УДК-543.056; 543.422

INTENSIFICATION OF SAMPLE PREPARATION FOR ATOMIC ABSORPTION BY PLASMA TREATMENT

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A new express method of sample preparation for the atomic absorption determination of noble metals in sulphide copper-nickel ores has been developed. The method is based on the use of plasma treatment on the stage of sample preparation. It allows one to improve the noble metal extraction degree, and to simplify and shorten the sample preparation stage as compared to the standard methods. The main effects of plasma treatment can be summarised as follows:

- Formation of hydrogen peroxide in the solution which acts as an additional oxidant.

- Fragmentation of ore particles that increases their specific surface and accelerates all transfer processes on the liquid-solid interface.

- Activation of atomic bonds on the solid surface of ore particles.

KEY WORDS: plasma treatment, sample preparation, atomic absorption, sulphide copper-nickel ore, noble metals

1. Introduction

The stage of sample preparation, which includes such long operations as drying, decomposition and concentrating, is still the most time- and labour-consuming stage of an analytical cycle. Methods of intensification of sample decomposition are based on the use of high-aggressive agents, elevated temperature and/or pressure as well as on the application of physical fields such as ultra-sound and electromagnetic irradiations [1, 2]. The use of the above physical fields is known to form free radicals, change structure and ion reactivity of solutions, intensify mass transfer processes, break polymeric chains, etc. [3].

A few examples of the successful application of the microwave radiation to accelerate drying and decomposition of samples were described in literature [3, 4]. In particular, low-temperature non-equilibrium plasma can be used for intensification of decomposition of samples [3]. However, the nature of the observed plasma effect has not been discussed yet.

In the present study, a new procedure for the express determination of noble metals, such as Pt, Ag and Pd, in sulphide copper-nickel ores is developed. The procedure is based on the plasma-chemical treatment of samples followed by atomic absorption analysis (AAA). Scanning electron microscopy (SEM) and Auger electron spectroscopy (AES) are used to study mechanisms of the effect of plasma discharge on samples at various sample preparation stages.

2. Experimental

2.1 Sample materials and chemicals

Samples of sulphide copper-nickel ores of the Norilsk deposit (Russia) with different Ag, Pt and Pd contents were used to develop a new procedure of the express determination of noble metal concentrations. The ore used consists of a mixture of three main minerals, namely: pyrotine (FeS), pentlandite ($(NiFe)_9S_8$) and chalcopyrite ($CuFeS_2$) which totally amount to 80% of the crude ore. The rest contains various compounds, mainly oxides and carbides, of iron, copper, nickel and cobalt. Platinum, palladium and silver are in the form of metallic impregnations in the ore. The concentrations of noble and other main metals (Fe, Cu and Ni) were preliminary determined by the independent methods such as flame and thermal-electric atomic absorption analysis. The samples for such analyses were prepared in

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a standard manner with the use of HF, HCl and HNO$_3$ acids [6]. The measured concentrations of noble metals are considered as the standard values and they are shown in Table 1.

Standard solutions of complex Pd, Pt, Au and Ag chlorides were used to prepare the standards for atomic absorption analysis. Concentrated high purity HF, HCl and HNO$_3$ acids were used for sample decomposition.

2.2 Procedures of sample preparation

Two different approaches were used for sample preparation with the aim to compare their effectiveness and thus to achieve the paper goal. The first approach includes the well-known standard procedure which is based on the acid decomposition [6]. The second approach is based on the proposed plasma-chemical treatment of samples. The main stages of both procedures are as follows.

1. In all the cases, 2.5 gram ore samples were first reduced to fine particles in a porcelain mortar and then annealed at 700°C for 1.5 h in air to remove sulphur and some other impurities.
2. The second stage was aimed at the sample dissolution. For the standard procedure, as-annealed samples were heated in a 3:1 mixture of the concentrated HCl and HNO$_3$ acids using a water bath. The standard heating time was 60 min. For the proposed plasma-chemical procedure, a combination of plasma discharge treatment and heating in the same acid solution was applied to as-annealed ore samples. The effectiveness of the plasma treatment was studied as a function of treatment time, acid volume and consecution of the applied operations.
3. Finally the solutions obtained during the dissolution stage were prepared for AAA. For the case of standard procedure, the dissolved ore samples were three times evaporated to a moist salt state. Before the second and the third evaporation, 5 ml of diluted (1:1) HCl was added to the solution. Then the solution was filtered and reduced to the volume of 50 ml with the use of 1M HCl. For the case of plasma-chemical treatment, the dissolved ore samples were evaporated only once with or without acid additions. Any further procedures were similar to those described above.

