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ION EXCHANGE TREATMENT OF GOLD- AND SILVER-CONTAINING WASTEWATERS FROM ELECTROPLATING PLANTS

Ion-exchange purification of rinsing baths from electrochemical silver- and gold-plating plants with silver and gold concentrations equal to 15.6 mg/dm^3 and 1.2 mg/dm^3, respectively, has been studied. The wastewaters have been consecutively treated by means of strongly acidic cation exchanger in the H-form, weakly basic anion exchanger in the OH-form and strongly basic anion exchanger in the OH-form. During the process three ion-exchange units have been used: 1) Lewatit S-100 – Lewatit MP-500 – Lewatit MP-62 (I), 2) Varion KSM – Varion ADAM – Varion ATM (II) and 3) Wofatit KS-10 – Wofatit AD-41 – Wofatit SZ-30 (III).

It has been found out that when all three ion exchange units are used, the volume of water purified of silver (up to specific conductivity of 50 $\mu s \cdot cm^{-1}$, according to the requirements for recycled water supply) ranges from 450 to 465 bed volumes, and the quantity of water purified of gold is 460–480 bed volumes.

The ranges of quantities of silver and gold retained by anion exchangers are 16.5–18.3 g/dm^3 and 2.4–3.2 g/dm^3, respectively. The anion exchangers are regenerated by means of 1.5 N NaOH or 1.5 N KCNS.

1. INTRODUCTION

The rinsing wastewaters from the electrochemical gold- and silver-plating plants contain certain quantities of silver or gold. Such wastewaters can be subject to ion-exchange treatment, aiming at their purification and recycling on one hand and concentration of the noble metals in the ion-phase for the purpose of their extraction and utilization by means of proper treatment on the other.

Only a few authors [1]–[8] have studied the possibility of ion-exchange extraction of gold and silver form wastewaters. A lot of different brands of strongly and weakly basic anion exchangers, including some specific ions, have been used. It has been established that silver-holding capacities of Amberlite IRA-68, AH-18 and AB-17 are 52 g/dm^3 [2], 153.6 mg/dm^3 [6] and 72–130 g/dm^3 [7], respectively,

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and those of Amberlite IRA-400, AH-18 and AP-2 are 3.7–10 g/dm^3 [5], 95.8 g/dm^3 [8] and 3.6–4.5 mg/dm^3 [9], respectively. In order to utilize the precious components it has been suggested to burn the loaded ion-exchangers or to renegate them by means of various agents (NH_4CNC, $CS(NH_2)_2$, H_2SO_4, etc). Silver and gold are extracted from the regeneration solutions due to electrolysis or settling by means of SO_2, mercury treatment in the form of amalgam, adsorption on activated carbon, etc. [1], [2], [5].

The studies carried out by different authors show that the composition of the water treated, the concentrations of its components and ion regeneration conditions are heavily dependent on ion exchange capacity, depth of ion exchanger and the degree of noble metal extraction, thus making it necessary to establish by experiment the optimum conditions of particular ion-exchange processes.

2. MATERIALS AND METHODS

The subject of this paper is to investigate the possibility of ion-exchange treatment of cyanide rinsing wastewater from electrochemical silver- and gold-plating plants. The silver and gold concentrations in such a wastewater are 15.6 mg/dm^3 and 1.2 mg/dm^3, respectively. The wastewaters (of specific conductivity equal to 450 $\mu s \cdot cm^{-1}$) were consecutively treated by means of strongly acidic cation exchanger in the H-form, weakly basic anion exchanger in the OH-form and strongly basic anion exchanger in the OH-form. The following ion-exchange units were used:

Lewatit S-100 – Lewatit MP-62 – Lewatit MP-500 (I)

Varion KSM – Varion ADAM – Varion ATM (II)

Wofatit KS-10 – Wofatit AD-41 – Wofatit SZ-30. (III)

Each ion-exchange column, 22 mm in diameter, has been loaded with 200 cm^3 of the respective ion exchanger. The experiments have been carried out under dynamic conditions. The specific loading during filtration cycle amounted to 15 dm^3/dm$^3 \cdot$ h. The gold, silver and cyanide ion concentrations were determined in the water after treatment and the specific conductivity was measured [9], [10].

