USE OF CONJOINT REACTIONS FOR EXTRACTION OF METALS FROM MINERAL RAW MATERIALS

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Abstract

In the article there are some data on extraction of metals into a solution from compound mineral raw materials by means of electrochemical leaching. Leaching reagent (sodium thiosulfate, etc.) was obtained at the same time with reaction of resolving metals in a solution of sodium alkali. Resource of sulfur for obtaining the leaching reagent was a composite sulfur-graphite electrode, which was used at metal resolution as a cathode and as an anode. At that there were obtained similar results on extraction of metals into a solution.

Keywords: Leaching, electrochemical reactions, composite electrode

Introduction

Increasing of scopes and variety of topics of research on development of hydrometallurgical methods of metal extraction into a solution are determined by deterioration of quality of recovered metal ore, involving multi-component and refractory raw materials into production, and by necessity of recycling of technogenic waste and secondary raw materials. For example, in the work (Mineyev G.G. etc, 1994) gold and silver resolving by resolvents of different types is introduced. In several developed technologies, gold is extracted from refractory sulfide gold ores and concentrates after their hydrometallurgical treatment for transition of compounds into resoluble state (oxidation of pyrite and arsenic pyrite in leaching autoclaves, nitric uncovering, bacterial leaching) (Lodeishchikov V.V. 1999; Kholmogorov A.G. etc, 2000). Hydrometallurgical preparation of sulfide concentrates allows obtaining chemical products, from which gold can be extracted by means of leaching with non-cyanide complexing reagents. Processes with application of thiocarbamide and thiosulfate solutions were used for extraction of gold from different mineral products (Mineyev G.G. etc, 1994; V.V. 1999; Kholmogorov A.G. etc, 2000; Gold Hydrometallurgy 1999; Kholmogorov A.G., Kononova O.N. ect, 2000). Apart from purely chemical methods of intensification of metal extraction into solutions, there are widely used physical and physicochemical methods of intensification of chemical reactions: destruction of crystal structures of mineral formations with mechanochemical processes and different physical effects, use of wave characteristics of chemical processes and so on. Technical methods, which are being developed for intensification of metal extraction into a solution, are designed to provide individualization of phases of precious metals and impurity elements for their selective extraction. According to results of this research it is obviously that recent research does not take into account forces of “adhesion” of basic minerals with minerals of enclosing rock, though many technologies are directed to overcome these forces (e.g., Khmelnitskaya O.D. etc, 2010; Groot E.A., Algebraistova N.K. 2010; Patent 2460814 Russia and others). For example, in (Khmelnitskaya O.D. etc, 2010) it is said that the reaction, limiting the rate of oxidation of the main mineral (which has a big effect on oxidation-reduction processes in sulfide-oxide systems), pyrite, is the stage of its chemical interaction with an oxidizing agent. Element sulfur, which is one of oxidation products, does not form conglomerates with pyrite particles due to dispergating action of oxide component of the concentrate. In view of overcoming difficulties at leaching, connecting with the above processes, application of electric current is very important in development of new technologies. It was shown that electrochemical treatment of solutions is an advanced method of intensification of leaching process. At low capital and operating costs and minimum impact on the environment electrochemical treatment will allow using “lean” and refractory mineral raw materials, providing integrity of mineral resources exploitation (Pavlova L. 2011). In (Vafaeian S. etc 2011) there is a method of intensification of cyanide leaching of Au in the presence of pyrite, chalcopyrite, sphalerite and chalcocite. It is shown that electrical treatment leads to decreasing negative influence of sulfide minerals on leaching process due to formation of galvanic pair with pyrite. Preliminary oxidation of sulfides accelerates cyanidation of Au. Reactions of transition of metals into solutions with different chemical composition by means of electric current – electrochemical leaching – takes a special place in research of electrochemical processes. Shulgin L.P. has undertaken a lot of researches on application of electrochemical processes on alternating current: on reduction and oxidation of different compounds in solutions, on study of resolving rate and other factors, occurring in solutions under influence of alternating current etc.([Celep Oktay etc 2011 and others). We can state that to date there was experimentally shown possibility of effective application of electric current with different parameters as a certain “chemical agent” for moving chemical balance to the required side. In the above works and others, in particular, it is shown that under influence of alternating and pulsating currents in solutions there are some different changes of physicochemical properties due to changes in solution structures, including structures of solvates and resolvents. Recent methods of extraction of metals into a solution from refractory ores are based on combination of traditional processing methods, which do not meet requirements of industrial production. Such methods do not provide effectiveness of extraction of metals from raw materials, do not provide reducing power consumption per ton of produced metal and reducing quantity of technogenic waste. It is caused by the following circumstances:

