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THE EFFECT OF ANODIC MATERIAL ON THE ELECTROCHEMICAL OXIDATION OF CYANIDES

The anodic oxidation of CN^- on graphite, copper and iron electrodes has been investigated. The effectiveness of the process has been estimated basing on such parameters as rate of anodic oxidation of cyanides, specific power consumption, current efficiency and degree of purification. It has been established that the effectiveness of electrochemical process depends on the nature of anodic material. The highest rate has been measured on the graphite electrodes.

1. INTRODUCTION

It is known that the nature of anodic material is a major factor responsible for its corrosion resistance and its effect on the rate of anodic process [1]–[4].

The aim of this work is to study the effect of the anodic material on the effectiveness of cyanide electrochemical oxidation, which allows us to develop an electrochemical method for purification of concentrated cyanide solutions.

2. EXPERIMENTAL

Graphite, copper and iron electrodes were investigated.

The graphite anodes were made of Zigri graphite (product of Germany) of the following characteristics:

high specific surface area – $32 \cdot 10^3$ m^2/m^3,
density – 1620 kg/m^3,
porosity – 22% ± 2.5,
specific resistance – $10 \cdot 10^{-6}$ Ωm.

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The copper electrodes were made of copper foil of 99.9% purity, and the iron ones – of steel, grade 1H 189T.

The effect of the electrode material on the effectiveness of CN^- anodic oxidation was studied by means of apparatus including electrochemical cell, multivoltmeter, ammeter and voltmeter (fig. 1) [7].

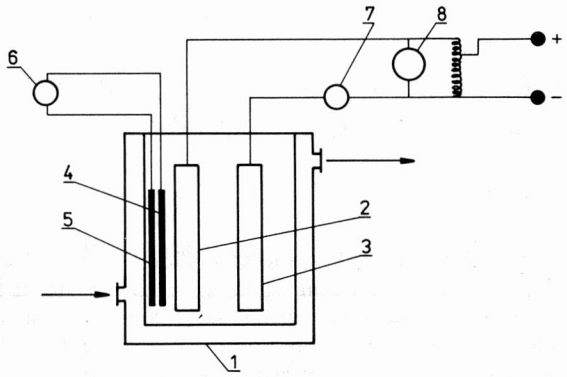

Fig. 1. Experimental installation
1 – thermostatic cell, *2* – anode, *3* – steel cathode, *4* – calomel electrode, *5* – platinum electrode, *6* – milivoltmeter, *7* – ammeter, *8* – voltmeter

Oxidation effectiveness was evaluated on the basis of the following parameters: rate of anodic oxidation of CN^- – V_0; current efficiency – η; specific power consumption – W; degree of purification – α. These parameters were determinated according to equations (1)–(4), respectively.

The rate of anodic oxidation of CN^- was determined according to the following equation [3]:

$$V_0 = (C^0 - C) \cdot V/t \cdot S \tag{1}$$

where:

V_0 – rate of oxidation (kg $CN^-/m^2 \cdot h$),
C^0 – initial CN^- concentration (kg/m^3),
C – final CN^- concentration (kg/m^3),
V – solution volume (m^3),
t – time of oxidation (h),
S – anodic surface area (m^2).

The current efficiency of CN^- oxidation process was determined by the equation [3]:

$$\eta = \frac{(C^0 - C)V \cdot 26.8}{I \cdot t} \times 100, \tag{2}$$

where:

η – current efficiency (%),

I – current intensity (A),

26.8 – Faraday constant (A · h/gram-equivalent).

Power consumption for the oxidation of 1 kg of CN^- was determined according to the following equation [3]:

$$W = I \cdot U \cdot t/1000(C^0 - C) \cdot V \tag{3}$$

where:

W – specific power consumption (kWh/kg CN^-),

U – cell potential (V).

