

Galvanochemical Purification of Liquid Radioactive Wastes in Sulphuric Acid Uranium Refining Pattern

YU. V. OSTROVSKIY¹, G. M. ZABORTSEV¹, R. L. RABINOVICH², V. R. KALK² and A. A. LAVELIN²

¹JSC "State Specialized Design Institute", Novosibirsk VNIPIET, Ul. B. Khmel'nitskogo 2, Novosibirsk 630075 (Russia)

E-mail: ost@vni Piet-nsk.ru

²JSC "Angarsk Electrolysis Chemical Combine", Irkutsk Region, Angarsk 665804 (Russia)

(Received April 4, 2008; revised July 30, 2008)

Abstract

Galvanochemical purification of liquid radioactive waste products of sulphuric acid uranium refining pattern has been studied by the example of wastewater from the Angarsk Electrolysis Chemical Combine as well as basic laws and features of this process have been determined.

Key words: wastewater, uranium, heavy and nonferrous metals, galvanochemical purification, galvanic couples, immobilization of galvanic slime

INTRODUCTION

Wastewaters containing uranium, heavy and nonferrous metals, as well as ammonium, fluoride, phosphate and sulphate ions are formed due to the production activity of the chemical plant of the Angarsk Electrolysis Chemical Combine (AECC).

Liming of wastewater by the suspension of calcium hydroxide, used at the plant for sedimentation of uranium ions, heavy and nonferrous metals, as well as subsequent feeding the pulp obtained to a reservoir for liquid waste products do not meet contemporary requirements for the environmental conservation. In this connection the question concerning the implementation of a more perfect technology is of currently central value.

For purifying the wastewater of sulphuric acid uranium refining pattern of the AECC chemical plant we offer a technology which provides a higher extraction level for uranium, heavy and nonferrous metals, fluorides, phosphates and sulphates as compared to liming, with a considerable decrease in the amount of solid radioactive wastes (SRW) subject to burial [1, 2].

The technology is based on galvanochemical wastewater treatment which provides the extraction of trace contaminants (uranium, heavy and nonferrous metal ions) in the presence of macro-pollutants (fluoride, phosphate and sulphates ions, ammonium ions) [3, 4].

The method of galvanochemical wastewater treatment is based on using the effect of short-circuited galvanic cells (galvanic couples) consisting of the mixture of two electroconductive materials with different values of the electrochemical potential, placed into the solution under treatment for dissolving one of the elements of the galvanic couple [5].

This paper presents the results of the studies on the influence of galvanic couple composition and processing conditions upon the efficiency of galvanochemical AECC wastewater treatment.

EXPERIMENTAL

The experiments on galvanochemical wastewater treatment were carried out using a vertical vibration galvanic coagulator unit with simultaneous wastewater and compressed air sup-

ply [6]. As the components of galvanic couples we used various waste products such as coke or graphite, iron and aluminium shavings with particle size ranging within 5–10 mm and the mass ratio of (3–4) : 1. Prior to the beginning of operation a galvanic couple was activated using 5–10 % HCl solution, and then it was washed with water.

The galvanochemical wastewater treatment included the adjustment of pH values with 10 % NaOH or H₂SO₄ solution, the processing in the galvanic couple field within a vibration galvanic coagulator unit, the aeration of a pulp with the compressed air, the adjustment of pH values using 10 % Ca(OH)₂ suspension, the precipitation and filtration of a sediment (galvanic slime) at the following parameters: $t = 18\text{--}20$ °C, wastewater to galvanic couple contact time $\tau = 5\text{--}30$ min, compressed air flow rate $Q_{\text{air}} = 2.0$ L/min, vibration frequency of the vibration galvanic coagulation unit $f = 30\text{--}55$ Hz, $\text{pH}_{\text{fin}} 9.0\text{--}12.0$, pulp aeration time $\tau = 1$ h. The experiments were carried out with model solutions those contained no uranium, as well as with uraniferous wastewaters from the AECC.