The regimes used for the sample preparation are listed in Table 2. The regime shown as Regime 1 corresponds to the standard procedure. Regimes 2-7 correspond to various regimes of the plasma-chemical procedure under development. The consecution of the operations used (Regimes 2-4), the duration of plasma treatment (Regimes 2, 5 and 6), and the amount and concentration of the acids used (Regimes 2, 7 and 8) were the main optimisation parameters.

2.3 Equipment and experimental methods

Plasma treatment of geological samples was performed using the laboratory reactor. The reactor represents a molybdenum glass cylinder with external water-cooling. The glass with a sample is placed into the reactor. The electrodes are set in parallel to each other in sockets of the removable cylinder head so that a lower part of the anode is plunged into the dissolved sample while a lower part of the cathode is located above the solution surface. The anode is made of platinum wire soldered into a glass tube. The cathode is made of a stainless steel rod. The reactor is pumped out with a vacuum pump. The described equipment allows one to treat powder samples moistened with small amount of the aggressive liquid chemicals (acids) and also allows sample mixing.

The parameters of power supply were as follows. The output DC voltage varied from 700 to 1500 V. The maximal load current was 0.25 A. The pulse voltage used for plasma initiation was usually 12-15 kV at a pulse duration of 1-1.5 ms. The voltage of plasma discharge, which is mainly dependent on the gas pressure used in the reactor, was usually equal to 750-900 V.

The effectiveness of sample decomposition was found to be a function of the plasma discharge current and the gas pressure. The preliminary studies made show that the discharge becomes unstable at pressures higher than 3×10^4 Pa while the solution starts to boil at pressures lower than 10^3 Pa. Thus, the optimal pressure range which was used in our experiments is $(0.5-1) \times 10^4$ Pa. The optimal current range is 40-50 mA. Increasing the current above 50 mA does not improve the decomposition effectiveness but promotes a very active boiling and spitting of the solution and, thus, destabilises the plasma treatment process. Lowering the current below 40 mA increases the treatment duration and reduces the extraction degree. The discharge becomes unstable when the current is lower than 15 mA.

The atomic-absorption spectrophotometer «Saturn-3P1» with a complex for thermal-electric atomisation «Grafit-2» was used for determination of the noble metal concentrations. All measurements were carried out in a concentration range corresponding to a linear dependence of the absorption signal versus element concentration. For all schemes showed in Table 2, the decomposition of samples followed by the measurement of analytical signals was performed three times to average the results

The degree of element extraction for a given procedure was calculated as a ratio of the average concentration C_k, which was measured using a given procedure to the known element concentration C_0. Closeness of the calculated C_k/C_0 ratio to 1 was considered as a measure of the completeness of the extraction process.

Chemical reactions, which take place in the solution in the course of plasma treatment, were monitored by the spectrophotometric method described in work [7]. In particular, the presence of a complex $[Ti \times H_2O_2]^{2+}$ compound gives evidence to the formation of peroxide in the solution.

Effect of plasma treatment on the surface composition and morphology of ore particles was mainly studied for the ore sample shown as No 1 (Table 1). Ore particles were taken for the microstructural studies on the following sample preparation stages:

1. As-received ore samples after milling to fine particles,
2. As-annealed ore particles (annealing at 700°C for 1.5 h),
3. As-annealed ore particles after decomposition in acids by the standard procedure (Regime 1, Table 2),
4. As-annealed ore particles after plasma-chemical decomposition (Regime 7, Table 2).

Morphology of individual particles was studied by SEM, while the surface analysis was performed by AES. The Auger analyses were performed in the ultra-high vacuum chamber (UHV) (about 10^{-7} - 5×10^{-8} Pa) of the scanning Auger microprobe JAMP-10S, JEOL. The ore samples treated in acid mixtures were dried before loading into the UHV chamber. The accelerating voltage of the primary electron beam and the beam current were 10 kV and 10 nA, respectively. The diameter of the beam was approximately 1 μm. The spectra were recorded in the derivative mode, $dN(E)/dE$ versus the kinetic energy, E with a cylindrical mirror analyser. The energy resolution, $\Delta E/E$, of the analyser used was approximately 0.6%. All spectra were recorded in an energy range 50-1000 eV with a step 1 eV. The following Auger peaks were detected and measured on the surface: Fe LMM series, C KLL, O KLL, S LMM, Ni LMM, Cu LMM, Cl LMM and Si LMM. A minimum of 15 - 20 spectra was usually accumulated from individual particles of any sample. The following formula was used for spectra quantification:

$$C_i = \frac{I_i S_i}{\sum I_j S_j}$$ (1)

Evidently the formula used is simplified because it does not take into account possible contributions of the matrix effects, electron backscattering as well as possible effects of the chemical inhomogeneity in nearest subsurface layers. However, the calculation results are considered as those sufficient for semi-quantitative estimations of the surface composition.

