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Electrochemical Method for Cyanide Regeneration from Acidic Thiocyanate Solutions

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Abstract

A method is studied aimed at the regeneration of cyanides via electrochemical oxidation of acidic thiocyanate solutions. The influence of reagents concentration, current density as well as the processing mode upon the efficiency of thiocyanate oxidation and the substance yield of cyanide was investigated for modelling and technological solutions.

Key words: thiocyanate, cyanide, electrochemical oxidation

INTRODUCTION

It is well known that the main source of thiocyanate aqueous solutions is presented by hydrometallurgical processes of gold and silver extraction from sulphide-containing ores and ore concentrates. The process of cyanation involves the interaction between cyanide and sulphur-containing species, for example, according to the following reactions [1]:

$$S^0 + CN^- \rightarrow SCN^- \quad (1)$$

$$S^{2-} + CN^- + H_2O + 1/2O_2 \rightarrow SCN^- + 2OH^- \quad (2)$$

$$S_2O_3^{2-} + CN^- \rightarrow SCN^- + SO_3^{2-} \quad (3)$$

Depending on the content of sulphur and the number of turnaround cycles the content of thiocyanates in technological solutions can vary within the range from several milligrams up to several tens grams per one litre. The formation of thiocyanates results not only in the increase in the reagent consumption in the process of cyanide leaching, but also exerts a negative effect on the sorption and desorption stages in the processes of sorption gold leaching [2]. Moreover, the excess recirculated water should be subjected to the destructive oxidation before discharging them into a tailing pit, which is connected with a considerable consumption of oxidizer for the destruction of thiocyanate complexes. At the same time, the high content of thiocyanates in spent technological solutions provides the profitability of processing them for the purpose of cyanide extraction [3].

In the process of cyanide regeneration from thiocyanates one can observe simultaneous carbon reduction and sulphur oxidation occurring in SCN^- complex accompanying with the formation free cyanide and sulphate according to the half-reactions presented below (the potentials presented being taken against the standard hydrogen electrode):

$$SCN^- + 4H_2O \rightarrow SO_4^{2-} + CN^- + 8H^+ + 6\bar{e} \quad (4)$$

$$E^0 = -0.490 \text{ V}$$

This reaction was studied earlier [4, 5] both with chemical oxidizers employed (hydrogen peroxide, ozone, sulphur dioxide, chlorine), and using the technique of electrolysis. However, the realization of this given process becomes complicated due to the further oxida-

tion of cyanide to produce cyanate according to reaction

$$CN^- + H_2O \rightarrow OCN^- + 2H^+ + 2\bar{e} \quad (5)$$
$$E^0 = 0.169 \text{ V}$$

The authors of [4] have established that at low pH values the contribution of reaction (5) is insignificant and thiocyanate is almost completely oxidized to produce cyanide:

$$SCN^- + 4H_2O \rightarrow SO_4^{2-} + HCN + 7H^+ + 6\bar{e} \quad (6)$$
$$E^0 = -0.399 \text{ V}$$

Thus, there are thermodynamic prerequisites for realizing the process of cyanide regeneration through the oxidation of thiocyanate-containing solutions. It should be noted that during the recent years the employing of direct electrochemical oxidation is considered to be more preferable due to the profitability of this method [1].

The present work is devoted to the presentation of results obtained from the studies on the process of cyanide regeneration via electrochemical oxidation of acidic thiocyanate solutions.

EXPERIMENTAL

The investigations were carried out using model solutions with the initial content of SCN^- complex of about 27 and 2.5 g/L, at pH 1–3. All the solutions were prepared using NH_4SCN and KSCN reagents of chemical purity grade. For real (technological) solutions the content of the liquid phase from the tailings of thiocyanate sorption leaching amounted to about 20 g/L, the content of free cyanides being about 0.1 g/L, pH 10. The solutions with the SCN^- complex content of 2.5 g/L were obtained through the dilution of the initial leaching filtrate. In order to gain the solution pH 1–3 we added sulphuric acid at a rate of 2 mL per 1 L of the solution.