The determination of uranium, heavy and nonferrous metals was carried out by means of photometric technique; sulphates were determined using a turbidimetric method. Fluorine ions were determined by a photometric method with a zirconium-alizarine indicator, the determination of phosphorus was performed via the oxidation in the solution by ammonium persulphate with an ammonium molybdate indicator [7, 8]. For the monitoring of photometric analyses we used a DR/2010 spectrophotometer (HACH, the USA).

RESULTS AND DISCUSSION

Galvanochemical purification of model wastewater

The rate of galvanochemical oxidation (dissolution) of galvanic couple components depends on the type of a galvanic couple, on the temperature and electrical conductivity of a medium, on the potentials and the size of galvanic couple components [5].

The choice of a galvanic couple is determined by a particular task concerning wastewater treatment. So, for the removal of heavy and nonferrous metal ions one use a Fe–C (coke) galvanic couple wherewith a determining role is played by iron oxohydrates [9], whereas for the removal of anions (for example, sulphate) an Al–C (coke) galvanic couple could be used wherewith purifying is carried out due to the formation of aluminum dihydroxo and tetrahydroxo sulphates [5].

In searching for an optimum galvanic couple in order to purify model wastewater whose composition is presented in Table 1, we have worked over the following modes of galvanochemical purification: 1) one-stage mode in the field of Fe–C galvanic couple; 2) one-stage mode in the field Fe–C and Al–C galvanic couples; 3) two-stage mode in the field of Fe–C galvanic couple (1st stage), and Al–C galvanic couple (2nd stage); 4) two-stage mode in the field of Fe–C and Al–C galvanic couples.

In the case of one-stage purification in the field of Fe–C and Al–C galvanic couples the latter are arranged in series: from the bottom a Fe–C galvanic couple is located, an Al–C galvanic couple being from the top. In the case of

TABLE 1

Parameters for various modes of model wastewater galvanochemical purification

Purifying method	pH_{ini}	pH_{fin}	Pollutants content, mg/L					
			Ni ²⁺	Cu ²⁺	Cr _{total}	F ⁻	P _{total}	SO ₄ ²⁻
Initial composition	2.0	-	500.0	500.0	10.0	295.0	114.0	20 815
One-stage mode in the field of Fe–C galvanic couple	4.0	10.0	15	0.5	0.0	6.5	0.1	3955
One-stage mode in the field of Fe–C and Al–C galvanic couples	4.0	10.0	5.5	83.0	0.0	30.1	0.0	4787
Two-stage mode in the field of Fe–C (1st stage), Al–C (2nd stage) galvanic couples	4.0	9.5	485	25	0.0	156	0.2	3892
Two-stage mode in the field of Fe–C and Al–C galvanic couples	4.0	9.3	19.0	19.0	0.0	18.0	0.2	1936

two-stage purification in the field of Fe-C galvanic couple (1st stage) and Al-C galvanic couple (2nd stage) there is a change of a galvanic couple in the vibration galvanic coagulator unit realized as well as adjustment of the solution acidity with sulphuric acid up to pH 6.5-7.5. Between the stages the sediment was separated.

The two-stage purification in the field of Fe-C and Al-C galvanic couples was carried out with no changing a galvanic couple in the vibration galvanic coagulator unit and consisted in double passing the solution through the galvanic coagulator: the first stage was performed at pH_{ini} 4.0 (Fe-C galvanic couple operating), whereas the second stage at pH_{ini} 10.0 occurred (Al-C galvanic couple operating). Between the stages the sediment was separated.

The results for various modes of galvanochemical purification of model wastewater at $\tau = 15$ min and $f = 40$ Hz are presented in Table 1.

A scarce influence of Al-C galvanic couple upon the extraction level for anions in the system under investigation with the total salt content up to 30-35 g/L is, to all appearance, caused by a high concentration of sulphate ions. In this connection we proposed a one-stage purification mode in the field of Fe-C galvanic couple as an optimum variant for galvanochemical purification of model wastewater.

