Updating of sewage – purification facilities of electroplating enterprises with counterflow ion-exchange filters

V F Torosyan, E S Torosyan, P D Sorokin, A A Telitsyn

Yurga Institute of Technology, Yurga, Russia

E-mail: torosjaneno@mail.ru

Abstract. The paper focuses on work of electroplating sewage-purification facilities of mechanical engineering production; drawbacks caused by specific features of physical and chemical processes of coagulation and technological malfunctions have been revealed. Additional equipment – ion-exchanging filters have been selected on the basis of designed methods, they make it possible for enterprises of mechanical engineering to implement conversion to water rotation systems.

1. Introduction

Materials of different chemical nature are used in mechanical engineering [1], and various physical and chemical processes are applied in surface and deep processing of materials, therefore, enterprises of this branch have both to provide high precision and reliability of produced machines [2], and use raw material reasonably, assure environmental safety of technological and production processes. Electro-plating industry is one of main sewage producers in mechanical engineering. Basic water pollutants in electro-plating industry are ions of heavy metals, non-organic acids and alkalis, cyanides, and surface-active substances. Here, scourage is considered the main source of toxic substances and simultaneously, the main user of water, as well as the source of sewage in electro-plating industry. In most electro-plating industries the volume of sewage is enormous because the method of workpiece washing isn't perfect and requires significant consumption of water (up to 2 m^3 and more per each 1 m^2 of workpieces surface). Nevertheless, none of available methods of electro-plating sewage purification can meet the current standards of industrial sewage; therefore, work optimization of purification plants is thought to be the urgent problem of machinebuilding enterprises.

While workpiece washing, in average 3300 t of zinc, 2400 t of nickel, 2500 t of copper, and dozens of thousands of other metals are taken from operating cell annually. One of the important problems in this industry is also failure of process solutions because extraneous organic and non-organic substances are stored up in electrolytes; and correlation of basic components in electroplating baths gets broken [3].

Sewage of spent solutions makes up 0.2–0.3 % of total sewage volume, but in terms of pollutant concentration its share is about 70 %. Volley of this sewage breaks operating mode of purification plants, and causes irretrievable loss of valuable materials. Unpurified or insufficiently purified sewage and other wastes containing non-ferrous metals, which get into water bodies, bring harm to national economy and environment because used in industry metals get lost, and their impact on environment is increasingly negative [4].

It is worth noting that enterprises of mechanical engineering can completely provide themselves with electrical and thermal energy. They take measures to remove admixtures and impurities of

industrial sewage, making them meet standards of maximum permissible concentration, and utilize liquid wastes in areas of persistent storage [5].

Chemical composition and concentration of sewage of electroplating industry is of high importance for purification plants of these enterprises, because electrolytes are contaminated by metal impurities in the course of electroplating due to dissolution of workpiece metals. Ions of copper, nickel, ferrum, zinc and other metals are taken by process water into sewage. The increase in concentration of impurity metals has a considerable negative effect on conductivity, hence, electro-chemical purification is damaged (electrical equipment fails).

2. Experimental part

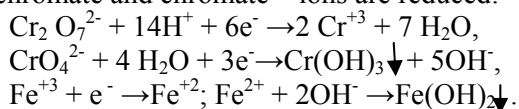Pursuant to SNiP 2.04.03–85 hexavalent chromium and other metals are removed from sewage as follows:

– concentration of ions of hexavalent chromium Cr+6 only is maximum 100 mg/l;

– total concentration of non-ferrous metals doesn't exceed 100 mg/l, concentration of each of them is maximum 30 mg/l;

– minimum total solid content of sewage is 300 mg/l and concentration of suspended materials is maximum 50 mg/l.

As we can conclude from the information on concentration of ions of heavy metals in chromium-containing sewage of electro-plating production at Yurga Machinebuilding Plant, their qualitative purification from hexavalent chromium can be performed provided that its concentration is maximum 50 mg/l.

A bath for catching valuable or particularly toxic components is placed on the site of electro-plating after the technological bath and before the washing cells in order to reduce contamination of sewage with these components. Used rinsing water from the catching bath is twice diluted process liquor. It can't be subject to purification, because process failure of purification plants is possible, as well as contamination of sewage and quantity of forming slime can increase.

Volleys of concentrated used solutions also disrupt acceptable operation of purification plants. Therefore, neutralization of used solutions at purification plants of enterprises can't be considered as an engineering solution being in line with current level of electro-plating [6].