3. RESULTS AND DISCUSSION

The results of the experiments are shown in table 1 and in figures 1 and 2. The data in table 1 shows that when all three ion-exchange units are used, the volume of water purified of silver (up to specific conductivity of 50 $\mu s \cdot cm^{-1}$ according to the requirements for recycled water supply) ranges from 450 to 465 bed volumes, and the volume of water purified of gold from 460 to 480 bed volumes. Moreover, the concentration of silver, gold and cyanide ions in the purified water is below 0.1 mg/dm^3, and the specific conductivity amounts to 1–3 $\mu s \cdot cm^{-1}$ (figures 1 and 2).

Table 1

Quantity of the water purified up to specific conductivity of 50 $\mu s \cdot cm^{-1}$ by using the ion-exchange units I–III

No.	Ion-exchange units	Waste-water contains	Purified water, bed volumes
I	Lewatit S-100 – Lewatit MP-62 – Lewatit MP-500	silver	465
II	Varion KSM – Varion ADAM – Varion ATM	silver	460
III	Wofatit KS-10 – Wofatit AD-41 – Wofatit SZ-30	silver	450
I	Lewatit S-100 – Lewatit MP-62 – Lewatit MP-500	gold	480
II	Varion KSM – Varion ADAM – Varion ATM	gold	475
III	Wofatit KS-10 – Wofatit AD-41 – Wofatit SZ-30	gold	460

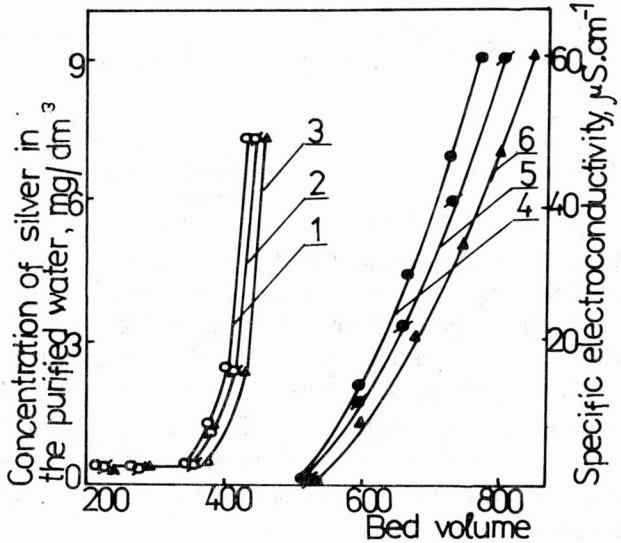

Fig. 1. Specific conductivity (*1*, *2*, *3*) and concentration of silver (*4*, *5*, *6*) in the filtrate after treatment of wastewater by means of ion-exchange unit I–III
1, *4*; *2*, *5*; *3*, *6* – I, II, III ion-exchange units, respectively

The data in figures 1 and 2 prove that silver breakthrough occurs at 520–550 bed volumes, white gold breakthrough – at 530–560 bed volumes.

The regeneration of the cation exchangers was carried out by means of 10% H_2SO_4 (6 bed volumes) at 5 $dm^3/dm^3 \cdot h$ of specific loading. It has been established that the average concentration of silver in the regeneration solutions ranges from 35 to 40 mg/dm^3, and that of gold from 0.8 to 1.0 mg/dm^3.

