ELECTROCHEMICAL OXIDATION OF SULPHIDE AND THIOSULPHATE IONS USING A HYDROCYCLONE ELECTROLYTIC CELL

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Abstract. A hydrocyclone electrolytic cell was applied for the oxidation of sulphide and thiosulphate ions in an aqueous solution. The mechanism and kinetics of the electrooxidation of sulphide were investigated. The oxidation process proceeded by a consecutive-parallel scheme of reactions. At sufficient flux rate of electrolyte and low current density the overall process rate was limited not by the mass transfer rate, but by the rate of the chemical reaction.

Key words: electrochemical oxidation, sulphide oxidation, hydrocyclone cell.

INTRODUCTION

Chromium tannery waste waters contain large quantities of organic and inorganic compounds, including toxic substances, such as sulphides and chromium salts. The sulphides have to be removed before treating the waste water in the aeration tanks, flotation cells, and a biopurification system to prevent the decomposition of sulphides and the emission of toxic hydrogen sulphides into the atmosphere. For that reason we proposed a selective sulphide removal process – the soft electro-chemical oxidation at a relatively low current density (0.2–2.0 A dm^{-2}) [1]. The process is selective for sulphide compounds, the large amount of organic matter remaining unoxidated. Sulphides are oxidized mainly to sulphate, according to a consecutive-parallel kinetic scheme, with thiosulphate as an intermediate product [2].

These investigations were carried out in undivided parallel-plate cells where, in spite of a small interelectrode gap and gas bubbling, the process rate may be essentially influenced by diffusional resistance to mass transfer between the

bulk of the liquid phase and electrode surface. Therefore, investigation of the possibilities for process intensification by enhanced turbulence of the electrolyte seems to be necessary.

The diffusional resistance can be significantly reduced by the use of swirling flow of the electrolyte within the cell [3]. Such a possibility is offered by a hydrocyclone cell (HCC) with a helical flow of electrolyte between the electrodes. An electrochemical HCC was developed by Dhamo [4] and used by us for the purification of electroplating waste water [5]. In these studies an HCC with a graphite anode and a tubular membrane, acting as vortex finder, were used.

In the present work the HCC was used for the electrochemical oxidation of sulphide in an aqueous solution. For that purpose a new design of the HCC with an undivided electrolyte room and a tubular titanium–manganese dioxide anode (TMDA) were used. The transformation of sulphide ion into thiosulphate and sulphate and the influence of the electrolyte flow rate on the overall process rate were investigated.

EXPERIMENTAL

Our investigations were carried out in an undivided HCC enclosed in a circulating system. The general arrangement of the experimental equipment is shown in Fig. 1. It consists of an HCC, a well-stirred electrolyte tank with a constant volume ($V = 3.0$ dm^3), and a rotary pump for electrolyte circulation. The flow rate of the circulating electrolyte was regulated in a range of 12 to 120 cm^3 s^{-1} by means of an adjustment valve. The stainless steel wall of the hydrocyclone inlet with a 50 mm diameter served as a cathode. The tubular TMDA with a 42 mm outlet diameter and 50 mm active height was situated in the centre of the hydrocyclone, acting simultaneously as a vortex finder. The electrolyte entered tangentially into the hydrocyclone and flew helically downward round the anode. The apex-valve of the cyclone was kept closed, so the whole electrolyte flow was issued from the hydrocyclone and recirculated. The experiments were carried out at the batch recycle mode of operation, the operation time varying from 1 to 8 h. During the experiment both the current and the electrolyte temperature were kept constant. The TMDA was prepared by repeated thermal combustion of manganese nitrate on a titanium plate treated previously with a hydrofluoric acid solution [6].