Electrochemical purification based on the method of electrical coagulation involves electrolytic solution of steel electrodes, which causes formation of ferrous iron ions (Fe^{2+}), as the result bichromate and chromate – ions are reduced:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2\,Cr^{+3} + 7\,H_2O,$$
$$CrO_4^{2-} + 4\,H_2O + 3e^- \rightarrow Cr(OH)_3\downarrow + 5OH^-,$$
$$Fe^{+3} + e^- \rightarrow Fe^{+2}; \; Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2\downarrow.$$

As the result of electrochemical reaction hydrogen ions concentration decreases in sewage and hydrogen ion exponent (pH) grows in pretreated waste water [2]. If there are cations of other heavy metals in water, they are reduced by ferrous iron in the course of exchange processes and are deposited alongside with chromium and ferrum hydroxides, some of these metals react with anions OH – transfer to poorly soluble hydroxides or are reduced on the cathode, losing their hydration film and sorbing on its surface.

pH values, providing removal of heavy metals via deposition on cathode, in the course of electrochemical purification are listed in Table 1 [7].

If Cr^{+6} concentration doesn't exceed 20 mg/l, initial value of pH is to be 4.5 – 5. If pH ≤ 3 the rate of electrochemical processes of Cr^{+6} reduction increases. If pH ≥ 6 specific consumption of electric power increases as conductivity of solution reduces and overvoltage grows on cathode because of hydrogen emission.

Table 1. pH of electrochemical purification

| Heavy metals	Cr^{6+} concentration, mg/l	pH
Trivalent chromium	–	3.5–4.0
Nickel	–	Minimum 7.0
Copper, zinc, cadmium	–	Minimum 4.5
Hexavalent chromium, copper, zinc	Maximum 20	6–7
	20–50	5–6
	50–100	4–6
Hexavalent chromium, cadmium, nickel	Maximum 50	6–7
	Minimum 50	5–6
Hexavalent chromium	Maximum 50	6–7

In the course of coagulation passivation of anodes takes place because on their surface a hydroxy film forms and decelerates electro dissolution of metal [8]. That is why, every other 30–60 minutes of electro-coagulators work it is necessary to change the polarity of electrodes, i.d. reversal of current on a rectifier. $Cr(OH)_3$ has amphoteric properties; at pH ≥ 12 it dissolves in redundant alkali and chromites form, i.d. ions of chromium can be transferred to solution again.

$Cr(OH)_3 + 3NaOH \rightarrow Na_3[Cr(OH)_6]$
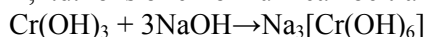
Hence, while acid chromium containing waste water is neutralized, excess dispensing of alkali is to be avoided. Polyacrylamide can be applied to remove hydroxides of metals and clarify waste water via flocculation.

As one can conclude from the analysis of experimental data on purification of electroplating waste water at Yurga Machinebuilding Plant, concentration of ferrum ions in pretreated water grows because ions Fe^{2+}, which are excessive over the needed quantity to reduce Cr^{+6}, are transferred from the surface into the solution. In this case pretreated waste water can be blown down in the aeration chamber before being transferred into the sedimentation tank in the aeration chamber.

As the result ions Fe^{2+} in ferrum hydroxide (II) are oxidized up to sparingly soluble ferrum hydroxide (III), and their total concentration in water decreases:

$4Fe^{2+} + 8OH^- + O_2 + 2H_2O \rightarrow Fe(OH)_2$,

$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$.
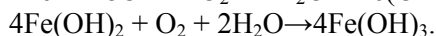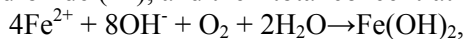
Water can be circulated twice through electrocoagulators to make purification of sewage the most efficiently. However, it is important to note that none of avaliable methods to purify electroplating sewage can provide independently all current standards of industrial waste waters; the latters are as follows:

- purification until the standards of maximum permissible concentration are met, especially those of ions of heavy metals;

- return of 90-95 % water into reverse cycle, low cost price of purification;

- small-size facilities, utilization of valuable components (acids, alkalis, metals).

Impossibility of meeting the environmental standards is worsened by poor financial situation at many enterprises. Therefore, from our point of view, a way to overcome this situation consists in modernization of means and methods of sewage purification and optimization of purification systems.

3. Discussion of results

Here, we think it is necessary to use additional equipment for afterpurification of sewage water. As the total replacement of equipment being at disposal of the enterprises, is hardly possible because of required investments, these new facilities are to be power-consuming, cost effective and meet the standards of productivity and efficiency of industrial sewage purification.

