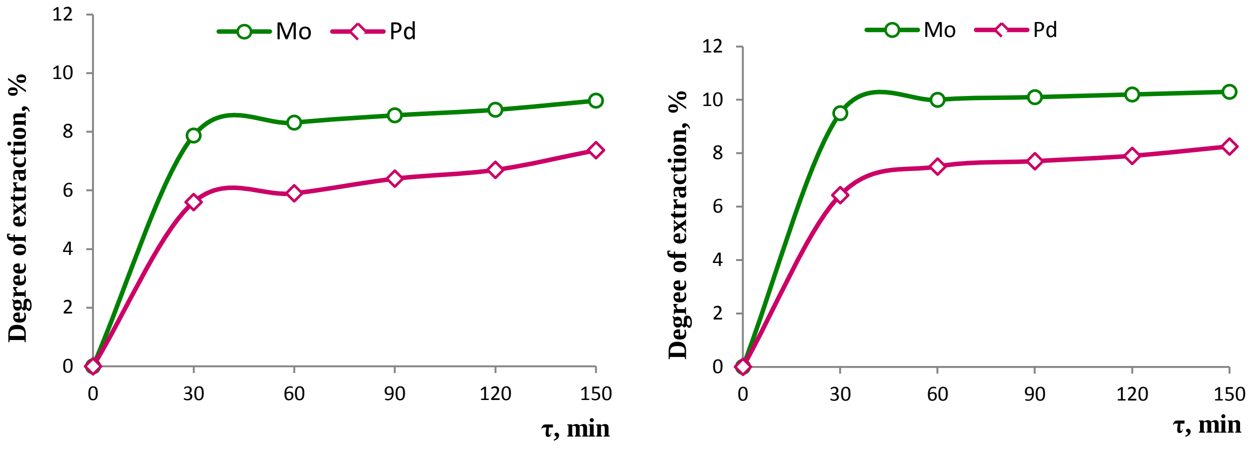

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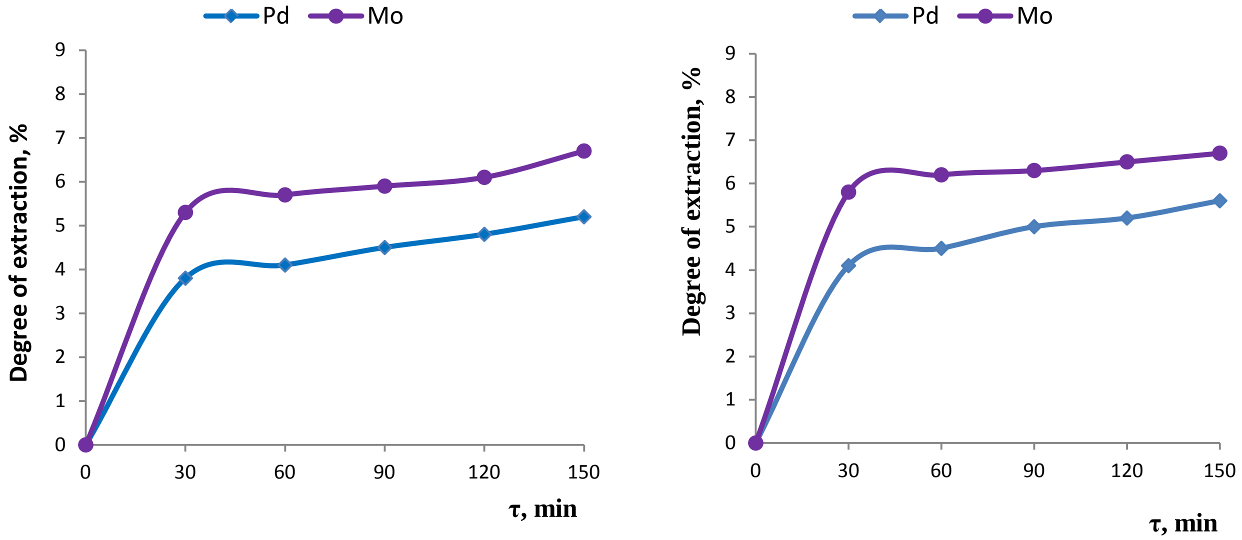
Figure 2. Dependence of degree of extraction of palladium and molybdenum from waste catalysts Pd/Al_2O_3 from concentration NaOH: a – 0,1 M; b – 0,5 M; c – 1,0 M; d – 2,0 M (i – 150 A/m^2, t – 25 °C)

