ФИЗИКАЛЫҚ ЖӘНЕ АНАЛИТИКАЛЫҚ ХИМИЯ
ФИЗИЧЕСКАЯ И АНАЛИТИЧЕСКАЯ ХИМИЯ
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Investigation of the processes of copper ions transition into a solution from oxide and sulfide compounds under the influence of organic complexing agents

The article describes the results of studying of the process of copper leaching from model grounds containing 0.02 % of copper oxide or copper sulfide, with solutions of natural and chemically modified complexing agents. The total amount of one ground sample was 500 g. The model grounds were placed in columns, and the solutions of complexing agents were passed through the columns at a given rate. Sodium humate, sulfonated and oxidized humic acid, native and oxidized fulvic acid, and sodium lactate were studied as leaching agents. It is shown that solutions of all reagents with a concentration of 0.01 % can produce a transition of copper into the solution from both the oxide and sulfide mixtures. It was established that oxidized and native fulvic acids and sodium lactate are most effective for copper extracting. For oxide copper minerals, the most effective complexing agent is the lactate ion, and an oxidized derivative of fulvic acid has a little lower efficiency. Further, less effective agents are the sulfonated humic derivative and the native fulvic acid which have approximately equal effectiveness. The sodium humate is less active and the oxidized humic derivative has lower efficiency. In the case of sulfide minerals, the most effective complexing agent is the oxidized derivative of fulvic acid. The lactate ion, the sulfonated humic derivative and the native fulvic acid are a little less effective agents. The sodium humate and the oxidized humic derivative have comparatively low efficiency. By the mathematical processing of kinetic data, the rate constants of copper leaching processes from model grounds were estimated. The values of the found constants are in the range from $1.05 \cdot 10^{-7}$ to $1.28 \cdot 10^{-7}$ s^{-1}. The kinetic curves for the transferring of copper ions to the solution under the action of complexing agents are characterized by a relatively small transition period and fast reaching concentrations which are close to equilibrium ones.

Keywords: humic acids, fulvic acids, sulphonated humic acids, oxidized fulvic acids, oxidized humic acids, malachite, kinetics of copper leaching.

Introduction

The development of methods for additional extraction of non-ferrous metals from poor and off-balance ores and dumps is an important and actual task due to permanent decreasing of mineral reserves in rich deposits. The purpose of the research is to develop methods for recovery off-balance metals in depleted copper deposits and dumps by transferring copper minerals to a soluble form with using of complexing agents and followed by fixation of copper ions on carbonate collectors.

The formation of malachite under natural conditions occurs in the presence of carbonate rocks in the zones of oxidation of sulfide copper deposits, as well as in places of development of copper deposits, in waste mines and dumps [1–7]. Earlier it was shown that for the intensification of this process it is expedient to use limestone as a carbonate collector and donor of carbonate ions, as well as the use of environmentally safe organic complexing agents [8, 9]. In order to investigate the processes that affect secondary mineral formation under these conditions, the effect of organic complexing agents on the solubility of copper minerals has been studied.

The main objective of the research is to describe the dissolution of sulfide and oxidized copper minerals under model conditions for the subsequent accumulation of copper ions on carbonate collectors, with using of various physicochemical methods. The scientific novelty is in the estimation of the efficiency of conversion of copper minerals into solution in the form of complex compounds with chemically modified organic ligands.

Experimental

The experiments were conducted to measure the effect of organic complexing agents and their sulfonated and oxidized derivatives on the process of mineral formation of basic copper carbonates on model grounds. The model grounds were mixtures of copper oxide or copper sulfide with inert filler consisting of a mixture of sand and perlite, the content of copper in the soils was 0.02 %. The total amount of one sample of ground was 500 g. Model grounds were placed in columns, through which solutions of complexing agents were passed at a given rate. Six types of complexing agents were used: the lactate ion in the form of a buffer mixture (conventionally designated as Lac), sodium humate (Hum-Na), free fulvic acid (Ful-H), sulfonated (Hum Sulf) and oxidized (Hum Ox) humic derivatives and oxidized derivative of fulvic acid (Ful Ox). The initial concentration of solutions of complexing agents was 0.01 %; the rate of passage of solutions through the columns was between 30 and 50 ml/h. The controlled parameter in carrying out these experiments was the concentration of copper in the solution. The current analytical control of copper in the solutions was carried out by the photometric method on the KFK-2 colorimeter with using of sodium dithiocarbamate [10].

