Extraction of Cyanides from Waste Solutions of Cyanidation of Flotation Concentrates from Kholbinskoye Gold Deposit

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Abstract

Processes that occur during extraction of cyanides from cyanidation solutions using centrifugal bubbling apparatuses (CBA) as reactors have been studied. In the eddy chamber of CBA (pH < 3), one can observe virtually complete removal of HCN from solution and precipitation of heavy metals in the form of insoluble compounds. The electronic absorption spectra of solutions treated in CBA suggest that destruction of $[Cu(CN)_x]^{x-1}$, oxidation of Cu^+ to Cu^{2+} by air oxygen, and oxidation of thiocyanates in the presence of $S_2O_3^{2-}$, forming HCN and SO_4^{2-}, are also accompanied by the emergence of stable intermediate products $(SCN)_2$ and $(SCN)_x$ of oxidation in solution.

INTRODUCTION

Cyanides are widely used in extraction of precious metals, mainly fine gold and silver, from sulphide-bearing ores. A significant part of cyanides in the form of simple and complex compounds remain in recycled solutions. Excess recycled water is subjected to purification including destructive oxidation of free and complex cyanides, and then it is released into open reservoirs or onto the land. At the same time, the waste solutions from processing of flotation concentrates contain cyanides in such quantities that recovery and recycling of these compounds in the form of NaCN become profitable.

The acidification – volatilization – reneutralization method (AVR process) is commonly used for cyanide recovery [1–3]. The method is based on distilling or blowing out volatile HCN formed after acidification of the waste processing solutions of cyanidation to pH 6–2.5 followed by absorption of HCN by alkaline solutions. The obtained sodium cyanide is recycled. Acidification is accompanied not only by binding of free cyanides into HCN, but also by destruction of complex cyanides of heavy metals to form additional hydrogen cyanide.

The stability of complex cyanides of heavy metals depends strongly on pH of water solutions (Fig. 1) [5].

Au^{3+}, Co^{2+}, and Fe^{2+} cyanides are stable in acidic media, while Zn^{2+} and Ag^+ complexes decompose practically completely even at pH 6. This behaviour of complex cyanides of heavy metals is in good agreement with the corresponding Eh – pH diagrams [5]. Obviously, the most complete removal of cyanides in the form of HCN by distilling would be expected for solutions acidified to pH < 3.
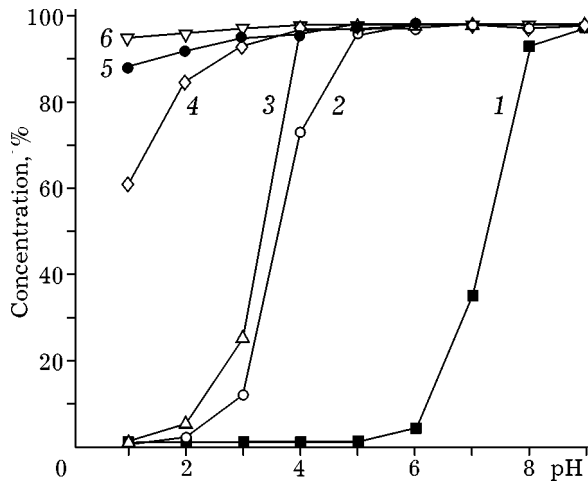
Fig. 1. Effect of pH on the stability of metal cyanide complexes in water solutions: $1 - Zn(CN)_4^{2-}$, $2 - Ni(CN)_4^{2-}$, $3 - Cu(CN)_3^{2-}$, $4 - Fe(CN)_6^{4-}$, $5 - Au(CN)_2^-$, $6 - Co(CN)_4^{2-}$.

Nevertheless, even in the case of pH 2–3, it is generally possible to extract and recycle no more than 75 % of cyanides from the real waste solutions of cyanidation containing 400–900 mg/l of copper [3]. This is attributable to the formation of sparingly soluble and rather stable (in acid solutions) compounds CuCN and copper, nickel, zinc, and iron ferrocyanides. In addition, the completeness and the character of decomposition of complex cyanides depend not only on pH and on the chemical composition of these compounds, but also on the availability of other anions and solute oxygen in solution, and also on the intensity of mass transfer in the reaction zone. These circumstances should be taken into account when using the AVR method.