The influence of the duration of model wastewater galvanochemical treatment in the field of Fe-C galvanic couple upon the efficiency of heavy and nonferrous metal ions removal has been demonstrated by the example of nickel and copper ions (Fig. 1). With the increase in the contact time value one can ob-

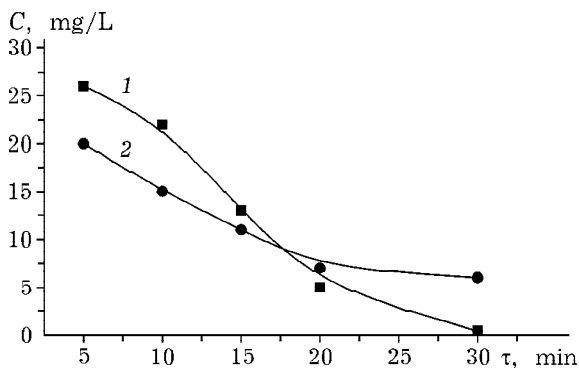


Fig. 1. Residual content of Ni^{2+} (1) and Cu^{2+} (2) ions in model wastewater depending on the contact time value (pH_{ini} 4.0, pH_{fin} 9).

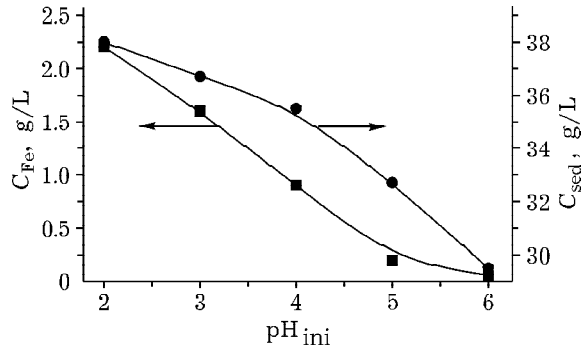


Fig. 2. Concentration of iron and ferriferous sediment in model wastewater depending on pH_{ini} .

serve a decrease in the residual content of nickel and copper ions. To all appearance, this fact is connected with of iron generation into the solution whose content amounts up to 2.0-2.5 g/L at $\tau = 15-20$ min, the content of the galvanic slime sediment amounting to 30-40 g/L. The efficiency of model wastewater purification at $\tau = 15$ min and pH_{fin} 9.0 with respect to sulphates amounts up to 97.7 %, whereas this value for fluorides, phosphates, nickel and chromium is equal to 99.5 %.

The most significant role in the extraction of heavy and nonferrous metal ions is played by iron oxohydrates [9] whose formation is de-

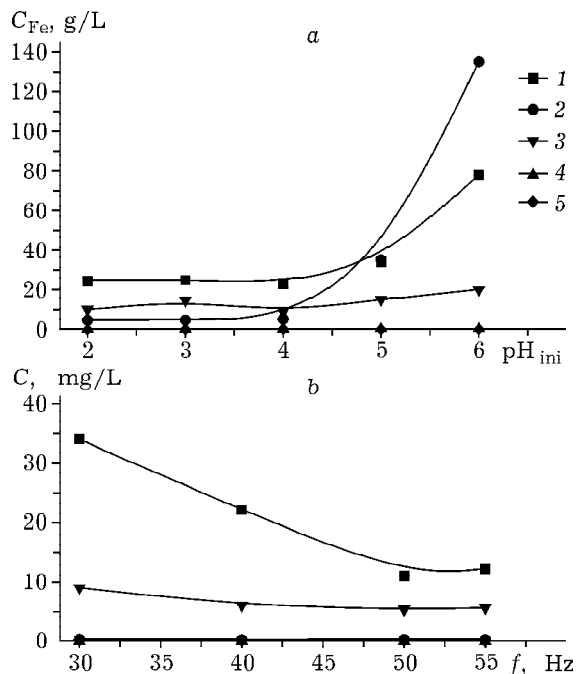


Fig. 3. Residual content of pollutants in model wastewater depending on pH_{ini} (a) and on the vibration frequency (b): 1 - Ni^{2+} , 2 - F^- , 3 - Cu^{2+} , 4 - Cr_{total} , 5 - P_{total} .

terminated by the acidity of the initial solution. Figure 2 demonstrates the influence of initial solution acidity for the value ranging within pH 2–6 upon the generation of iron into the solution as well as upon the content of the sediment. The effect of the same parameter on the efficiency of purification for model wastewater in the field of Fe–C galvanic couple at $\tau = 15$ min and $\text{pH}_{\text{fin}} 9$ is presented in Fig. 3, *a*.