The degree of purification (α) was determined by the formula:

$$\alpha = \frac{C^0 - C}{C^0} \cdot 100 \ (\%). \tag{4}$$

CN^- concentrations in the model solutions and in effluent cyanide solutions (before and after purification) were determined spectrophotometrically with pyridine barbituric acid, in the presence of chloramine T [4]. The latter interacts with CN^- forming cyanogen chloride, which reacts with pyridine to give a colour compound that has an absorption peak at $\lambda_{max} = 580$ nm. Its absorption spectrum was measured with Spekol-10 photometer using cuvettes of a 1.0×10^{-2} m thick absorption layer. The relative standard deviation of the method is 5.4%.

3. RESULTS AND DISCUSSION

The results concerning the effect of anodic material on the electrochemical oxidation of cyanides are presented in fig. 2 and tables 1–4. The data obtained show that oxidation of CN^- ions takes place on all anodes under study. The process is most effective when graphite electrodes are applied. They yield a maximum degree of purification ($\alpha = 100\%$) in the shortest time and at the lowest power consumption. The rate of electrochemical oxidation reaches its highest value ($V_0 = 0.035$ kg of $CN^-/m^2 \cdot h$) when graphite electrodes are used. For the other electrodes, it is arranged in the following descending order:

$$V_0 \text{ graphite} > V_0 \text{ copper} > V_0 \text{ iron}.$$

Investigations show that iron and copper anodes cannot yield a 100% purification, and the residential CN^- concentration is above 4.0×10^{-4} kg/m^3.

The iron anodes have low oxygen overpotential ($a = 0.75$; $b = 0.06$ V) [5] and are, therefore, unsuitable in the cases of solutions containing complex cyanides that are difficult to oxidize. Due to anodic polarization phenomenon, the dissolution of anode occurs causing additional pollution of the solutions by metal cations.

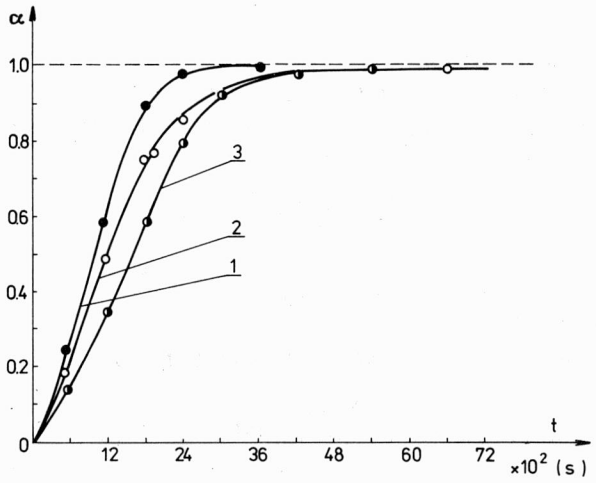

Fig. 2. Dependence of α on the duration of electrolysis and the nature of anodic material
1 – graphite, *2* – copper, *3* – iron, pH – 11.00, *i* – 50 A/m²

Table 1

Parameters of CN^- oxidation on copper anodes
C^0 – 0.170 kg/m³, V – 1.0×10^{-3} m³, I – 1.0 A, S – 4.0×10^{-3} m², U – 3.2 V, pH – 11.00

Electrolysis duration $a \cdot 10^2$ (s)	CN^- concentration C (kg/m³)	Purification degree α (%)	Oxidation rate V_0 (kg CN^-/m²·h)	Specific power consumption W (kWh/kg CN^-)
0	0.1700	0.0		
6	0.1400	17.6		
12	0.0890	47.8		
18	0.0440	74.1		
25	0.0340	80.0		
30	0.0153	91.0		
36	0.0085	95.0		
42	0.0051	97.0	0.014	37.6
48	0.0034	98.2		
54	0.0028	98.3		
60	0.0010	99.4		
66	0.0004	99.7		
77	0.0004	99.7		

The studies conducted proved that of all anodes under investigations these made of graphite are most suitable for cyanide electrolytic oxidation. Unfortunately they have technological disadvantages, described by Sharma [6]. Such disadvantages

arise under conditions of industrial electrolysis of cyanides, i.e. in an aggressive medium, at high concentration, voltage (potential) and temperature.