This work presents the results of our studies on processes that occur during extraction of cyanides from recycled processing solutions of the hydrometallurgy department of the gold-processing plant (Kholbinskiy mine) using centrifugal-bubbling apparatuses (CBA) as reactors for AVR processes. Winning of gold at the mine is realized by flotation concentration of ore followed by leaching of the metal in cyanide form from the concentrates. The plant uses closed-loop recycled water supply without fresh water make-up and without waste disposal. The dam and the bottom of the tailings pond are permanently in the frozen state to prevent underground filtration of solutions. Reagent sewage

treatment using $CaOCl_2$ as an oxidation agent is provided in case of emergency.

EXPERIMENTAL

Reagents and methods for determining concentration of substances in solutions

For experiments with model solutions, reagents of chemically pure or analytically pure grade were used. The composition of the real waste solutions of cyanidation, mg/l: the total content of cyanides and thiocyanates was 580–3600, including thiocyanates 780–2360, iron 46.0–126.0, copper 300–800, zinc 2–50, nickel 9–32, silver 10–25, thiosulphates 1500–3300, sulphites 60–80, sulphates >1000, chlorides >300, pH 9.5–11.0.

The concentrations of thiocyanates in solutions were determined by photometric measurement of $Fe(SCN)_3$ [6]; that of cyanides, by the Bucksteg method with volatilization in the form of HCN; and that of thiosulphates, by the iodometric method [8]. Atomic absorption analysis for heavy metals was conducted on an AAS Perkin Elmer 3110 device. Absorption spectra of solutions were registered on a UV-VIS Aglent-8453 instrument.

Centrifugal bubbling apparatuses for AVR processes

The design of CBA (Fig. 2) involves a cylindrical case whose upper part has a separation
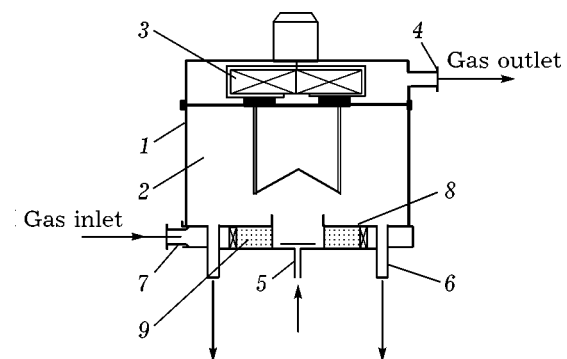

Fig. 2. Schematic diagram of a centrifugal bubbling apparatus: 1 – cylindrical case; 2 – separation zone; 3 – fan; 4 – gas outlet; $5, 6$ – fitting pipes for liquid feed and discharge; 7 – gas inlet; 8 – swirler; 9 – rotating gas-liquid layer.

zone, a fan, and a gas outlet and the bottom part has fitting pipes for liquid feed and discharge, a gas inlet and a guiding device (swirler). The swirler is a ring with tangential slots for gas twisting.

The operating principle of CBA is letting the gas pass through a rotating liquid layer held by the gas stream in the eddy chamber. When the fan is switched on, the gas passes through the slots of the swirler and entrains the liquid in the swirl, forming a rotating gas-liquid layer inside the apparatus. Through the central fitting pipe the gas and liquid enter the separator that uses the centrifugal and inertial forces to let the gas and liquid out of the reactor.

A CBA with an air-flow rate of $140-160 \ \mathrm{m^3/h}$ (liquid flow rate 60-80 l/h) and an industrial module of two devices mounted in series with an air-flow rate of up to $8000 \ \mathrm{m^3/h}$ were used for our experiments. Air stripping of solutions to remove HCN was conducted in a device with two swirlers installed in succession; HCN absorption by a NaOH solution was carried out in a CBA with three swirlers. The industrial module afforded $2.5-3 \ \mathrm{m^3}$ of cyanide solutions to be processed per hour by means of the AVR method.