The anion exchangers were regenerated by means of 1.5 N NaOH or 1.5 N KCNS (6 bed volumes, specific loading 5 $dm^3/dm^3 \cdot h$). The average concent-

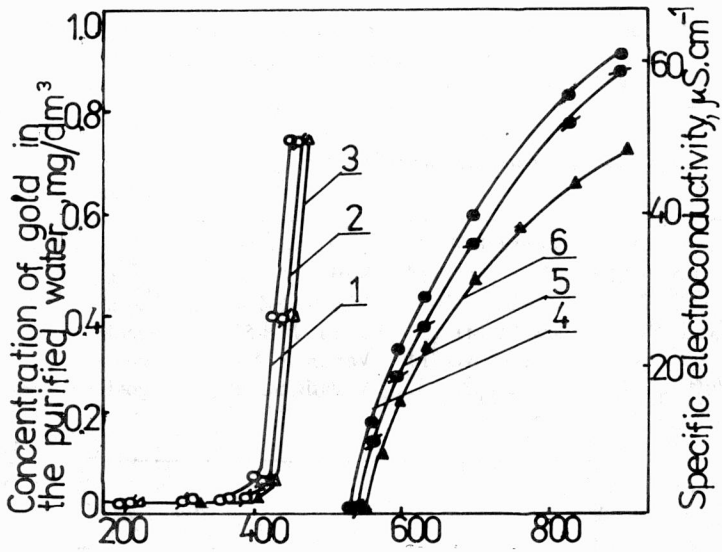

Fig. 2. Specific conductivity (*1*, *2*, *3*) and concentration of gold (*4*, *5*, *6*) in the filtrate after treatment of wastewater by means of ion-exchange unit I–III
1, *4*; *2*, *5*; *3*, *6* – I, II, III ion-exchange units, respectively

rations of silver in the regeneration solutions for various anion exchangers regenerated using NaOH and KCNS range from 320 to 340 mg/dm^3 and from 640 to 660 mg/dm^3, respectively. The average concentrations of gold are 45–50 mg/dm^3 and 65–70 mg/dm^3. The above-mentioned results prove that the regeneration process is more efficient when KCNS is used as regeneration agent (figures 3 and 4).

The considerably higher concentrations of noble metals in the regeneration solutions of the anion exchangers as compared to those of the cation exchangers show that the bulk concentration of silver and gold in the form of cyanide complexes is retained in the anion exchangers.

The ion exchangers regenerated in such a manner have been used for two more cycles of saturation–regeneration. It has been found that the duration of the three cycles when utilizing KCSN as regeneration agent does not significantly differ, whereas the volume of the water treated during the second and the third cycles when applying NaOH as regeneration agents is smaller.

Although during consecutive steps of rinsing water treatment, i.e., strongly acidic cation exchanger – weakly basic anion exchanger – strongly basic anion exchanger, the requirements for recycled water supply are met, the concentrations of silver and gold retained in the ion-exchangers are comparatively small (210–240 mg of silver per 1 dm^3 of cation exchanger and 4.8–6.0 mg of gold per 1 dm^3 of cation exchanger as well as 3800–4000 mg of silver per 1 dm^3 of anion exchanger and 390–400 mg of gold per 1 dm^3 of anion exchanger). Hence, the concentrations of precious metals in