The oxidation of thiocyanates was carried out in an electrochemical cell with the separation and with no separation between the anodic and cathodic space by means of a MF-4SK cation-exchange membrane. A lead plate or platinum foil was used as an anode material. The working area of the anode amounted to 5 cm^2; the volume of anolyte was 28 mL. The cathode represented platinum foil or nickel grating; 1 M H_2SO_4 solution was used as a catholyte. The cell was fed by electric current from a PI-50-1.1 potentiostate.

The electrolysis of solutions was performed employing a galvanostatic mode during certain time with no blowing-out as well as with a simultaneous blowing-out of the hydrocyanic acid formed. Air was fed into the cell by means of a peristaltic pump. The hydrocyanic acid blown out was trapped in an absorbing vessel filled with 10 % NaOH solution. After the electrolysis the electric current was switched off, whereas the blowing-out of hydrocyanic acid was continued during 1 h additionally, thereby the content of CN^- in the anolyte amounted to 1–6 % of total cyanide obtained.

The initial and residual content of SCN^- in modelling and real solutions was determined by means of permanganatometric technique. The content of cyanide in the electrolyte and in the absorption vessel was determined by means of argentometric assay with the use of (4-dimethylaminobenzylidene)rhodanine as an indicator [6].

RESULTS AND DISCUSSION

Thermodynamic calculations demonstrate that the regeneration of cyanide could be carried out according to reaction (6) provided that the potential on the anode would be higher than −0.4 V. The rate of thiocyanate oxidation should be determined by the current density on the electrode and the concentration of substrate in the electrolyte. With the decrease in thiocyanate content the cyanide formed could undergo the further oxidation to produce cyanate. However, at pH < 6 cyanide exists mainly in the form of hydrocyanic acid which is much more difficultly amenable to the further oxidation. In this connection, a forced removal of HCN formed should also promote the increase in its yield.

In order to choose the conditions necessary for performing the process of tiocyanate oxidation in an acidic medium we have conducted experiments with modelling solutions. The experiments were aimed at determining the influence of the current density, the quantity of electricity passing through the cell, and the blowing-out of the hydrocyanic acid formed upon the kinetics and efficiency of cyanide regeneration process at the two values of the initial SCN^- content.

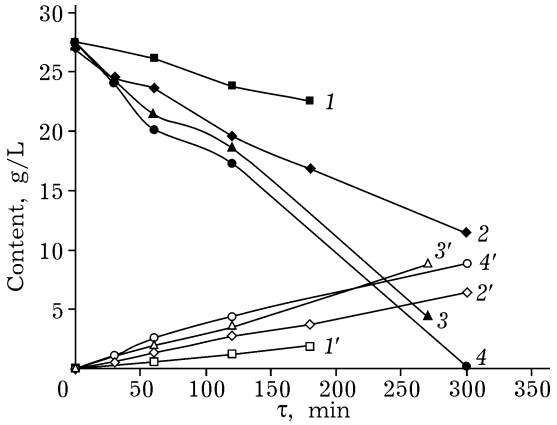

Fig. 1 Content of thiocyanate (*1*–*4*) and cyanide (*1′*–*4′*) depending on the electrolysis time (τ) at different values of current density, mA/cm^2: 25 (*1*, *1′*), 50 (*2*, *2′*), 75 (*3*, *3′*), 100 (*4*, *4′*).

The influence of blowing-out the hydrocyanic acid formed in the course of SCN^- oxidation upon the substance yield of cyanide was investigated employing a platinum anode with the current density of 100 mA/cm^2, using a cell with no membrane. At the initial SCN^- content of 2.7 g/L the substance yield of cyanide was equal to 74.1 % and 60.5 % for 1.5 h electrolysis with blowing-out and without blowing-out, respectively. With increasing the content of thiocyanates up to 27 g/L and for 2 h electrolysis duration with blowing-out and with no blowing-out the yield of cyanide amounted to 64.5 and 41.5 %, respectively. The reduction of the substance yield in the electrolysis with no blowing-out could be connected, to all appearance, with the accumulation of cyanide ions and their further oxidation to yield cyanate ions. At a higher content of thiocyanate, when the amount of cyanide formed increases, the performing of electrolysis with the forced removal of HCN exerts a considerable effect on the yield of the latter.

