

## Leaching process intensification of gold-bearing raw materials

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### Abstract

**Purpose.** Research on the process intensification of gold-bearing product hydrometallurgical processing based on mechanochemical milling of the initial sulphide material.

**Methods.** Mechanochemical activating (oxidation) of sulphide gold-bearing concentrate under conditions of superfine milling, sulphite-thiosulphate leaching of the milled product after liquid phase separation. The float concentrate sample with a particle size of  $-0.074$  mm, the Au content is 15.5 g/t is tested. When loading into the mill of an initial concentrate sample weighing 300 g, 600 ml of a calcium hydroxide solution with a concentration of 143 g/l are added. The weight of balls loaded into the mill in relation to the concentrate weight is 10:1. The remainder of the solid product after milling is subjected to leaching with a sulphite-thiosulphate reagent.

**Findings.** A sharp increase in the milled product of 10  $\mu\text{m}$  fractions (from 14.05 to 34.63%) has been determined, and the mass fraction of gold in the final milling product decreases from 15.5 to 13.0 g/t. This corresponds to the recovery of gold into solution at this stage at the level of 16%. It has been found that with an additional supply of 1 g/l of copper sulphate for copper in the process of milling, it is possible to reduce the gold content in the milled product to 8.3 g/t. Thus, the recovery of gold into solution at the stage of milling increases from 16 to 48%. During the milling process, partial leaching of gold by reagents formed from its own sulphur has been revealed. It has been found that the transition of gold into solution is caused by the formation of a water-soluble hydrosulphide complex of gold during milling (AuS). As a result of leaching with the reagent, an additional 27% of gold has been recovered.

**Originality.** Phase transformations of the sulphide gold-bearing beneficiary product as a result of mechanochemical activation have been determined. For the first time this process has been implemented to intensify the leaching process of gold-bearing mineral raw materials.

**Practical implications.** The research results can be used in technological processes for the processing of refractory gold-bearing ores and technogenic raw materials.

**Keywords:** float concentrate, gold, sulphur, milling, mechanochemical activation, reagent, recovery, solution, oxidation, leaching

### 1. Introduction

It is known that the technology of hydrometallurgical processing of gold-bearing sulphide raw materials includes two main process stages [1]-[4]. At the first process stage, the raw materials are oxidized with the conversion of sulphur, iron and arsenic into elements with a higher degree of oxidation. This is accompanied by the destruction of gold-retaining matrices of minerals, such as pyrite, arsenical pyrite, and also provides more favorable conditions for the access of reagents to gold particles leached from the raw materials. The success of the second stage of raw material processing, which is directly related to the transfer of gold into solution, is determined mainly by the depth of raw material oxidation. At the same time, in the case of using a sulphite-thiosulphate composition as a reagent for dissolving gold, this condition has specificity somewhat different from other reagents. This is conditioned by the fact that in this case the rock-forming sulphide minerals and the reagent contain sulphur as the main element. Moreover, as it was

indicated in our previous publications [5], [6], sulphur in combination with hydrothermal waters are the “causers” of gold ore deposit formation.

Sulphur with water, forming in the natural environment various oxygen-free, and with the access of air, oxygen chemical compounds (hydrosulphides, sulphides, thiosulphates, etc.) become in some cases solvents of gold, in others, in combination with gold, they are transformed into an insoluble state. Thus, on the way from the bowels to the earth's surface, gold in compounds with sulphur and, depending on the pH and Eh of the medium, is repeatedly dissolved and precipitated. These natural processes indicate the possibility of using the sulphur in the sulphide raw materials, partially or completely, as a reagent in the technology of gold recovery in the processes of its dissolution and precipitation from solutions.