Table 1. Concentrations of main and noble metals in enriched sulphide copper-nickel ores

Ore No	Concentration, mas. %			Concentration, g/ton		
	Fe	Cu	Ni	Pt	Pd	Ag
I	26,70	5,30	2,88	47,58	116,10	19.10
II	29,27	13,80	2,10	41,70	131,16	81,00
III	21,50	5,70	2,00	-	96,20	60,50

3. Results and discussion

3.1 Atomic absorption spectroscopy

The degrees of Ag, Pd and Pt extraction, C_k/C_0 were measured as a function of various parameters of the plasma treatment and shown in Fig. 1. The extraction degrees obtained by the standard procedure (Regime 1, Table 2) are shown as horizontal straight-line segments in Fig. 1 to compare the effectiveness of various sample preparation procedures. The role of consecution of the operations used is
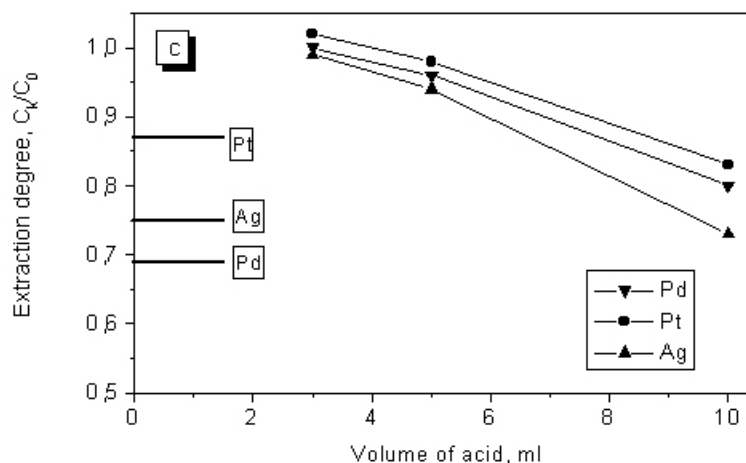
illustrated in Fug. 1a where the values of C_k/C_0 are plotted as a function of heating time performed before the plasma treatment. The total heating time, which includes both pre-heating before the 10 min plasma treatment and after-heating, is constant and equal to 50 min for all regimes under comparison (Regimes 2-4, Table 2). It is found platinum is easily extracted and the Pt extraction degree obtained by any regime of the plasma treatment is comparable with that obtained by the standard procedure. For the other two elements, the plasma treatment regimes under comparison do not show any significant improvement as compared to the standard procedure. However, the use of plasma treatment before heating (Regime 2, Table 2) is usually more effective than that after heating. It appears the plasma discharge produces a stronger effect on a fresh solution when the probe is not dissolved by the acid yet, while it has a weaker influence on the probe after a prolonged acid dissolution.

Figure 1b illustrates a non-monotonic dependence of the extraction degree with plasma treatment time. The plasma treatment for 10 min provides the best extraction degree among the regimes studied. The reason of such an extremal dependence seems to be clear. Any further increase of the treatment time over 10 min heats up the solution and destabilises the decomposition process. On the other hand, a decrease of the treatment time below the optimal value does not allow to complete the extraction process.

Fig. 1. Extraction degree (C_k/C_0) of Ag, Pt and Pd plotted as a function of: a) time of pre-heating in an acid mixture before the plasma treatment, b) time of plasma treatment, c) volume of HCl acid used for the plasma treatment. Three horizontal line segments show the extraction degrees for Pt, Pd and Ag obtained by the standard procedure

Figure 1c demonstrates the effect of acid amount on the extraction degree. The use of a small liquid amount, which is sufficient to cover the sample with a thin acid layer only, is shown to provide the most effective extraction while any further increasing the acid layer thickness decreases the effectiveness of treatment. The effect of liquid amount seems to be connected with configuration of the electrical field applied to the ore sample. In particular, the increase of acid layer promotes defocusing of the electric field tension over the total surface of liquid. If the sample is covered with a very thin liquid layer, the plasma discharge focuses just on the ore sample and thus provides the effective sample decomposition.

As follows from the results obtained, the plasma treatment by Regime 7 (Table 2) provides the highest extraction degree. The ore probe is first treated by the plasma discharge for 10 min at the current 50 mA and the gas pressure 10^4 Pa. The next stages include addition of HCl, evaporation of the obtained solution and finally filtering of the sediment. The obtained probe is ready for atomic absorption analysis.

