

Displayed results of work point out to possibility of selective extraction of required component without dissolution of all material and allow to devise criteria for estimation of efficiency of MA for rare metal concentrates and to apply MA for improvement of available technologies purposefully.

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Rhenium and platinum extraction from dead-catalysts of oil processing with the use of electrochemical hydrochlorination

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The behaviors of platinum, rhenium and dead catalysts KR-108 (TS 2177-019-04610600-99) in hydrochloric solutions have been investigated.

The unique construction of an electrochemical set for the processing of dead reforming catalysts, permitting to produce the chlorinating agent "in situ" (directly in technological process) and extract platinum and rhenium simultaneously, have been developed and introduced into the research process.

Experiments with use of the burnt and not burnt catalysts, and also in addition subjected to crushing have been conducted.

The degree of extraction of valuable components for the burnt and not burnt catalyst are practically equal (platinum – 87.2%, rhenium – 84.1% and platinum – 89.1%, rhenium – 87.5% accordingly), however for processing of the burnt catalysts are necessary more long time of their finding in a reactionary zone on 8-10 hours.

Dependence of degree of extraction on time of process of electrochemical hydrochlorination has been received.

It has been established, that crushing of the catalyst till the size of particles of an order of 0.1 mm allows to raise extraction degree: platinum – 98.2%, rhenium – 91.4%.

Solubility of a basis of the crushed catalyst at electrochemical hydrochlorination has been investigated.

It has been shown, that use of the cathode with the developed surface on the basis of graphite materials allows reaching residual concentration of platinum and rhenium to concentration in some milligramme and less. The technological scheme of processing of the dead reforming catalyst via electrochemical hydrochlorination, by which metal concentrate containing rhenium and platinum is formed, has been suggested.

Key words: catalysts, platinum, rhenium, processing, electrochemical hydrochlorination, electrochemical allocation.

Recently rhenium recycling issue is quite actual. This is related to many factors but mostly to the rise of metal prices because of recently occurred demand-supply disbalance on rhenium market. Special interest of Russian Federation in this problem is connected with the lost of the basic industrial facilities and raw rhenium materials at the end of XX century. These facilities and materials have been remained in union republics (Kazakhstan, Armenia, Uzbekistan) after USSR disintegration. This led to the almost total dependence of domestic

machine engineering on the rhenium import. A significant amount of rhenium and its compounds is utilized in catalyst production (14% of rhenium application), which have high activity and selectivity in various organic and hetero-organic synthesis reactions [1–5]. Therefore dead catalysts represent a promising rhenium resource.

The results of the investigation of platinum, rhenium and dead catalyst CP-108 (Standard 2177-019-04610600–99) behavior in hydrochloric-acid solutions are given within this paper. The central technological

* O. V. Chernyshova, Assistant Professor, e-mail: oxcher@mail.ru; Chair of Chemistry and Technology of Rare and Scattered Metals named after K. A. Bolshakov, Lomonosov Moscow University of Fine Chemical Technology; V. I. Chernyshov, Chief Executive Officer, Innovation Enterprise "TETTRAN" LLC, Moscow, Russia.

idea is to join hydrochlorination process with chlorinating agent generation in situ (directly in technological process) and electrochemical extraction of platinum metals and rhenium from dead catalysts.

Special equipment has been developed and produced for the investigations on the technology development of the electrochemical platinum and rhenium extraction from dead catalysts. General view of the equipment is presented in Fig. 1.

The equipment represents the combination of electrolytic cell, reactor, filter, heat exchanger, pump, power supply and an additional device which provide nonstop platinum, palladium and rhenium dissolution from the catalyst and their extraction on the cathode.

Platinum and rhenium dissolution from the catalyst takes place in the reactor, the support grid is located in the reactor bottom. The filter is settled under the grid and prevents the catalyst falling. On the reactor cover there are the electrolyte-supply connection, the electrolyte and gas outlet connection to the filter, breather valve for the air outlet at the system pouring and agitator shaft gland. On the bottom of the reactor there is the connection for the electrolyte, chlorine and hydrogen mixture supply from the electrolytic cell. The propeller type agitator is driven by the motor-reductor, the rotation rate of the agitator makes from 0 to 5 rotations per minute. The electrolyte with unreacted gases goes from the reactor to the filter where the gases separate from the electrolyte and their evacuation into the gas purification system occurs. There are two connections in the filter cover, one being for the electrolyte flow and the second one being the gas mixture outlet. In the bottom of the filter electrolyte the outlet to the heat exchanger is settled. The heat exchanger is made from quartz glass and it is filled with distilled water with the jacket for electrolyte circulation. Thermometer and electrical heater of 1,000 watt, connected to lab autotransformer, are located in this volume. Then electrolyte is pumped over (the rate of the electrolyte inlet flow is regulated within 0.5–50.0 l/h) into the fluoroplastic electrolytic cell, with the use of the surge pump made from fluoroplastic material, where anode and cathode space being separated with membrane. The electrolytic cell is connected to the regulated current source HY3010. In order to conduct balance experiments, the device is connected to the reactor with high capacity which equipment is identical to the basic one.