At most Kazakhstan deposits, gold in ore occurs in fine association with sulphide minerals of iron, arsenic, copper and other non-ferrous metals (pyrite, arsenical pyrite, chalcocopyrite, etc.). In addition, a number of gold ore deposits

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contain carbon. The fine association of gold in minerals, the presence of carbon and other impurities in the lower valence forms ( $\text{Fe}^{++}$ ,  $\text{As}^{+++}$ ,  $\text{S}^{-}$ ) create insuperable difficulties for the recovery of gold when they are directly exposed to cyanide solvents. For this reason, these types of ores are usually classified as refractory raw materials. Among the deposits with such types of ores in Kazakhstan are Bakyrchik, Bolshevik, Maikain, Akbakai and many others, which contain more than a third of the explored gold reserves of the republic. When using the cyanide process for such types of ores, a number of additional technological methods are required, which mainly consist in the preliminary oxidation of raw materials – radical roasting of the ore or concentrate; by bacterial oxidation; by treatment with nitric acid in the presence of pure oxygen under high pressure in an autoclave (redox-process) or under normal conditions in the presence of air oxygen (Nitrox or Arseno processes), etc. Even with the involvement in the ore processing technology of the indicated, rather complex, additional technological stages, in a number of cases (at Bakyrchik, Bolshevik, etc.) it is still not possible to achieve acceptable rates of gold recovery from raw materials. At the same time, all the mentioned methods do not ultimately exclude the environmental hazard of the process resulting from the use of a cyanide reagent at the final stage of the technology [7]-[10].

These problems in the processing of refractory types of gold-bearing raw materials can be solved by using an environmentally friendly reagent based on thiosulphate compounds instead of cyanides in the technology of their processing [11], [12].

Methods for leaching gold and silver with ammonium or sodium thiosulphate solutions in the presence of sulfite ions and copper are well known in world practice [13], [14]. The use of the reagent is primarily intended for processing of ores unsuitable for leaching with traditional cyanide solutions (coppery, manganic, carbonaceous, etc.). The experience of Canadian researchers [15] on the use of a thiosulphate reagent for leaching rhyolite ore has the following composition: 3 g/t of gold, 113 g/t of silver and 7 kg/t of manganese dioxide. The process is conducted at a temperature of 25-60°C, duration up to 3 hours, with a solution of the following composition (%): 1-42  $\text{S}_2\text{O}_3^{2-}$ ; 0.7  $\text{NH}_3$ ; 0.15-6.0  $\text{CuSO}_4$ . With an increase in temperature, the degree of gold and silver recovery increases and after 3 hours of leaching at 50°C it reaches 90 and 70%, respectively. In the absence of thiosulphate ion, gold solubility is very low.

In another paper [16], a thiosulphate reagent is used to recover silver from refractory ore containing copper, selenium, tellurium, and manganese. The process is conducted at a temperature of 40-50°C. The required salt composition of the solution is maintained by adding elemental sulphur and its dioxide. Under such conditions, 90% of silver is recovered into the solution from the ore with a silver content of 456 g/t and manganese 10.5%. There is a method [17], used for thiosulphate leaching of refractory manganese-containing ore of the following composition: 0.4 g/t of gold, 343 g/t of silver, 2.1% of manganese. The leaching process is performed with a solution concentration of 18%  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  in the presence of 3% ammonium sulphite, 2% ammonium hydroxide, and 4 g/l of copper. The recovery of silver is 93.2%, gold – 86.7% at the consumption of ammonium thiosulphate of 3.6 kg, ammonium sulphite of 1.35 kg, copper of 0.45 kg per ton of ore. In the paper [18], the influence of the concentration of ammonium thiosulphate, ammonia and copper in solution on the recovery of gold during the leaching of sul-