RESULTS AND DISCUSSION

*Air stripping of cyanidation solutions
to remove HCN in CBA*

Previously [8], we have demonstrated that the rates of chemical reactions in CBA and the completeness of cyanide removal by the AVR method depend strongly on the intensity of mass transfer, which, in turn, is controlled substantially by the rotation rate of the gas-liquid layer. Residence time of the gas-liquid layer in CBA during air stripping is 15-60 s (one to four treatments in the swirler). The volumetric rates of reactions involving the transformations of thiocyanates and cyanides in the rotating gas-liquid layer of CBA were calculated from the loss of the total concentration of cyanides and thiocyanates and comprised 9.5-13.7 mol/(l h), which is $45-65$ times higher than the rates of the same processes in a bubble type column.
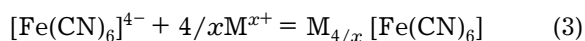
As noted above, acidification of waste solutions leads to dissociation of the complex cyanides of heavy metals:
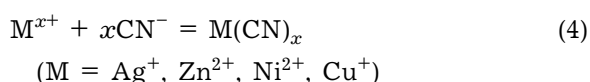
$$\mathrm{M}^{x+}(\mathrm{CN})_y^{(x-y)} \leftrightarrow \mathrm{M}^{x+} + y\mathrm{CN}^- \qquad (1)$$
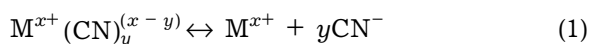
and to binding of cyanide ions into HCN:

$$\mathrm{H}^+ + \mathrm{CN}^- = \mathrm{HCN} \qquad (2)$$

The liberated metal ions react with iron cyanides $[\mathrm{Fe(CN)_6}]^{4-}$ (if any) in solution to form ferrocyanides sparingly soluble in acid media:

$$[\mathrm{Fe(CN)_6}]^{4-} + 4/x\mathrm{M}^{x+} = \mathrm{M}_{4/x}[\mathrm{Fe(CN)_6}] \qquad (3)$$

or $\mathrm{M(CN)}_x$ type compounds:

$$\mathrm{M}^{x+} + x\mathrm{CN}^- = \mathrm{M(CN)}_x \qquad (4)$$
$$(\mathrm{M = Ag^+, \ Zn^{2+}, \ Ni^{2+}, \ Cu^+})$$

The precipitation sequence $\mathrm{Zn^{2+}} > \mathrm{Fe^{2+}} > \mathrm{Ni^{2+}} > \mathrm{Cu^+}$ is controlled, on the one hand, by dissociation of cyanide complexes at different pH values (see Fig. 1) [4] and on the other hand, by the stability of ferrocyanides in acid media [9].

Figure 3 shows the kinetic curves of removal of common cyanides, thiocyanates, and copper from processing media. The data obtained testify that virtually complete removal of HCN and heavy metals from the solution is observed within a minute in the eddy chamber of CBA under conditions of intense mass transfer at pH < 3. This leads to 100 % absorption of hydrogen cyanide in an alkali solution. Copper thiocyanates comprise the bulk of the deposit; they form by the reaction

$$[\mathrm{Cu(CN)}_x]^{x-1} + x\mathrm{H}^+ + \mathrm{SCN}^-$$
$$= x\mathrm{HCN} + \mathrm{CuSCN} \qquad (5)$$
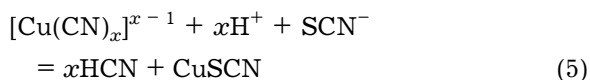
Oxidation of thiocyanates in CBA

