

Electric Spark Method of Purification of Galvanic Waste Waters

Abstract. The purification of multicomponent galvanic waste water by the electric-spark method using metal loading (Fe, Al) and low-voltage (up to 1000 V) equipment have been carried out.

Streszczenie. Przeprowadzono oczyszczanie wieloskładnikowych ścieków galwanicznych metodą iskry elektrycznej za pomocą urządzeń do ładowania metali (Fe, Al) i niskonapięciowych (do 1000 V). (Metoda elektroiskrowa oczyszczania wód odpadowych galwanicznych)

Keywords: electro spark method, water treatment, galvanic processes, water quality.

Słowa kluczowe: metoda elektroiskrowa, uzdatnianie wody, procesy galwaniczne, jakość wody.

Introduction

The most important pollutants of wastewater are heavy metals. Sources of heavy metals are enterprises of the chemical, metallurgical industry and other removal of heavy metals ions from discharges, in particular galvanic plants, is one of the most difficult tasks of wastewater treatment. Water quality is a very important aspect of a country's sustainable development. Quality of water is equally important to the quantity available [1-7].

Coagulation methods for wastewater treatment from heavy metal ions are the most effective and used [8-15].

In electro coagulation methods of galvanic wastewater treatment adsorption-active hydroxides of iron or aluminum are formed by electro erosion by electrolytic dissolution of steel or, respectively, aluminum anodes. In this case, phenomena such as water electrolysis, particles' polarization, electrophoresis, redox processes and the interaction of electrolysis products with each other can occur in the electrolyzer. Galvanic coagulation method consists in passing waste water through a galvanic coagulator that contains an active anode and cathode mixture, for example, coke, aluminum, iron [16] etc.

Electric spark discharge in metal-containing reactors is proposed as an alternative to existing methods for purification of galvanic drains. The method is also an effective way for producing coagulated active metal oxides and hydroxides [17].

In this case, the main attention was directed to expanding the capabilities of the method, aimed primarily at the component cleaning of galvanic drains, by increasing the operating voltage from 300-600 V to 3-15 kV, and using monometallic metal loading (granules of one metal). This allowed the purification of concentrated galvanic drains containing Cr(VI) to 1000 mg/dm³. However, the further implementation of this approach turned out to be economically inexpedient due to the high cost and limited resource of high-voltage equipment, its increased danger and low process productivity.

The object of this work is to study the influence of technological parameters (specific energy, frequency characteristics of electrical impulses, flow patterns of purified water) on the efficiency of the process of cleaning multicomponent galvanic drains in reactors with combined metal loading using low-voltage (up to 1000 V) electrical equipment.

Increasing the efficiency of the cleaning method will significantly reduce the concentration of heavy metals, which in turn will contribute to solving a number of environmental problems of enterprises [18].

Materials and methods

The materials for the experimental treatment were real wastewaters after various galvanic production operations,

which is supplied to the treatment facilities of a machine-building enterprise. Galvanic wastewater are multicomponent composition containing ions (Cr⁶⁺, Ni²⁺, Cu²⁺ & Zn²⁺). A mixture of iron and aluminum granules with a diameter from 4 to 6 mm was selected as the material for metal loading. This choice is due to the following facts: the positive result of complex water purification from heavy metal ions during high-voltage electric discharges in reactors with granular metal loading and the use of these materials [19]; the traditional use of steel or aluminum electrolytically soluble anodes during the implementation of the electrocoagulation method for treatment galvanic wastewater [8, 9]; experience in stabilizing spatially distributed discharges in a layer of aluminum and iron granules with using low-voltage (up to 1000 V) electrical equipment [20].

To implement low-voltage electric discharges between the granules of metal loading, a push-pull (charge/discharge) electric circuit based on semiconductor switches was chosen (Fig. 1). The clocks were formed by the signals of the rectangular pulse generators (PG1, PG2), connected by the output/input of synchronization, either with a preset frequency of the master oscillator (PG1), or by an external trigger (S). Pulse isolation transformers (IT) were used to decouple the power and control circuits.