phide concentrates is studied. It has been revealed that at a temperature of 50°C, L:S = 1:3, concentration (mol/l):  $\text{NH}_4\text{OH}$  2-4,  $(\text{NH}_4)_2\text{SO}_4$  0.5-0.8,  $(\text{NH}_4)_2\text{S}_2\text{O}_3$ , copper of 2 g/l, under conditions of pulp aeration with air, the recovery of gold reaches 95%. There is information on the use of thio-sulphate leaching in relation to the processing of complex pyrite raw materials of the following composition (g/t): Au – 12.31; Ag – 1390; in (%): Cu – 5.95; Pb – 4.38; S – 28.34; Zn – 1.33; Fe – 26.04; Si – 28.34. Under optimal conditions for conducting the leaching process, the recovery of gold and silver into the solution is achieved at the level of 93.38 and 85.64%, respectively. In another case [18], the ore of the following composition (%): Si – 3.97;  $\text{Al}_2\text{O}_3$  – 3.97; Fe – 2.0;  $\text{Fe}_2\text{O}_3$  – 3.3; CaO – 2.7; S – 0.34;  $\text{K}_2\text{O}$  – 2.97; Au – 21.8 g/t; Ag – 90.2 g/t is leached with a solution of sodium thiosulphate (40-80 g/l) in an ammonia medium ( $\text{NH}_4\text{OH}$  10-15 g/l) in the presence of copper sulphate (6-8 g/l) at 80°C for 1.5-2.0 hours. The recovery of gold into solution in this case reaches 97%. As applied to the refractory carbonaceous ores of the State of Nevada [19], the preliminary oxidation of the raw material with oxygen in an autoclave is used. Ore composition: Au – 5-7 g/t, carbon – 6-7%, sulphur – 1.5-2.5%. The milled ore is processed in an autoclave at a temperature of 185-235°C. Then, ammonium thiosulphate (3-11 g/l), ammonium sulphite (0.1 g/l), copper (0.1 g/l) are dosed into the cooled pulp at pH = 8.7. The leaching lasts for about 2 hours at 40-55°C. Gold recovery is up to 80%. The patent [20] presents the results of thiosulphate leaching of a similar type of ores, but with preliminary microbiological oxidation of raw materials and the use of a percolation method for leaching lump ore (-15 mm). Ore composition: 1.8 g/t of Au, 1.2% of carbon, 1.3% of sulphide sulphur. The duration of microbiological oxidation is 14 days, percolation leaching is 13 days. The composition of the leaching solution: 15 g/l of ammonium thiosulphate, 1 g/l of ammonia, 60 mg/l of copper. Gold recovery is 68%. For comparison, the recovery of gold by the cyanide method under similar process conditions is only 1% due to the sorption properties of the carbon present in the ore in relation to the cyanide complex of gold.

Chinese researchers studied the influence of thiosulphate concentrations,  $\text{Cu}^{2+}$  and  $\text{NH}_4\text{OH}$  on the recovery of gold from sulphide concentrates. It has been revealed that the recovery of 95% is achieved at 50°C, L:S = 1:3 under conditions of pulp aeration at concentrations (mol/l):  $\text{NH}_4\text{OH}$  is 2-4;  $(\text{NH}_4)_2\text{SO}_4$  is 0.5-0.8;  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  is 0.2-0.3; Cu is 3 g/l. In the absence of thiosulphate, as well as at its high content, the recovery does not exceed 20% [21].

The recovery of precious metals is performed with a solution of ammonium thiosulphate from refractory ore containing copper, selenium, tellurium and manganese. Moreover, manganese content is more than 0.5% [22]. The optimum temperature is 40-50°C. To prevent the decomposition of thiosulphate, the concentration of sulfite ion in the reagent is maintained at more than 0.05%. The ammonium thiosulphate and sulphite concentrations are maintained with sulphur dioxide and elemental sulphur. This solution is used to process ore with a silver content of 456 g/g and manganese content of 10.5%. As a result, silver recovery is up to 90%.

It is believed that thiosulphate leaching of gold can be used in cases where the use of cyanide solutions is impossible or prohibited. Such cases, in particular, are underground leaching and processing of gold-bearing concentrates in the conditions of copper production [23], [24].

## 2. Experimental procedure

Research on the leaching process intensification of the gold-bearing product (flotation concentrate) has been performed based on mechanochemical activation using fine milling in a laboratory ball mill. In order to leach the product of processing, air oxygen is supplied to the mill instead of expensive pure oxygen. Additional supply of copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) in the process of milling accelerates the process of gold dissolution due to the oxidation of gold. To create an alkaline medium, calcium hydroxide solution ( $\text{Ca}(\text{OH})_2$ ) is used, which dissociates with the formation of  $\text{OH}^-$  ions, creating an alkaline medium. It has been determined that, as a result of mechanical activation, gold is partially leached due to its own sulphur in the starting raw material, which acts as a leaching reagent during the milling process. As a result, the mass fraction of gold in the final milling product significantly decreases from 15.5 to 13 g/t, which corresponds to the recovery of gold into solution already at this stage at a level of approximately 16%.

When maintaining all the regime parameters of milling, the addition of copper sulphate during the process (at the rate of 1 g/l for copper) makes it possible to reduce the gold content in the milled product to 8.3 g/t. At the same time, at the milling stage, the recovery of gold into solution increases from 16 to almost 48%.

In our studies, the first stage of the oxidation process of sulphide raw materials is replaced from autoclave to a simpler version of mechanochemical processing, carried out by finer milling of the initial sulphide material.