Synthesis of modified complexing agents

Sodium humate (manufactured by LLC «NVP BashIncom», Ufa, Russia) and free fulvic acid (manufactured by Tagrow Co., Ltd., USA) were used as initial complexing agents. The content of water-soluble fulvates in fulvic acid was 96 % from the dry residue with a fulvic acid content of 70 %, the moisture content was 10 %; for the sodium humate, the content of the main substance was not less than 80 %, the rest 20 % represent mainly with water. To characterize the compounds, infrared spectra were registered (Fig. 1 and 2).

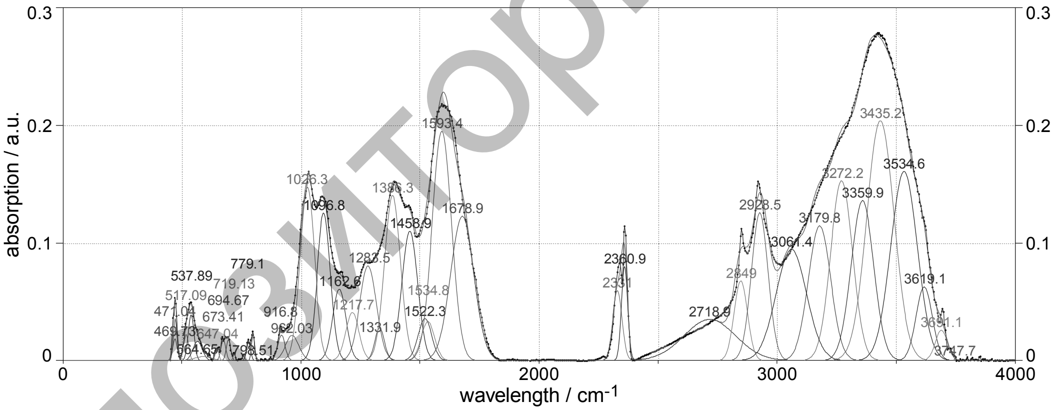

Figure 1. Infrared spectrum of the initial humate

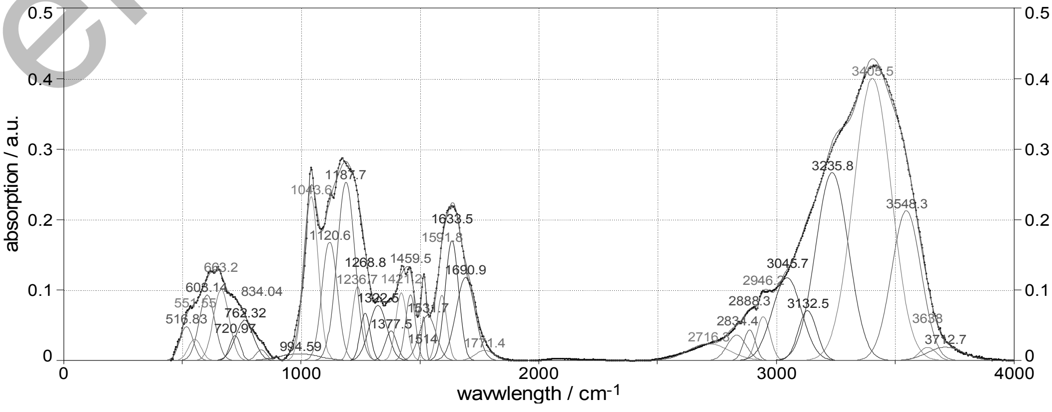

Figure 2. Infrared spectrum of initial fulvic acid

It can be seen from the figures, the starting compounds are characterized by a complex structure of absorption spectra, among which one can distinguish regions related to the vibrations of functional groups (500–1400 cm^{-1}), the range of vibrations of carbonyl groups at 1635–1640 cm^{-1} [11], a wide absorption band of bound water near 3410–3440 cm^{-1}. The IR spectrum of humate also clearly shows the vibrations of free water molecules.

The initial treatment of the starting materials consisted in their heat treatment at 80–90 °C to remove excess moisture and volatile compounds. Two main variants were used for the chemical modification of the starting compounds. First, treatment with oxidants for both a general growth in the number of oxygen-containing functional groups, which, as a rule, exhibit good complexing properties, and to increase the oxygen content in them and, accordingly, to enhance their electron-donating properties and to extend the chemical affinity for metal ions. Second, another variant of the chemical modification involves the introduction of sulfonate groups into the structure of compounds. These groups, in accordance with reference [12], contribute to an increase in the solubility of the humic compounds with content of metals, and, as a result, intensificare their geochemical mobility.

