Chemistry for Sustainable Development **20** (2012) 309–314

UDC 541; 621. 359. 7

Purifying Man-Caused Wastewaters and Technological Solutions from Heavy Metal Ions and Arsenic

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(Received August 2, 2011; revised September 28, 2011)

Abstract

A process of purifying complex multicomponent technological solutions with the use of a combined sorption-and-electrochemical method was studied. By the example of processing the technological solutions from the Belovo Zinc Plant and from the sulphuric acid workshop of the Ural Mining and Processing Company, a potentiality of combined using the adsorption and electrochemical stages for efficient extracting of HMI and arsenic up to attaining required MPC standards for discharging the solutions into a sewage system was demonstrated. This allows reducing to a significant extent the hazard inherent in the wastewaters and technological solutions, improving the environmental situation around the enterprises and reducing the metal loss.

Key words: man-caused wastewater, heavy metals, arsenic, electrolysis, flow-through porous cathodes

INTRODUCTION

The problem of purifying industrial waste waters from heavy metal ions (HMI) is relevant for many operating and shutdown enterprises. In order to solve the problem, it is efficient to use combined physicochemical methods. For example, the technology based on electrolysis with flow-through porous cathodes and adsorption onto naturally occurring mineral brucite, tested in the course of purifying of washing solutions resulting from a number of electroplating processes (chromating, galvanizing, copper plating, nickel plating, *etc*.) allows one to extract metals up to MPC level [1–3].

The washing solutions considered by the authors of [1–3] were simple in composition and contained 1 or 2 kinds of metals to remove. However, waste waters and technological solutions with complicated polyionic composition are to a greater extent widespread in hydrometallurgy, the composition of those, alongside with HMI could contain high-toxic impurities, for example, arsenic.

The aim of this work consisted in evaluating the efficiency of using a combined sorption-and-electrochemical method for purifying complicated multicomponent technological solutions.

EXPERIMENTAL

As the subject of inquiry, we used real man-caused waste water taken from the sewage reservoir of the Belovo Zinc Plant (BZP) and technological solutions taken from the sulphuric acid workshop of the Ural Mining and Processing Company those additionally contain arsenic.

The evaluation of the efficiency of electrowinning the metals onto flow-through porous

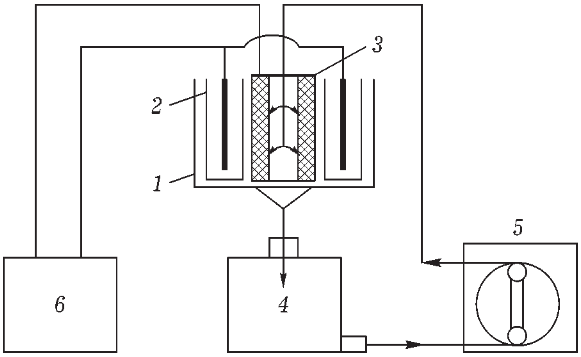

Fig. 1. Schematic diagram of experimental electrolysis unit: *1* – electrolyzer, *2* – anode chamber, *3* – cathode block, *4* – buffer tank for the solution, *5* – peristaltic pump, *6* – power supply.

cathodes was performed with the use of a laboratory setup consisting of an electrolyser, a pump, a buffer tank for the solution and a DC source (Fig. 1). As the flow-through cathodes, we used porous materials with different fixed geometrical surface area (30 cm^2), metallised sintepon [4], KNM and VNG-30 carbon felt, iron wool. With almost identical parameters the VNG-30 felt exhibits a higher (an order of magnitude) electrical conductivity as to compare with the KNM felt [5]. The anode material was presented by graphite. For the separation of the cathode and anode spaces of the electrolyser we used a MA-40 anion exchange membrane.

The concentration of metals in the initial and final solutions was determined using atomic emission spectroscopy (an IRIS Intrepid II XSP emission spectrometer with inductively coupled plasma, Thermo Fisher Scientific, the USA). The determination error for metals ranged within 0.03–1.5 %. For the rapid determination of copper and zinc in the course of electrolysis we used voltammetry with renewable graphite electrode [6]. The electrolysis of wastewaters and technological solutions was performed in a circulation mode at a fixed volume flow rate amounting to 18 L/h; the volume of the solution portion under treatment was equal to 1 L. All potential values are presented with respect to silver chloride reference electrode.