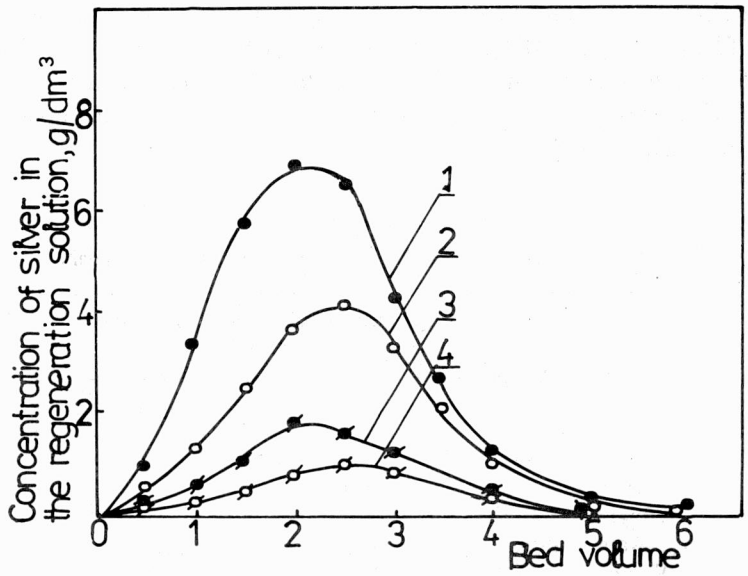

Fig. 3. Regeneration curves of Lewatit MP-500 saturated (*1*, *2*) and partially saturated (*3*, *4*) with silver
1, *3* – KCNS as regeneration agent, *2*, *4* – NaOH as regeneration agent

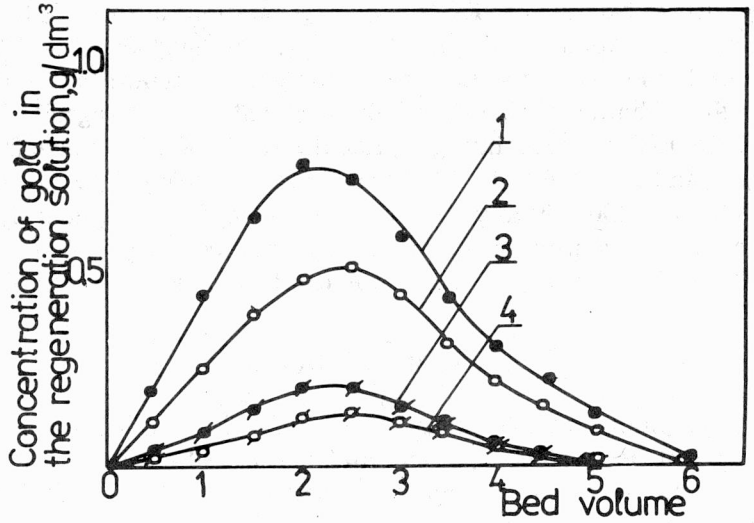

Fig. 4. Regeneration curves of Lewatit MP-500 saturated (*1*, *2*) and partially saturated (*3*, *4*) with gold
1, *3* – KCNS as regeneration agent, *2*, *4* – NaOH as regeneration agent

the regeneration solution are low and additional experiments have been carried out to establish the possibility of complete saturation and regeneration of the anion exchangers investigated.

Table 2 shows the quantity of silver and gold retained by the anion exchangers during the filtration cycle. It has been established that 1.0 dm^3 of anion exchanger retains 16.5–18.3 g of silver or 2.4–3.2 g of gold. The anion exchangers investigated are capable of retaining smaller quantities of silver and gold than those described by some authors [2], [5]–[8].

Table 2

Quantity of silver or gold retained by the anion exchangers

Anion exchanger	Quantity of silver or gold retained g/dm^3	
	Silver	Gold
Lewatit MP-500	17.8	2.8
Varion ATM	16.9	2.5
Wofatit SZ-30	16.5	2.4
Lewatit MP-62	18.3	3.2
Varion ADAM	17.5	2.8
Wofatit AD-41	17.3	2.7

Our investigations were undertaken to examine regeneration of saturated anion exchangers, using NaOH or KCNS as regeneration agents under the same conditions as those applied to non-saturated ion-exchangers.

It has been found that the average silver and gold concentrations in this case are higher than these characteristic of partially saturated ion-exchangers. When NaOH and KCNS are used as regenerating agents, the yields of silver range from 1500 to 1600 mg/dm^3 and from 2600 to 2700 mg/dm^3, respectively. The average concentrations of gold are 230–240 mg/dm^3 and 370–380 mg/dm^3, respectively. Gold and silver can be extracted from these solutions during electrolysis. The regeneration solutions obtained after NaOH regeneration can be used in the electroplating baths.

