Oxidation of Thiocyanates in Acid Media in a Cell with a Pt Anode and a Gas-Diffusion Cathode Generating Hydrogen Peroxide from Oxygen

T. A. KENOVA and V. L. KORNIENKO

Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Ul. K. Marxa 42, Krasnoyarsk 660049 (Russia)

E-mail: kvl@icct.ru

(Received May 16, 2003; in revised form July 3, 2003)

Abstract

The kinetics of thiocyanate oxidation in acid media using a cell with or without a membrane and with a platinum anode and a gas-diffusion cathode producing hydrogen peroxide has been studied. The influence of reagent concentration, current density and electrochemical cell design on the oxidation rate of SCN^- has been investigated.

INTRODUCTION

Despite the high toxicity of sodium cyanide, cyanidation of gold-containing raw materials remains the major technique for extracting noble metals. Waste and return waters containing simple and complex cyanides and thiocyanates must be subjected to thorough purification from highly toxic components before discharge or recycling.

Various methods are used for detoxication of discharge in gold-mining industry. The choice of the method is dictated by the composition and concentration of contaminants, by the amount of discharge, *etc.* [1].

Recently, the efforts of researchers were devoted to a search for ecologically safe and simple methods of wastewater treatment including extraction of valuable components and removal of harmful components. From this viewpoint, electrochemical methods possess a number of advantages: they use a pure reagent (electron); less by-products are formed if at all [2].

Using electrochemical oxidation of cyanide-containing discharge permits one to simultaneously decrease the concentration of hazardous compounds and lower the cost of detoxication due to regeneration of reagents based on cyanide compounds. The method is based on the reaction of electrooxidation of thiocyanate ions to cyanide and sulphate ions. At low concentrations of SCN^- exceeding the MPC but not sufficient for extraction of CN^-, oxidation can be carried out to the stage of formation of less toxic compounds [3].

Destructive oxidation of cyanides and thiocyanates with hydrogen peroxide permits one to attain a considerable ecological effect due to decreased mineralization of wastewaters.

It is known that the rate of oxidation with hydrogen peroxide is determined by the H_2O_2/substrate ratio and increases considerably when one introduces into the system metals with variable valence, catalyzing the degradation of hydrogen peroxide to form highly reactive hydroxyl and perhydroxyl radicals ($HO^{\bullet}$, $HO_2^{\bullet}$) [4].

A method has been proposed [2] for detoxification of wastewaters from cyanides and thiocyanates with hydrogen peroxide in the presence of iron (III) compounds at pH 2.8–3.6. This technique makes it possible to recycle a considerable part of sodium cyanide and to avoid recontamination of solutions.

As is known, anodic treatment of wastewater in a cell without a membrane generates large amounts of hydroxyl radicals on Pt, PbO_2 and SnO_2 anodes during water oxidation [5, 6]:

$$2H_2O \rightarrow 2HO^{\bullet} + 2H^+ + 2\bar{e} \quad (1)$$

Moreover, using a gas-diffusion cathode producing hydrogen peroxide from oxygen can form perhydroxyl radicals [5]:

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HO_2^{\bullet} \quad (2)$$

$$O_2 + H^+ + \bar{e} \rightarrow HO_2^{\bullet} \quad (3)$$

It was demonstrated [7] that destructive oxidation of thiocyanates in alkaline media in a membraneless cell with a platinum anode and a gas-diffusion cathode generating HO_2^- from O_2 occurs more efficiently than direct oxidation only on a platinum anode.

The goal of the present work is to study thiocyanate oxidation in acid media in a cell with a platinum anode and gas-diffusion cathode producing hydrogen peroxide from oxygen in the presence of iron (II).

EXPERIMENTAL

Experiments were carried out on model solutions with initial concentrations of SCN^- from $1.7\ 10^{-2}$ to $7.8\ 10^{-2}$ mol/l in a 0.1 M H_2SO_4 solution.

For oxidation of thiocyanates, we used a cell with separated anode and cathode spaces (three-chamber cell) and a cell without separation (two-chamber cell). A soot gas-diffusion electrode served as cathode, and a platinum plate as anode. The dimensions and characteristics of the gas-diffusion electrodes are presented in [7]. Fe(II) in the form of an $FeSO_4$ solution was used as a catalyst of hydrogen peroxide decomposition; the salt was added to the electrolyte before the start of electrolysis.

Hydrogen peroxide was obtained by electric reduction of oxygen in a gas-diffusion cathode in a galvanostatic regime at current densities of 250 and 500 mA. The electrolysis temperature was 15–20 °C.

The residual concentration of SCN^- was estimated by photometry of Fe(III) thiocyanate complexes after complete degradation of hydrogen peroxide [8].