Studying the potentialities of HMI and arsenic sorption extraction from the industrial solutions of complicated composition was performed using both naturally occurring and thermally modified brucite. Earlier it was reported [7] concerning high sorption properties of brucite with respect to HMI. Brucite represents a mineral belonging to the class of hydroxides, it has a layered structure, the chemical formula being $Mg(OH)_2$. The sorption capacity of

TABLE 1

Initial and final composition of the BZP solution under different conditions of electrolysis

Metals	Metal concentration, mg/L					
	Initial solution	Solutions after electrolysis				
		1	2	3	4	5
Cu	750	30	1.2	9.0	0.3	0.3
Zn	400	150	19.6	173	8.8	9.8
Pb	5	4	1.3	3.0	0.4	0.4
Mn	24	16	4.7	23	13.0	6.0
Al	15	14	0	8.0	0	0
Ni	5	5	0.5	4.0	0.7	0.7
Cd	3	3	0.4	0.9	0.4	0.3
Fe	2	2	0	780	0	0
Co	1	1	0.26	1.6	0.3	0.2
pH	4.3	1.3	7.0	2.1	8.0	7.1

Note. Electrolysis conditions: solutions Nos. 1, 2 – porous cathode made of metalized sintepon, I = 3 A, τ = 60 min, electrolysis without separation (soln. No. 1) and with separation (soln. No. 2) of electrode spaces; solutions Nos. 3, 4 – porous cathode made of iron wool, I = 2 A, τ = 60 min, electrolysis without separation (soln. No. 3) and with separation (soln. No. 4) of electrode spaces, $\varphi = -1.5$ V, τ = 60 min; soln. No. 5 – porous carbon felt cathode made of carbon felt KNM, electrode spaces separated, $\varphi = -1.6$ V, τ = 60 min.

the mineral with respect to metals in mono solutions as well as in joint presence thereof ranges from 900 to 115 mg/g to decrease in the following order: Cu > Zn > Cd > Co > Ni > Mn. The thermal treatment of brucite results in forming any modified forms of the mineral with a “defective” crystalline structure and a developed specific surface area; those differ to a considerable extent from naturally occurring samples in adsorption capacity [8].

The sorption experiments were performed under static conditions *via* varying the concentrations, wherefore the brucite with the grain size ranging within 10-50 μm was added to the solution; the solution was stirred with the help of a magnetic stirrer during 30 min and further the solid was separated *via* filtration. The kinetics of sorption process in a static mode exhibits a 30- to 50-fold increasing the rate, when stirring the solution with brucite is performed using an ultrasonic disperser.

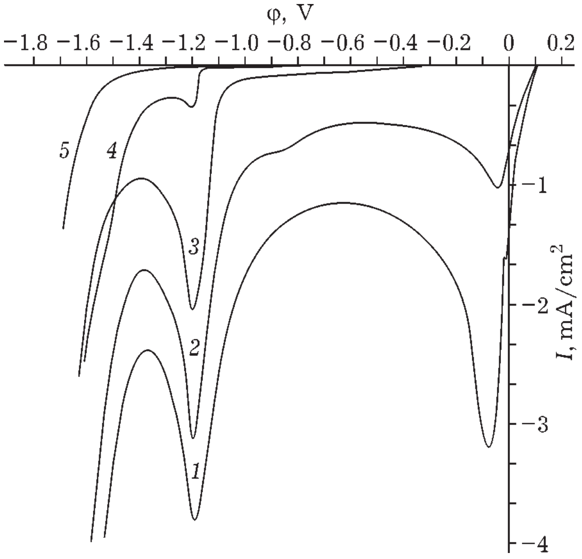

Fig. 2. Extraction of Cu and Zn from the man-caused solution taken from BZP onto the cathode made of metallised sintepon (electrolysis with the separation of the electrode spaces, galvanic mode, $I = 3$ A): *1* − initial solution, *2*−*5* − the solution after processing for 15 (*2*), 30 (*3*), 45 (*4*) and 60 min (*5*).

RESULTS AND DISCUSSION

Processing the technological solutions the Belovo Zinc Plant

More detailed information about the composition of the starting solutions from BZP and the final solutions after electrolysis under different experimental conditions are listed in Table 1. It is seen that the basic macro components of the solutions taken from BZP are presented by copper and zinc, whose content is equal to 400 and 750 mg/L, respectively. The contents of other metals in solution and is significantly lower at 1−20 mg/L.

The cathodic polarization curve for the initial solution taken from BZP is presented in Fig. 2 (curve *1*). The method of supplements demonstrated that the cathodic polarization curves within the potential range of less than 0.1 V correspond to copper deposition, whereas at $\varphi < -1.2$ V zinc is observed to deposit, and an intense evolution of H_2 is observed for the potential values more negative than −1.4 V. The cathodic polarization curves presented here reflect for different moments of time the dynamics of depositing copper and zinc onto the cathode of metallised sintepon separated from the anode by an ion exchange membrane.