The investigation concerning the current density effect on the kinetics of SCN^- oxidation was carried out using a cell with a membrane with a Pb/PbO_2 anode at current density values of 25, 50, 75 and 100 mA/cm^2 for the solutions with the initial SCN^- content of 27 g/L and at current density values of 50 and 100 mA/cm^2 for the solutions with the SCN^- content of 2.7 g/L, with simultaneous hydrocyanic acid blowing-out.

Taking into account the results obtained for the yield of cyanide with the use of given electrochemical cell and for the residual content of thiocyanate we have plotted the change in the content of SCN^- and CN^- against time at various current density values (Fig. 1). The initial content of thiocyanate ions amounted to 26.93 and 27.5 g/L. One can see that the rate of thiocyanate oxidation increases with the increase in current density. A similar relationship is observed for the change in the content of cyanide formed. For 5 h of electrolysis at the current density values of 50 and 100 mA/cm^2 the content of SCN^- is observed to decrease down to 11.44 and 0.15 g/L, with the content of CN^- reaching 6.39 and 8.89 g/L, respectively. At the current density of 75 mA/cm^2 after 4.5 h electrolysis the content of CN^- amounted to 8.75 g/L with the reduction of the residual thiocyanate content down to 4.31 g/L. It has been revealed that at a low initial content of thiocyanate (2.7 g/L) the increase in current density from 50 to 100 mA/cm^2 does not exert any considerable effect on the rate of its oxidation.

In the course of cyanide regeneration there are two conjugated reactions such as (4), (5) occurring, so we investigated the influence of the quantity of electricity passed through the cell upon the efficiency of thiocyanate oxidation ($(C_0 - C)/C_0$, %) and the yield of cyanide at the values of current density chosen (Figs. 2, 3). One can see that the efficiency of oxidation and the yield of cyanide exhibit a decrease with the increase in current density. For the solutions with a low initial content of thiocyanates at equal quantity of electricity passed (0.25 A · h) and the current density value of 50 and

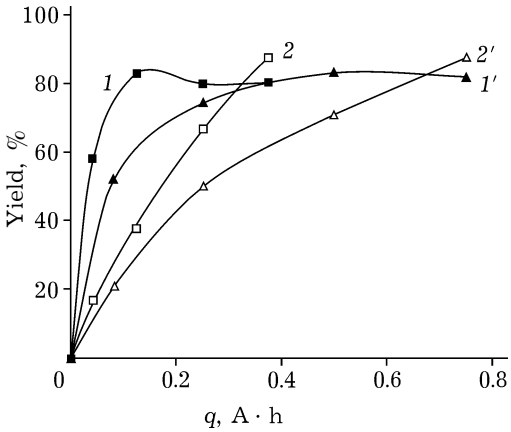

Fig. 2. Substance yield of cyanide (*1*, *1′*) and the efficiency of thiocyanate oxidation (*2*, *2′*) depending on the quantity of electricity *q* (at the initial SCN^- content of 2.7 g/L). Current density, mA/cm^2: 50 (*1*, *2*), 100 (*1′*, *2′*).