- chemical processes in nonorganic water solutions are studied insufficiently, as scientific notation of single-component liquids structure are quite indistinct, and research of liquid solutions structure, especially multi-component solutions, is more complicated problem;
- conjoint electrochemical reactions, which occur in solution volume, are not also fully studied;
- there are not fully studies chemical reactions, which allow reducing quantity of operations in the processing chain “ore – technology – metal”.

We have developed a method of electrochemical leaching of nonferrous and noble metals from compound, refractory and technogenic raw materials by means of combined process of electrochemical obtaining of leaching and simultaneous transition of metals into solution (Beisembetov I.K. 2012). Metals are leached in solution of sodium alkali. A composite sulfur-graphite electrode (Certificate of Authorship USSR: 4693944.04 17.03.89) is applied as a resource of leaching reagent and its electrochemical treatment allows obtaining sodium thiosulfate and other sulfur-bearing sodium compounds in alkali solution. In our research on electrochemical leaching, sulfur-graphite electrode was applied as a cathode and as the anode. In this article there are some results on leaching of gold and silver from compound raw materials in laboratory conditions by means of conjoint electrochemical method.

Data and Results:

Experiments on extraction of nonferrous and noble metals from compound mineral raw materials using a sulfur-graphite electrode were carried out with the use of gold and silver concentrate. The concentrate composition, %: Au – 31 g/t; Ag – 68.5 g/t; Cu – 1.2; Pb – 41.0; Ba – 9.4; Ti -5.1; Zn – 0.3; Cr – 0.5; Mn – 0.2; Co – 0.1; As – 3.4; Sb – 0.02. Preliminarily regrounded material was reclaimed by quartering. Then using the InnovXSystems X-ray fluorescence spectrometer in six sub-samples of reclaimed starting material, concentrations of elements (metals and nonmetals: chlorine, sulfur, arsenic, stibium) were determined, after that average values of concentrations on each element were calculated.

In the work there was used a particle of monodisperse material – gold and silver concentrate with particle size -0.16 + 0.074 mm (95 %) and with specific surface of 4.5 m^2.

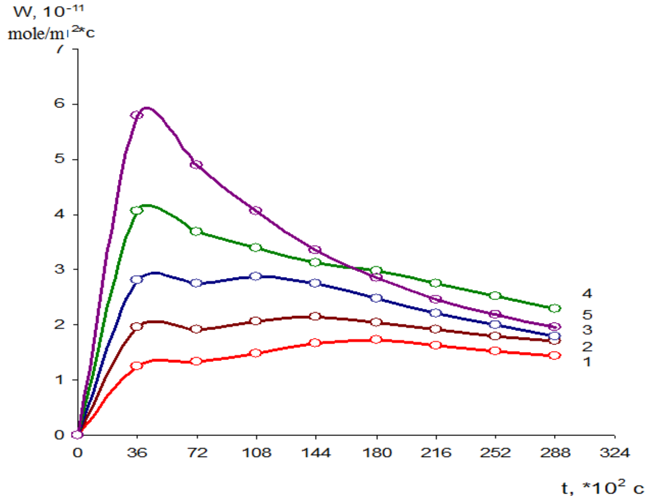
Experiments were carried out in a thermostated reaction cell with three-electrode system, which consists of the working electrode, reference electrode and auxiliary electrode. A sulfur-graphite electrode was used as the cathode. A silver-chloride electrode was the reference electrode and a graphite electrode was the anode.

25 g of a sub-sample concentrate was put into the reaction vessel in solid to liquid ratio 1:10, sodium hydroxide solution of required concentration and volume 250 ml was poured. The vessel was heated up to required temperature. Electric leaching was held at current density i, equal to 200 A/m^2. The solution was mixed, and turnover rate of the mixer was 480 rpm. Solutions with concentration of sodium hydroxide NaOH: 0.1 M, 0.3 M, 0.5 M, 1.0 M and 2.0 M were used at the research.