Figure 4 presents the results of air stripping and absorption of HCN during the AVR process in CBA. Curve *1* is plotted from data for common cyanides in solutions before and after treatment in CBA; curve *2* is drawn from the results of CN^- determination in the absorbing solution of NaOH. It is evident that the contents of cyanides in the absorbing solution of NaOH are, on the average, 30 %
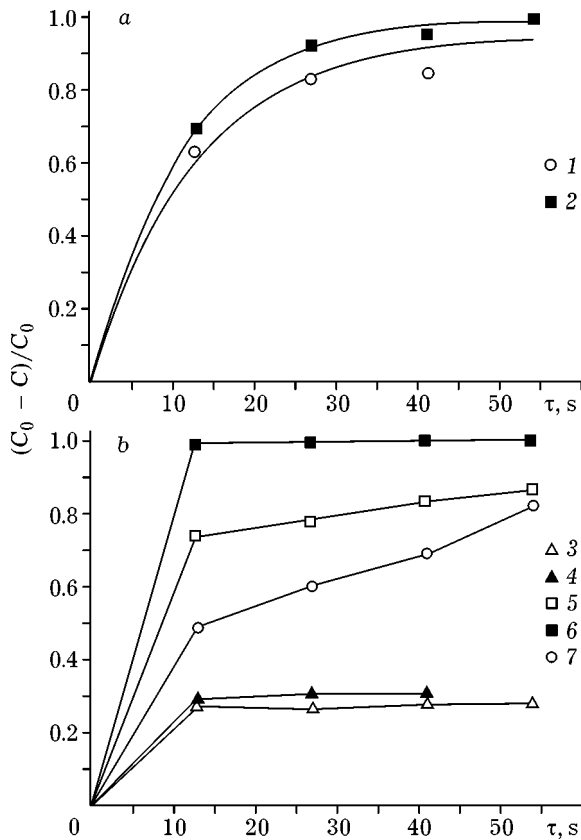
Fig. 3. Kinetics of removal of common cyanides *(a)*, thiocyanates, and copper *(b)* during treatment of processing solutions in CBA (C_0 is the initial concentration, and C is current concentration, mg/l): *1, 2* – CN^-; *3, 4* – SCN^-; *5, 6* – Cu; *7* – $S_2O_3^{2-}$; pH: 3.7 (*1, 3, 6, 7*), 2.4 (*2, 4, 5*).

higher than one might expect even in the case of complete dissociation of complex cyanides of heavy metals. Hence, the additional quantity of cyanides formed in the absorbing solution due to oxidation of SCN^-.

The diagram Eh – pH (Fig. 5) plotted with thermodynamic data [10] confirms that thiocyanates are unstable in the $HSCN$ – H_2O system. Oxidation of thiocyanates can form sulphur [11] or thiocyanogen $(SCN)_2$ [12] as intermediate products, which depends on conditions. The first scheme is realized in the presence of Cu^{2+} and with thiosulphates or sulphites present in solution. Under these conditions, thiocyanates are actively oxidized to HCN and SO_4^{2-}.

Treatment of cyanidation solutions in CBA under conditions of intense mass transfer at pH < 3 results in decomposition of $[Cu(CN)_x]^{x-1}$, oxidation of Cu^+ to Cu_{2+} by air oxygen according to the scheme
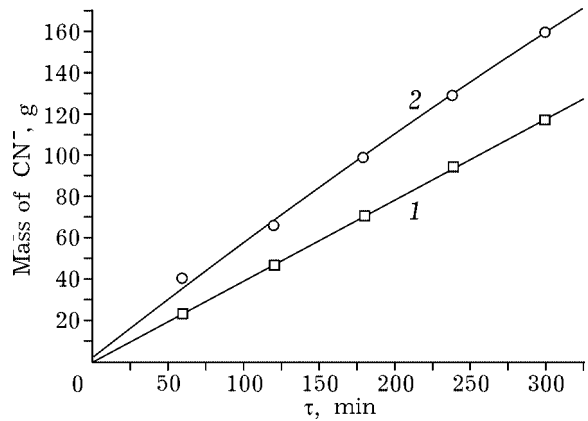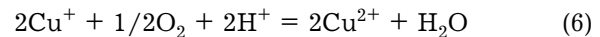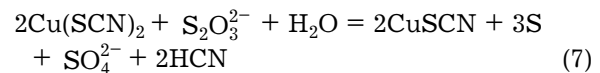

Fig. 4. Air stripping to remove HCN *(1)* and HCN absorption *(2)* in CBA (solution feed rate in CBA is 1 l/min, pH 2.47). At inlet to CBA: C_{CN^-} = 633 mg/l, C_{SCN^-} = 1837 mg/l; at outlet from CBA: C_{CN^-} = 245.5 mg/l, C_{SCN^-} = 1008 mg/l.

$$2Cu^+ + 1/2O_2 + 2H^+ = 2Cu^{2+} + H_2O \qquad (6)$$
$$E^0 = 1.076 \text{ V}$$

HCN formation:

$$2Cu(SCN)_2 + S_2O_3^{2-} + H_2O = 2CuSCN + 3S + SO_4^{2-} + 2HCN \qquad (7)$$

and oxidation of sulphur:

$$S + 4H_2O = SO_4^{2-} + 8H^+ + 6e^- \qquad (8)$$
$$E^0 = -0.357 \text{ V}$$

This mechanism is supported by the character of variation of $S_2O_3^{2-}$ and copper concentrations after treatment of cyanide solutions in CBA (see Fig. 3).