The samples for analysis were taken from the electrolyte at the beginning and at the end of the process. The sulphide ions were precipitated from the solution as CdS, dissolved in a hydrochloric acid solution, and titrated iodometrically. In the filtrate both the thiosulphate and sulphite ions were titrated iodometrically, separating the sulphite ions by formaldehyde [7]. Practically no sulphite ions existed in our electrolytic solutions. The concentration of the sulphate ion was determined using an ion chromatograph (sorbent RM 25–40 µm, eluent – phthalic acid, pH 4.36, detector – Knauer spectrophotometer, $\lambda = 260$ nm).
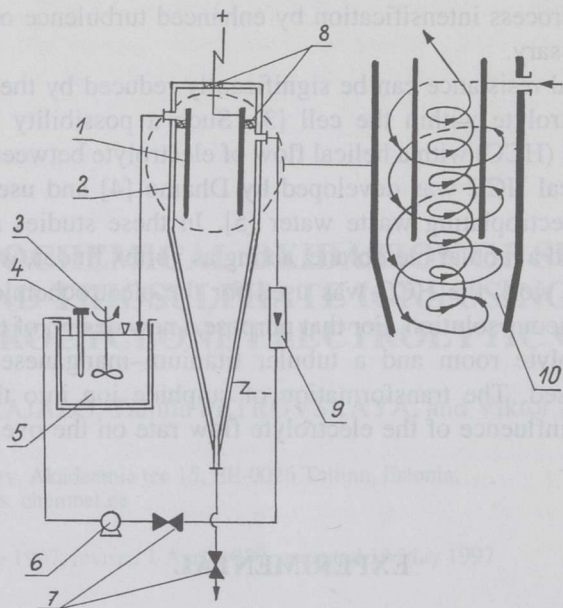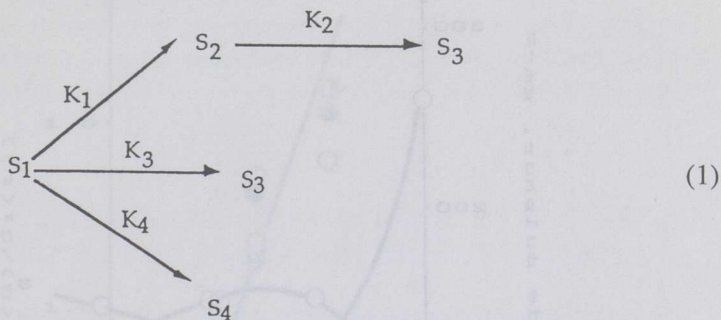
Fig. 1. Scheme of the experimental equipment. *1*, anode; *2*, hydrocyclone wall (cathode); *3*, stirrer; *4*, temperature regulation; *5*, tank; *6*, rotary pump; *7*, valves; *8*, Teflon gaskets; *9*, flow meter; *10*, scheme of the electrolyte flow.

As electrolytes synthetic solutions containing (as initial concentration) 260–280 g m^{-3} sulphide, 40–60 g m^{-3} thiosulphate, and 19–23 g m^{-3} sulphate were used.

RESULTS AND DISCUSSION

As mentioned above, our experiments were carried out at the batch recycle mode of operation. In Fig. 2 the contents of sulphide, thiosulphate, and sulphate sulphur depending on time at a constant current density of 0.89 A dm^{-2}, temperature 22 ± 1 °C, and electrolyte flow rate 120 cm^3 s^{-1} are shown. The curves obtained at other flow rates were similar. In all cases the concentration of the sulphide sulphur was continuously decreasing and that of the sulphate sulphur continuously increasing in time. The concentration curve of thiosulphate as an intermediate product had its maximum. All the concentration curves were in good agreement with those obtained in the parallel-plate cell [2, 8]. Thus, we can conclude that in the HCC the oxidation proceeds by the same consecutive-parallel scheme of reactions as it was established in the parallel-plate cell:

$$
\begin{array}{c}
\quad\quad\quad S_2 \xrightarrow{\;K_2\;} S_3 \\[4pt]
\nearrow^{K_1} \\[2pt]
S_1 \xrightarrow{\;K_3\;} S_3 \\[2pt]
\searrow_{K_4} \\[4pt]
\quad\quad S_4
\end{array}
\tag{1}
$$

Here S_1 is the molar concentration of sulphide, S_2 the concentration of thiosulphate, S_3 the concentration of sulphate, and S_4 the concentration of elementary sulphur. K_1, K_2, K_3, and K_4 can be regarded as products of the reaction rate constant k_i and specific electrode area a_e. Supposing the first order for electrochemical oxidation reactions, the following system of rate equations can be obtained:

$$dS_1/dt = -a_e(k_1 + k_3 + k_4)S_1, \tag{2}$$

$$dS_2/dt = a_e(k_1 S_1 - k_2 S_2), \tag{3}$$

$$dS_3/dt = a_e(k_2 S_2 + k_3 S_1), \tag{4}$$

$$dS_4/dt = a_e k_4 S_1, \tag{5}$$

where t is the process time, and a_e the specific area of anode; $a_e = S_A V$, S_A is the anode area, and V is the electrolyte volume. Equations (2)–(5) can be regarded as a kinetic model of the sulphide electrooxidation process.