Synthesis of oxidized derivatives from the initial complexing agents

The prepared starting materials were treated with 10 % hydrogen peroxide solution at room temperature for 24 hours. The reaction mixture was evaporated on a sand bath; the residue was dried in a drying oven at 110 °C to constant weight. Infrared spectra of oxidized derivatives of the complexing agents are presented in Figures 3 and 4.

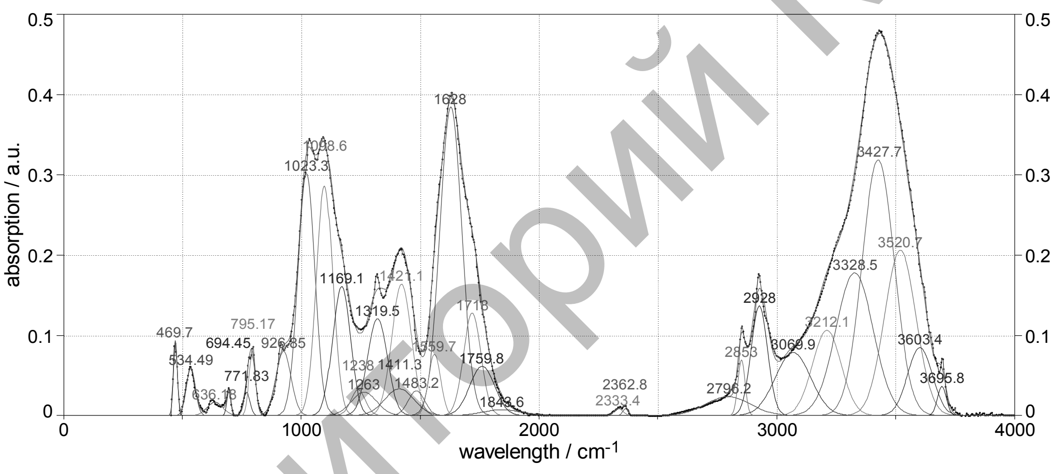

Figure 3. Infrared spectrum of oxidized humate

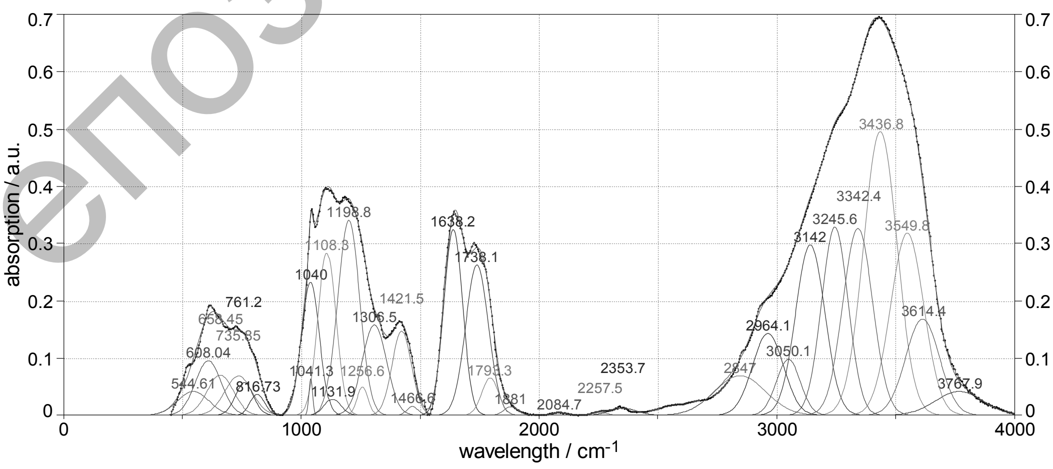

Figure 4. Infrared spectrum of oxidized fulvic acid

The main differences between the spectra of the modified compounds and the spectra of the initial substances consist in an increase in the intensity of absorption of carbonyl groups at 1635–1640 cm^{-1} for humic and fulvic acids, which indicates an increase in their mole fraction in the oxidation process. For fulvic acid, an additional peak of ketone groups appears at 1730 cm^{-1}. An increase in the number of these functional groups leads to an increase in water solubility and a tendency to formation of complexes with the metal cations that are part of the carbonate collectors, i.e. calcium and magnesium.

Synthesis of sulfonate derivatives from the initial complexing agents

The starting materials were treated with a dilute solution of sulfuric acid (concentration 32 %) at the boiling point of the solution for 4 hours in a cup for evaporation. During the reaction, fulvic acid completely dissolved in the reaction medium, where it could not be isolated. The infrared spectrum of the humic derivative is shown in Figure 5.