It is worth saying that among available methods of waters and sewage purification ion-exchanging methods are practically the most efficient ones. Therefore, this work focuses on selection of

equipment, necessary for afterpurification of sewage water of electroplating production at the enterprises of mechanical engineering. The equipment will be selected on the basis of designed methods of calculation and according to requirements for efficiency of purification system being at disposal of Yurga Machinebuilding Plant [9].

The following characteristics of ion-exchanging filters are thought to be basic structural, technological, as well as technical and economical ones: productivity up to 40 m^3/h, filtering fill – cationite KY–2–8, anionite AB–17–8, which provide practically complete removal of ions of heavy metals in industrial tests. Necessary reconstruction predetermines also the replacement of forward feeding of water to be purified by the counterflow one, from our point of view, it is reasonable and economical, technologically and environmentally efficient. Here we take into consideration the advantages of counterflow feeding technology:

- low layers of ionite (the last ones down pretreated water) are subject to deep regeneration with excessive reagent;

- the second regeneration of ion-exchange resin with untreated exchanging capacity is not required (material isn't used evenly), consumption of the reagent can be reduced.

Conversion of forward feeding ion-exchange filters to the counterflow one makes it possible:

- to increase efficiency of filters by means of available facilities;

- to reduce annual filling of material because of advanced technology;

- to reduce quantity of salt, acid and alkali needed for regeneration (8–10 %);

- to decrease chloride, acid and alkali discharge;

- to cut down water consumption for needs of filters (up to 50 %) [10].

Methods to calculate basic technological characteristics of cationite filter type XB–042–1

Number of flows (Q), transferred to filters – 40 m^3/h. Total concentration of cations – 0.54 g·equ/m^3.

Cationite filter XB–042–1 (Table 2) is used for ion-exchanging purification.

Table 2. Technical parameters of cationite filter type XB–042–1

Parameter	Value
Diameter of filter	1000 mm
Area of filtering	0.8 m^3
Volume of filtering fill	1.6 m^3
Filtering fill	Cationite KY–2-8 (Table 3)

Table 3. Chemical characteristics of cationite KY–2-8

Characteristic	Standard	
	Supreme grade	First grade
Granulometric composition: dimensions of grains, mm	0.315–1.25	0.315–1.25
Inclusion volume of power fraction, %, minimum	96	95
Efficient dimensions of grains, mm	0.40–0.55	0.35–0.55
Coefficient of homogeneity, maximum	1.7	1.8
Mass concentration of moisture, %	43–53	43–53
Full static exchanging capacity, mmole/cm^3 (mg equ/cm^3), minimum	1.9	1.8
Specific volume, cm^3/g in H-form, maximum	2.8	2.8
Osmotic stability, %, minimum	94.5	90
Apparent density of commercial cationite, g/dm^3	750–800	750–800

The running facilities of industrial sewage purification are to be equipped with 3 cationite filters – 2 operating ones and 1 in reserve.

Filtering rate is equal to:

V_f = 40/1.6 = 25m^3/h, permissible – 30 m3/h, where 1.6 – volume of filtering fill.

Working exchanging capacity of cationite is computed pursuant to the formula:

$$E_{wc}^{k} = \alpha_k E_{gen}^{k} - K_{ion} q_k \sum C_w^{k},$$ (1)

where α_k – coefficient of regeneration efficiency, is accepted to be 0.85, E_{gen}^{k} – full exchanging capacity of cationite, accepted to be 1000 g·equ/m^3, qk – specific water consumption to wash cationite after regeneration, accepted to be 5 m^3 per 1 m^3 of cationite, K_{ion} – coefficient needed to take into consideration the type of ionite, for cationite it is accepted to be 0.5, $\sum C_w^k$ – total concentration of cations in cleaning water (when cationite washing by ionizated water).

Hence: E_{wc}^{k} = 0.85 · 1000 – 0.5 · 5 · 0.5 4= 840 g·equ/m^3.

Duration of working cycle is determined:

$$t_f = \frac{YE_{wc}^{k} n}{Q \sum C_w^{k}}$$ (2)

where Y – volume of fill filter, is accepted to be 1.6 m^3, n – number of working filters.

t_f = 1.60 · 2 · 840/40 · 0.54 = 12 hours.

Frequency of filter switching on for regeneration is 12/2 = 6 hours.

Reagent consumption for regeneration:

Consumption of 100 % acid for regeneration of one cationite filter is computed according to the formula:

$$T_k = \frac{YE_{wc}^{k} \cdot B}{1000}$$ (3)

where B – specific consumption of acid, it is accepted to be 100 g/g·equ.