Integration of Eq. (2) gives

$$\ln[S_1(0)/S_1(t)] = a_e(k_1 + k_3 + k_4)t. \tag{6}$$

The dependence of $\ln[S_1(0)/S_1(t)]$ on time is shown in Fig. 3. The experimental data points were obtained at the same current density (0.89 A dm^{-2}) but at different flow rates of the electrolyte. As it can be seen, the experimental data points are close to a linear plot, thereby verifying the first order of the sulphide oxidation reaction. The value of $(k_1 + k_3 + k_4)$ calculated from the slope of the linear plot in Fig. 3 is close to that obtained at the parallel-plate cell [2].

The overall rate of an electrochemical reaction may be limited by the rates of both the chemical reaction and the diffusional mass transfer. If we suppose the sulphide electrooxidation to be a diffusion controlled process then the overall rate constant must depend on the flow rate. In the purification of electroplating waste water in an HCC an important role of mass transfer was demonstrated in [4, 5].
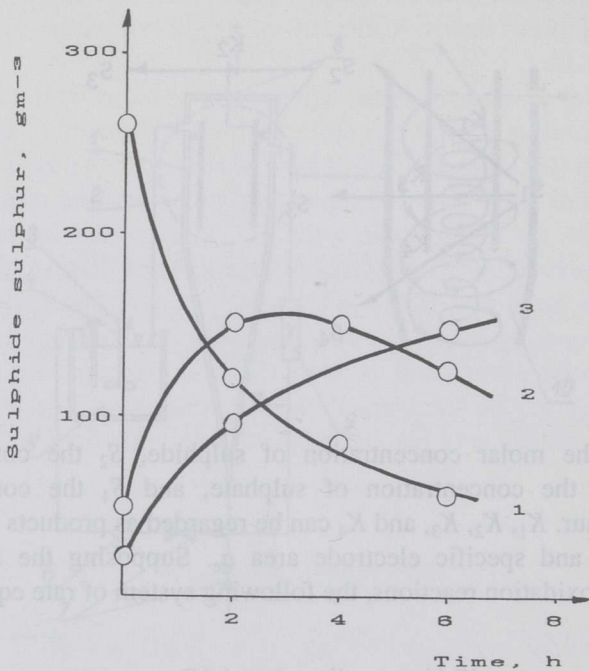
Fig. 2. Dependence of sulphide (*1*), thiosulphate (*2*), and sulphate (*3*) sulphur concentration on time. Current density 0.89 A dm^{-2}, electrolyte flow rate 120 cm^3 s^{-1}, temperature 22±1 °C.

The mass transfer rate in an HCC at batch recycle mode of operation was described in [4] as

$$-dS_1/dt = \tau^{-1}[1 - \exp(-K_L/Q)]S_1, \qquad (7)$$

where $K_L = \pi DLK$, K is the mass transfer coefficient, m s^{-1}; D and L the diameter and length of the anode, m; Q is the volumetric flow rate, m^3 s^{-1}; τ is the mean residence time of the electrolyte in a tank, s; t is the process time, s. Equation (7) is valid on the following conditions:

(1) the spiral movement of the electrolyte round the anode may be approximated to plug flow;

(2) the electrolyte reservoir has constant volume and can be regarded as a perfectly stirred tank;

(3) the volume of the HCC is very small compared with that of the tank, therefore the change of sulphide concentration in time is very small as compared to the concentration change in the length of the HCC.
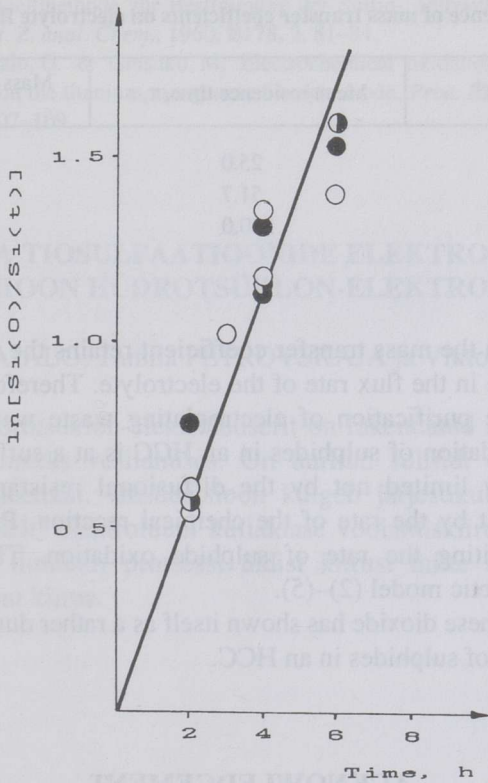
Fig. 3. Dependence of $\ln[S_1(0)/S_1(t)]$ on time. Current density 0.89 A dm^{-2}. Flow rates: ● 120 cm^3 s^{-1}, ○ 58 cm^3 s^{-1}, and ◑ 12 cm^3 s^{-1}.

