The use of electrohydropulse treatment of waste solutions in refining production for the recovery of platinum group metals

D Yu Parfenov 1, V S Ratushnyak 1, E S Ilyin 1, A V Yuryev 1, V O Kolmakov 1

1Krasnoyarsk, Krasnoyarsk Railway Institute, branch of the Irkutsk Railway Engineering University

Abstract. The high cost of precious metals and environmental requirements lead to the need for the completeness of their extraction from primary and secondary raw materials. During the processing of primary raw materials, waste solutions are produced that contain low-concentration precious metals, which must be removed from the process. To prevent losses and comply with environmental protection requirements, it is necessary to extract precious metals from waste solutions. The complexity of this task lies in the low concentration and chemical forms of the presence of precious metals in aqueous systems. The cementation method, currently used for the extraction of precious metals, has several disadvantages: the duration of the process, high-energy consumption, etc. To increase the efficiency of the method used, it is necessary to pre-treat the solution with the goal of labilizing the noble metal complexes. The purpose of the experiment: determination of the optimal modes of the electrohydropulse (EHP) method for intensifying the process of additional extraction of platinum group metals (PGM) and heavy non-ferrous metals from industrial solutions of refining production. As a result of the study, the necessary materials were selected to create the reactor and electrode systems, the volume of the laboratory reactor was determined. Trial launches of the installation were carried out, according to the results of which a pulse current generator (PCG) was configured. A series of tests was carried out, based on the results of which conclusions were drawn about the possibility of using this method to activate stock solutions.

1. Methods for the recovery of precious metals from waste process solutions

The following methods for the recovery of precious metals from process solutions are widely used:
1 Cementation.
2 Sorption.
3 Electrolysis.
4 Galvano-coagulation.

Cementation is one of the first and most common methods for isolating PGMs from effluent solutions. The driving force of the cementation process is the difference between the real redox potential (RRP) of the cementing metal and the ions of the metal being deposited to the solution [1, 2, 3].

This method is effective with a high concentration of precious metals in solution (more than 20 mg / l). The process of cementation lasts about 20 - 24 hours, since the destruction of the durable complex compounds of precious metals requires a long time, which implies high energy costs. The temperature of the solution is 80 - 90 °C during the whole cementation process, the solution usually is heated with direct steam.

Sorption is widely used at gold mining enterprises. This operation is most often used for the following types of solutions:
• productive solutions of heap and in-situ leaching;
• discharge of the thickeners containing cyanide complexes of gold and silver;
• stock solutions after gold electrolysis;
• filtrates after the filtration of cyan-containing sorption tailings;
• solutions of the industrial sewage of the plants after the preliminary separation of the solid phase [4].
The disadvantages of this method are the large dependence of sorption on the forms of valuable components in the solution, the relatively long duration of sorption and the small capacity of sorbents, and in relation to precious metals - the complexity, and in some cases, the impossibility of desorption.

Electrolysis is the process of the isolation of the constituent parts of solutes or other substances on the electrodes that are the result of the secondary reactions on the electrodes, which occurs when an electric current passes through the solution or the electrolyte melt. The disadvantages of electrolysis are high energy consumption, the need for frequent replacement of the electrolyte, cleaning of the electrodes and the fundamental impossibility of the complete extraction of valuable components.

Galvano-coagulation is the method based on the effect of a galvanic iron (aluminum) -cox or iron (aluminum, copper) -cox element, placed in the solution to be purified. Due to the difference in electrochemical potentials, iron is polarized anodically and goes into solution, followed by precipitation in the form of oxyhydrates, on the surface of which there are adsorbed the negatively charged anions. Coke or copper in the galvanic couple is polarized in the cathode way, as a result of which there is electrodeposition of cations on the cathode [5, 6]. Thus, the metals are extracted from solutions. The disadvantage of this method is a relatively low degree of extraction of metals (about 80-90%) from the solution and the formation of a significant amount of slime sediment.

2. Method to improve the efficiency of precious metals extraction from solutions

Stabilization of precious metal complexes is the most promising method for increasing the efficiency of extraction. Chemical and physical methods can be used for labialization: complexing agents, electrochemical activation, activation of iridium complexes by autoclave chlorination, microwave radiation, UV radiation, and other methods.