Mechanical activation to a greater or lesser extent leads to a change in the structural and physical-chemical properties of minerals, especially surface ones. The research performed to date makes it possible to compile a fairly complete list of physical-chemical changes in the mineral substance and the transformation of materials during dispersion.

An analysis of publications on the mechanical chemistry of minerals indicates the versatility and complexity of the physical-chemical processes that occur during mechanical activation, thereby leading to conclusion that the degree of reactivity of minerals is determined both by a change in the fine crystalline structure, an increase in the surface, as well as by the processes accompanying mechanical processing – solid-phase reactions. When studying the examples of using the activation by milling for the purpose of intensifying extraction, the emphasis is made on combining activation with leaching, but this does not exclude the possibility of separating these procedures. If the technological scheme allows activation by dry milling before leaching, then the processes should be divided, as material activated by dry milling in most cases is leached better [23]. The experiments described in these works indicate the possibility of intensifying the selective recovery of elements during the chemical beneficiation of ores and real prospects for the use of this method.

According to the existing concepts [25], [26], the mechanochemical activation of products is characterized by three process stages. If at the first stage there is practically no interaction between the milled particles, then at the second stage the interaction begins to grow and manifests itself in their aggregation due to the van der Waals forces. At the third stage, this process stops and is replaced by the formation of chemical bonds between the particles. If, based on these concepts, we attribute the +74  $\mu\text{m}$  fraction obtained during milling to an aggregated finer class, then it can be

assumed that the total content of material with a particle size of -10  $\mu\text{m}$  in the final product increases by more than 60%. It is expected that in the process of milling, according to the mechanisms indicated above, there is a partial leaching of gold by reagents formed from its own sulphur.

The paper [27] presents the results of experimental research on the use of mechanical activation in the processing of ores and technogenic materials. At the stage of mineral preparation, the efficiency has been confirmed of using the electroflotation activated solutions and complex reagents. Technological solutions are proposed to reduce the losses of finely-dispersed and chemically-bound gold during the processing of gold-bearing materials, based on a directed change in the properties of the surface of minerals. The efficiency of using the mechanochemical activation process for various aspects of the technological chain has been experimentally confirmed. These include a reduction in the sorption properties of materials, the development of microfractures in oxidized ores for the penetration of leaching solutions into mineral aggregates, the oxidation of the surface of primary ores, and the removal of films from the surface of minerals. Indicators of technological resistance of the studied ores and technogenic materials have been revealed – a high proportion of gold chemically-bound with atoms of the main and auxiliary mineral-forming elements.

It is known that the technology of hydrometallurgical processing of gold-bearing sulphide raw materials includes two main process stages. At the first process stage, the raw materials are oxidized with the conversion of sulphur, iron and arsenic into elements with a higher degree of oxidation (based on the redox-process).

This is accompanied by the destruction of gold-retaining matrices of minerals, such as pyrite, arsenical pyrite, and also provides more favorable conditions for the access of reagents to gold particles leached from the gold-bearing raw materials. The success of the second stage of raw material processing, which is directly related to the transfer of gold into solution, is determined mainly by the depth of raw material oxidation. At the same time, in the case of using a sulphite-thiosulphate composition as a reagent for dissolving gold, this condition has specificity somewhat different from other reagents. This is conditioned by the fact that in this case the rock-forming sulphide minerals and the reagent contain sulphur as the main element. Moreover, as it was indicated in our previous publications [1], [6], sulphur in combination with hydrothermal waters are the “causers” of gold ore deposit formation. Sulphur with water, forming in the natural environment various oxygen-free, and with the access of air, oxygen chemical compounds (hydrosulphides, sulphides, thiosulphates, etc.) become in some cases solvents of gold, in others, in combination with gold, they are transformed into an insoluble state. Thus, on the way from the bowels to the earth's surface, gold in compounds with sulphur and, depending on the pH and Eh of the medium, is repeatedly dissolved and precipitated. These natural processes indicate the possibility of using the sulphur in the sulphide raw materials, partially or completely, as a reagent in the technology of gold recovery in the processes of its dissolution and precipitation from solutions.