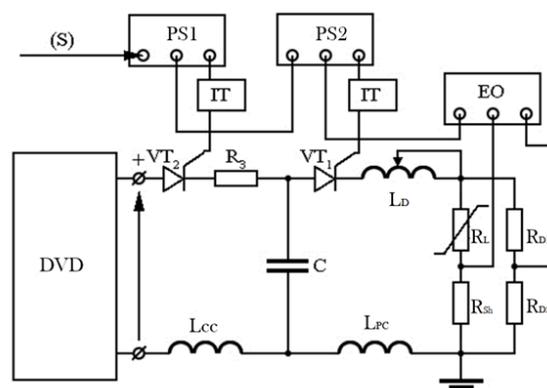


Fig. 1. The electric circuit of a low-voltage source of discharge currents

The charging circuit consists from a direct voltage driver (DVD), a thyristor (VT₂), an ohmic charging resistance (R₃), a capacitor bank (C), and a charging circuit's own inductance (L_{cc}). The voltage generator (VD) was assembled from a universal power source UIP-1 (Tallinn Measuring Instruments Plant, up to 600 V±0.5%, installed power 1500 W) or - serially connected oil autotransformer, transformer and bridge diode rectifier.

The structure of the discharge circuit includes a high-speed power thyristor (VT₁), an additional multi-section inductance (L_D), an electric spark load (R_L), a low-impedance coaxial shunt (R_{sh}), and a self-inductance circuit (L_{pc}). In parallel with the spark load, a voltage divider (R_{d1}, R_{d2}) was connected.

The discharge current and voltage at the interelectrode gap are recorded with an OWON XDS 3202E oscilloscope, using a divider and shunt of own manufacture. The general view of the laboratory device is in the Fig. 2.



Fig. 2. The general view of the experimental device

The determination of the content of heavy metals in the start and treated water was carried out in accordance with the current regulatory documents [21-23].

The efficiency of the galvanic waste waters treatment process was studied by varying the specific processing energy, the amount of stored energy, pulse parameters, and the height of the metal load.

Results and discussions

The choice of the range of variation of parameters and processing schemes is based on the following assumptions. The specific energy is varied taking into account the data given in paper [13], which relates to the purification from highly concentrated solutions of heavy metal ions (from 8500 mg/dm³ – total content of heavy metals and up to 600 mg/dm³ Cr⁶⁺, respectively) with high-voltage electric discharges in reactors with granular metal loading in a column electro coagulator.

We used data on the electric spark method for producing highly dispersed powders of metals and alloys to select the energy value per pulse (W_p) [14]. As shown, this process can be implemented with pulse repetition frequencies (f) up to several kHz using capacitor banks with capacities from 10 to 120 μ F. For research, we chose a capacitance corresponding to the middle of the range - 65 μ F. Charging voltage was determined experimentally. To do this, first set the charging voltage (U_0), which corresponds to the extremum of the relative energy release in the interelectrode gap of the dispersion reactor to the stored energy of the capacitor bank (formula 1)

$$(1) \quad \eta_w = \frac{W_p}{W_0} = \frac{\int_0^{\tau_1} i(t)u(t)dt}{W_0},$$

where is W_p - energy that is released in the interelectrode gap of the reactor during one discharge pulse, J; $W_0 = C \cdot U_0^2 / 2$ - energy stored by the capacitor bank to the beginning of the discharge, J; τ_1 , $i(t)$ and $u(t)$ are the

discharge time, discharge current (time dependence), and the voltage on the electrode gap (time dependence), respectively, calculated from the results of oscillography (Fig. 3).

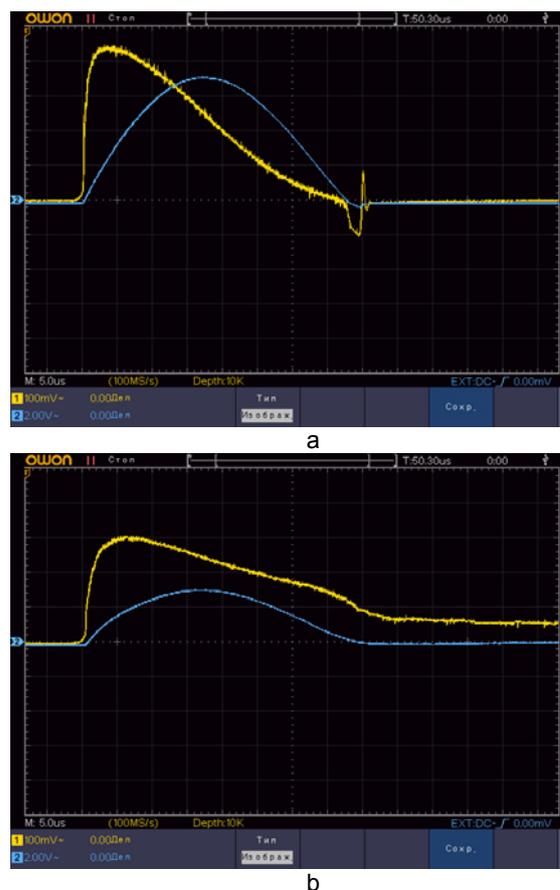


Fig. 3. Oscillograms of the discharge current (blue curve) and voltage on the interelectrode gap (yellow curve) for $\eta_w \sim 0,95$ (a) and $\eta_w \sim 0,8$ (b)