The electro-impulse effect is one of the ways to activate the solution. EHP is a method based on breaking complex compounds and speeding up chemical reactions. This method does not replace the existing methods, but is an addition to them. The EHP method is actively used to accelerate the chemical reactions in various areas of the national economy (in metallurgy — activation of the lime mortar; in agriculture — activation of bio solves (bacterial explosion); in chemical industry — acceleration of reactions, in particular, to intensify the leaching process of platinum-palladium catalysts). The use of EHP method speeds up processes significantly (2-5 times) when replacing the traditional types of activation, that is, increasing the temperature of the solution, expensive catalysts, mechanical and ultrasonic methods.

The main properties of the EHP discharge, affecting the activation of solutions:
- significant (tens of kV / cm) electric field strength;
- values of the current in a pulse are up to tens of kA and, as a result, the large values of the magnetic field;
- pressure in the pulse is 10-100 atm;
- the temperature in the discharge zone is up to 30 000 °C;
- the ultraviolet radiation;
- the X-rays (the level of XR depends on the voltage);
- the cavitation effect.

The possible variants of the technology are electrohydropulse activation - cementation with iron; electrohydropulse activation - galvanic-coagulation on the pair of coke - iron or on the filler of coke – iron - aluminum. In both cases, reducing agents may be added. The studies of the possibility to use pulse technologies to intensify the leaching process of platinum-palladium catalysts [6] showed the recovery up to 98% by treating a catalyst with an energy of 15 kJ; the catalyst is most active in the first 30 minutes of treatment.

At Krasnoyarsk Institute of Railway Transport, patent studies were conducted, covering more than 130 documents (58 applications and 76 abstracts of the Russian inventions) devoted to the extraction of precious metals. Most of the inventions were connected with cementation or sorption [7,8].

The considered methods have a number of disadvantages, such as, the long duration of the process, a significant increase in the volume of effluent, high energy consumption, the high cost of facilities and sorbents. In this connection, in the research conducted with the help of the EHP method, the method was chosen as the most optimal one. It extends the existing methods and is easily integrated into the existing system; it is characterized by relatively low power consumption [9].

3. Installation description
The installation includes the pulse current generator and the reactor with an electrode system.

The main technological characteristics of the developed equipment.

1) Pulsed current generator.
The PCG should have the following characteristics: the maximum energy per pulse is 0.3 kJ; voltage on electrodes is from 5 to 10 kV; current between the electrodes is from 2 to 10 kA; the repetition rate of micro pulses is from 0.5 to 2 Hz; the maximum power consumption of the installation is 2 kWh; the power supply of the generator from the network of alternating voltage is 220 ± 22 V [10,11,12,13].

2) Reactor (Figure 1).

![Figure 1. Photo of the reactor](image)

The reactor has a housing (working chamber), a cover, an electrode system, and it is positioned on a support platform with fasteners. The system of electrodes consists of the units: negative and positive electrodes.

The volume of the reactor is 1 l. The working chamber of the reactor was made of HDPE as per GOST 22689.2-89, the cover and the electrode system are made of grade VT1-0 titanium as per GOST 19807-91 and
of titanium alloy OT4 as per GOST 26492-85. The choice of these materials was due to the use of the reactor for working with chemically aggressive liquids. Other elements of the reactor that are not in contact with the medium being processed (washers, nuts, tuckers, etc.) are made of general-purpose St3 steel, GOST380-2005. The overall dimensions of the reactor are 310x110x140 mm.

3) Electrode system.
   It consists of two electrodes: positive and negative. The electrode material is polyurethane, titanium, iron.

4. Manufacture of reactor and electrode systems
Some parts of the reactor (metal elements, mainly: electrodes, washers, glasses, lugs, covers, tuckers, studs, etc.) are produced according to the design documentation (DD) at the industrial enterprises of Krasnoyarsk. Figure 2 shows the assembly drawing of the reactor.

![Figure 2. Schematic of the reactor](image)

Some structural elements (washers for electrodes, an insulator of a positive electrode) were made in the Student Design Bureau of "Engineering Solutions". The technology for manufacturing parts from molded polyurethane (PMC780) was developed and mastered for this purpose. This technology has the following operations:
1) Preparing the surface of the form (cleaning, applying a release agent to prevent the form from sticking to the model).
2) Mixing A and B components in a ratio of 2A: 1B.
3) Mixing the components.
4) Degassing under vacuum.
5) Pouring the mixture into the form.
6) Cure for 48 hours.