Integration of Eq. (7) gives

$$\ln[S_1(0)/S_1(t)] = \tau^{-1}[1 - \exp(-K_L/Q)]t, \qquad (8)$$

which also describes a linear function of $\ln[S_1(0)/S_1(t)]$ vs. t. From the slope of the straight line we can calculate the mass transfer coefficient as

$$K = -Q(\pi DL)^{-1}\ln\{1 + \tau t^{-1}\ln[S_1(t)/S_1(0)]\}. \qquad (9)$$

The calculated values of mass transfer coefficients are given in the Table.

Dependence of mass transfer coefficients on electrolyte flow rate

Flow rate, $Q \times 10^6$, m^3 s^{-1}	Mean residence time, τ, s	Mass transfer coefficient, $K \times 10^3$, m s^{-1}
120	25.0	3.04
58	51.7	3.04
12	250.0	3.06

As it can be seen the mass transfer coefficient retains the same value in spite of a tenfold increase in the flux rate of the electrolyte. Therefore, we can say that differently from the purification of electroplating waste water, the rate of the electrochemical oxidation of sulphides in an HCC is at a sufficient flux rate and low current density limited not by the diffusional resistance in the laminar electrolyte layer, but by the rate of the chemical reaction. Probably a chemical intermediate is limiting the rate of sulphide oxidation. The process can be described by the kinetic model (2)–(5).

Titanium–manganese dioxide has shown itself as a rather durable anode material for electrooxidation of sulphides in an HCC.

ACKNOWLEDGEMENT

REFERENCES

1. Petrovskaya, T. & Rajalo, G. Electrochemical oxidation of sulphides in tannery waste water. *Proc. Estonian Acad. Sci. Chem.*, 1992, **41**, 4, 194–199.
2. Rajalo, G. & Petrovskaya, T. Selective electrochemical oxidation of sulphides in tannery wastewater. *Environ. Technol.*, 1996, **17**, 605–612.
3. Legentilhomme, P. & Legrand, J. Overall mass transfer in swirling decaying flow in annular electrochemical cells. *J. Appl. Electrochem.*, 1990, **20**, 216–222.
4. Dhamo, N. An electrochemical hydrocyclone cell for the treatment of dilute solutions: Approximate plug-flow model for electrodeposition kinetics. *J. Appl. Electrochem.*, 1994, **24**, 745–750.
5. Rajalo, G., Petrovskaya, T., Glushko, M. & Ahelik, V. Purification of electroplating waste water using a hydrocyclone electrolytic cell. *Proc. Estonian Acad. Sci. Chem.*, 1996, **45**, 3/4, 169–175.
6. Slesarenko, O. A., Zharskij, I. M., Letsko, V. V. & Voropaev, L. E. SU Patent 1546516 AI, 1990.

7. Szkeres, L. Eine Schnellmethode zur Bestimmung der Sulfid-, Polysulfid- und Thiosulfationen nebeneinander. *Z. anal. Chem.*, 1960, **B178**, 2, 81–84.

8. Petrovskaya, T., Rajalo, G. & Glushko, M. Electrochemical oxidation of sulphide and thio-sulphate ions on the titanium-manganese dioxide anode. *Proc. Estonian Acad. Sci. Chem.*, 1994, **43**, 3, 107–109.

SULFIID- JA TIOSULFAATIOONIDE ELEKTROKEEMILINE OKSÜDATSIOON HÜDROTSÜKLON-ELEKTROLÜÜSERIGA

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Diafragmata hüdrotsüklon-elektrolüüserit on rakendatud sulfiid- ja tiosulfaat-ioonide oksüdeerimiseks vesilahuses. On uuritud sulfiidi elektrooksüdatsiooni mehhanismi ja kineetikat. Oksüdatsioon kulgeb järjestikulis-paralleelse reakt-siooniskeemi kohaselt. Elektrolüüdi küllaldase voolamiskiiruse ja vähese voolu-tiheduse korral ei limiteeri protsessi üldist kiirust mitte massiülekande, vaid keemilise reaktsiooni kiirus.