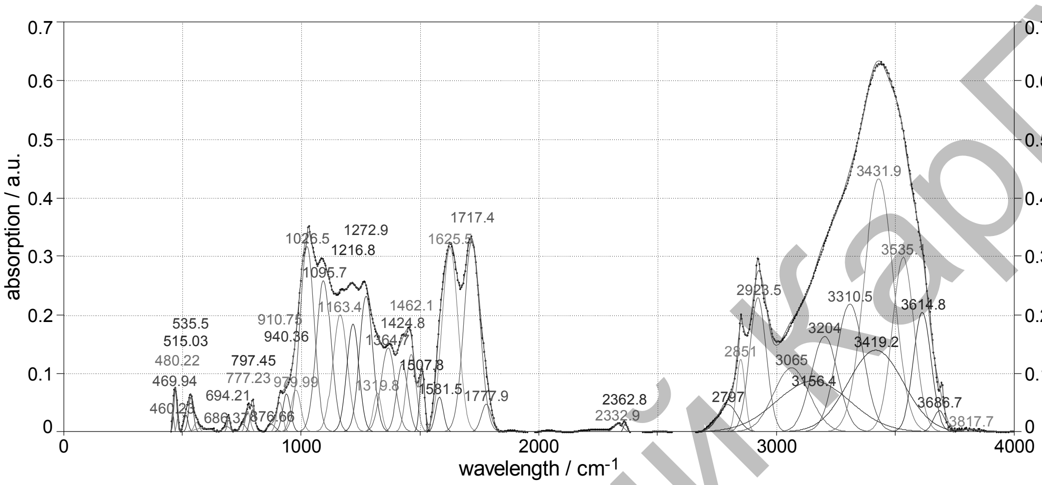

Figure 5. Infrared spectrum of sulfonated humate

The presence of sulfate groups in the structure of the sulfonated derivative is confirmed by an absorption band at 1261 cm^{-1}. It should be noted that along with sulfonation, other processes occur, including the formation of ammonium salts of sulfuric acid with amino groups of humic acid and also the formation of ketone groups (1703 cm^{-1}), apparently in the hydrolysis of unsaturated esters and polysaccharide chains.

Results and discussion

Collection of data on the transfer of copper into a solution from model grounds with the using of complexing agents was carried out over a period of 50 weeks. All types of complexing agents showed appreciable activity for the dissolution of copper from sulfide and oxide minerals. Figures 6–9 show the copper content in solutions passing through the columns. For convenience of perception, the obtained values are divided into four groups: data on the humic complexing agents for the copper oxide and for copper sulfide, and, similarly, on the fulvic complexing agents (together with lactate ion) for copper oxide and copper sulfide. The scale on the ordinate axis is the same for all plots.

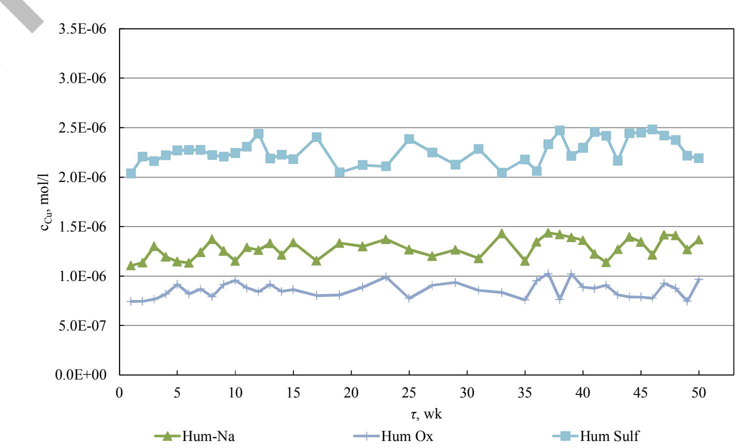

Figure 6. Dependences of copper extraction from copper oxide into solution by humic complexing agents

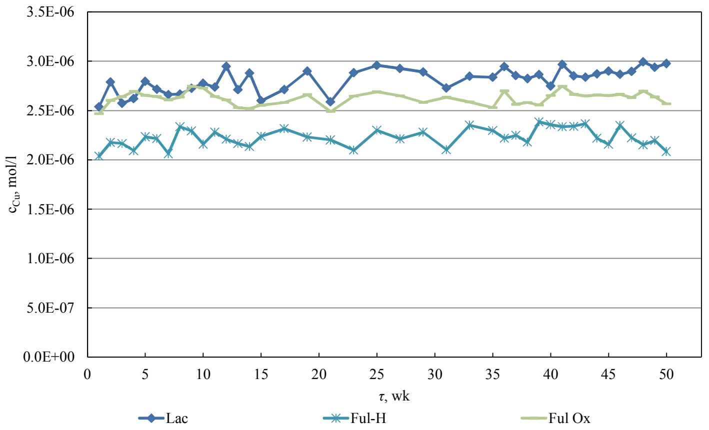

Figure 7. Dependences of copper extraction from copper oxide into solution by fulvic complexing agents and lactate ion

It can be seen from the graphs given, the copper extraction rates in the solution are quite stable, although they are relatively sensitive to the rate of passage of solutions through the columns, and show a certain tendency to increase with time.