For the Fe–C galvanic couple, a considerable decrease in the efficiency of model wastewater galvanochemical purification from the ions of heavy and nonferrous metals is observed at $\text{pH}_{\text{ini}} > 5.0$ (see Fig. 3, *a*). To all appearance, this fact could be connected with a decrease in iron generation level as well as in total amount of the galvanic slime sediment within the solution processed (see Fig. 2).

The vibratory fluidization allows one to optimize the operation of Fe–C galvanic couple due to permanent refreshing the surface of the galvanic couple elements and removal of the diffusion restrictions. The effect of vibration frequency of the vibration galvanic coagulator unit on the galvanochemical purification of model wastewater at $\tau = 15$ min, $\text{pH}_{\text{ini}} 4.0$ and $\text{pH}_{\text{fin}} 9.0$ is presented in Fig. 3.

As opposed to the nitrate systems [4] an increase in the vibration frequency of the vibration galvanic coagulator unit within the range of $f = 30$ – 55 Hz under these conditions results in insignificant growth of the galvanochemical purification efficiency whose curve flattens out at $f > 50$ Hz (see Fig. 3, *b*). The content of the sediment in this case increases from 35.5 to 53.5 g/L, which, to all appearance, could be caused by more intense galvanic couple consumption.

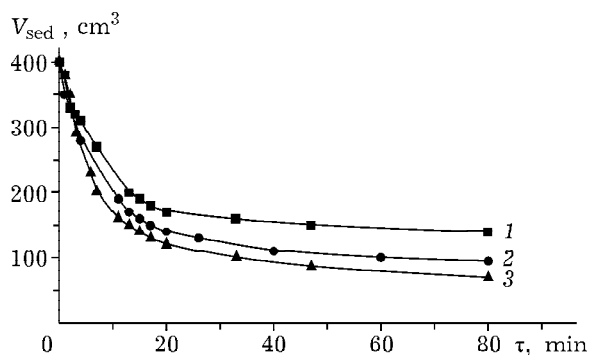


Fig. 4. Kinetics of galvanic slime sedimentation with the use of various alkaline reagents: 1 – 10% $\text{Ca}(\text{OH})_2$ (suspension), 2 – the mixture of 10% $\text{Ca}(\text{OH})_2$ and 10% NaOH (1:1), 3 – 10% NaOH.

TABLE 2

Composition of wastewater samples from the AECC

Sample No.	Pollutants content, mg/L						
	U_{total}	Ni^{2+}	Cu^{2+}	$\text{Cr}_{\text{обш}}$	F^-	Fe_{total}	P_{total}
1	0.47	7.0	2.4	34.0	570	490	76 800
2	0.01	25.0	2.5	0.082	4100	15	16 400
3	0.80	72.0	27.0	4.5	360	590	80 500
4	0.43	0.93	0.26	0.61	1200	95	7500
5	0.62	11.0	1.8	5.6	2100	42	6600

One of the key points of a technology for wastewater treatment consists in the separation of sediment. Figure 4 demonstrates the results of galvanic slime sedimentation obtained in the process of galvanochemical purification of model wastewater in the field of Fe–C galvanic couple at $\tau = 15$ min, $f > 50$ Hz, $\text{pH}_{\text{ini}} 4.0$ with the subsequent alkalization up to $\text{pH}_{\text{fin}} 9.0$ using various alkaline reagents.

High level of galvanic slime sedimentation is observed under adjusting the value of wastewater pH by adding NaOH solution or its mixture with $\text{Ca}(\text{OH})_2$ suspension. Owing to this, one can succeed in achieving a high wastewater purification level with respect to many components. However, the use of alkaline reagents results in the contamination of wastewaters with sodium ions.

Thus, wastewater treatment in the field of the Fe–C galvanic couple is worthwhile to be carried out under the following conditions: $\tau = 15$ – 20 min (being in a good agreement with the data from [5]), $f = 50$ Hz, $\text{pH}_{\text{ini}} = 3.0$ – 4.0 , $\text{pH}_{\text{fin}} 9.0$.