The redox-process proceeds at high temperatures (250-300°C) and pressures (16-20 atm), in a nitric acid medium and in the presence of pure oxygen. The process requires very high capital and operating costs. Gold is recovered from the solid remainder of the process by leaching with cyanide

solutions. Sulphur in the autoclave is oxidized to the maximum 6-valence state and entirely in the form of ballast sulphate compounds is sent to the dump. Known from the same series, the so-called Nitrox or Arseno processes, differ from the previous process in that they are realized without pressure under normal conditions and in an air atmosphere. However, in this case, due to the lack of oxidizing potential, sulphide sulphur is oxidized only to an intermediate phase – the elemental state. This causes a low gold recovery during the subsequent cyanidation of the solid remainder, since elemental sulphur, settling on the surface of gold particles, makes it difficult for the solvent to access them. In our studies on this topic, due to the use in an autoclave instead of an acidic alkaline medium, it becomes possible to transfer this process to a milder regime (excess pressure 5 atm instead of 20 atm, temperature 100-120°C instead of 250-300°C). The negative effect of the partially elemental sulphur formed in this case can be avoided by using a solid remainder of sodium sulphite with a small addition of thiosulphate as a reagent for leaching. When sodium sulphite reacts with elemental sulphur, sodium thiosulphate is formed and, thus, a sulphur film is removed from the solid particles and at the same time the main reagent for gold leaching is regenerated. Thus, along with the solution of an important technological problem, it is possible to transfer part of the sulphur as a ballast product from the initial sulphide raw material into the category of a useful element. In general, with approximately comparable gold recovery rates compared to the cyanide process, in this case, the additional effect of reducing the environmental burden and economic costs is obvious.

The first stage of the oxidation process of sulphide raw materials is replaced from autoclave to a simpler version of mechanochemical processing, carried out by finer milling of the initial sulphide material.

The initial stage of pyrite oxidation is the formation of ferrous sulphate and elemental sulphur:



Elemental sulphur easily interacts with alkalis with the formation of a whole range of oxygen and oxygen-free sulphur compounds:



These reactions indicate the possibility of the formation of sodium thiosulphate and hydrosulphide compounds during the milling of raw materials in an alkaline medium and a high probability of the formation of water-soluble gold complexes with the indicated sulphur anions, as evidenced by many publications. It should be mentioned one of them [28], which seems to be the most interesting due to the fact that it studies these processes more thoroughly and is used by the authors as an evidence base for their theory of the formation of hydrothermal gold deposits with the participation of these processes.

According to this theory, when hydrothermal solutions are formed in deep horizons of the earth under conditions of low presence of oxygen and low values of oxidation-reduction potential (ORP), gold occurs in solutions, most likely in the form of a hydrosulphide complex ( $\text{AuS}$ ). As the solutions come to the surface and the ORP increases, this complex is destroyed with the release of gold, which is commonly called as early or high-temperature gold. At the

same time, favorable conditions are created for the formation of a thiosulphate sulphur compound and the corresponding water-soluble thiosulphate complex of gold. Subsequent deeper changes in the Eh-ph medium lead to another destruction of this complex with the formation of a gold deposit.

To conduct technological research, a laboratory ball mill MSHL-1 of 2.3l is used. The research methodology provides for the milling of the concentrate in an alkaline medium in the presence of air oxygen as an oxidizing agent. The lack of the possibility of continuous air supply in this mill design forces the milling process to be carried out with stops of the apparatus for periodic supply of fresh air portion through the loading hatch.

### 3. Results and discussion

Research on mechanochemical activation has been performed using a flotation concentrate sample from the Akbakai gold recovery plant with a particle size of 0.074 mm, a content of Au is 15.5 g/t, As is 0.058%, S is 22.6%. When loading into the mill an initial sample of the concentrate weighing 300 g, 600 ml of a calcium hydroxide solution with a concentration of 143 g/l are added. Steel balls are loaded at a ratio of 1:10 to the concentrate weight. Milling is conducted for 60 min with the mill stopping every 2 min for air blowing. Measurements of the medium ph have the values of 9.0-9.5. At the same time, the ORP varies within the Eh values from -0.176 to -0.186v.

Table 1 presents the sedimentation analysis results of initial raw material, and Table 2 presents the sedimentation analysis indicators after milling.