A few samples of the known noble metal contents (Table 1) were decomposed by Regime 7 and analysed by AAA. When comparing the measured concentrations with the standard values shown in Table 1, the deviations of the experimental data from the regression line shown in Fig. 2 are considered as a measure of the procedural error. All data points obtained for Pd, Pt and Ag lie within the confidence interval. The repeatability of the results was wholly satisfactory and the relative standard deviation did not exceed the value of 0.05.

Table 2. Regimes of the sample preparation procedures used in experiments

Regime No	Acid volume in solution, ml	Plasma treatment time, min	Heating time in acid mixture, min			Notes
			Before plasma treatment	After plasma treatment	Total	
1	10	0	0	0	60	1, 3
2	10	10	0	50	50	2, 4
3	10	10	25	25	50	2, 4
4	10	10	50	0	50	2, 4
5	10	5	0	50	50	2, 4
6	10	15	0	50	50	2, 4
7	3	10	0	0	0	2, 5
8	5	10	0	50	0	2, 5

Notes:
(1) Concentrated mixture of HCl and HNO_3 acids is used for the standard procedure (Regime 1).
(2) Diluted (1:3) mixture of HCl и HNO_3 acids is used for plasma-chemical treatments by Regimes 2-8.
(3) After heating for 60 min, solution is three times evaporated to moist salts. Before the second and the third evaporations, 5 ml of diluted (1:1) HCl is added to the solution.
(4) Single evaporation is performed without acid addition.
(5) 5 ml of diluted (1:1) HCl is added before single evaporation.

The use of plasma treatment by the optimised regime allows one to reach the 100% extraction of noble metals while the experimental time is reduced from 5-7 h to 0.7 h. The use of plasma treatment also reduces the number of operations and the consumption of chemicals as compared to the standard procedure of sample preparation.

Since the system under study consists of three phases, such as air – electrolyte – solid sample, one can suppose that the observed plasma-induced acceleration of sample dissolution is caused either by some processes in the solution or by the direct plasma effect on the solid probe.
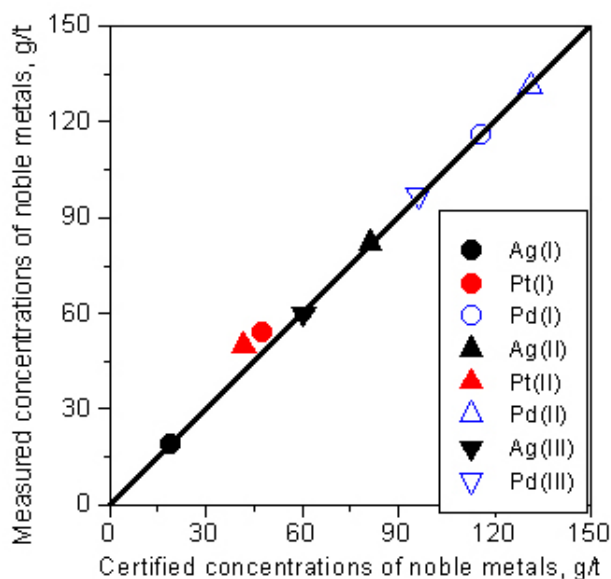
Fig. 2. Deviations of the results of atomic absorption determination from the regression curve for three geological samples with the known Ag, Pt and Pd concentrations

A special idle solution of the acid mixture was prepared and plasma treated by the regimes described in Table 2 to study possible mechanisms of the plasma effect. Formation of hydrogen peroxide was observed in the treated solution by the spectrophotometry. The formation of solvated electrons and various radicals ($H^\bullet$, $OH^\bullet$) in electrolyte solutions under the influence of low-temperature non-equilibrium plasma discharge was already described in literature [9, 10]. The observed formation of hydrogen peroxide results from their recombination. The newly formed H_2O_2 takes part in oxidation-reduction reactions in the solution. It can act as an additional oxidant together with nitric acid and in combination with a complexing agent (hydrochloric acid) to dissolve Pt, Pd and Ag. This observation agrees qualitatively with the results in Fig. 1a which illustrates the maximal effectiveness of the plasma treatment at early stages of sample preparation. Evidently, the earlier the additional oxidant forms, the more effective dissolution proceeds in the course of posterior heating.

Evidently, some changes of the surface microstructure and microchemistry of crystalline ore particles, such as formation of additional reactive centres, phase transitions with possible concomitant deformations, etc, can take place in the course of plasma treatment and heating. Auger electron spectroscopy studies were performed for ore sample No 1 in both as-received and as-treated states. The effect

of the standard treatment procedure (Regime 1, Table 2) on the microchemistry and microstructure was compared with that of the most effective plasma chemical treatment (Regime 7, Table 2).