4. CONCLUSIONS

The experimental data allows us to conclude that rinsing wastewaters from electroplating can be treated effectively and purified of silver or gold of concentrations of 15.6 mg/dm^3 and 1.2 mg/dm^3, respectively. In the process, incorporating three consecutive steps, the wastewater is subject to ion-exchange treatment on strongly acidic cation exchanger in the H-form, weakly basic anion exchanger in the OH-form and strongly basic anion exchanger in the OH-form. The water purified meets the requirements for recycled water supply.

It has been established that the capacity of the anion exchangers as regards silver and gold are 16.5–18.3 g/dm^3 and 2.4–3.2 g/dm^3, respectively. Regeneration of anion exchangers by means of KCNS yields regeneration solutions with concentrations of

silver and gold ranging from 2.6 to 2.7 g/dm^3 and from 0.37 to 0.38 g/dm^3, respectively. Noble metals can be obtained from these solutions when treated properly.

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OCZYSZCZANIE METODĄ WYMIANY JONOWEJ ŚCIEKÓW GALWANIZERSKICH ZAWIERAJĄCYCH SREBRO I ZŁOTO

Oczyszczano wody popłuczne z galwanizerni metodą wymiany jonowej. W oczyszczanych ściekach zawartość srebra wynosiła 15,6 mg/dm^3, złota natomiast 1,2 mg/dm^3. Ścieki stopniowo oczyszczano na silnie kwaśnych kationitach (H), słabo zasadowych kationitach (OH) i silnie zasadowych anionitach (OH). Podczas procesu oczyszczania stosowano trzy następujące układy jonowymieniaczy: 1) Lewatit S-100 – Lewatit MP-500 – Lewatit MP-62 (I), 2) Varion KSM – Varion ADAM – Varion ATM (II) oraz 3) Wofatit KS-10 – Wofatit AD-41 – Wofatit SZ-30 (III).

Stwierdzono, że kiedy używano trzech układów jonowymieniaczy, objętość ścieków oczyszczanych ze srebra (do wartości przewodnictwa właściwego 50 $\mu s \cdot cm^{-1}$) wynosiła 450–465 objętości złoża, a ze złota – 460–480 objętości złoża.

Na wymieniaczach anionowych zatrzymywało się 16,5–18,3 g srebra/dm^3 i 2,4–3,2 g złota/dm^3. Wymieniacze jonowe regenerowano za pomocą 1,5 N NaOH lub 1,5 N KCNS.

ОЧИСТКА МЕТОДОМ ИОНООБМЕНА ГАЛЬВАНИЧЕСКИХ СТОЧНЫХ ВОД, СОДЕРЖАЩИХ СЕРЕБРО И ЗОЛОТО

Очищали гальванические промывные воды методом ионообмена. В очищаемых сточных водах содержание серебра составляло 15,6 мг/дм^3, золота зато 1,2 мг/дм^3. Сточные воды постепенно очищали на сильно кислотных катионитах (Н), слабо щелочных катионитах (ОН) и сильно щелочных анионитах (ОН). Во время процесса очистки применяли три следующие системы ионообменников: 1) Lewatit S-100 – Lewatit MP-500 – Lewatit MP-62 (I), 2) Varion KSM – Varion ADAM – Varion ATM (II), а также 3) Wofatit KS-10 – Wofatit AD-41 – Wofatit SZ-30 (III).

Установили, что при употреблении трех систем ионообменников объем сточных вод, очищаемых от серебра (до значения удельной проводимости 50 мс $\cdot$ /см$^{-1}$) составлял 450–460 объемов слоя, а от золота – 460–480 объемов слоя.

Аниониты задерживали 16,5–18,3 г серебра/дм^3 и 2,4–3,2 г золота/дм^3. Ионообменники регенерировали при помощи 1,5 N NaOH или 1,5 N KCNS.