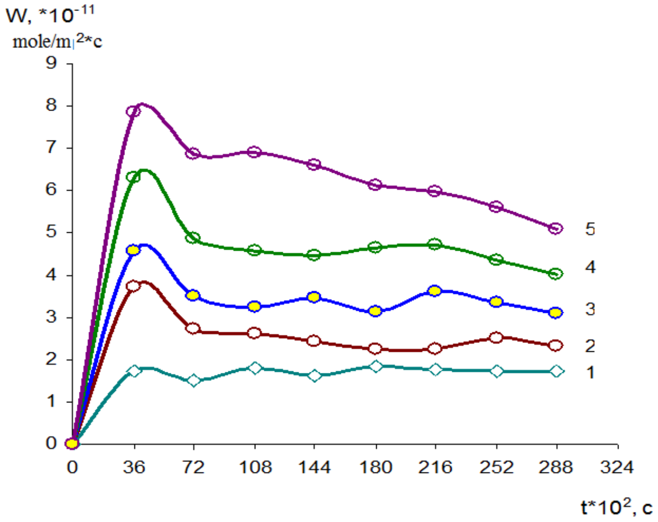
Assays of gold, silver and other metals in liquid and solid phases were held using the atomic absorption spectrometer “contr AA 300” in accordance with standard methods. For preparation of samples of basic material and leaching cakes there was used Sample fast deterioration system “Microwave Reaction System” of “Multiwave 3000” brand produced by ”Anton Paar” Company. Assay of accompanying metals was held by mean of InnovXSystems X-ray fluorescence spectrometer. IR-spectroscopic research of solutions and solid samples was conducted using IR-Fourier-spectrometer “Avatar 370”.

It was determined that in the experiment conditions there was a reaction of oxidation of sulfur, which is included in the composite electrode with formation of sodium polysulfides (tiosulfate-, sulfite-, sulfate-, hydrosulfide- and sulfide-ions). And all the listed anions, except sulfate-ion, can form complex anions with noble and accompanying metals.

Results of research of specific rate of gold resolving in sodium hydroxide solutions of different concentration are shown in Figure 1. Figure 2 shows relationship of specific rate of silver resolving with leaching time. In Figures 1 and 2 we can see that specific rate of gold and silver resolving increases quite fast in the first 60 minutes of leaching. Then resolving rate is reduced, at that reducing rate of silver resolving is inconsequent, in contrast with rate of gold resolving. It may mean change in silver solving process (settling-out, stopping of reaction due to change in the structure of leached solution etc.). It is also obvious that process of conjoining reactions of obtaining leaching agent and reaction of transition of metals into a solution in the same volume may be a very effective method for treatment of compound and refractory mineral raw materials, as recent methods of extraction of metals into a solution from refractory ores are based on combination of traditional processing methods, which at the present time do not meet requirements of industrial production, do not provide effectiveness of extraction of metals from raw materials, do not provide reducing power consumption per ton of produced metal and reducing quantity of technogenic waste.



C_{NaOH}: 1 – 0.1 M; 2 – 0.3 M; 3- 0.5 M; 4- 1.0 M; 5 – 2.0 M
Figure 1. Relationship of specific rate of gold resolving with leaching time in sodium hydroxide solutions of different concentration.



C_{NaOH}: 1 – 0.1 M ; 2 – 0.3 M; 3- 0.5 M; 4- 1.0 M; 5 – 2.0 M
Figure 2. Relationship of specific rate of silver resolving with leaching time in sodium hydroxide solutions of different concentration.

Below there are experimental data on leaching of nonferrous and noble metals by electrochemical method, using the sulfur-graphite electrode as the anode. The graphite electrode served as the cathode. Other leaching conditions are the same as the above.

Figures 3 and 4 show data on relationship of specific rate of gold and silver resolving in 0.1 M of sodium hydroxide solution at different current densities (50-200 A/m^2). As we can see in Figures 3 and 4, specific rate of metal resolving increases fast in the first 30 minutes of leaching, that is maximum rate of solving is achieved twice as fast as using sulfur-graphite electrode as the cathode. At that reducing rate of resolving is consequent both for gold and silver.