A further increase in the charging voltage facilitates the transition of the discharge into a technically and technologically unacceptable oscillatory mode. The maximum value of η_w , can reach 0,9-0,95, however, to increase the degree of adaptability of regulation of the level of charging voltage in the context of the technological tasks of the work, the selected value of η_w did not exceed the values of 0,8-0,85. The energy values in pulse in this range ranged from 3,6 J to 4,5J, respectively.

One of the most important characteristics of a high-voltage electric discharge is the time of the pulse, the change of which, when the energy is fixed in a single pulse, leads to a redistribution between the ratio of the amount of material of the granules transferred from solid to gaseous or liquid. There is a redistribution of micro- and nanopowders of metal in terms of dispersion, morphology, and other characteristics, which is accompanied by a change in its coagulation properties. In this case, the characteristics of the electric discharge plasma also change. Galvanic wastewater was processed in two modes: short powerful pulses (duration 38 μ s) and long pulses (duration up to 200 μ s) of lower power (Fig. 4). The specific processing energy in both cases remained constant and amounted to 130 galvanic drains in metal-loaded reactors is the height of the latter, which in this study varied from h to $h/2$. The electrical parameters were chosen based on the best result ($W_{sp} = 130$ J/dm³; pulse duration - 38 μ s; $W_p = 4,5$ J).

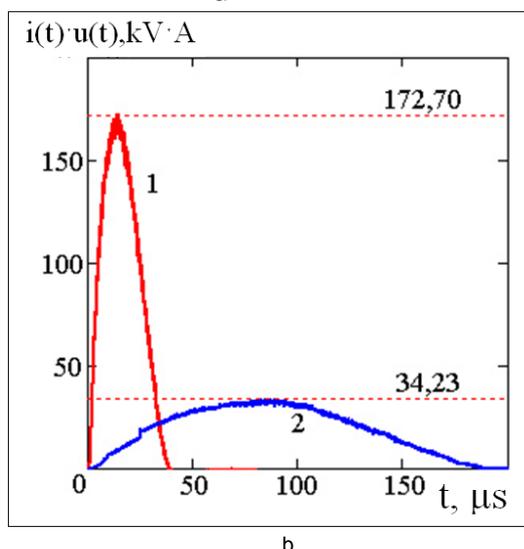
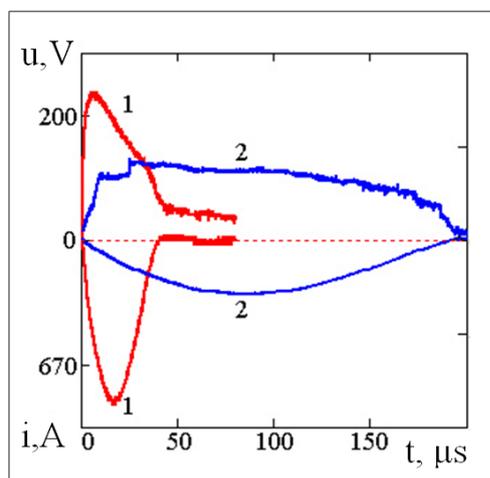


Fig. 4. Temporal dependences of the voltage at the interelectrode gap of the reactor and the discharge current (a) and the power allocated to the electric spark load (b)

In the process of experimental work, various technological, electrical, and energy parameters changed. The initial data of galvanic waste water are presented in table 1.

Influence of the specific energy on the purification degree of the galvanic wastewater at a pulse duration of 38 μ s and energy per pulse $W=4,5$ J is presented in table 2.

Influence of the pulse time on the degree of purification of the galvanic wastewater at fixed energy in the pulse ($W=4,5$ J) and specific energy ($W_{sp}=130$ KJ/dm³) is presented in table 3.