From Table 1 one could also see that the efficiency of the electrochemical extraction of Cu and Zn depends to a great extent on the separation between the electrode spaces. In the course of electrolysis without separating the cathode and anode chambers, the process is accompanied by acidifying the solution to pH 1.3 owing to the evolution of O_2 at the anode and the formation of H^+ ions. This effect facilitates the release of hydrogen at the cathode resulting in decreasing the cathode current yield and an abrupt decreasing the level of Cu and Zn extraction, regardless of the nature of the cathode. The residual copper content amounts to 9−30 mg/L and that for zinc ranges within 150−173 mg/L. When iron wool is used as the flow-through cathode, there occurs a significant dissolution of iron in the acidic environment (iron concentration increases from 2 to 780 mg/L), which indicates that the material is unfit for electrochemical processing these solutions without separating the electrode spaces.

The separation of electrode chambers with an anion exchange membrane causes the source of solution acidification near the anode to be eliminated and to at the expense of the parallel evolution of hydrogen at the cathode and

TABLE 2

Effect of pH on the efficiency of metal extraction from BZP waste technological solution using reagent method

Metals	Metal content, mg/L				
	Initial	Residual			
	Solution pH				
	4.1	7.0	8.0	9.0	10.5
Al	15	0	0	0.01	0.07
Cd	3	2.32	1.18	0.01	0.03
Co	1	0.77	0.32	0.004	0.05
Cu	750	15.5	4.5	0.06	2.10
Fe	2	0	0	0	0.01
Mn	24	7.9	3.8	0.01	0.08
Ni	5	2.85	0.20	0.002	0.016
Pb	5	0.07	0.04	0.02	0.01
Zn	400	99.2	17.5	0.06	1.21

results in alkalization catholyte to pH 10–10.5, which increases to a significant extent the level of metal extraction. So, in this case copper can be extracted to attain the concentration of 0.3–1 mg/L, whereas the residual concentration of zinc can be reduced to 19 mg/L, which is considerably lower as compared to acidic solutions. Comparing different porous cathodes between each other, it should be noted that under the conditions of the separation of the electrode spaces they provide similar results for metal recovery. However, the most low residual concentration values are observed in the case when the KNM is used. Most likely, this is connected with a higher specific surface of the KNM and with the growth of its conductivity according as metal is deposited. Alongside with improving the operation conditions of the porous cathode due to shifting the H2 evolution potential toward the cathode range due to alkalizing the solution, the increase in the level of extraction could be partly connected with chemical precipitation of metals in the form of hydroxides. This is confirmed by the results of the reagent purification of the solutions taken from BZP obtained for different pH values, which can be adjusted by means of adding NaOH solution thereto (Table 2).

It is seen that already at pH 7.0 there is an almost complete deposition of Al and Fe, as well as 98 % of Cu, 75 % of Zn and approximately 50 % of other metals observed. With increasing the pH value of the solution up to 8.0 the level of metal extraction increases up to 99.4 % for Cu, 96 % for Zn, 66 % for Cd, up to 73 % for Co, up to 86 % for Mn, 84 % for Ni. At pH 9.0, an almost complete extraction all the metals from the man-caused solutions occurs. Further increase in the acidity up to pH 10.5 results in lowering the recovery performance due to a partial dissolution of hydroxides. In this connection, the optimum solution pH value in the course of the reagent purification amounts to pH 9.

From Table 1 one can see that fort all the tested variants of HMI electrowinning the residual concentrations in the solution after electrolysis exceed the MPC value corresponding to wastewater discharging into the Novosibirsk

TABLE 3

Changing the chemical composition of waste technological solution BZP from after electrolysis and after-treatment sorption onto naturally occurring and modified brucite

Metals	Metal content, mg/L			MPC, mg/L
	Purified soln. after electrolysis	Naturally occurring brucite	Modified brucite	
Cd	0.35	0.004	0.009	0.1
Co	0.23	0.04	0.0007	0.1
Cu	0.75	0	0.01	0.1
Fe	0	0	0	1.0
Mn	5.9	1.6	0.0008	0.3
Ni	1.45	0.1	0.003	0.1
Pb	0.85	0.03	0.06	0.1
Zn	15.1	0.02	0.0086	0.1

TABLE 4

Composition of the initial solution and the solutions after the removal of arsenic, under electrolytic HMI extraction and sorption after-treatment using brucite. Electrolysis with a flow-through cathode made of carbon-fibre felt VNG-30, $\varphi = -0.9$ V

Metals	Metal content, mg/L									
	Initial solution	After As removal	Duration of electrolysis, h				Sorption treatment			
			1	2	3	4	I	E, %	II	E, %
Al	4.7	4.2	4.5	4.8	4.7	5.0	0.06	98.8	0.06	98.8
As	50.3	5.8	6.3	5.3	4.0	3.6	0	100	0	100
Cr	2.0	0.3	0.7	0.7	0.6	0.7	0	100	0	100
Cu	1139	926	496	129	64	3.2	0.13	95.9	0.05	98.4
Fe	419	9.4	67	66	68	77	0	100	0	100
Mn	1.6	2.2	1.8	1.8	1.6	1.6	1.6	0	1.6	0
Ni	20.8	0.9	6.1	6.6	6.8	7.6	0	100	0	100
Pb	4.9	2.9	2.7	2.0	1.0	0.7	0.02	97.1	0.02	97.1
pH	1.1	1.0	0.9	0.8	0.8	0.7	4.9	–	4.9	–

