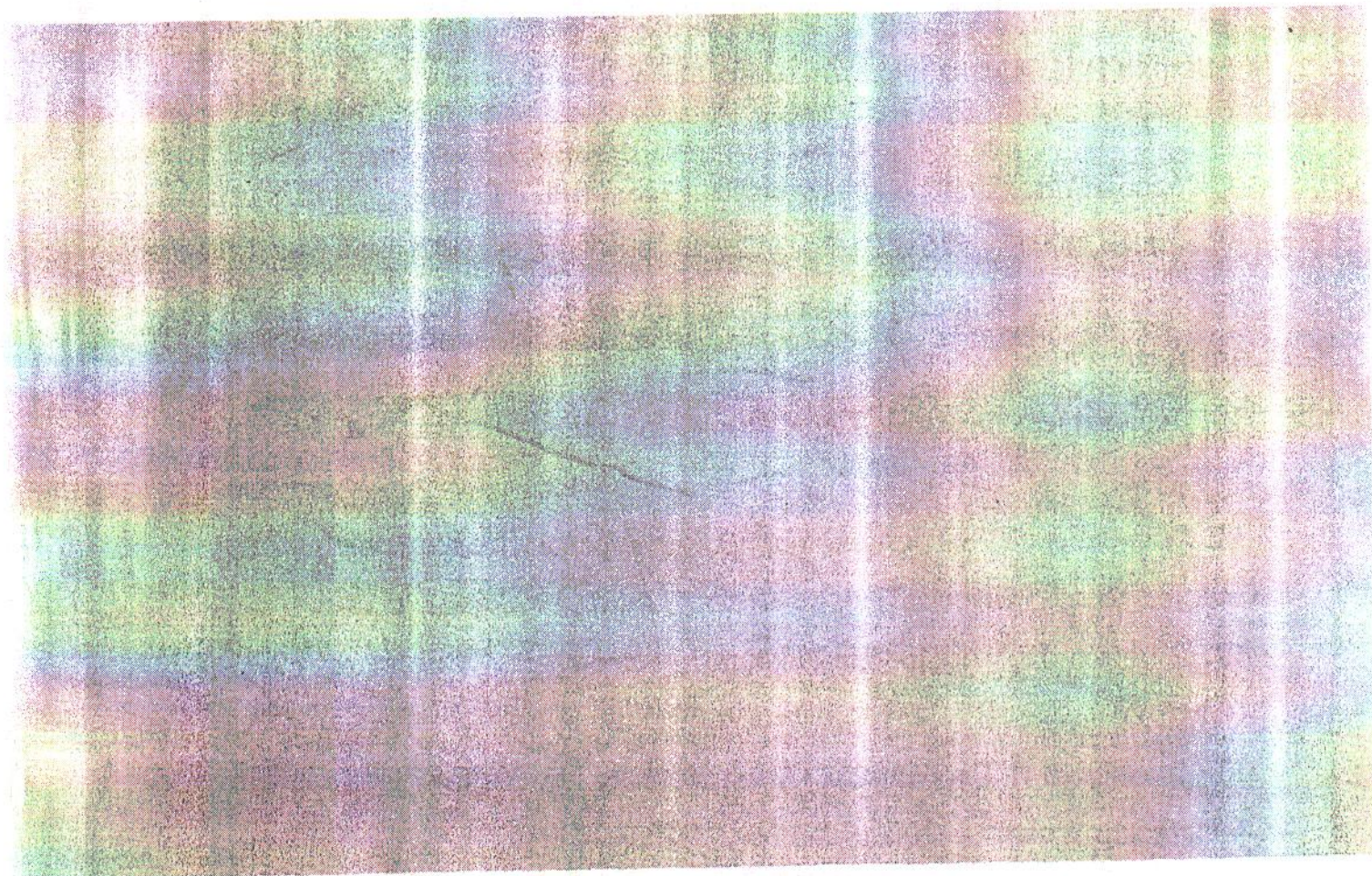


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Using ferritised galvanic slurry in the processes of purification of effluents to remove ions of heavy metals

E.S. Klimov and V.V. Semenov

The authors present the results of examination of the process of purification of effluents containing ions of heavy metals, using ferritised galvanic slurry. It is shown possible to use the slurry for the intensification of the process of clarification of water and increase of the density of the deposit in the reagent purification of effluents by limestone milk. The technology of purification of galvanic effluents developed on the basis of the experimental results, is based on the introduction of the suspension of ferritised slurry together with limestone milk into the neutralisation reactor with subsequent additional sorption purification using the dried refined ferrite deposit. After saturation, the sorbent is mixed together with the initial uncontaminated slurry and subjected to ferritisation.