Table 1. The initial data of a zero sample of galvanic wastewater

| Parameters | No. sample | Parameter's value | The concentration of heavy metal ions, mg/dm ³ | | | | pH |
|-------------------------------|------------|-------------------|---|------------------|--|------------------|------|
| | | | Ni ²⁺ | Zn ²⁺ | Cr ⁶⁺ + Cr ³⁺ | Cu ²⁺ | |
| Original galvanic waste water | 0 | - | 1,20 | 0,26 | 1,27 | 0,06 | 7,45 |

Table 2. Influence of the specific energy on the purification degree of the galvanic waste water

| Parameters | No. sample | Parameter's value | The concentration of heavy metal ions, mg/dm ³ | | | | pH |
|-------------------------------------|------------|-------------------|---|------------------|--|------------------|-----|
| | | | Ni ²⁺ | Zn ²⁺ | Cr ⁶⁺ + Cr ³⁺ | Cu ²⁺ | |
| Specific energy, kJ/dm ³ | 1 | 130 | 0,03 | 0 | 0,0002 | 0,00 | 7,3 |
| | 2 | 65 | 0,05 | 0,03 | 0,0023 | 0,01 | 8,2 |

Table 3. Influence of the pulse time on the degree of purification of the galvanic wastewater

| Parameters | No. sample | Parameter's value | The concentration of heavy metal ions, mg/dm ³ | | | | pH |
|-------------------------|------------|-------------------|---|------------------|--|------------------|------|
| | | | Ni ²⁺ | Zn ²⁺ | Cr ⁶⁺ + Cr ³⁺ | Cu ²⁺ | |
| Pulse duration, μ s | 3 | 38 | 0,03 | 0,00 | 0,0002 | 0,003 | 7,34 |
| | 4 | 200 | 0,02 | 0,00 | 0,0002 | 0,003 | 7,33 |

Influence of energy in a pulse on the degree of purification of galvanic galvanic wastewater at a fixed specific energy ($W=130$ KJ/dm³) and a slight change in the pulse duration (from 38 to 40 μ s) is presented in table 4.

Table 4. Influence of energy in a pulse on the degree of purification of galvanic galvanic waste water

| Parameters | No. sample | Parameter's value | The concentration of heavy metal ions, mg/dm ³ | | | | pH |
|---------------------------------|------------|-------------------|---|------------------|--|------------------|------|
| | | | Ni ²⁺ | Zn ²⁺ | Cr ⁶⁺ + Cr ³⁺ | Cu ²⁺ | |
| The stored energy in a pulse, J | 5 | 4,5 | 0,03 | 0,00 | 0,0002 | 0,003 | 7,34 |
| | 6 | 5,5 | 0,025 | 0,04 | 0,0017 | 0,005 | 7,97 |

Influence of the metal loading height on the degree of purification of galvanic galvanic wastewater at a fixed all other parameters ($W=130$ J/dm³; pulse duration 38 μ s; $W_{sp}=4,5$ J) is presented in table 5.

Analysis and comparison of the data in the tables 1-5 allows us to draw the following conclusions. Flow-through purification of galvanic drains to MPC standards using the electric spark method with granular metal loading and a low-voltage (up to 1000 V) source of discharge currents is technologically feasible and quite effective.

Table 5. Influence of the metal loading height on the degree of purification of galvanic galvanic waste water

| Parameters | No. sample | Parameter's value | The concentration of heavy metal ions, mg/dm ³ | | | | pH |
|--------------------------|------------|-------------------|---|------------------|--|------------------|------|
| | | | Ni ²⁺ | Zn ²⁺ | Cr ⁶⁺ + Cr ³⁺ | Cu ²⁺ | |
| The metal loading height | 7 | h | 0,03 | 0,00 | 0,0002 | 0,003 | 7,34 |
| | 8 | h/2 | 0,15 | 0,15 | 0,0026 | 0,015 | 7,84 |

Conclusion

After study it is quite clear that the electric spark method is effective during multicomponent galvanic drains purification. In the experiment combined metal loading (Fe, Al) and low-voltage (up to 1000 V) equipment were used. The research showed that the degree of purification depends on the specific energy of the treatment, the height of the metal loading of the reactor, and weakly depends on the pulse energy and the rate of its input into the medium being processed. The experiment gave good results. So, the concentrations of heavy metals (Ni^{2+} , Zn^{2+} , ΣCr^{6+} and Cr^{3+} , Cu^{2+} , ΣFe) in the treated water are significantly lower than their MPC values.

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