Electrochemical hydrochlorination technology was chosen for the treatment of dead catalysts of oil processing. This technology involves the operation of conversion of the precious components into the solution in “softer” conditions compared with the technologies described in the works [6–13]. The solution with 10% of hydrochloric acid was used for extraction at 80–90 °C. At electrochemical hydrochlorination of the catalysts, the shape and the state of the catalyst substrate has a great importance because it significantly influences on the residual concentration of the precious components in the catalyst and on the substrate dissolution extent in the break solution.

As usual, deactivated catalysts go to the processing after thermal treatment during the chemical equipment unloading.

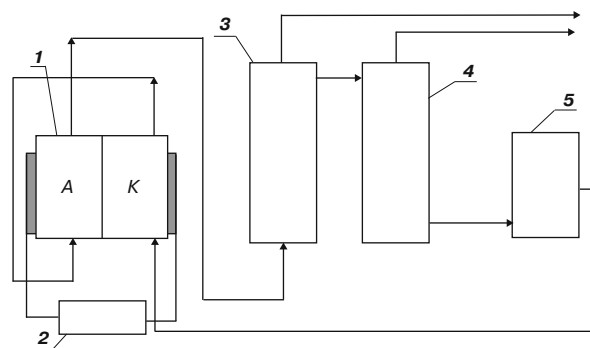


Fig. 1. General view of the equipment for the investigation of electrochemical technology of platinum and rhenium extraction from dead catalysts:
1 – electrolytic cell with anode (A) and cathode (C) space separation; 2 – power supply; 3 – reactor; 4 – filter; 5 – heat exchanger

ing. To decrease the solubility of the catalyst substrate, which consists of different modifications of aluminium oxide, it is additionally roasted with the conversion into hardly soluble modification $\alpha\text{-Al}_2\text{O}_3$. But this process requires heating overcharge as well as complex and expensive thermal equipment. Mechanical grinding of the catalysts is often applied to rise the extraction ratio of the precious components, which makes possible to shorten the step of platinum metals conversion into the solution.

A number of experiments on the roasting and not roasting and also grinding catalyst treatment with the use of laboratory device have been carried out to choose the technology alternatives. The catalysts without grinding have been treated without mixing because it was necessary to apply much force under the laboratory conditions to the stirrer, and the reactor was mechanically damaged when catalyst pieces had an abrasive effect on the parts and the sides of the construction.

When treating the catalysts without grinding, the analysis on the precious components content has been carried out. The samples were taken from three reactor zones: the catalyst from upper covering zone, central and lower zone which directly contacts with the support grid of the reactor. The results of technological experiments are represented in Table 1.

Samples of the catalyst from different reactor zones had different view: the catalyst from the upper zone remained the same, the catalyst from the central zone was significantly lighter and changed its shape because of the sharp side rounding and the catalyst from the lower zone lost its mechanical strength and converted partially into the light powder.

Pretreatment of the catalyst	Extraction, %					
	Upper zone		Central zone		Lower zone	
	Pt	Re	Pt	Re	Pt	Re
Without roasting	75.2	78.5	85.6	82.0	89.1	87.5
Roasting	73.4	74.2	81.5	79.3	87.2	84.1

Pretreatment of the catalyst	Extraction, %		Substrate loss, %
	Pt	Re	
Without grinding	89.1	87.5	14.82
Grinded	98.2	91.4	28.44

The Table 1 shows that there is no considerable difference between roasted catalyst and the catalyst without roasting in terms of the precious components extraction, but the treatment of the roasted catalyst takes more time by 8–10 hours of the presence in the reaction zone. The elongation of the roasted catalyst breaking can be explained by the formation of stronger passivating oxide layer on the platinum surface because the roasting influence takes place only on the platinum breaking.

At the catalyst roasting, formation of the volatile rhenium compound – rhenium anhydride Re_2O_7 – was proposed. But rhenium was not observed in the cold zone during roasting conducted in the dual-ampoule furnace in air flow. This indicates the presence of rhenium in the catalyst in the form which doesn't react with atmospheric oxygen, with the formation of rhenium anhydride.

As soon as the catalyst, destroyed during breaking from the lower part of the reactor, had minimal content of the precious components, the experiments with grinded catalyst were conducted. The results are presented in Table 2.

The data presented in the table show that the catalyst grinding makes possible to raise the precious components extraction from the catalyst. The samples of liquid and solid phases have been periodically taken during electrochemical hydrochlorination; calculation of the extraction ratio of the precious components has been done on the basis of the analysis data. The varying of the extraction ratio is given in the Fig. 2.