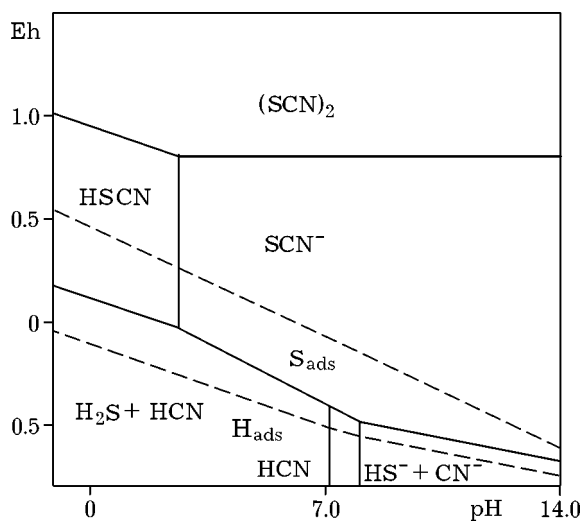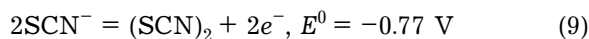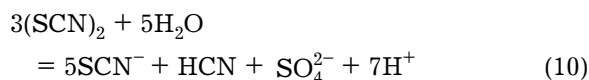Fig. 5. Diagram potential – pH for the HSCN – H_2O system [11].

The second scheme of thiocyanate oxidation in aqueous solutions through thiocyanogen formation,

$$2SCN^- = (SCN)_2 + 2e^-, \, E^0 = -0.77 \, V \qquad (9)$$

also gives rise to HCN and SO_4^{2-} as end products.

Hydrolysis of thiocyanogen in aqueous solutions according to the scheme

$$3(SCN)_2 + 5H_2O$$
$$= 5SCN^- + HCN + SO_4^{2-} + 7H^+ \qquad (10)$$

described in the literature may be considered to be an integrated process as there is much evidence in favour of intermediate compounds, often more stable than $(SCN)_2$ [13−18].

It was shown that, e. g., thiocyanogen can form $(SCN)_x$ polymers not only in non-aqueous solvents such as glacial acetic acid [13] and acetonitrile [16], but also in aqueous media when thiocyanates are oxidized with hydrogen peroxide [17] or Fe(III) compounds [18].

Thiocyanogen is generally identified by its characteristic absorption at $\lambda_{max} = 295$ nm in the UV-VIS spectra [19]. The wide absorption band with $\lambda_{max} = 300$ nm in the region 280−320 nm, whose intensity increases appreciably with the content of SCN^- in aqueous solution during oxidation of HSCN, was explained by the presence of thiocyanogen together with the stable intermediate $(SCN)_3^-$ [17]:

$$(SCN)_2 + SCN^- = (SCN)_3^- \qquad (11)$$
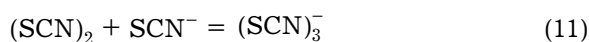
Moreover, the intense peak appearing at $\lambda_{max} = 320$ nm in the absorption spectrum was attributed to the formation of $(SCN)_3^-$ as an intermediate during electrooxidation of iron (III) thiocyanate in an aqueous 0.1 M solution of $HClO_4$ [18].

The two peaks (at 320 and 283 nm) observed in the absorption spectra of the oxidation products of SCN^- in acetonitrile were attributed to the trithiocyanate ion and thiocyanogen, respectively [20]. Two peaks (at 250 and 288 nm) were observed in the absorption spectra of fresh solutions of thiocyanogen in acetic acid [13]. For thiocyanogen obtained by oxidation of $Pb(SCN)_2$ with bromine in CCl_4 (curves 1, 2) and in glacial acetic acid (curves 3,