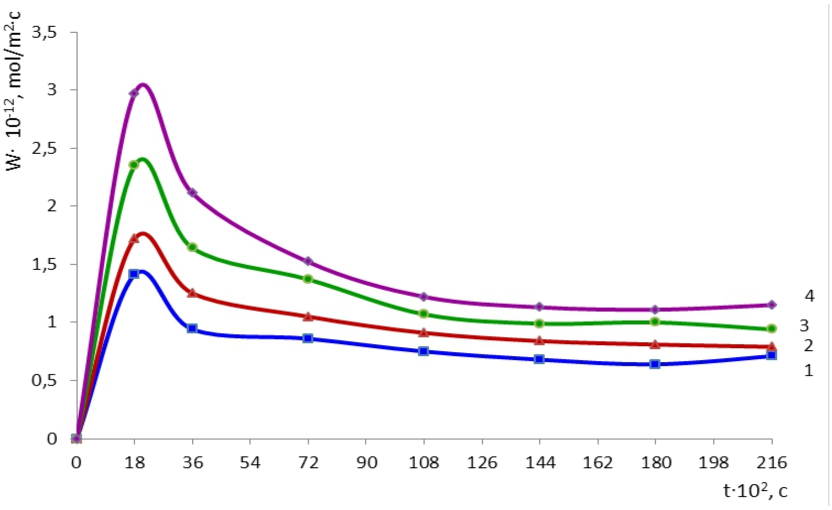


Figure 3. Specific rates of gold leaching processes depending on current density, A/m^2: 1 – 50, 2 - 100, 3 - 150, 4 – 200

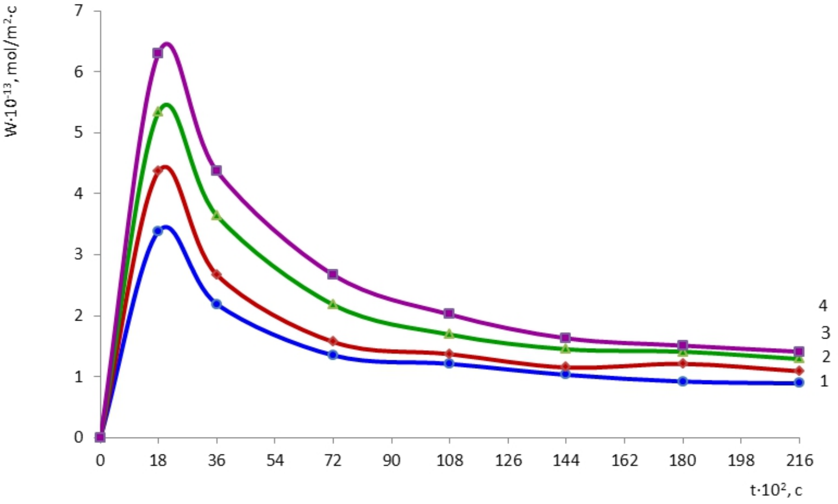


Figure 4. Specific rates of silver leaching processes depending on current density, A/m^2: 1 – 50, 2 - 100, 3 - 150, 4 – 200

Increasing current density leads to consequent increasing specific rate of reaction of metal transition into a solution. The same results were obtained also for data on leaching in solutions containing sodium hydroxide, M: 0.2; 0.5; 1.0; 2.0 and 5.0.

As it is known, mechanism of chemical reactions in nonorganic water solutions is studied insufficiently, as scientific notations about structure of single-component liquids are quite indistinct, and research of liquid solutions structure, especially multi-component solutions, is more complicated problem. Next publications will represent our researches on particularities of solutions formed during electrochemical leaching using the sulfur-graphite electrode. Only few IR-spectra of leaching solutions are described in this article as an example.