Recovery of palladium from spent catalysts on the basis of carbon is significantly lower than that of catalysts based on alumina (Figure 3). This is due to the high adsorption capacity of the carbon carrier. Extraction of molybdenum into a solution has similar mechanism but rate of extraction is slightly higher than the recovery of palladium as sodium molybdates are more soluble in water than the palladium compounds. With the increase of concentration of the alkaline solution the rate of recovery of palladium (Pd) from spent carbon-based catalyst (C) is increased from 0.5 to 0.8%.



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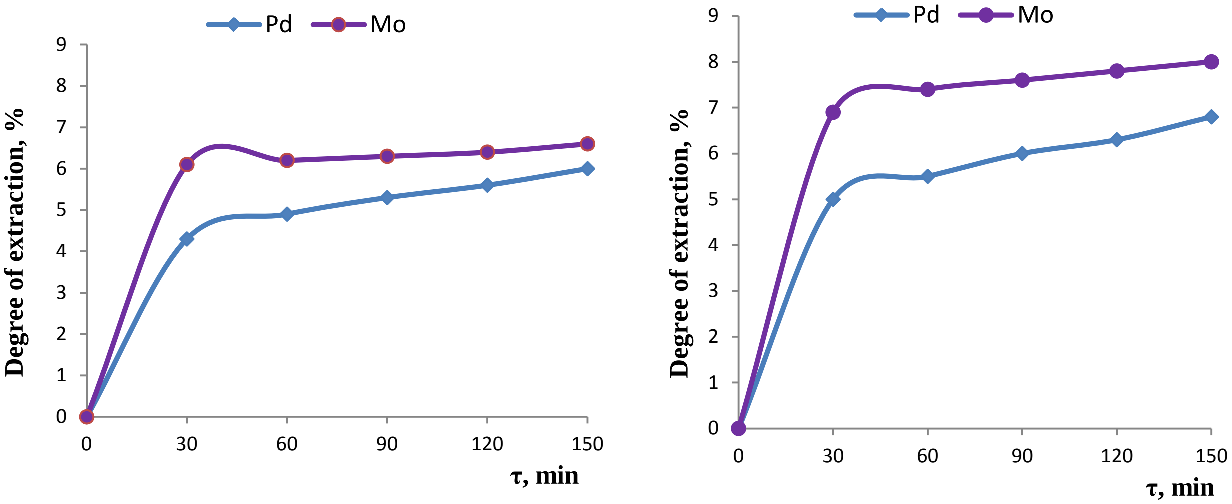

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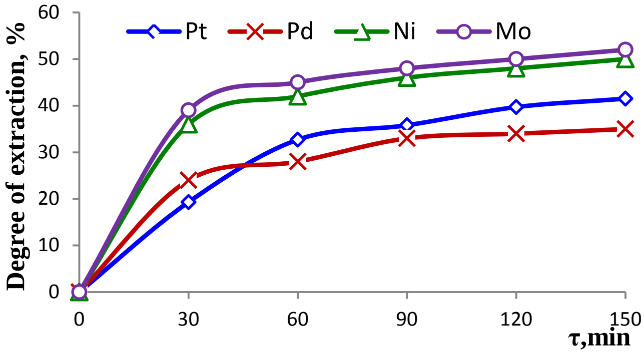
Figure 3. Dependence of degree of extraction of palladiumum and molybdenum from waste catalysts Pd/C from concentration NaOH: a – 0,1 M; b – 0,5 M; c – 1,0 M; d – 2,0 M (i – 150 A/m^2, t – 25 °C)