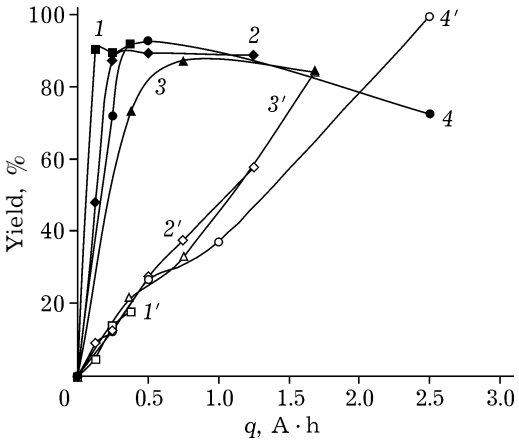

Fig. 3. Substance yield of cyanide *(1–4)* and the efficiency of thiocyanate oxidation (*1′–4′*) depending on the quantity of electricity *S* passed through the cell (at the initial SCN^- content of 27 g/L). Current density, mA/cm^2: 25 (*1*, *1′*), 50 (*2*, *2′*), 75 (*3*, *3′*), 100 (*4*, *4′*).

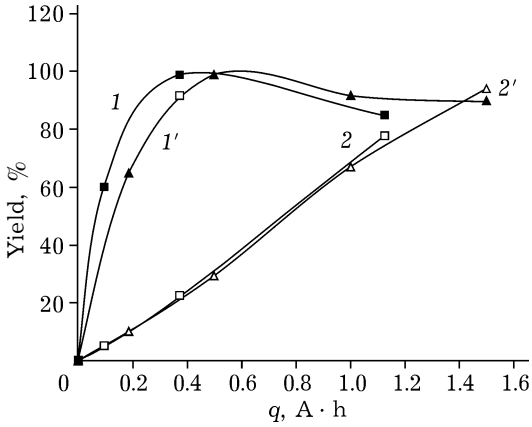

Fig. 4. Substance yield of cyanide (*1*, *1′*) and the efficiency of thiocyanate oxidation (*2*, *2′*) depending on the quantity of electricity passed for leaching solutions (at the initial SCN^- content of 20.21 g/L). Current density, mA/cm^2: 75 (*1*, *2*), 100 (*1′*, *2′*).

100 mA/cm^2 the efficiency of oxidation amounted to 66.7 and 50 %, and the yield of cyanide was equal to 79.8 and 74.1 %, respectively. On the contrary, with the increase in the content of SCN^- up to 27 g/L the efficiency of SCN^- oxidation does not depend on current density amounts to about 30 % at the charge value of 0.5 A · h passed through the cell. With the increase in the quantity of electricity the efficiency of oxidation is observed to be lower at a higher value of current density on the anode.

The maximum yield of cyanide is observed at the current density of 25 mA/cm^2, whereas it exhibits a decrease with the increase in current density the substance yield value at the same quantity of electricity passed. Thus one could assume that with the increase in current density the rate of thiocyanate oxidation grows and, as a consequence, there is an increase in the amount of cyanide which has no time for removing from the reaction zone at a given blowing-out rate. As a result, the portion of current that falls at the further oxidation of cyanide exhibits an increase, which gives rise to a decrease in the efficiency of thiocyanate oxidation as well as to lowering the substance yield of cyanide.

The electrolysis of sorption leaching tailing pulp filtrate taken from the Olympiadinskaya Gold Extraction Factory was carried out at the current density of 75 and 100 mA/cm^2. According to the analysis performed within the day of testing, the initial content of thiocyanates amounted to 20.21 g/L.

In the course of the investigations we have established that the dependence of SCN^- and CN^- content on the electrolysis duration for real solutions exhibits the same character as for modelling systems. With the increase in the current density value from 75 up to 100 mA/cm^2, the rate of thiocyanate oxidation grows. The residual content of SCN^- amounted to 0.59 g/L after 2.5 h electrolysis with the current density of 100 mA/cm^2 and 4.46 g/L after 3 h electrolysis and current density of 75 mA/cm^2. The substance yield for cyanides ranges up to 67.7% and 84.8 %, respectively.