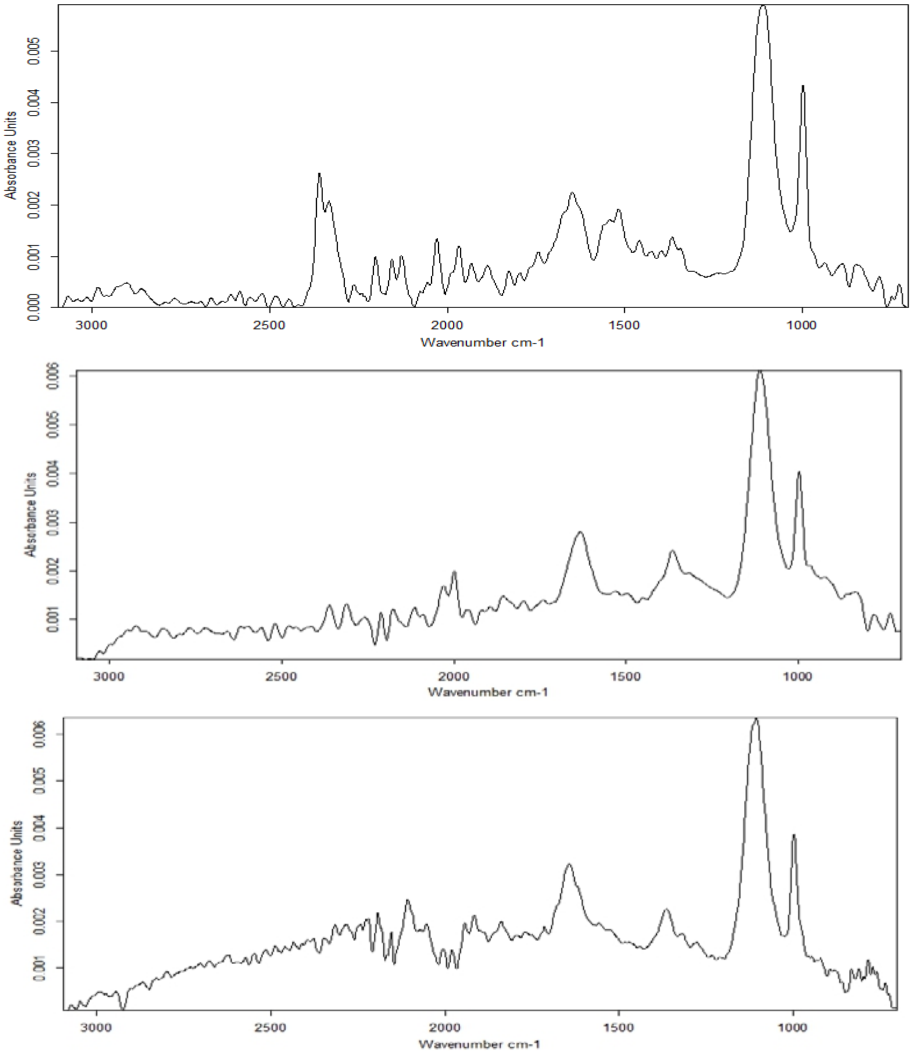


Figure 5. IR-spectra of leaching solutions after 1, 2 and 3 hours (from top to bottom)

IR-spectroscopic assay of leaching solutions showed that the studied solutions have compound microstructure and contain different thio-compounds of sodium. For example, Figure 5 shows IR-spectra of solutions obtained after leaching of concentrate with 0.1 M NaOH solution at current density 150 A/m^2, after 1, 2 and 3 hours of holding the experiment. In particular, in the spectra there were detected groups $[S_2O_3]^{2-}$ 1113 cm^{-1}, 996 cm^{-1} and group $[SO_3]^{2-}$ - 1113 cm^{-1}, 996 cm^{-1}. Titrimetric analysis for combined content of thiosulfate- and sulfite-ions also showed the presence of the both ions in reaction medium. In addition, the spectra character points to considerable changes of molecular composition of the solutions during leaching.

Conclusion

As it follows from the above experimental data, metal leaching process by means of conjoint electrochemical reactions by means of a sulfur-graphite electrode runs successfully both in the case of using the sulfur-graphite electrode as an anode and in the case of using the sulfur-graphite electrode as a cathode. Indications of effectiveness of metal extraction into a solution generally coincide. It points to the fact that limiting processes in these reactions are reactions of oxidation, complex formation and succeeding transition of metal compounds into water solution, not reactions of leaching formation. This circumstance also confirms that cumulative period of resolution reaction does not play an essential role in running processes.

There was developed an innovative method of matching reactions of leaching obtaining and reactions of transition of metals into a solution by means of composite sulfur-graphite electrode, which allows essentially shortening the processing chain “mineral raw materials – metal” and using sulfur, which is waste of petrochemical production.

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