Introduction

In the production cycle of the majority of engineering, instrument making and other plants, extensive use is made of various galvanic processes, characterised by a number of special features [1]. On the one hand, this requires large quantities of clean water and, on the other hand, it is characterised by the formation of a large volume of liquid waste: as effluents (EF), spent electrolytes and various concentrates. The most toxic contaminating substances of galvanic waste by the ions of heavy metals (IHM), characterised by the cancerous, teratogenous and mutagenous effects [2].

At present, there is a large number of methods of purification of the galvanic waste, with the sorption-ion exchange process is characterised by the highest efficiency. However, these methods are not used widely in industry because of the high price of sorbents and the need for the regeneration

of these substances. At the same time, investigations are carried out in recent years show that expensive synthetic sorbent is maybe replaced by cheaper natural materials or production waste (for example, the deposits of effluents) [9].

According to the experimental results obtained in [4, 9], the deposits, formed in ferritic cleaning of the effluents of galvanic production are characterised by any high absorption capacity in relation to the cations of the heavy metals and organic substances. However, the production of these deposits is economically not efficient because it requires a high consumption of energy for heating the entire volume of the effluents to a temperature of 70-80 °C. It is more efficient to use ferrite deposit is from concentrated suspension is of galvanic slurry [3]. The resultant ferritised galvanic slurry contains the defects of the crystal lattice resulting in a large increase of the adsorption properties and, consequently, these sub-

stances can be used for the deep cleaning of the effluents [2, 9].

In our previous work, we investigated the process of chemical stabilisation (ferritisation) of actual slurry obtained from individual companies [7, 10]. The experimental results obtained in these investigations were used for the development of the technology making safe galvanic waste, based on mixing of the suspension of the slurry with the solution of the iron salt (II), alkalisation of the mixture to pH 9-10, heating to 60-70 °C, bubbling and subsequent dehydration of the produced ferrite deposits.

The aim of the present work was the investigation of the process of purification of galvanic effluents in order to remove the ions of heavy metals with the application of ferritised slurry.

The experimental section

The ferrite deposits, used in the experiments for the investigation of the process of cleaning of effluents to remove the cations of the metals, were produced in the lab laterally conditions from actual slurry from engineering production. The gross content of metals in the absolutely dry slurry, mg·kg⁻¹: copper 3680, nickel 470, lead 350, zinc 10280, chromium 4270. The modelling galvanic effluents were presented by the solutions of the salt of iron (II and III), chromium (III), nickel and copper with the required concentration. The solutions were prepared from the the agents of the chemical and analytical grade using distilled water. The actual effluents and limestone milk 40 reagent cleaning process were taken from the station for the neutralisation of galvanic effluents of engineering companies.

The sorption purification of effluents using ferritised slurry was carried out using the following procedure. The ferrite deposits were dried out a temperature of 105 °C, ground and subsequently screened to the fraction with the particle size 0.1-0.25 mm. The required amount of the ferritised slurry was introduced into the vessel with the galvanic effluents. Subsequently, the vessel was covered with a tight lid and shaken for

the required period of time. Subsequently, the ferritised slurry was filtered on a filter, and the filtrate was analysed for the content of the ions of metals.

The purification of the effluents using the limestone milk was carried out by the generally accepted technology. In reagent purification of the effluents using the ferritised slurry, the container with the solution to be purified was mixed with the addition of the suspension of ferritised slurry with a moisture content of approximately 95% (the mass content of the ions of heavy metals and the solid phase of the ferritised slurry was 1:10). Subsequently, the mixture was alkalised using limestone milk to pH 7-8. After completing the process of purification, the remaining deposited was filtered-off and the filtered was analysed for the content of the ions of heavy metals.

Analysis of the water for the content of the ions of heavy metals was carried out by the spectral photometric methods [6] using FEK-56M photocolormeter. The value of pH was inspected using H-130 ion meter.

The experimental results and discussion

According to the literature data [8, 11], the efficiency of cleaning of the effluents is affected by a large number of factors: the mass ratio $D = \text{Me}^{n+} : \text{FGS}$ (the dose of the sorbent), the treatment time of the effluents, the value of pH established after the introduction of the sorbent into the effluents. In the investigations, we determined and optimised the main parameters of the cleaning process.