3.2 Scanning electron microscopy

The specific surface of particles was found to increase under exposure to the plasma discharge. It is illustrated by the SEM microphotographs of individual particles in Fig. 3.

As is seen in Fig. 3a, the particles of as-milled ores exist in the form of relatively fine particles with a high specific surface. The average diameter of such particles, *d*, is equal to approximately 16 μm. Such morphology basically forms in the course of sample milling and is dependent on the characteristics of strength and plasticity and structure of original ore pieces. The ore under studying is a complex conglomeration of the natural minerals, mainly oxides and sulphides, and disseminated noble metals. The principal minerals have sufficient strength and rather limited plasticity. The milling used for the ore pieces reduction first leads to the fracture of weaker interfaces between the mineral particles and then to the fracture (pounding) of mineral particles themselves. As a result, a typical morphology of the ground powder with sharp edges and a rather high specific surface is observed (Fig. 3a).

After annealing at 700°C the average particle size increases to 47 μm. The specific surface decreases because of agglomeration of disperse particles into coarser conglomerates (Fig. 3b). Some fusible phases, e.g. sulphides, decompose and partly evaporate and the S bulk content decreases. Softening of the fusible phases promotes the observed rounding-up of ore conglomerates as is seen in Fig. 3b. The decrease of the S content is the main goal of preliminary annealing. The presence of sulphide anions in the solution is known to promote formation of low- or insoluble sulphides in the course of sample dissolution. In particular, both formation of noble metal sulphides and co-precipitation of noble and main metals are possible. Evidently, both effects hamper the noble metal dissolution and decrease the extraction degree.
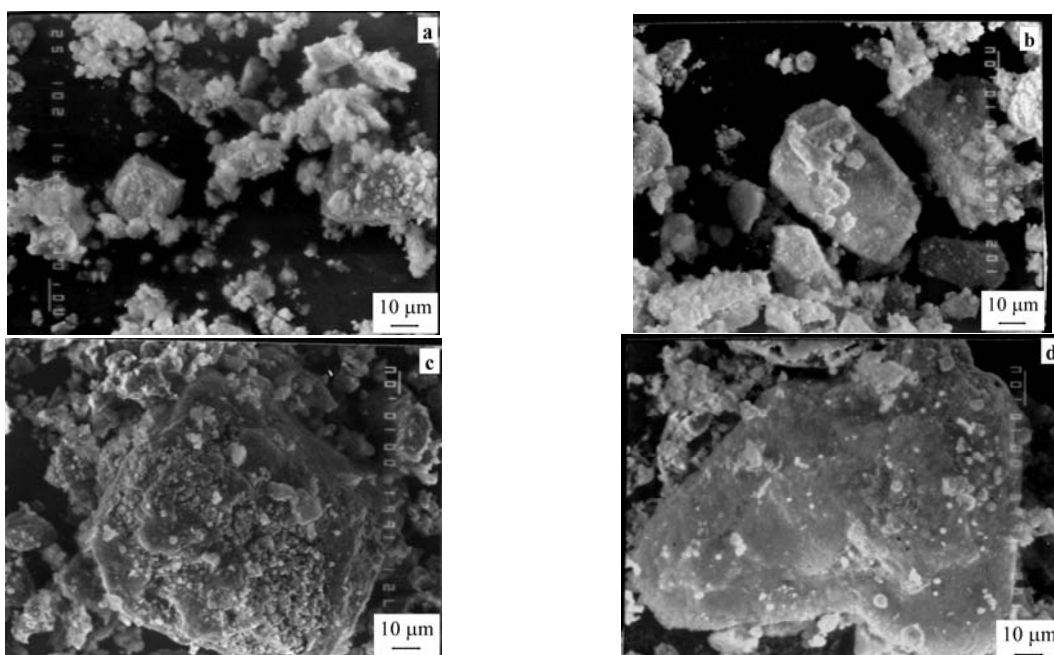
Fig. 3. Scanning electron micrographs of individual particles of the sulphide copper-nickel ore No 1 (x1000) a) as-milled, b) as-annealed at 700°C for 1.5 h, c) as-heated in acid mixture for 60 min, d) as-treated by plasma for 10 min

Short- and long-time heating in a mixture of the hydrochloric and nitric acids by the standard technique [6] does not lead to any essential changes in the particle size and morphology (Fig. 3c).