During the electrochemical hydrochlorination the structure of the catalyst was noted to be significantly changed. The initial catalyst powder view changed due to low particle dissolution with formation of the pulp, the number of small particles reduced and, at the end of the process, the significant amount of remained catalyst particles had blue, black, brown and red colour. Roentgen fluorescent analysis (roentgen fluorescent analyzer VRA-30 Carl Zeiss Jena) showed the significant amount of rhenium

Product	Mass, g	Mass loss, %
Initial catalyst	200.00	–
Catalyst residue, drying at 110 °C	193.03	3.49
Catalyst residue, tempering at 950 °C	143.11	28.44
Al content in the electrolyte in terms of Al_2O_3	67.58	–

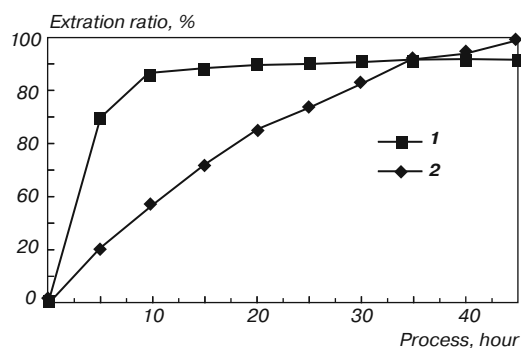


Fig. 2. Relation between Re and Pt extraction ratio and the duration of electrochemical hydrochlorination:
1 – Re; 2 – Pt

and iron in them, it can be induced by the presence of hardly dissolving with the use of hydrometallurgical methods rhenium and iron compounds in the particles.

Duration of the process has a great influence on the precious components extraction ratio from the catalyst.

For rhenium dissolution, it is enough to treat the catalyst with the acidic solution, 75–80% of total rhenium dissolving. The rest rhenium dissolves much more slowly and with the use of electrochemical hydrochlorination which allows to raise rhenium extraction ratio up to 88–90%.

Relation between Re and Pt extraction ratio and duration of electrochemical hydrochlorination of the grinded catalyst (Fig. 2) indicates that platinum extraction is the slowest process at the catalyst treatment. This fact correlates with the investigations on platinum dissolution behavior because passivating oxide layer of this metal is the most stable and it takes much time to destroy it [15].

When breaking the catalyst, the incomplete dissolution of the substrate consisting of aluminium oxide is occurred. Solubility of aluminium oxide depends on the substrate modification. Aluminium oxide has a large number of lattice structure modifications determining the reactivity of this compound. According to the technology, the solubility of the catalyst substrate is decreased after high temperature roasting at 1200–1300 °C with conversion of aluminium oxide into α -modification. But this method is connected with high power inputs and it requires special equipment for its realization.

When conducting electrochemical hydrochlorination in the solution with 10% of hydrochloric acid, solubility of the catalyst substrate was 28.44%. The treated catalyst unloaded from the reactor and dried at 110 °C had low mass loss. The tempering of the residue at 950 °C led to mass loss of about 25% which can be explained by the formation of hydrated aluminium chloroxo-compounds. Mass loss of the catalyst correlates with the data on aluminium content in the electrolyte. The experimental results are presented in Table 3.

The exceed of total electrolyte residue and aluminium dissolved in the electrolyte was 10.69 g, which can be explained by the formation of new solid phase on the basis of hydrated aluminium chloroxo-compounds. This excludes secondary application of the residue as the catalyst substrate.

Data on aluminium content in the electrolyte (in terms of Al_2O_3) are given for the balance experience with the catalyst

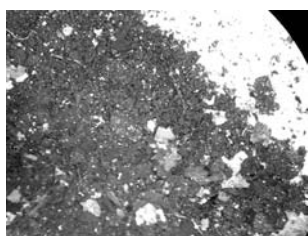


Fig. 3. Microphotography of the cathode residue

load of 200 g and for the sum of electrolyte volume of 3 l. When treating 1600 g of the catalyst in the same electrolyte volume, aluminium content was 47.45 g/l or totally 273.75 g in terms of Al_2O_3 , it was 17.11% mass loss of the catalyst substrate.

In terms of aluminium chloride, its concentration in the solution was 241.81 g/l. Literature data [16] show that aluminium chloride solubility is 32.7% at 80 °C and it slightly depends on the solution temperature, for example, the solubility is 31.9% at -55 °C. This fact makes possible to conclude in advance that aluminium chloride solubility in the electrolyte limit has been probably reached. Decrease of aluminium chloride concentration in comparison with reference data is caused by the same ion action (chloride ion in this case) which reduces aluminium chloride solubility. The electrolyte is expected to be in balance with formed solid phase on the basis of the catalyst substrate in the subsequent work.