**Table 1. Sedimentation analysis of initial raw material**

Indicators for the original product (concentrate)		
µm	gram	%
+74	14.16	14.67
74-40	18.55	19.22
40-20	18.48	19.14
20-10	31.78	32.92
10-0	13.56	14.05
Total	96.53	100.0

**Table 2. Sedimentation analysis after initial raw material milling**

Sedimentation analysis indicators after milling		
µm	gram	%
+74	21.58	25.63
74-40	1.2	1.43
40-20	14.18	16.88
20-10	17.95	21.37
10-0	29.1	34.63
Total	84.01	100.0

As it follows from Tables 1 and 2, there is a sharp increase in the milled product of 10 µm fraction (from 14.05 to 34.63%) and the +74 µm fraction (from 14.67 to 25.63%).

These, at first glance, contradictory results have a quite understandable scientific content. According to existing concepts [28], [29] the mechanochemical activation of products is characterized by three stages of the process. If, at the first stage, there is practically no interaction between the milled particles, then at the second stage the interaction begins to grow and manifests itself in their aggregation due to the van der Waals forces. At the third stage, this process stops and is replaced by the formation of chemical bonds

between the particles. If, based on these concepts, we attribute the +74  $\mu\text{m}$  fraction obtained during milling to an aggregated finer class, then it can be assumed that the total content of material with a particle size of -10  $\mu\text{m}$  in the final product increases by more than 60%. In the process of milling according to the above mechanisms, the gold is partially leached by reagents formed from its own sulphur. As a result, the mass fraction of gold in the final milling product significantly decreases from 15.5 to 13.0 g/t, which corresponds to the recovery of gold into solution already at this stage at a level of approximately 16%. As it is known, the addition of divalent copper ions to the gold dissolution process accelerates the process due to the gold oxidation. Therefore, further an experiment is conducted with the addition of copper sulphate sulphide concentrate to the milling process (at the rate of 1 g/l for copper), while maintaining all the previous regime parameters of milling. As a result, the gold content in the milled product is reduced to 8.3 g/t, that is, the recovery of gold into solution at the milling stage increases from 16% to almost 48%. A sub-sample of 100 g of the obtained milled product after separation of the liquid phase is subjected to sulphite-thiosulphate leaching in a 2-liter magnetic stirrer in the following regime:

- ratio of S:L - 1:10;
- content of sodium sulphite in the solution - 100 g/l;
- content of sodium thiosulphate in the solution - 50 g/l;
- content of copper in the solution - 1 g/l;
- pH of the medium 9.0-9.5, Eh from +0.034 to +0.084v;
- leaching time - 4 hours.

Analysis of the cake after leaching has revealed the gold content in it to be 6.1 g/t, that is, the recovery of gold into solution at this stage is about 27%. The most probable reserve for increasing this indicator at this stage of the process is to increase the leaching time.

Figure 1 shows the stability ratios between some compounds in water at a temperature of 25°C and a pressure of 1 atm. As a reagent for oxidation, chlorine is used, which, in active and ionic forms, can also be a complex-forming agent in a water-soluble gold compound.

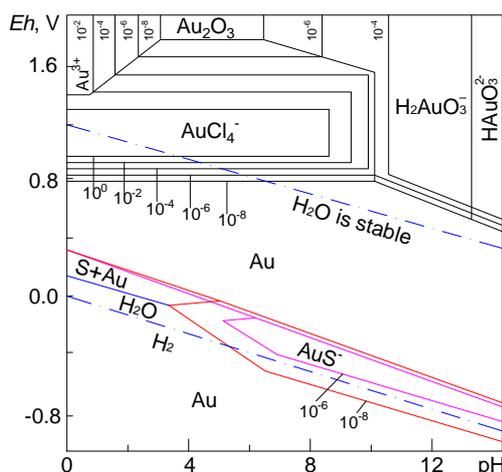


Figure 1. Stability ratios between some compounds of gold in water at 25°C and 1 atm. The sum of dissolved chloride components is  $10^{-1}$  mol/l and the sum of dissolved sulphur is  $10^{-1}$  mol/l (according to Garels)

Analysis of the cake after leaching has revealed the gold content in it to be 6.1 g/t, that is, the additional recovery of gold into solution at this stage is about 27%. The indicators

of gold recovery into solution with such a simple instrumentation of the processes could be considered acceptable, but some negative factors accompanying this method reduce the advantages of the technology. Measurements of pH and Eh of the medium in the course of the experiments performed indicate that gold leaching occurs mainly according to the hydrosulphide version, and the zone of stable existence of the soluble hydrosulphide complex of gold in our case is located approximately in zone "A" (Fig. 2).