Galvanochemical purification of the AECC wastewaters

The galvanochemical purification in the field of the Fe–C galvanic couple was performed samples of wastewater from the AECC whose composition is presented in Table 2. After adjusting the pH value of the medium, the wastewaters were processed with the help of a vibration galvanic coagulator; then the samples were aerated, alkalified up to $\text{pH}_{\text{fin}} 9$ and a precipitate was separated.

The results of galvanochemical wastewater treatment at $\tau = 15$ min, $\text{pH}_{\text{ini}} 3$ and $f = 40$ Hz are presented in Table 3. There are also the parameters of wastewater sample No. 5 pre-

TABLE 3

Purification efficiency for wastewater samples *via* the galvanochemical method and the method of liming

Sample No.	Level of contaminant extraction*, %						
	U _{total}	Ni ²⁺	Cu ²⁺	Cr _{total}	F ⁻	Fe _{total}	P _{total}
1	95.6	95.5	98.2	>99.9	96.5	~100	97.5
2	98.1	87.6	98.9	98.2	97.6	99.3	87.7
3	98.7	74.7	99.8	99.3	94.4	~100	98.5
4	97.7	77.4	86.5	96.9	98.1	99.2	95.3
5	>99.2/97.7	99.1/26.9	98.6/41.6	99.3/99.4	99.9/99.5	99.9/36.0	97.5/74.6

*The first value is obtained *via* galvanochemical purification, the second value is observed after purification by the method of liming.

sented for purifying by the method of liming at pH_{fin} 12. It is seen that the use of the galvanochemical method for different composition wastewater purification from uranium, heavy and nonferrous metals is much more efficient as compared to the method of liming.

The latter does not provide efficient extraction of nonferrous metal ions (such as nickel, copper), since it is first of all aimed at the sedimentation of uranium (the extraction level value amounting to 97.7 %), requiring for adjusting the wastewater acidity value up to pH_{fin} 12 (see Table 3). To all appearance, at pH_{fin} 12 the dissolution of nickel and copper hydroxides uses to begin, whereas calcium sulphate formed under liming of wastewater exhibits much lower sorption characteristics than iron oxohydrates from the galvanic slime.

The galvanic wastewater treatment results in a satisfactory separation of phases. The sedimentation rate value for the galvanic slime is

equal to 40.0 mm/min, which allows one to use thin-layer sediment traps for separating the galvanic slime. The application of flocculating agents based on various polyacrylamide modifications improves the coagulation.

After settling and filtering dark green sediments were obtained (the mixture of iron (II) and (III) hydroxides). The composition of different kinds of galvanic slime dried at 105 °C is presented in Table 4.

The galvanic slime obtained due to wastewater treatment contains up to 35 g/t of uranium, and it could be transmitted to the extraction processing for the extraction of uranium. Another way to use the galvanic slime consists in immobilizing the slime into glass ceramics by means of mixing with montmorillonite clay, pressing granules with subsequent drying and calcination at the temperature of 1000–1050 °C. The leaching rate value for the glass ceramics obtained with the effect of surface fusing amounts to less than $0.7 \cdot 10^{-5}$ g/(cm² · day) [2].

TABLE 4

Composition of galvanic slime obtained for the AECC wastewater treatment

Component	Mass fraction, %
U _{total}	0.0009–0.0035
Ni ²⁺	0.015–0.14
Cu ²⁺	0.005–0.021
Cr _{total}	0.028–0.12
NH ₄ ⁺	0.05–2.15
SO ₄ ²⁻	1.9–14.3
F ⁻	1.3–27.0
P _{total}	0.02–0.068
Fe _{total}	5.1–25.0

Note. The contents of the sediment amounted to 20–25 g/L.

CONCLUSION

The investigations carried out have demonstrated that the use of the galvanochemical method allows one to purify efficiently the AECC wastewaters from the impurities of uranium, heavy and nonferrous metals. The ways are proposed to recycle the galvanic slime obtained.

Acknowledgements

Authors express sincere gratitude to the researchers of the Novosibirsk VNIPIET Design and Research Institute A. A. Shpak, S. P. Yakobchuk and T. I. Vastrukhina for assistance in carrying out the experiments.

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