Note. I – natural brucite (2 g/L), II – modified brucite (1 g/L); *E* – the level of sorption extraction of the metal.

sewage system (Table 3). Therefore, it is necessary to carry out additional purifying the wastewaters. The sorption electrochemical method suggested by the authors consists in the use of the sorption purification with the help of brucite. For this purpose, solutions Nos. 3 and 4 (see Table 1) were joined together, further the separate portions of this solution (1 L in volume) was added either with 2 g/L of naturally occurring brucite, or with 1 g/L of modified brucite. The results of analyzing the solution before and after the sorption procedure are presented in the Table 3.

It can be seen that the sorption after-treatment of the solutions by modified brucite occurs very efficiently to allows extracting the macrocomponents (Cu and Zn) up to the MPC level, with significant reducing the concentration of other substances (Cd, Co, Mn, Ni, Pb). Thus, using the modified brucite provides obtaining much more pure waste water with a half consumption of the sorbent.

Processing the technological solutions of sulphuric acid production containing arsenic

The solutions taken from sulphuric acid production are characterized by a complicated ionic composition, a high concentration of copper (≥1000 mg/L), sulphuric acid (pH ≈ 1) and arsenic (up to 50 mg/L) (Table 4).

In the course of the purification such wastewaters, first of all a problem was posed concerning the removal of arsenic from the solution in the form of an insoluble compound suitable for burial. It is known that arsenic uses to form insoluble compounds with magnesium ($K_{sp}(Mg_3(AsO_4)_3) = 2.1 \cdot 10^{-20}$) [9]. Data from [10] confirm the stability of the compounds resulting from of arsenic adsorption on brucite in aqueous media. Furthermore, it should be noted that brucite exhibits high alkalinity properties, whereby this mineral could be used for the neutralization of acidic solutions.

These studies resulted in determining the conditions whereby the addition of brucite in

TABLE 5

Composition of precipitates with arsenic obtained in the course of sorption purification with the use of naturally occurring and modified brucite

Brucite	Sorbent consumption, g/L	Precipitate composition, %						
		As	Mg	Fe	Cu	Pb	Zn	Mn
Naturally occurring	3.5	1.63	6.61	27.43	12.25	9.54	0.18	0.01
Modified	2.0	4.21	16.63	18.86	3.23	6.62	0.25	0.03

the solution containing As and HMI, allows one to segregate arsenic in the form of insoluble compounds with magnesium, iron ($K_{sp}(FeAsO_4) = 5.8 \cdot 10^{-21}$) [9] with the minimum content of other metals. Table 4 demonstrates the chemical composition of the technological solution after the removal of arsenic, whereas Table 5 shows the composition of the precipitates obtained thereof. Residual arsenic concentration in this case is equal to 5.8 mg/L; however depending on the composition of the solution and on the consumption of brucite this value can vary from trace amounts up to 6.4 mg/L (MPC = 0.05 mg/L). The copper content exhibited a 19 % decrease; the iron content exhibited a 98 % decrease.

After removing the prevailing amount of arsenic and iron by means of brucite the solutions become slightly acidified (pH 4–5). This fact reduces the efficiency of the electrolytic purification of these solutions from HMI due to the blocking of the working surface of the porous electrode by hydroxide flakes and clogging the cathode. In this connection, in order to avoid the hydrate formation the solutions were acidified to pH ≈ 1 after the removal of arsenic. The rate of Cu extraction from such solutions is much higher, thus during 4 h the concentration of copper diminishes from 955 to 3 mg/L (see Table 4). The same table demonstrates the dynamics of extraction of other metals with the use of the cathode made of carbon felt VNG-30. Since the residual concentration of HMI exceeds the MPC level, it is required to perform additional sorption purification with the use of brucite. As it can be seen from Table 4, the sorption after-treatment of the solutions with the help of brucite provides a high level of HMI removal up to the MPC level required for solutions discharged into a sewage system.

CONCLUSION

Thus, by the example of processing the technological solutions from the Belovo Zinc Plant and from the sulphuric acid workshop of the Metallurgical Plant of the Ural Mining and Metallurgical Company we have demonstrated a potentiality of combined using the adsorption and electrochemical stages for efficient extracting of HMI and arsenic up to attaining required MPC standards for discharging the solutions into a sewage system. This allows reducing to a significant extent the hazard resulting from the technological solutions, improving the environmental situation around the enterprises and reducing the metal loss.

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