As a result, washers and electrode insulator with the specified insulation and strength characteristics were produced.

5. Test methodology

For the experiments it is necessary to simulate the process of cementation. The existing cementation process is carried out as follows. The containers designed for the cementation process were loaded with scrap metal to 2/3 of their volume, then they pour the stock liquor and heat it for 20-24 hours and partially mix the solution with direct steam, the temperature of which is up to 160°C. The solution in the process of cementation is heated to 90°C, the temperature is controlled by steam consumption.

To simulate the process, 3 electric tiles were taken (to heat the solution), 3 cups for grouting with a volume of 1 liter (as a replacement for cementing baths), 3 kg of steel nails.

A 1.5-liter beaker was used for pretreatment of the solution (pH adjustment, addition of additive reagents, etc.).

- Before the experiment, the nails were degreased with a detergent and boiled for 10 minutes in a solution of hydrochloric acid.
- All three cementation cups, with a volume of 1 liter, were numbered in order and each one was loaded with 1 kg of nails.
- The reactor was installed in a cabinet with the subsequent connection to the PCG.
- 20 liters of solution were delivered after the first cementation to a canister.
- 1 kg of the reducing agent of Na2S2O3 was taken to add it to the solution in order to exclude the possibility of recovery of the complex compound after its destruction.
- The process was carried out at pH = 1. Acidification was performed with sulfuric acid.

Preparation of the solution for cementation, acidification of the solution, namely, mixing and addition of the reducing agent were done in a 1.5-liter beaker. Subsequently, the prepared solution in equal volumes was sent to the beaker for cementation and to the reactor, where it was treated with an electro pulse effect. The treated solution was poured into a cementation beaker. Thus, dehumidification by cementation was compared when the solution was pre-treated by an electric pulse and when it was not pre-treated.

During the experiments, the number of pulsed discharges and in some cases the discharge energy varied. During the experiment, the expediency of acidification was checked before or after the EHP treatment. The addition of the reducing agent also varied in time; the addition of the reducing agent was also done with conventional cementation, in order to assess the effect of the EHP effect on the cementation process.

6. Plan of experiments

The program of the experiments was designed for 2 types of solutions brought to the shop for extraction by cementation.

For solution number 1.

1. One liter of the initial solution was taken into a measuring cup heated to 80-90 °C; steel of a 3-5 steel grade was used as a cementator filling 2/3 of the volume of the glass. The solutions are taken for the analysis of precipitation-based chemical analytical method (CAM) in Central Factory Laboratory (CFL). Two samples are taken for analysis: initial one and that one after cementation. The samples were analyzed with CAM. The experiments were done for varying periods of time.

2. One liter of the initial solution was taken into the measuring cup; it was prepared for the EHP treatment. It was heated to 80-90 ° C; steel of the 3-5-5 grade was used as the cementator metal filling 2/3 of the glass volume. The solutions were taken for analysis with CAM - CFL. The experiments were done for varying periods of time and number of pulses.

3. The initial solution (V = 2 l), to which a reducing agent is added (allowing one to exclude the restoration of the original properties of the solution), was divided. One liter was taken for electro pulse treatment, and then for cementation; the rest was taken for the cementation process. The solutions were taken for the analysis with CAM – CFL. The experiments were done with varying periods of time and number of pulses.

For solution number 2.

1. One liter of the initial solution was poured into a measuring cup heated to 80-90 ° C. Steel of a 3-5 grade was used as a cementator filling 2/3 of the volume of the glass. The solutions were taken for the analysis of CAM - CFL. Two samples were taken for the analysis: initial one and that one after cementation. The samples were analyzed by CAM. The experiments were done for different periods of time.

2. One liter of the initial solution was poured into the measuring cup prepared for the EHP treatment. It was heated to 80-90° C; steel of the 3-5-5 grade was used as a cementator metal filling 2/3 of the glass volume.
The solutions were taken for the analysis of CAM - CFL. The experiments were done for different periods of time and number of pulses.