In contrast to the standard procedure, the proposed plasma treatment essentially changes the fine structure of individual particles. While the average size of many particles remains unchanged, a clearly visible fragmentation of the particles is observed as illustrated in Fig. 3d. In particular, numerous cracks and pores are seen to form on the powder surface exposed to the plasma treatment. In fact, the original ore particles become transformed into agglomerates of smaller fragments. These fragments

are separated between each other by the newly formed interfaces but they, however, do not split up into separate elements.

The observed fragmentation under plasma treatment is caused by either the opening of internal interfaces, which have already existed in the particles, or by the formation of new interfaces. In the first case, e.g., interparticle surfaces, which were formed as a result of sintering of disperse particles into coarse agglomerates on the stage of preliminary annealing, could be open. In the second case, the processes of selective evaporation or dissolution of some unstable phases could lead to the formation of new interfaces.

The typical fragment size is 5-7 μm while the average particle size of as-treated samples is still 47 μm. Therefore, the proposed plasma treatment reduces the effective size of ore particles by 7-10 times or increases the specific surface of the particles, which is proportional to d^2, by 49-100 times. Evidently, the increase of the specific surface of solid samples intensifies diffusion, dissolution, adsorption, desorption and other transport processes at solid-liquid interfaces and, thus, promotes acceleration of sample preparation stage. This conclusion agrees with the experimental results shown in Fig. 1a and Fig. 1c. As is seen in Fig. 1a, the most effective way for sample preparation is the use of plasma treatment before acid decomposition. Evidently, the preliminary plasma treatment provides an intensive particle fragmentation while the extraction of noble metals in the course of heating is then intensified by the increased surface of liquid-solid contacts. When using a small acid amount, a very thin acid layer forms above the powder surface. This provides a much better focusing of the plasma discharge on the sample surface that results in a more effective extraction of the noble metals (Fig. 1c).

3.3 Auger electron spectroscopy study of ore samples at various sample preparation stages
3.3.1 As-received samples

The results of AES analyses are summarised in Table 3. Not only the specific surface but also the surface composition of ore particles changes in the course of sample preparation as is evidenced by AES. Evidently, the composition changes influence all interactions at the liquid-solid interface.

Table 3. Surface composition (at. %) of three main minerals measured by AES at various stages of sample preparation

№	Mineral	Fe	Cu	Ni	S	O	C	Cl	Ca
				As-milled state					
1	Pentlandite	7,6	-	7,3	15,3	7,5	62,3		
2	Chalcopyrite	15,2	13,6	-	34,9	6,6	29,4		
3	Pyrotine	10,6	-	-	7,9	11,4	70		
4	Pyrotine	10,8	-	-	23,9	7,9	57,3		
				As-annealed state					
5	Pyrotine	33,2	-	-	-	46,6	20,1		
				After acid treatment					
6	Pentlandite	33,1	-	13,7	-	51,1	-	2,0	-
7	Chalcopyrite	29,5	12,4	-	-	50,2	-	1,6	6,1
8	Pyrotine	35,3	-	-	-	46,6	-	2,0	15,9
				After plasma-chemical treatment					
9	Pentlandite	30,8	-	11,2	-	44,9	-	-	12,9
10	Chalcopyrite	27,1	7,6	-	-	46,5	18,6	-	-
11	Pyrotine	35,9	-	-	-	38,6	25,4	-	-
12	Pyrotine	27,9	-	-	2,6	27,6	41,6	-	-

The studied ore samples are known to be non-uniform in chemical composition. They consist of three principal minerals and many impurities and impurity phases. When analysing individual particles in their as-milled state it is possible to identify the main minerals. The number of pyrotine particles amounts up to 80% of the total number of the studied particles. The pentlandite and chalcopyrite particles totally come to the rest 20%. This observation is consistent with the results of bulk chemical analysis (Table 1). If iron, copper and nickel are mainly located in the principal minerals, then pyrotine, pentlandite and chalcopyrite form 76, 8 and 16 mas. % of the ore samples, respectively.