Figure 1 shows the dependence of the degree of purification of the effluents $\alpha = (C_{in} - C_f) \times 100\% / C_{in}$ (where C_{in} is the initial total content of the ions of heavy metals in the effluents, mg·l⁻¹; C_f is the total final content of the ions of heavy metals in purified water, mg·l⁻¹) with other conditions being equal, on the dose of the sorbent.

The experimental results indicate that the minimum mass ratio $\text{Me}^{n+} : \text{FGS}$, required for the purification of the effluents to remove the cations of the metals to the required

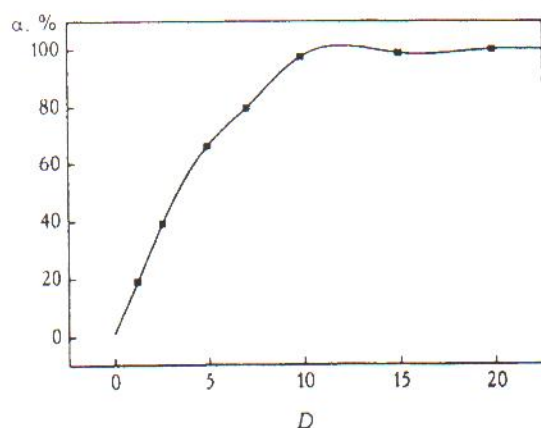


Fig. 1 Dependence of the degree of purification of effluents (α) on the dose of the sorbent (D)

standard values, is 1:10. The small improvement of the quality of water was recorded at $D = 1:15$. A further increase of the dose of the sorbent as almost no effect on the efficiency of purification of the effluents.

The degree of purification of the effluents with increase of the treatment time increases to a specific level and, subsequently, the given factor, like the dose of the sorbent, as almost no effect on the efficiency of cleaning. In the experiments, it was established that the optimum duration of the process of cleaning of the effluents is 60-90 minutes.

The ferritised galvanic slurry, obtained in the process of ferritised nation of galvanic the slurry, is characterised by end coli re-

serve and, consequently, the addition of these substances into the purified effluents result in the change of the initial value of pH. In examination of the effect of this parameter on the efficiency of the cleaning process it was established that at the pH value of 8-9 of the concentration of zinc and chromium in the purified water rapidly decreases, and at pH 7-7.5 the concentration of copper, nickel and I am decreases. Examination of the process of purification of the mixed effluents shows that of the most efficient removal of all the metals is recorded at the pH value of 7.5-8.5. If necessary, of this value is obtained by the addition of alkali or acid substances (Ca(OH)_2 , H_2SO_4).

The investigations carried out on the simulation effluents, have made it possible to determine the optimum conditions of the process of purification of the effluents to remove the ions of heavy metals [5]. The experimental results were used in the purification of galvanic effluents from engineering production plants.

The data on the reagent (with and without the application of ferritised galvanic slurry) and sorption purification of the actual galvanic effluents are presented in Table 1.

The application of the ferritised galvanic slurry in the processes of reagent and sorption purification of galvanic effluents to remove the ions of heavy metals makes it possible to increase greatly the efficiency of

Table 1 Comparative indicators of the efficiency of reagent (with and without the application of ferritised galvanised slurry) for adsorption cleaning of galvanic effluence (for reagent cleaning: $\text{pH}_{\text{ini}} = 4.67$, $\text{pH}_{\text{fin}} = 7.32$; for sorption cleaning: m_{Me}^{n+} ; $m_{\text{FGS}} = 1:10$, process time 80 min, pH after addition of FGS - 7.64)

Extracted metal	Initial metal concentration, $\text{mg}\cdot\text{m}^{-1}$	Reagent cleaning				Sorption cleaning using FGS	
		without FGS		with FGS			
		C_{fin} , $\text{mg}\cdot\text{m}^{-1}$	α %	C_{fin} , $\text{mg}\cdot\text{m}^{-1}$	α %	C_{fin} , $\text{mg}\cdot\text{m}^{-1}$	α %
Nickel	31.46	0.82	97.39	0.07	99.78	0.01	99.97
Copper	23.30	1.38	94.32	0.21	99.14	0.05	99.79
Chromium	60.43	1.81	97.00	0.83	98.63	0.30	99.50
Zinc	20.54	1.30	93.67	0.41	98.00	0.16	99.22
Iron	74.12	1.70	97.71	1.02	98.62	0.26	99.65

Comment: C_{con} is the final content of metal in purified water; α is the degree of cleaning of EF ($\alpha = (C_{\text{ini}} - C_{\text{fin}}) \cdot 100\% / C_{\text{ini}}$).

these processes. If in the neutralisation of the effluents using limestone milk the mean degree of purification in respect of all the metals is 96.0%, then after the addition of a specific amount of the suspension of ferritised galvanic slurry this parameter increases to 98.8%. In sorption purification of effluents, the degree of purification is already 99.6%.