T_k = 1.60 · 840 · 100/1000 = 134.4 кг.

Concentration of regenerating solution of acid Cp is 1.2 kg·equ/m^3.

Reclaim is transferred from cationite filter, its volume is:

$$V_{кат} = \frac{YE_{wc}^{k}}{C_p}$$ (4)

V_{kam} = 1.6 · 1/1.2 = 1.3 m^3.

Cationite backwash is carried out by treated water with intensity 3 l/sec·m^2.

Water consumption per one filter is 3 · 1.6 = 4.8   l/sec or 17.28 m^3/h for 15 minutes of backwash or 0.25 h.

Water quantity per one filter is 17.28 · 0.25 = 4.32 m^3.

For after regeneration washing water is used in proportion 5 volumes of water per 1 m^3 of resin, then: $Q_{отм}$ = 1.6 · 5 = 8 m^3.

It takes 60 minutes to wash.

Total consumption of water per one filter is: 4.32 + 8 = 12.32 m^3/24 hours.

Backwash and washing of filters are carried out by treated water from technological water supply system. As the result of calculations basic technological parameters were obtained for cationite filter (Table 4).

Table 4. Technological parameters of cationite filter

Parameters	Units	Quantity
Efficiency	m^3/h	40
Volume of filtering	m^3/h	25
Duration of filtering cycle	h	12
Between – regeneration period	h	6

Parameters	Units	Quantity
Consumption of H_2SO_4 per regeneration period (2 filters)	kg/24 hours	268.8
Concentration of regenerating solution	kg-equ/m^3	1.2
Water consumption A) preparing of regenerating solution B) for backwash C) for washing	m^3 m^3 m^3	2.0 4.32 8.0

Methods to calculate basic technological characteristics of anionite filter type XB–040–1

Number of flows, transferred to filter – 40 m^3/h, initial concentration of anions in water is 0.5 g·equ/m^3.

For ion-exchanging purification we used cation filter type XB–040–1 (Tables 5, 6)

Table 5. Technical parameters of anionite filter type XB–040–1

Parameter	Value
Diameter	1000 mm
Filter area	0.8 m^3
Height of filtering layer	2 m
Volume of filtering fill	1.6 m^3
Filtering fill	Anionite AB–17-8

Table 6. Chemical characteristics of anionite AB–17–8

Parameter	Standard	
	Supreme grade	First grade
Granulometric composition: dimensions of grains, mm	0.315–1.25	0.315 – 1.25
Inclusion volume of power fraction, %, minimum	95	93
Efficient dimensions of grains, mm	0.4–0.6	0.6
Coefficient of homogeneity, maximum	1.7	1.8
Mass concentration of moisture, %	35–50	35–50
Full static exchanging capacity, mole/cm^3 (mg equ/cm^3), minimum	1.15	1.00
Specific volume, cm^3/g in H-form, maximum	3.0±0.3	3.0±0.3
Balanced static exchange capacity, mmole/cm^3, minimum	1.00	0.90
Dynamic exchange capacity with full regeneration, mole/m^3, minimum	700	690
Osmotic stability, %, minimum	92.5	85.0
Apparent density of commercial cationite, g/dm^3	750–800	750–800
Working temperature, maximum, °C	100	
Working range, pH	1–14	

Running facilities of industrial sewage purification are to be equipped with 3 anionite filters – 2 working ones and one in reserve.

Filtering rate is equal to:

V_f = 40/1.6 = 25 m³/h whereas the permissible one is 30m³/h, where 1.6 – volume of filtering fill.

Working exchange capacity of anionite is computed according to the formula:

$$E_{wc}^{an} = \alpha_{an} E_{gen}^{an} - K_{ion} q_{an} \sum C_w^{an} \qquad (5)$$

where αk – coefficient of regeneration efficiency, it is accepted to be 0.9, E_{gen}^{an} – full exchange capacity of anionite is accepted to be 500 g·equ/m³, q_{an} – specific consumption of water for washing anionite after regeneration, it is accepted to be 24 m³ per 1 m³ of anionite, K_{ion} – coefficient, which takes into consideration ionite type; it is accepted to be 0.8, $\sum C_w^{an}$ – total concentration of anions in washing water, g·equ/m³.

Hence: E_{wc}^{an} = 425 g·equ/m³.