Humic complexants generally show a lower efficiency when copper is transferred to the solution; nevertheless, average values in the transition of copper to solution are observed for the sulfonated humic derivative. At the same time, the humic complexing agents show approximately the same efficiency with respect to the oxide and copper sulfide.

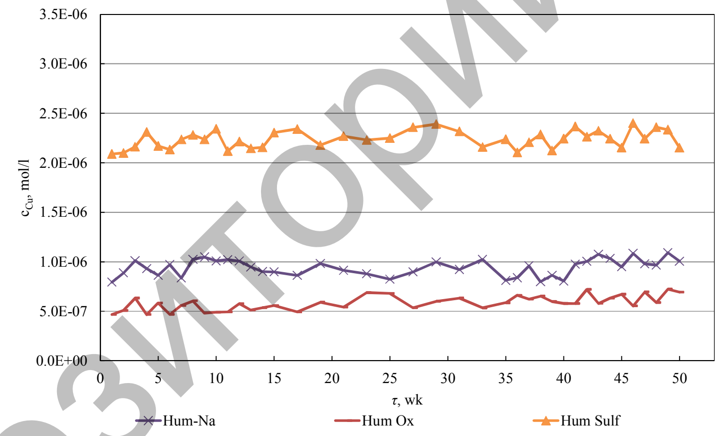

Figure 8. Dependences of copper extraction from copper sulfide into solution by humic complexing agents

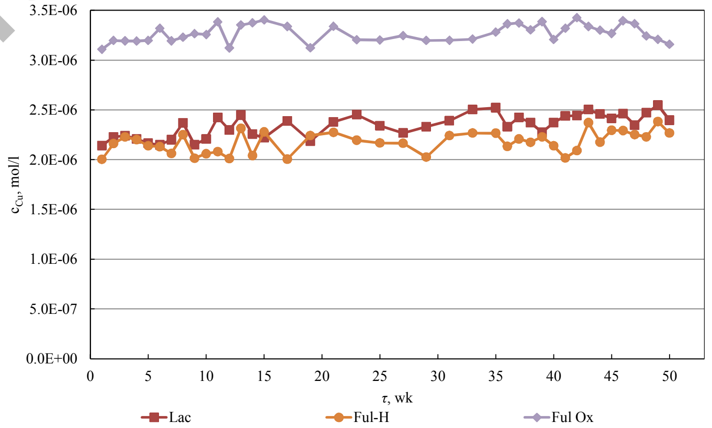

Figure 9. Dependences of copper extraction from copper sulfide into solution by fulvic complexing agents and lactate ion

For the other group of complexing agents, the oxidized derivative of fulvic acid has higher efficiency for copper sulfide. The lactate ion and the oxidized fulvic acid have a little lower efficiency for copper oxide. For copper sulfide, the lactate ion has less efficiency.

For chemically modified humic derivatives, the sulfonate derivative is more effective than sodium humate, and the oxidized derivative has a little lower efficiency. The oxidized derivative of fulvic acid has a higher efficiency than the native fulvic acid. For these compounds, Figures 10 and 11 show the kinetic curves of the copper ions transition into the solution with complexing agents at the initial stages of time.

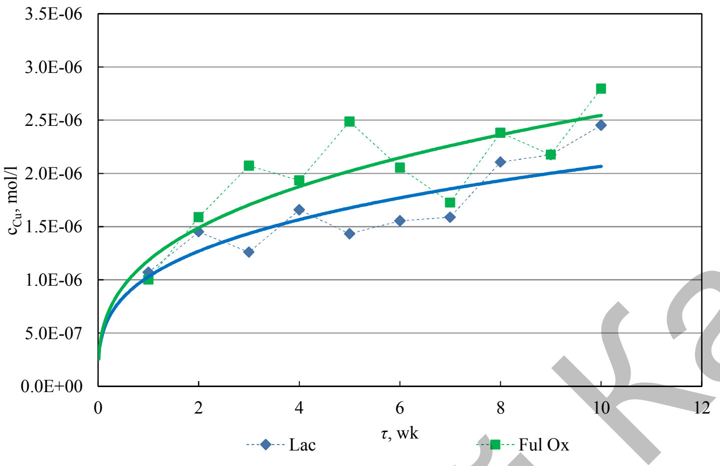

Figure 10. Kinetic curves for the lactate ion and oxidized derivative of fulvic acid for copper oxide