RESULTS AND DISCUSSION

As is known, the intermediates obtained in the course of hydrogen peroxide degradation possess higher chemical activity than the peroxide itself. In acid media with additions of H_2O_2 degradation catalysts, conditions for obtaining highly reactive $HO^{\bullet}$ and $HO_2^{\bullet}$ radicals are realized. Of critical importance is generation of a sufficient amount of such radicals in the system.

A commonly accepted scheme of radical generation in an H_2O_2 + Fe(II) system is the following sequence of reactions [4]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^- \quad (4)$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^- \quad (5)$$

$$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O_2 \quad (6)$$

In a membraneless electrochemical cell using a Pt anode, $HO^{\bullet}$ radicals can be generated by oxidation of water according to reaction (1); when Fe(II) salts are added to the solution, the radicals are additionally generated in the bulk of electrolyte by reaction (4) – so-called electro-Fenton process [9].

The kinetics of the oxidation process was studied on model KSCN solutions in a 0.1 M H_2SO_4 solution with concentrations of SCN^- from $1.7\ 10^{-2}$ to $7.8\ 10^{-2}$ mol/l, pH ≅ 2.

In the course of the experiments, correlations have been found between the oxidation rate of thiocyanate and the initial concentration of SCN^-, initial iron concentration, and current density in cells having a cation-exchange membrane and in cells having no membrane.

The initial oxidation rates of thiocyanates W_0 were estimated from the slope ratio between the tangent and the initial segments of the kinetic curves of SCN^- oxidation (Table 1). One can see that the initial oxidation rate increases with the initial content of thiocyanate and iron salt, and with the hydrogen peroxide concentration in the cell determined by the electrolysis current.

To study the effect of hydrogen peroxide concentration on the oxidation kinetics of SCN^-,

TABLE 1

Dependence of thiocyanate oxidation rate on the reagent concentration

Electrolysis current (H_2O_2 production rate, mA)	Thiocyanate concentration C_{SCN^-}, 10^{-2} mol/l	Iron concentration $C_{Fe^{2+}}$, 10^{-3} mol/l	Initial oxidation rate W_0, 10^{-3} mol/(l min)
	Three-chamber cell		
500	1.7	3.8	1.05
500	2.5	3.8	1.10
500	7.8	3.8	1.30
250	1.7	3.8	0.30
500	1.7	3.8	1.05
500	1.7	1.5	0.57
500	1.7	3.8	1.05
500	7.8	6.8	1.30
500	7.8	1.5	1.30
	Two-chamber cell		
500	7.8	1.5	1.90
500	7.8	6.8	1.80
500	1.7	1.5	1.27
500	1.7	2.7	1.37

we used a cell with a membrane and with Fe(II) salt additions. The initial concentration of SCN^- was 1.7 10^{-2} mol/l, the $FeSO_4$ concentration was 3.8 10^{-3} mol/l. As the electrolysis current increased from 250 to 500 mA, the initial oxidation rate of thiocyanates increased by a factor of more than three. The efficiency of oxidation was 43 and 96 %, respectively, the quantity of electricity passed being 0.125 A h. This is indicative of a dependence of the thiocyanate oxidation rate on the H_2O_2/Fe(II) ratio, which is in accordance with the data of [4]. A change in this ratio can alter the mechanism of the catalytic decomposition of H_2O_2, the concentrations of intermediates and the substrate oxidation rate, respectively.

Using different cell constructions and an anodic process concurrent with hydrogen peroxide formation on a cathode, one can change the concentrations of intermediates and thus the rate of the process.

Figure 1 presents the kinetic curves of thiocyanate oxidation in an acid medium in a cell with a membrane and without a membrane by different oxidation methods. One can see that oxidation of thiocyanates is more efficient when it uses hydrogen peroxide, a cell without a membrane and the electro-Fenton method (curves *3* and *4*); oxidation of SCN^- on a Pt anode (curve *2*) and oxidation using Fenton reagent in a cell with a membrane (curve *1*) were less efficient. Conversion of thiocyanates after 30 min of electrolysis was 71 and 82 % in a cell without a membrane and 50–52 % in anodic oxidation and in oxidation by the classical scheme with Fenton reagent.

The increased rate of electro-Fenton oxidation of thiocyanate is associated with the increased concentration of hydroxyl radicals formed by reaction (4) in the bulk electrolyte or by reaction (1) in the near-anode layer, which agrees with the data of [9]. In both anodic oxidation and oxidation in a cell with a membrane (classical Fenton reagent), the concentration of hydroxyl radicals depends on only one of these reactions. Moreover, one has to take into account that in a membraneless cell, direct anodic oxidation of SCN^- is possible.