Duration of working cycle is determined according to the formula:

$$t_f = \frac{Y E_{wc}^a n}{Q \sum C_w^a} \qquad (6)$$

where Y – volume of fill filter – 1.6 m³, E_{wc}^a – working exchange capacity, C_n – total concentration of anions in water, it is accepted to be 0.5 g equ/l.

t_f = 1.6 · 425/40 · 0.5 = 34 hours.

Frequency of filter switching on for regeneration: every 17 hours.

Alkali consumption for regeneration of one filter is:

$$P_щ = \frac{Y E_{wc}^a \cdot B}{1000} \qquad (7)$$

$P_щ$= 1.6 · 425 · 40/1000 = 28.8 kg.

Concentration of regenerating solution

T_p = 1.2 kg·equ/m³.

Regenerate is transferred from anionite filter, its volume is:

$$V_{an} = \frac{Y E_{wc}^{an}}{T_p} \qquad (8)$$

V_{an} = 1.6 · 0.425/1.2 = 0.9 m³.

Backwash of anionite is carried out by technological water with intensity 2 l/sec·m².

Water consumption per one filter is: 2 · 0.8 = 1.6 l/sec or 5.76 m³/h if backwash lasts 20 min or 0.33 hours.

Water quantity per 1 filter is 5.76 · 0.33 = 1.90 m³.

For after regenerating washing it is necessary to take 15 volumes of water per one volume of loaded resin.

$Q_{отм}$ = 1.6 · 15 = 24 m³.

Duration of filter washing is 2 hours.

Total consumption of water for washing of 1 filter is: 1.90 + 24 = 25.9 m³/24 hours.

As the result of calculation we obtained basic technological characteristics of anionite filter (Table 7).

Table 7. Technological parameters of anionite filter

Parameter	Unit	Quantity
Efficiency	m³/h	40
Volume of filtering	m/h	25
Between-regeneration period	h	17
Consumption of NaOH for filter regeneration	kg/24 hours	28.8

Parameter	Unit	Quantity
Concentration of regenerating solution	kg equ/m^3	2
Water consumption A) for preparing of solutions B) for backwash C) for washing	m^3 m^3 m^3	1.0 1.90 24.0

4. Conclusions

1. Available methods of electroplating sewage purification are insufficient to meet the current standards of industrial sewage independently:
- purification until the maximum permissible concentration is obtained, especially for ions of heavy metals;
- return of 90–95 % of water into reverse cycle;
- small-sized dimensions of facilities, utilization of valuable components (acids, alkalis, metals).

2. Ion-exchange filters as additional equipment for after purification of sewage in the system of coagulation make it possible to stop wastes discharge of enterprises and implement the transition to water circulation system.

3. Conversion of available forward feeding ion-exchange filters to the counterflow conditions of operating will enable:
- to increase the efficiency by means of available equipment;
- to reduce annual filling of material due to advanced technology;
- to reduce the consumption of salt, acid, alkali for regeneration (8–10 %);
- to decrease wastes of chlorides, acids, and alkali;
- to shorten water consumption for needs of filters (up to 50 %).

4. Methods of calculation of basic structural, technological, technical and economic characteristics of ion-exchange filters can also be used for their different productivity and various filtering ionites.

5. Modernization of purification plants carried out by counterflow feeding ion-exchange filters makes it possible for the enterprise to reduce parameters of water consumption and solve the problem of raw materials saving.

References

[1]   Chinakhov D A 2011 *Applied Mechanics and Materials* vols 52-54 pp 442-447
[2]   Solodsky S A, Brunov O G., Zelenkovsky A F 2012 *Welding International* vol 26 **4** pp 314−317.
[3]   Aksenov V I, Ladygichev M G, Nichkova I I, Nikulin V A, Klyan S E, Aksenov E V 2005 *Water economy of industrial enterprises* (M.: Teplotechnik)
[4]   Kolesnikov V A and Menshutina N V 2005 *Analysis, design of technologies and equipment for sewage* purification (M.: DeLiprint)
[5]   Technological process of industrial sewage purification in workshop № 48 of Yurga Machinebuilding Plant
[6]   *Industrial ecology* (Mode of access: http://prom-ecologi.ru/?p=61)
[7]   *Center of Education* (Mode of access http://edu.dvgups.ru/METDOC/ITS/GIDRA/TEOROS OV/METOD/UP_2/frame/frame_ tema2. htm)
[8]   *Industrial water purification* (Mode of access http://www.teh-g.ru/filtr-fsd.html)
[9]   Technological process of electroplating sewage purification at Yurga Machinebuilding Plant
[10]   Vinogradov S S 1998 *Environmental friendly electro-plating industry*