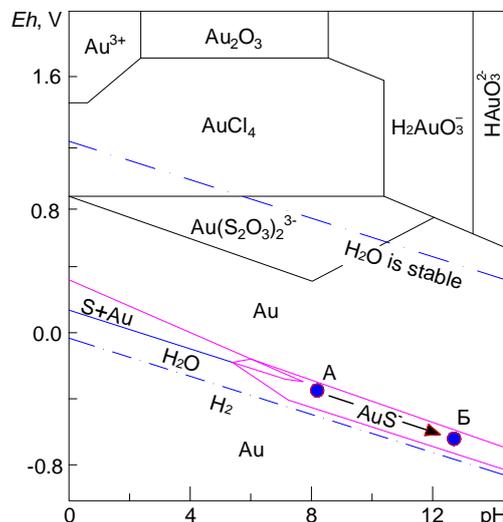


Figure 2. Stability ratios between some compounds of gold in water at 25°C and 1 atm with account of the thiosulphate ion equilibrium activity. The sum of dissolved chloride components is  $10^{-1}$  mol/l and the sum of dissolved sulphur is  $10^{-1}$  mol/l

The diagrams presented in Figures 1-3 are in good agreement with the conclusions of the author and give a complete pattern of the zones of stable existence of soluble gold compounds within the Eh-pH coordinates, as well as the dependence of the activity of these compounds in water on the ORP value. These data provide good guidance when planning and assessing the results of current and future technological research on this topic.

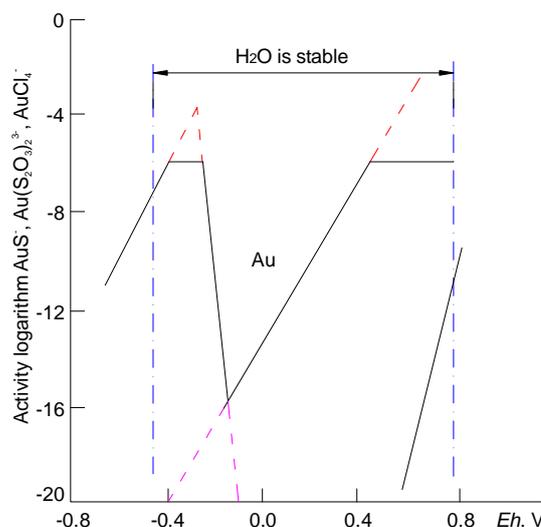


Figure 3. Dependence of the activity (concentration) of some gold compounds in water on the value of the ORP value at 25°C and 1 atm, pH = 8.0. The sum of dissolved sulphur is  $10^{-1}$  mol/l

The indicators of gold recovery into solution with such a simple instrumentation of the processes could be considered acceptable, but some negative factors accompanying this method reduce the advantages of the technology. Measurements of pH and Eh of the medium in the course of the experiments performed indicate that gold leaching occurs mainly according to the hydrosulphide version, and the zone of stable existence of the soluble hydrosulphide complex of gold in our case is located approximately in zone "A" (Fig. 2). As it follows from Figure 3, the area of gold existence in such a compound is characterized by a relatively limited range of medium Eh values. It is difficult to maintain the parameters of real technological processes in such a range, and given that these processes occur mainly on the earth's surface, the situation is complicated by the inevitable contact of productive solutions with air oxygen. This, in turn, can lead to uncontrolled sedimentation and loss of gold between technological stages. Indeed, the calculations performed by the authors in the work [29] and presented graphically in Figure 3 indicate that the area of existence of the water-soluble hydrosulphide gold complex is limited by narrow values of Eh from -0.470 to -0.170v. This is especially contrasting against the background of the thiosulphate compound indicators, where such a zone is much wider and ranges from -0.170 to +0.760v. Concerns about the above risks in the implementation of the gold recovery technology according to the hydrosulphide version are confirmed by a separately conducted experiment. In order to increase the sulphide and elemental sulphur dissolution according to reactions 1-3, an experiment was conducted with a higher alkali dosage (pH more than 11). It was expected that the process of hydrosulphide gold complex formation would continue more intensively and in the direction indicated in Figure 2 by the arrow towards point "B". However, the result turned out to be negative, with a significant decrease in the degree of gold dissolution. Probably, the ORP parameters of the medium exceeded the limits of the water-soluble hydrosulphide gold complex existence. Another reason for the failure can also be a sharp reduction in the formation of a complex-forming hydrosulphide anion due to the reversal of the sodium sulphide hydrolysis reaction [30] due to the creation of a significant excess of alkali in the solution.