The unexpectedly higher rate of oxidation conducted in a membraneless cell in the absence of iron salts (see Fig. 1, curve *4*) is most probably due to the understated results of analysis. Since estimating the residual concentration of SCN^- requires that the solution be absolutely free from hydrogen peroxide, analysis was carried out in a few days after the

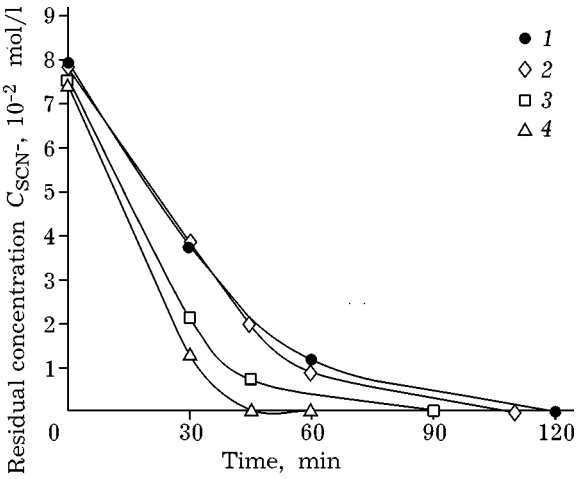

Fig. 1. Kinetic curves of thiocyanate oxidation in acid media (initial concentration of SCN^- is ~7.8 10^{-2} mol/l, I = 500 A): *1* – oxidation with Fenton reagent in a cell with a cation-exchange membrane; *2* – anodic oxidation; *3* – electro-Fenton oxidation; *4* – oxidation with hydrogen peroxide produced in the gas-diffusion cathode.

experiment because in acid media H_2O_2 decomposes slowly. In this case, thiocyanates may be oxidized with hydrogen peroxide that remained unchanged during electrolysis.

In the presence of iron salts, the oxidation rate increased by a factor of ~2 when the concentration of Fe(II) was raised from 1.5 10^{-3} to 3.8 10^{-3} mol/l. The electrolysis current was 500 mA, and the initial SCN^- concentration was 1.7 10^{-2} mol/l. Conversion of thiocyanates was 41 and 62 %, respectively, after 10 min of electrolysis. At a concentration of SCN^- of 7.8 10^{-2} mol/l, even a fourfold increase in the Fe(II) concentration did not change the initial oxidation rate (see Table 1). Therefore, one can assume that the rate of thiocyanate oxidation depends on the concentration of the resulting iron thiocyanate complex, which is a more active catalyst of hydrogen peroxide degradation than iron aqua ions [4].

When the process is run in a membraneless cell, it should be borne in mind that direct oxidation of thiocyanates on a platinum anode in acid media occurs by the reaction

$$SCN^- + 4H_2O \rightarrow SO_4^{2-} + CN^- + 8H^+ + 6\bar{e} \quad (7)$$

i. e., it forms cyanide ions which can undergo either further oxidation or hydrolysis, forming toxic hydrogen cyanide.

It is noteworthy that at high initial concentrations of thiocyanates the process may be carried out in a membraneless cell for cyanide regeneration and recycling to the leaching process. However, at low SCN^- concentrations this method is not economical and even ecologically unsafe when no effort is taken to trap the released HCN^-. In this case, the most acceptable method of oxidation of thiocyanates seems to be oxidation in alkaline media [7].

CONCLUSION

It has been established that oxidation of thiocyanates in an acid medium in a membraneless cell with a gas-diffusion cathode generating hydrogen peroxide from O_2 and with a platinum anode in the presence of Fe(II) salts occurs more efficiently than in a cell with a membrane.

REFERENCES

1 B. A. Tsybikova, A. A. Ryazantsev, S. Ts. Khankhasaeva *et al.*, *Khimiya v interesakh ustoichivogo razvitiya*, 8 (2000) 445.
2 Pibrre M. Bersier, Topics in Current Chemistry, Springer-Verl., Berlin *etc.*, 1994, vol. 170, p. 114.
3 M. A. Meretukov, A. M. Orlov, Metallurgiya blagorodnykh metallov: zarubezhny opyt, Metallurgiya, Moscow, 1991.
4 A. Ya. Sychev, V. G. Isaak, *Uspekhi khimii*, 64, 12 (1995) 1183.
5 E. Brillas, R. M. Bastida and E. Liosa, *J. Electrochem. Soc.*, 142, 6 (1995) 1733.
6 O. J. Murphy, G. D. Hitchens, L. Kaba and C. E. Verotsko, *Wat. Res.*, 27 (1992) 443.
7 T. A. Kenova, V. L. Kornienko, *Khimiya v interesakh ustoichivogo razvitiya*, 10 (2002) 307.
8 Yu. A. Lourie, Analiticheskaya khimiya promyshlennykh stochnykh vod, Khimiya, Moscow, 1984.
9 E. Brillas, E. Mur, J. Casado, *Electrochem. Soc.*, 143, 3 (1996) 49.