3. A reducing agent was added to the initial solution (V = 2 l), allowing one to exclude the restoration of the initial properties of the solution. One liter was taken for electro pulse treatment and then – for cementation; the other was taken for cementation. The solutions were taken for the analysis of CAM – CFL. The experiments were done for different periods of time and number of pulse.

7. Analysis of the results of the experiment

During the project, the following experiments were conducted:

- preliminary EHP treatment before cementation;
- preliminary EHP treatment with the addition of a reducing agent (sodium thiosulfate) before cementation;
- EHP treatment followed by sludge solution;
- EHP treatment with the subsequent sludge and additional processing before cementation.

Steel shavings, nails and graphite were used as the cementing agents.

The analyses of the samples were done with WSS (working standard solution) and CAM methods. The EHP treatment has a beneficial effect on the recovery of base metals (BM) during cementation, as shown in Figure 3.

![Figure 3. Chart of the EHP effect on the NB extraction.](chart)

CM-1 Initial solution, 2-1 conventional cementation (heating + stirring), 2-2 EHP treatment (8 kV, 100 imp., Heating + stirring), 2-3 EHP processing + reducing (8 kV, 100 imp., heating + mixing). All the samples had 2-hour cementation, which is 22 hours less than the usual cementation time.

The results of the experiments are presented in Table 1.
Table 1. Results of additional metal extraction of PGM by cementation with and without EGP treatment.

| №  | Samples                                      | Pt       | Pd       | Rh       | Ir       | Time h |
|----|---------------------------------------------|----------|----------|----------|----------|--------|
|    |                                             | content, mg/l | content, mg/l | content, mg/l | content, mg/l |        |
|    | Initial solution                            | 30       | 0.0      | 0.5      | 3.7      | 4.8    | 0.0    | -      |
|    | Conditional cementation                      | 7.2      | -76.0    | <0.5     | 0.0      | -73.0  | 0.0    | -85.4  | 3      |
|    | EHP processing (8 kV, 50 imp., heating + mixing) | 3.4      | -88.7    | <0.5     | 0.0      | -73.0  | <0.5   | -89.6  | 3      |
|    | Cementation with reducing agent (heating + mixing) | 9.3      | -69.0    | <0.5     | 0.0      | -81.1  | 0.9    | -81.3  | 3      |
|    | EHP processing + reducing agent (8 kV, 50 imp., heating + stirring) | 5        | -83.3    | <0.5     | 0.0      | -91.9  | 1.3    | -72.9  | 3      |
|    | Initial solution                            | 27.3     | 0.0      | <0.5     | 0.0      | 3.2    | 0.0    | 5      | 0.0    | -      |
|    | Without EHP, day of sediment                | 25       | -8.4     | <0.5     | 0.0      | -28.1  | 3.6    | -28.0  | 2      |
|    | EHP 200 pulses 8.2 kV, sludge day           | 23.6     | -13.6    | <0.5     | 0.0      | 0.6    | -81.3  | 3.1    | -38.0  | 2      |

Table 1 shows that the influence of the EHP method increases the extraction of PGM from the stock liquors during the cementation time within 2 and 3 hours. Also, two-hour solutions were not cemented, as a result of which the sediment rate fell in the samples, while in the sample processed with EGP, the sediment was rather marked, and the sampling showed the decrease in PGM in these samples.

Figure 4. The effect of solution treatment on the cementation process.

Figure 4 shows the influence of the EHP treatment with and without a reducing agent on the additional extraction process. The comparison is made against the conventional cementation with and without a reducing agent. CM-4 initial solution, 8-1 ordinary cementation, 8-2 EGP treatment (8 kV, 50 imp., heating + mixing), 8-3 cementation with a reducing agent (heating + mixing), 8-4 EGP processing + reducing agent (8 kV, 50 imp., heating + mixing), all cementation processes lasted for two hours.

8. Conclusion

The experiments have shown the effect of EHP on the recovery of PGM and the possibility of its use in industrial production. To establish the optimal processing parameters, it is necessary to upgrade the power...
section of the power generation plant to 2 kJ, and also to change the reactor design so that it can withstand 2 kJ loads. In connection with the change in properties (characterized by turbidity) of the solution within an hour, development of a method of rapid analysis is in demand.

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