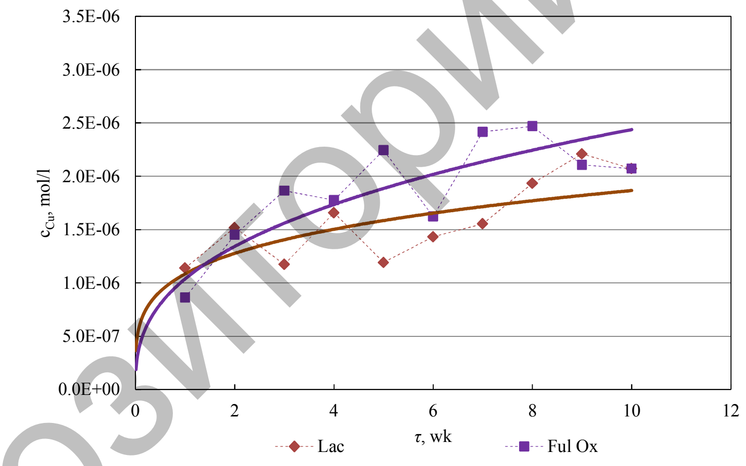

Figure 11. Kinetic curves for the lactate ion and the oxidized derivative of fulvic acid for copper sulfide

It can be seen from the figures, the kinetic curves for the dissolution of copper oxide and sulfide compounds with the participation of the complexing agents are characterized at the initial stage by a very steep rise, followed by a gradual increase in the concentration of copper ions in the solution to equilibrium. Analysis of the graphical shapes of kinetic curves allows us to conclude that the equilibrium value of the concentration of copper ions in solution for the lactate ion is in the range 2.5–3 µmol/l, and for the oxidized derivative of fulvic acid is in the range 3–3.5 µmol/l.

Since the rate of accumulation of products during the dissolution of copper compounds obeys the relations $dc/dt<0$ and $d^2c/dt^2<0$, the processes correspond to a simple chemical reaction with a low order of reaction in the final product, which slowly approaches equilibrium concentrations. Under the considered conditions, the proceeding reaction is heterogeneous, and due to the low dissolution rates of the copper compounds, the interface area can be considered a constant value, and the concentration of the complexing agent in the solution is also maintained at a constant level. Thus, the concentration of the initial substances does not have a decisive influence on the kinetics of the process (that is, they enter the kinetic equation in the form of constants). Formally, the kinetics of the reaction can be described by the reaction product, that is, by the concentration of copper in the solution, which enters the kinetic equation as the difference between some conditional initial concentration of copper in the solution that is greater than the true equilibrium concentration of copper in the solution:

$$\upsilon = k([\mathrm{Cu}]_{\mathrm{init.}} - [\mathrm{Cu}^{2+}]).$$

When the equation is differentiated, all constants are transformed into a new constant. The linearization of the resulting equation by logarithm gives an array of velocities in the investigated interval (Fig. 12, 13).

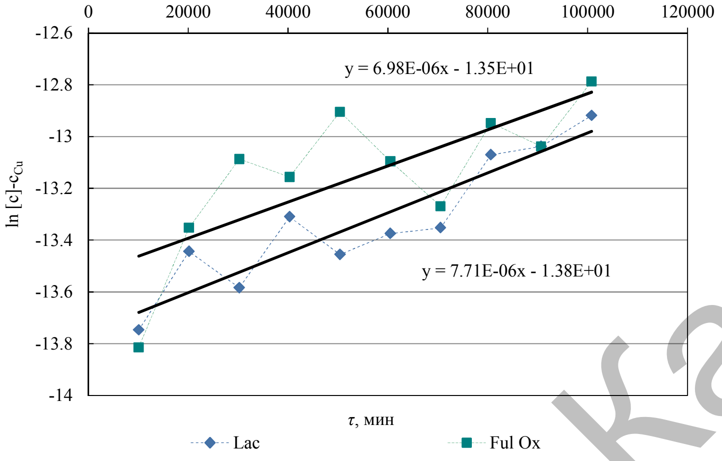

Figure 12. Kinetic equations of lactate ion and oxidized fulvic acid derivative for copper oxide in logarithmic form