Table 2

Parameters of CN^- oxidation on iron anodes
C^0 – 0.170 kg/m³, V – 1.0×10^{-3} m³, I – 1.0 A, S – 4.0×10^{-3} m², U – 4.80 V, pH – 11.00

Electrolysis duration $a \cdot 10^2$ (s)	CN^- concentration C (kg/m³)	Purification degree α (%)	Oxidation rate V_0 (kg CN^-/m²·h)	Specific power consumption W (kWh/kg CN^-)
0	0.1700	0.0		
6	0.1462	14.0		
12	0.1103	35.1		
18	0.0731	57.2		
24	0.0369	78.3		
30	0.0146	91.5	0.014	56.5
36	0.0114	93.3		
42	0.0054	96.9		
48	0.0034	98.0		
54	0.0025	98.5		
60	0.0015	99.1		
66	0.0007	99.6		
72	0.0007	99.6		

Table 3

Parameters of CN^- oxidation on graphite anodes
C^0 – 0.170 kg/m³, V – 1.0×10^{-3} m³, I – 1.50 A, S – 6.0×10^{-3} m², U – 2.30 V, pH – 11.00

Electrolysis duration $a \cdot 10^2$ (s)	CN^- concentration C (kg/m³)	Purification degree α (%)	Oxidation rate V_0 (kg CN^-/m²·h)	Specific power consumption W (kWh/kg CN^-)
0	0.1700	0.0		
6	0.1270	25.3		
12	0.0710	58.2		
18	0.0220	87.1	0.0346	16.84
24	0.0040	97.6		
30	0.0020	98.8		
36	0.0000	100.0		
42	0.0000	100.0		

All of these facts account for the actuality of the investigations into making graphite anodes of high corrosion resistance. This is the area of our further investigations [7].

Table 4

Dependence of η on anodic material
C^0 – 0.170 kg/m^3, V – 1.0×10^{-3} m^3,
I – 1.0 A, S – 4.0×10^{-3} m^2, pH – 11.0

Anodic material	Yield by current (%)
graphite	21.1
copper	14.6
iron	11.6

4. CONCLUSIONS

The anodic oxidation of CN^- on graphite, copper and iron electrodes has been studied. The highest rate of the process as well as the highest degree of cyanide solution purification have been measured on the graphite electrodes. Technology of purification of highly concentrated cyanide solutions will be developed on the basis of laboratory results.

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WPŁYW MATERIAŁU ANODOWEGO NA ELEKTROCHEMICZNE UTLENIANIE CYJANKÓW

Badano anodowe utlenianie cyjanków na elektrodach wykonanych z grafitu, miedzi i żelaza. Wydajność procesu oszacowano na podstawie takich parametrów, jak: szybkość anodowego utleniania cyjanków, jednostkowe zużycie energii, wydajność prądowa oraz stopień oczyszczenia. Ustalono, że efektywność procesu elektrochemicznego zależy od właściwości materiału anodowego. Największą szybkość utleniania zmierzono na elektrodzie grafitowej.

ВЛИЯНИЕ АНОДНОГО МАТЕРИАЛА НА ЭЛЕКТРОХИМИЧЕСКОЕ ОКИСЛЕНИЕ ЦИАНИДОВ

Исследовано анодное окисление цианидов на электродах, выполненных из графита, меди и железа. Эффективность процесса оценена на основе таких параметров, как: быстрота анодного окисления цианидов, специфическое потребление энергии, токовая эффективность и степень очистки. Было установлено, что эффективность процесса зависит от свойств анодного материала. Самую большую быстроту окисления измерили на графитном электроде.