Typical surface compositions of individual particles in as-milled state are shown in Table 3. The measured ratios of the surface concentrations of Cu/Fe and Ni/Fe are very close to their stoichiometric ratios. Therefore, no surface enrichment or depletion of Fe, Cu or Ni is observed. Oxygen and sulphur are usually recorded on the particle surface of all minerals. Combination of these elements can lead to the formation of complex oxy-sulphides. The S surface concentration usually exceeds the stoichiometric value that is expected for FeS. This can be caused by either the presence of FeS_2 in the ore or by the S and O surface segregation.
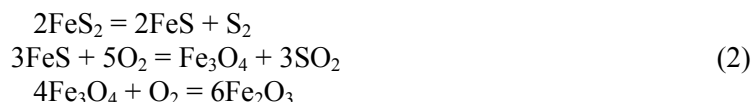
A very high level of the C Auger peak is a typical feature of as-milled ore samples. The C concentration calculated by (1) varies from 30 to 70 at. %. Based on the analysis of C KLL 272 eV peak fine structure (Fig. 4) one can conclude that carbon on the particle surface exists in a form of either hydrocarbon compounds or elemental (adsorbed) carbon [11, 12]. A more precise identification of the chemical state of the measured carbon peak is hindered by insufficient energy resolution of the analyser used. Evidently, the intensive milling of ore particles leads to the opening or creation of new surfaces, formation of broken bonds with a high reactivity which are saturated by the carbon and oxygen atoms from the atmosphere.

Fig. 4. Fine structure of the C KLL 272 eV Auger peak recorded from the surface of various compounds: a) iron carbide, b) graphite, c) hydrocarbon organic compound, d) as-milled particles of the sulphide copper-nickel ore No 1e) as-plasma-treated particles of the sulphide copper-nickel ore No 1

Two different types of particles shown as No 3 and 4 in Table 3, which differ with respect to the S/O surface ratio, are typical for as-milled pyrotine samples. The observed S/O ratio varies from 0.5 to 3.
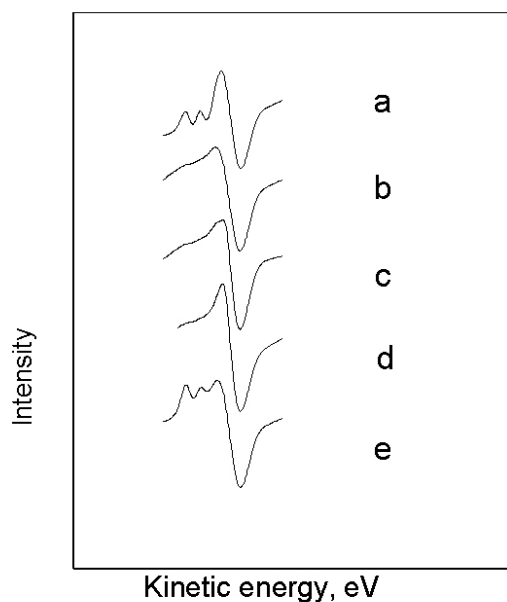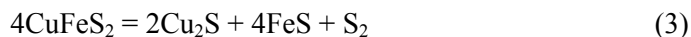
3.3.2 As-annealed samples

The preliminary annealing at 700°C leads to an abrupt decrease of the carbon concentration and removes sulphur from the surface. The typical surface composition of as-annealed particles is shown in Table 3 (particle No 5). The Fe and O atoms dominate on the surface that gives evidence to a strong surface oxidation during annealing. The Ni and Cu Auger peaks are not recorded on the surface. Most probably, this is due to a specific oxidation of the surface when the oxide layer forms by means of the cross diffusion of oxygen and iron to the interface. As is follows from the O/Fe Auger peak ratios, the oxide composition varies from magnetite (Fe_3O_4) to haematite (Fe_2O_3). In some cases, mixed non-stoichiometric oxide compositions are also observed.

Chemical reactions which take place during the annealing at 700°C in air are described as follows. Pyrotine first oxidises to magnetite and then to haematite. If there is some pyrite (FeS_2) in the ore, then it first dissociates to form pyrotine and then oxidizes. The principal high-temperature oxidation reactions are as follows

$$2FeS_2 = 2FeS + S_2$$
$$3FeS + 5O_2 = Fe_3O_4 + 3SO_2 \qquad (2)$$
$$4Fe_3O_4 + O_2 = 6Fe_2O_3$$

Similar reactions, which describe decomposition of the original compounds followed by oxidation of the newly formed sulphides and combustion of redundant free sulphur, can be written for the other two minerals. For example, for chalcopyrite:

$$4CuFeS_2 = 2Cu_2S + 4FeS + S_2 \qquad (3)$$

3.3.3 Samples after standard treatment

Iron and oxygen continue to dominate on the particle surface after acid treatment by the standard procedure. Typical surface compositions are illustrated in Table 3 (particles 6-8). In contrast to as-annealed particles, copper and nickel are seen on the surface of some as-treated particles while carbon and sulphur are not usually recorded. In many cases, calcium (5-15 at.%) and chlorine (usually 1-2at.% but not more than 10 at.%) appear on the surface of particles after 50 min heating in an acid mixture. The most probable source of calcium seems to be some Ca-containing phases in the ore particles which become uncovered in the course of the acid treatment. Since chlorides are not contained in the original ore, the recorded chlorine ions seem to precipitate on the surface from the acid solution. As a result, the effective chlorine concentration in the solution decreases. This reduces the effectiveness of sample dissolution and thus the extraction degree of noble metals with increasing heating time.