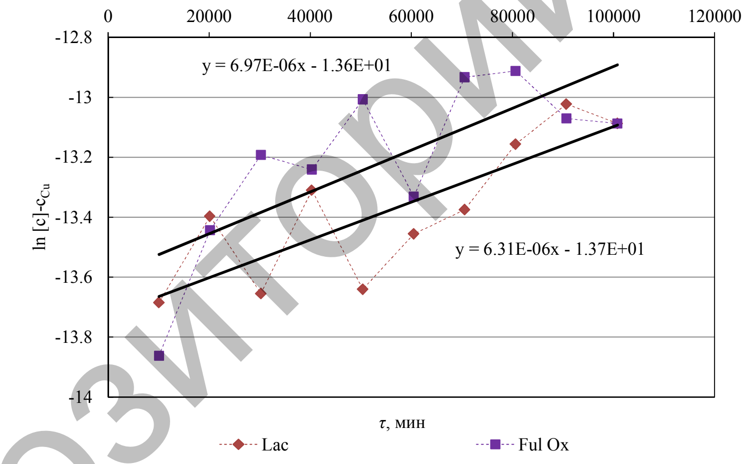

Figure 13. Kinetic equations for the lactate ion and oxidized fulvic acid derivative for copper sulfide in a logarithmic form

The dependences obtained are satisfactorily described by the equation of a straight line. The rate constant for the reaction involving the oxidized fulvic acid derivative is the same value $1.16 \cdot 10^{-7}$ s^{-1} in both cases, whereas in the lactate-ion reaction the rate constant is $1.28 \cdot 10^{-7}$ s^{-1} for copper oxide and $1.05 \cdot 10^{-7}$ s^{-1} for copper sulfide. Thus, the oxidized derivative of fulvic acid has the same efficiency with respect to oxide and sulfide minerals, and the lactate ion has a somewhat higher efficiency in the case of oxide minerals.

Conclusion

The kinetic curves of the transition of copper ions to the solution under the action of complexing agents are characterized by a relatively small transition period and a rapid yield to the steady-state regime. The absence of an induction period and early attainment of concentrations close to equilibrium indicate a good ability to transfer copper ions to the solution for the selected complexing agents.

The use of chemical modification of chelating agents, as a rule, promoted their effectiveness. Nevertheless, the oxidized humic derivative showed a little lower efficiency than the original sodium humate. In general, the investigated complexing agents are placed in following series in accordance with their effectiveness in the case of copper oxide:

Hum Ox < Hum-Na < Ful-H < Hum Sulf < Ful Ox < Lac,

and in the case of copper sulfide:

Hum Ox < Hum-Na < Ful-H < Hum Sulf < Lac < Ful Ox.

For oxide copper minerals, the most effective complexing agent is the lactate ion, and the oxidized derivative of fulvic acid has a little lower efficiency. Less effective agents are the sulfonated humic derivative and the native fulvic acid which have approximately equal effectiveness. The sodium humate and the oxidized humic derivative are least effective agents. In the case of sulfide minerals, the most effective complexing agent is the oxidized derivative of fulvic acid. The lactate ion, the sulfonated humic derivative and the native fulvic acid are a little less effective agents. The sodium humate and the oxidized humic derivative have comparatively low efficiency.

The effectiveness of the complexing agents studied can be given some relative quantitative assessment if it is described their ability to transfer copper ions into solution as compared to the concentration of copper in the solution obtained by passing pure water through the column without the participation of complexing agents. This concentration is 0.15 μmol/l in average. In view of this, the above series can be written for the case of oxide minerals as:

5.6 Hum Ox < 9.1 Hum-Na < 15.1 Ful-H < 15.3 Hum Sulf < 17.6 Ful Ox < 19.6 Lac,

and for the case of sulfide minerals:

4.5 Hum Ox < 6.4 Hum-Na < 14.9 Ful-H < 15.2 Hum Sulf < 16.5 Lac < 22.1 Ful Ox.

Thus, among studied complexing agents the lactate ion and the oxidized derivative of fulvic acid are the most effective complexants towards both copper oxide and sulfide minerals.