Comparison of the degree of extraction of molybdenum and palladium from catalysts with various carriers shown that this factor is quite significantly affects on the degree of metal extraction. One cannot ignore the factor that different catalysts with different working life have varying degrees of poisoning, which affects the recovery of metals by an electrochemical method. However, in this case, a low recovery of palladium and other metals from the spent catalyst on carbon support is likely due to the high adsorption ability of carbon, in particular adsorption of noble metals. To test this assumption about spent catalysts series of comparative experiments were carried out by electrochemical extraction of metals from spent catalysts, where catalysts pre-washed with plenty quantities of aromatic hydrocarbon mixtures. For this purpose the mixture was prepared from spent catalysts Pt / Al_2O_3 and Pd / Al_2O_3 (Table 1), and it was washed repeatedly with benzene, until the change of color of solvent.

Figure 4 shows the kinetic curves of extraction of platinum, palladium, molybdenum and nickel from a mixture of spent catalysts after washing with benzene.



C_{NaOH} = 2,0 M, t = 25 °C, i = 150 A/m^2

Figure 4. Dependence of degree of extraction of palladium and molybdenum from waste catalysts Pt/Al_2O_3 и Pd/$Al_2O_3$from concentration

The values of the degree of extraction of metals from spent catalysts, previously washed from the coke formation is significantly higher than that spent catalysts not pretreated, Mo - 52%, Ni -50%, Pd - 35%, Pt - 41,5%.

The conclusion is obvious, one of the reasons hampering the recovery of useful metals from spent catalysts of petrochemical processes is their high coking.

The use of carriers such as active alumina and coal, to which are applied catalytic elements, also create difficulties for the complete removal of precious metals. In a liquid phase leaching due to the high value of the surface area of gamma-alumina and activated carbon (200 m^2 / g) are always two competitive processes occur: desorption of noble metal compounds to the solution from the catalyst surface and the reverse sorption on it. This reversible equilibrium for their displacement requires multiple procedures of leaching and washing, which ultimately is not always ensure the completeness of extraction of metals. The latter fact also leads to the inevitable energy losses and increasing the consumption of reagents due to the necessity of processing of large volumes with low concentrations of valuable components. These drawbacks ultimately determine high irreversible loss of recoverable metals. Waste catalysts characteristic that change the basic parameters of the electrochemical leaching within the boundaries defined optimum conditions of formation of thiosulfate ions (current density of 150 A/m^2 and the concentration of NaOH 0,5 ÷ 2,0 M) has no significant effect on the degree of extraction of metals and practically non-ferrous metals are not extracted from spent catalysts. The most important factor affecting the yield of metal in the solution is the concentration of alkali. However, given the experimental data and a wide range of applications of platinum metals and that the role of the platinum group metals, becomes more and more important with each passing year, it is necessary to continue research in selected scientific - technical direction. Experiments were performed to determine the optimal parameters of leaching man-made materials (spent catalysts of petrochemical production) in order to extract the precious metals.

Conclusion

Optimum conditions for leaching platinum and palladium from spent catalysts of various types are the following: temperature 40 ° C, concentration of NaOH - 2.0 M and a current density of 350 A/m^2. Factors affecting the recovery of metals in solution are the nature of the active phase and the support which define the structure and properties of the spent catalysts (Table 2).

Table 2. The recovery of metals from secondary raw materials at the optimal parameters

Optimal parameters	Parameter	Extract from spent catalysts , %			Extract from spent catalysts after washing,%		
		Pt	Pd	Mo	Pt	Pd	Mo
Concentration of electrolyte - C_{NaOH}, M	1,0 - 2,0	25	10	38	52	28	49
Density of current (i), A/м^2	250 - 350						
Temperature (t), °C	45 - 55						
The ratio of liquid to solid, S:L (solid - liquid)	6:1 -10:1						
Speed of mixing (ω), rpm	240 - 480						

Extraction of palladium (Pd) from spent catalysts on carbon (Pd / C) is significantly lower than on-alumina catalysts (Pd / Al_2O_3), which can be explained by the adsorption capacity of coal - carrier.

It has been established that the pre-washing the spent catalyst with an organic solvent can significantly increase the effectiveness of the leaching from 25 to 52%.

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