3.3.4 Samples after plasma treatment

The typical surface compositions of particles treated by the plasma discharge are shown in Table 3 (particles 9-12). The measured concentrations correspond either to the stoichiometric Fe_2O_3 and Fe_3O_4 or to their mixture. Both calcium and chlorine are not usually detected. Carbon, which was removed during the preliminary annealing, is again recorded on the surface of as-treated particles. Any further heating of the particles in the acid does not remove the carbon signal.

The fine structure of the C KLL Auger peaks recorded from the surface of as-milled and as-treated particles was compared with that of some standard compounds, such as graphite, Fe_3C and hydrocarbons (Fig. 4a-e). As-milled samples (Fig. 4d) usually exhibit the carbon peak shape similar to the shape of either adsorbed carbon (Fig. 4b) or organic hydrocarbons (Fig 4c). After plasma treatment the carbon peak shape (Fig. 4e) changes and corresponds to a mixture of the carbide (Fig. 4a) and adsorbed carbon (Fig. 4b) signals.

Therefore, the use of plasma discharge promotes surface carbide formation. First, the plasma treatment cleans the surface removing the adsorbed atoms and simultaneously activates all atomic bonds on the surface. The newly formed broken bonds are very reactive [13]. Such atoms cannot be vacant for a long time and they work for the formation of new bonds. The carbon atoms adsorbing on the surface neutralize the broken bonds, form the surface carbides and thus passivate the surface. As follows from AES data, the surface passivation prevents precipitation of the chlorine atoms and thus protects against depletion of the acid solution.

Summarizing, one can suppose the plasma treatment influences the surface of ore samples by at least two ways. The first mechanism is connected with the increase of the specific surface of particles due to the observed particle fragmentation that intensifies the process of noble metal dissolution. This conclusion is evidenced by the available electron microscopy data and agrees with the well-known fact that any sample refining usually facilitates its decomposition [14].

The second mechanism is connected with the observed plasma-induced modification of the surface atomic bonds. This effect prevents washing–out of the chlorine atoms and maintains a high dissolution rate.

The plasma discharge also influences chemical reactions in the acid solution. As a result, hydrogen peroxide forms there and acts as an additional oxidant together with the nitric acid. Under the presence of the complexing agent (hydrochloric acid) this intensifies sample dissolution.

4. Conclusions

The use of plasma treatment allows one to simplify decomposition of the copper-nickel sulphide ore samples and preparation of the working solution for atomic absorption analysis.

The developed procedure of sample treatment with the use of plasma discharge provides the quantitative extraction of Pt, Pd and Ag into the solution. As compared to the known standard procedure of acid decomposition the proposed plasma treatment is a less time- and labour-consuming procedure and it also decreases the consumption of reagents.

Based on the AES, SEM and spectrophotometry data, the influence of plasma treatment on the ore samples can be summarized as follows:

- The plasma discharge forms a strong additional oxidant in the solution, such as hydrogen peroxide, that intensifies dissolution of Pd, Pt and Ag.

- The specific surface of ore particles strongly (up to 100 times) increases due to the plasma treatment that accelerates all chemical and physical transfer processes on the liquid-solid interface.
- The plasma treatment activates atomic bonds on the solid surface that influences their adsorption activity.

5. Literature

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Вісник Харківського національного університету. 2005. №669. Хімія. Випуск 13(36). Т.М. Деркач, Ф.А. Чмиленко, А.В. Крайников. Обработка плазмой геологических образцов для интенсификации пробоподготовки.

В работе описана новая экспресс-методика атомно-абсорбционного определения благородных металлов в сульфидных медно-никелевых рудах, основанная на использовании плазмы пониженного давления. Обработка плазмой образцов руды, помещенных в небольшое количество смеси кислот, приводит к улучшению степени извлечения таких благородных металлов, как платина, серебро и палладий, упрощает и сокращает время пробоподготовки. Проведенные спектрофотометрические, электронномикроскопические и оже-спектроскопические исследования показали, что действие плазмы на систему раствор – твердая проба сводится к образованию в растворе дополнительного окислителя пероксида водорода; резкому увеличению удельной поверхности частиц руды, что способствует интенсификации физико-химических процессов на границе раздела раствор-проба; активизации атомных связей на поверхности твердой пробы, вследствие чего меняется ее адсорбционная способность.