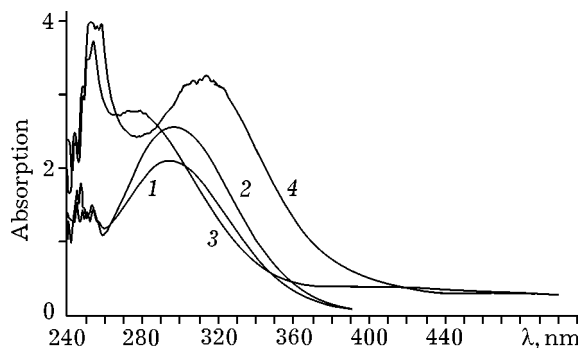Fig. 6. Absorption spectra of thiocyanogen: 1, 3 − solutions are obtained by oxidation of $Pb(SCN)_2$ with bromine in CCl_4 and CH_3COOH; 2, 4 − solutions 1, 3 after an excess of KSCN has been added.

4), our data (Fig. 6) reproduce the results of [13]. The difference lies in the fact that the peaks corresponding to the absorption maxima lie at $\lambda_{max} = 254$ and 273 nm. The absorption peak at 254 nm, whose intensity increases considerably after addition of excess KSCN to the solution, is attributed to $(SCN)_3^-$ or to some other, more condensed thiocyanate. The emergence of a compound of this kind in solution causes the second peak to shift in the long-wavelength range of the spectrum ($\lambda_{max} = 315$ nm).

When the AVR process is conducted in CBA (pH < 3), reactions (6) and (7) proceed quickly and the concentration of thiocyanates decreases sharply in solutions even after 15 s of treatment in the eddy chamber of CBA (see Fig. 3). After further treatment, the concentration of thiocyanates decreases slowly as practically all copper precipitates from the solution. The peaks that are responsible for the emergence of the oxidation products of thiocyanates (thiocyanogen or its polymeric modifications $(SCN)_x$) are absent from the absorption spectra of the solutions (Fig. 7, curve 1). However, after the precipitate has been separated and allowed to settle for a few days, the liquid contains a small amount of amorphous suspended solid, percolating through the paper filter and dissolving in NaOH. Addition of NaOH to the solution gives rise to two maxima (at 267 and 285 nm), whose intensity increases with pH (see Fig. 7, curves 2, 3). One maximum ($\lambda_{max} = 285$ nm) was attributed to thiocyanogen $(SCN)_2$, and the other to $(SCN)_x^-$, where $x \geq 3$. This was in-
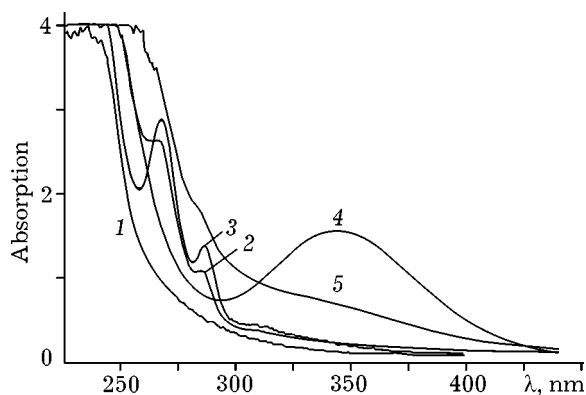
Fig. 7. Absorption spectra of cyanidation solutions after air stripping to remove HCN in CBA and separation of the precipitate: *1* − pH 2.65; *2* − pH 3.75; *3* − pH 9.0; *4* − solution *2* + Cu^{2+}, pH 3.75; *5* − solution *4* + NaOH, pH 6.25.

ferred from comparison of the given spectrum and the spectra of thiocyanogen (see Fig. 6) and also from the fact that addition of Cu^{2+} to the solution (pH 3.75) forms copper complexes $Cu(SCN)_x^+$ strongly absorbing in the region 345 nm (see Fig. 7, curve *4*), which are less stable than $Cu(OH)_2$ in alkaline media (see Fig. 7, curve *5*).

CONCLUSIONS

Treatment of cyanidation solutions of sulphide flotation concentrates in centrifugal bubbling apparatuses under conditions of intense mass transfer at pH < 3 leads not only to practically complete extraction of cyanides in the form of HCN from the aqueous phase, but

also to production of more hydrogen cyanide due to regenerative oxidation.

A mechanism is suggested whereby the conversion of thiocyanates in CBA occurs both by oxidation by air oxygen in the presence of copper ions and thiosulphates and through formation of thiocyanogen.

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