The studies on the oxidation efficiency and cyanide the cyanide substance yield dependence on the quantity of electricity passed through

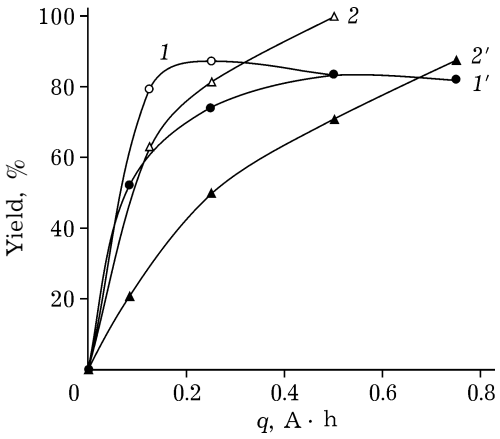

Fig. 5. Substance yield of cyanide (*1*, *1′*) and the efficiency of thiocyanate oxidation (*2*, *2′*) depending on the quantity of electricity (*q*) passed through the cell for the leaching solution (*1*, *2*) and a modelling solution (*1′*, *2′*) at the current density value of 100 mA/cm^2.

the cell have demonstrated that just as it is for modelling solutions, the substance yield grows with the reduction of current density, whereas the oxidation efficiency does not depend on the current density chosen at the passed quantity of electricity amounting to 1 A · h (Fig. 4). A higher oxidation efficiency for real solutions (67.1 %) in comparison with the modelling solution (37.3–48 %) at equal quantity of electricity passed could be caused, to all appearance, by a difference in the initial content thiocyanates in the solutions (~25 %).

In addition, the leaching solutions contain Cu^{2+} ions those could play in the presence of atmospheric oxygen the role of a catalyst for thiocyanate oxidation under the conditions of intense mass transfer [7]. It counts in favour of such mechanism of thiocyanate oxidation (as an addition to the electrochemical mechanism) that there is an essential difference in the efficiency of oxidation observed at rather close SCN^- content (Fig. 5). For modelling solution (the initial SCN^- content of 2.7 g/L) and real (2.5 g/L) solutions at the quantity of electricity passed if 0.25 A · h the efficiency of oxidation amounted to 50.0 % and 87.3 %, and the yield of cyanide was 74.1 % and 81.2 %, respectively.

CONCLUSION

The studies carried out have demonstrated that the electrochemical method allows one to perform efficient regeneration of cyanides from acidic solutions of thiocyanates. It has been established that the processes of electrochemical thiocyanate oxidation to produce cyanides in acidic media exhibit a similar character both for real and modelling solutions. The oxidation of thiocyanates with simultaneous blowing-out hydrocyanic acid allows considerably reducing their content in the filtrate of tailing pulps resulted from the sorption leaching. Cyanide formed in the course of oxidation could be extracted with a high substance yield (70–80 %) and returned into the technological process, simultaneously decreasing the consumption of oxidizers at the decomposition limit of cyanides and thiocyanates from the solutions of tailing pulps.

REFERENCES

1 M. M. Botz, D. Dimitriadis, T. Polglase *et al.*, *Mineral & Metallurgical Proc.*, 18, 3 (2001) 126.
2 V. K. Sovmen, V. N. Gus'kov, A. V. Bely *et al.*, Pererabotka Zolotonosnykh Rud s Primeneneniyem Bakterialnogo Okisleniya v Usloviyakh Kraynego Severa, Nauka, Novosibirsk, 2007.
3 M. A. Meretukov, A. M. Orlov, Metallurgiya Blagorodnykh Metallov: Zarubezhny Opyt, Metallurgiya, Moscow, 1991.
4 I. R. Wilson, G. M. Harris, *J. Am. Chem. Soc.*, 82 (1960) 4515.
5 Canada Pat. No. 1188250, 1985.
6 Yu. Yu. Lurie, Analiticheskaya Khimiya Promyshlennykh Stochnykh Vod, Khimiya, Moscow, 1984.
7 A. A. Kochanov, A. A. Ryazantsev, A. A. Batoeva *et al.*, *Chem. Sust. Dev.*, 12 (2004) 445.
URL: http://www.sibran.ru/English/csde.htm