When treating the catalyst, platinum and rhenium pass into the electrolyte solution, which is continuously pumped through the electrolytic cell. Metals precipitate in the electrolytic cell in the form of metal powder, precipitation is presented in the photo (Fig. 3). The residue is black fine-dispersed powder, the particles taken from the cathode surface have metallic luster. Composition of the cathode residue from the technological process of the CP-108 catalyst treatment with current density of 5.0 A/cm² equals to: 64.2% of Pt; 10.2% of Re 2.5% of Mo; 4.3 % of Fe; 10.8% of insoluble residue.

In Fig. 4 the process flowsheet is presented describing the treatment of dead catalysts of oil processing with the use of the electrochemical method.

The process flowsheet includes following technological operations:

- prior grinding of the catalyst;
- electrochemical hydrochlorination of the catalyst;
- washing of the catalyst and cathode residue;
- correction of the technological solution composition;
- evaporation of rinsing water and electrolyte for the purpose of aluminium and iron chlorides removal.

The flowsheet can be organized in such way that electrochemical hydrochlorination and catalyst washing may take place in the same technological string. At washing, the electrolytic cell discharged from the cathode residue, joins in the workflow scheme so that the washing solution passes only through the cathode chamber of the electrolytic cell. At washing solution circulation through the system, the washing of the catalyst from the process solution containing the precious components takes place and partial platinum and

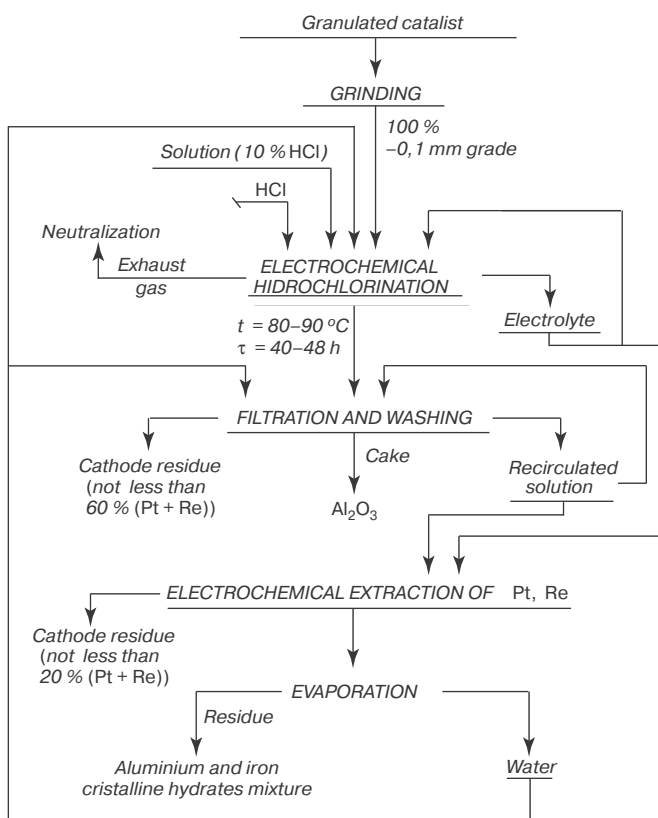


Fig. 4. The process flowsheet describing the treatment of dead catalysts of oil processing with the use of electrochemical hydrochlorination

rhenium precipitation in the form of metal concentrate occurs. Additional platinum and rhenium precipitation is possible because washing solution has lower concentration of the dissolved chlorine and its oxo-acids and their compounds. Use of the cathode with the advanced surface on the basis of the graphite materials allows to obtain residual platinum and rhenium content in some milligrams and less. The data on precipitation on the graphite tissue are given in the Table 4.

Proposed technological sheet has following advantages.

1. No preliminary roasting of the catalyst.
2. The absence of gas collecting system and gas purification of roasting gases.
3. Combination in one technological process of dissolution and extraction of the precious components.
4. Production of precious components in the form of the metallic concentrate with high content of noble metals.
5. Suitability of concentrate for individual metals production with the use of known technologies.
6. High extraction ratio of precious components.

Table 4
Dependence of Pt and Re residual concentration in the electrolyte on the cathode material

Cathode material	Residual concentration, g/l	
	Pt	Re
Titanium electrode	0.056	0.115
Graphite tissue	0.003	0.037

7. Considerably reduced volume of working solutions and sewage.

8. Simple compact instrumental and technological scheme with minimum non-standard equipment.

9. Minimum reagents.

10. Conduction of the process in technological solutions with low concentration of mineral acids.

11. Technological process control with possible automation.

12. Absence of the catalyst overworks.

The conducted investigations and laboratory experiments showed the electrochemical hydrochlorination to be a promising technological treatment of secondary rhenium materials combining high efficiency and simple ecological technological scheme.

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