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Д.Б. Гоголь, И.Е. Рожковой, Д.Л. Пономарев, В.Н. Фомин

Органикалық комплекстүзуші әсерінен тотықты және сульфидті қосылыстардан мыс иондарының ерітіндіге көшу үдерісін зерттеу

Мақалада құрамында 0,02 % оксиді мен сульфиді бар топырақтағы мысты табиғи және химиялық модифицирленген комплекстүзушілердің ерітінділерімен сілтісіздендіру үрдісін зерттеу нәтижелері келтірілген. Грунттың бір үлгісінің жалпы мөлшері 500 г. Комплекстүзуші ерітінділері берілген жылдамдықпен өткізілетін бағаналарға топырақтың үлгілері орналастырылды. Сілтісіздендіргіш агенттер ретінде натрий гуматы, сульфирленген және тотыққан гумин қышқылы, табиғи және тотыққан фульвоқышқыл және натрий лактаты зерттелді. Барлық реагенттердің 0,01 %-дық ерітінділері оксидті және сульфидті қоспалардан мыстың ерітіндіге өтуіне септігін тигізеді. Ең тиімді мысты топырақтан алып шығаруды тотыққан және табиғи фульвоқышқыл мен натрий лактаты көрсетті. Лактат-ион мыстың оксидті минералдары үшін неғұрлым тиімді кешенді түзгіш болып табылады; тотыққан туынды фульвоқышқылының тиімділігі неғұрлым азырақ. Төмен тиімділікке ие агенттер сульфатталған гуматты туынды мен еркін фульвоқышқылы болып табылады, олар тиімділігі бойынша жуықтағанда бірдей. Натрий гуматының белсенділігі баяу, бұл жағдайда тотыққан гуматты туынды неғұрлым аз тиімділікке ие болады. Сульфидті минералдар жағдайында ең тиімді комплекстүзуші болып фульвоқышқылдың тотыққан туындысы табылады. Лактат-ион, сульфатталған гуматты туынды мен еркін фульвоқышқылы тиімділігі неғұрлым төмен агенттер ретінде есептеледі. Натрий гуматы мен тотыққан гуматты туындының тиімділігі салыстырмалы түрде төмен. Кинетикалық мәліметтерді математикалық өңдеу нәтижесінде мысты топырақтардан сілтісіздендіру процестерінің жылдамдықтарының константалары анықталған. Олардың шамалары $1{,}05\cdot10^{-7}$-тен $1{,}28\cdot10^{-7}$ с$^{-1}$ дейін аралығында. Мыстың иондарының ерітіндіге ауысуының кинетикалық қисықтары кешенді түзгіш әсерінен аздаған ауыспалы кезең мен тепе-теңдік күйге жақын концентрацияға жылдам қолжеткізумен сипатталды.

Кілт сөздер: гумин қышқылдары, фульвоқышқылдары, сульфирленген гуминді қышқылдары, тотыққан гуминді қышқылдары, тотыққан фульвоқышқылдары, малахит, минералдар қалыптастыру, мыс шаймалау кинетикасы.

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Изучение процессов перехода ионов меди в раствор из оксидных и сульфидных соединений под действием органических комплексообразователей

В статье описаны результаты изучения процесса выщелачивания меди из модельных грунтов, содержащих 0,02 % оксида или сульфида меди, растворами природных и химически модифицированных комплексообразователей. Общее количество одного образца грунта составляло 500 г. Модельные грунты размещались в колонках, через которые с заданной скоростью пропускались растворы комплексообразователей. В качестве выщелачивающих агентов исследованы гумат натрия, сульфированная и окисленная гуминовая кислота, нативная и окисленная фульвокислота, а также лактат натрия. Показано, что растворы всех реагентов с концентрацией 0,01 % вызывают переход меди в раствор как из оксидной, так и из сульфидной смеси. Установлено, что наиболее эффективны для извлечения меди окисленная и нативная фульвокислота и лактат натрия. Для оксидных минералов меди наиболее эффективным комплексообразователем является лактат-ион, окисленное производное фульвокислоты обладает немного меньшей эффективностью. Далее менее эффективными агентами являются сульфированное гуматное производное и свободная фульвокислота, которые приблизительно равны по эффективности. Гумат натрия менее активен, окисленное гуматное производное имеет более низкую эффективность. В случае сульфидных минералов наиболее эффективным комплексообразователем является окисленное производное фульвокислоты. Лактат-ион, сульфированное гуматное производное и свободная фульвокислота являются немного менее эффективными агентами. Гумат натрия и окисленное гуматное производное имеют сравнительно низкую эффективность. Путем математической обработки кинетических данных установлены константы скоростей процессов выщелачивания меди из модельных грунтов. Значения найденных констант находятся в пределах от $1{,}05\cdot10^{-7}$ до $1{,}28\cdot10^{-7}$ с$^{-1}$. Кинетические кривые перехода ионов меди в раствор под действием комплексообразователей характеризуются сравнительно малым переходным периодом и быстрым достижением концентраций, близких к равновесным.

Ключевые слова: гуминовые кислоты, фульвокислота, сульфированные гуминовые кислоты, окисленные гуминовые кислоты, окисленные фульвокислоты, малахит, минералогенез, кинетика выщелачивания меди.

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