The reduction of the residual content of the ions of heavy metals in reagent purification of the effluents with the application of ferritised galvanic slurry may be explained by the fact that the ferrite deposits are a heavy component, which makes it possible to increase the intensity of the processes of clarification of the effluents and increase of the density of the deposit [9]. The ferritised galvanic slurry results in the coalescence of the fine-dispersion and colloidal particles of the hydroxides of metals and, consequently, reduce the concentration of the ions of heavy metals in the purified water. The experimental results show that in comparison with the conventional conditions of neutralisation, the rate of clarification of the effluents increases 3-3.5 times, and the volume of the resultant deposit decreases 1.5-2 times.

The results of the experiments make it possible to propose the following technological method of purification of galvanic effluents in order to remove the cations of metals using the ferritised galvanic slurry (Fig. 2).

In the ferritisation reactor 1 after carrying out the process making safe the galvanic slurry, we obtain the suspension of the ferritised galvanic slurry which is separated into two floors. The required volume of the suspension is applied to the reactor for neutralisation of galvanic effluents in order to reduce the consumption of $\text{Ca}(\text{OH})_2$, intensify the processes of clarification of the effluents, and increase the density of the deposit. The other part of the ferritised galvanic slurry is dehydrated on the filter 2 and, subsequently, transferred to the reception container 3 and, using the screw feeder 5, it is directed to drying into the heating device 5. The dried ferritised galvanic slurry

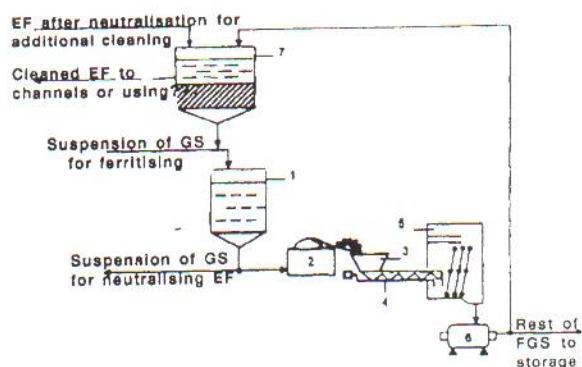


Fig. 2 The technological diagram of the purification of galvanic effluents to remove metal cations using ferritised galvanic slurry: 1) the ferritisation reactor; 2) filter; 3) the receiving container; 4) the screw feeder; 5) the heater; 6) the ball meal; 7) the reaction for sorption purification of the galvanic effluents.

is transferred into the ball meal 6 for redefining. The sorption additional cleaning of the effluents is carried out in the reaction vessel 7 which receives the liquid phase from the desilter and the required amount of the leave find ferritised galvanic slurry. After completing the processes of purification and holding, the water is discharged into the channel system (or supplied for a reputed application), and the contaminated ferritised galvanic slurry is mixed with the initial galvanic slurry and directed into the ferritisation reactor 1. In the proposed technological system, it is necessary to increase the volume of the sorbent and, consequently, the excess of the sorbent maybe realised by another company law transferred to storage as the waste of safety range IV.

The main advantages of the proposed technology of purification of the galvanic effluents to remove the ions of heavy metals include:

- the possibility of producing the cheap sorbent in the conditions of industrial plants;
- the absence of any need for the application of additional areas and reagents for the regeneration of ferritised galvanic slurry;
- the possibility of repeated application of purified water;
- the possibility of application of the given technology without any significant changes in the existing system for reagent purification of the effluents using the limestone milk.

Conclusions

- 1 The application of ferritised slurry in the sorption cleaning of galvanic effluents to remove the ions of heavy metals results in the degree of purification of 99.6%.
2. In comparison with the conventional conditions of reagent purification, the application of ferritised the slurry increases the rate of clarification of the effluents by a factor of 3-3.5 and reduces the volume of the deposit by a factor of 1.5-2.

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