It is obvious that in order to create more "comfortable" conditions for performing technological processes in practice, a transition to another zone is required, to the zone of stable formation of gold thiosulphate complex. According to calculations, this zone in Figure 3 is located at pH = 8, for example, in a wider Eh range from -0.170 to +0.760. However, pressure is required to enter this zone when air oxygen is used as the oxidizing agent. Under normal conditions a stronger oxidizing agent is required. For these purposes, chlorine can be used as a reagent, which, in active and ionic forms can be both an effective oxidizing agent and a complex-forming agent in a water-soluble gold compound (Fig. 1). In addition, obtaining chlorine in water solution from sodium chloride in an active form by the electrochemical method is a relatively simple task.

#### 4. Conclusions

Research has been conducted on mechanochemical activation by milling of the factory-made sulphide gold-bearing concentrate in an alkaline medium. The process was performed in a laboratory mill with a capacity of 2.3 l at

S:L = 1:2, and the ratio of loading the steel balls to the concentrate weight was 10:1. During the milling time of 30 min, the solid material of the -10 µm class has increased from 14 to 60%. With the measured parameters of the milled medium (pH = 8-9 and Eh from -0.18 to -0.19v), approximately 16% of gold has been recovered into the liquid phase of the mill. With the addition of 1 g/l divalent copper ions to the milling process, the recovery of gold into the liquid phase has increased to 48%.

It has been found that the transition of gold into solution is caused by the formation of a water-soluble hydrosulphide complex of gold during milling (AuS<sup>-</sup>).

The remainder of the solid product after milling was subjected to leaching with a sulphite-thiosulphate reagent in the mode: S:L=1:10, the content of sodium sulphite is 100 g/l, sodium thiosulphate is 50 g/l, copper is 1 g/l, at pH = 9.0-9.5, and process time of 4 hours. The continuous air supply to the reaction medium made it possible to maintain the medium Eh during the leaching process at a level of +0.030 to +0.080v. As a result, about 27% of gold has been recovered into the solution additionally.

An in-depth analysis of the performed research results has been made. It has been substantiated that the practical use of data obtained in the technology of gold recovery is associated with certain risks due to the relatively limited range of stable existence formed under the conditions of mechanochemical activation of the raw materials of the hydrosulphide gold complex.

In the process of leaching the gold-bearing raw materials, instead of the cyanide process, we used an environmentally friendly method of thiosulphate leaching.

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## Інтенсифікація процесу вилуговування золотовмісної сировини

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**Мета.** Дослідження з інтенсифікації процесу гідрометалургійної переробки золотовмісного продукту на основі механохімічного подрібнення вихідного сульфідного матеріалу.

**Методика.** Механохімічне активування (окислення) сульфідного золотовмісного концентрату в умовах надтонкого подрібнення, сульфід-тіосульфатне вилуговування подрібненого продукту після відділення рідкої фази. Дослідження проведено на пробі флотоконцентрату крупністю -0.074 мм, вміст Au – 15.5 г/т. При масі, що завантажується в млин вихідної проби концентрату 300 г, додавали 600 мл розчину гідрат окису кальцію концентрацією 143 г/л, маса куль, що завантажуються в млин по відношенню до маси концентрату 10:1. Залишок твердого продукту подрібнення піддавався вилуговуванню сульфід-тіосульфатним реагентом.

**Результати.** Встановлено різке зростання у подрібненому продукті фракцій 10 мкм (з 14.05 до 34.63%), а масова частка золота в кінцевому продукті подрібнення знизилася з 15.5 до 13.0 г/т, що відповідає вилученню золота у розчині на цій стадії на рівні 16%. Встановлено, що додаткова подача в процесі подрібнення мідного купоросу 1 г/л по міді дозволила знизити вміст золота у подрібненому продукті до 8.3 г/т, а вилучення золота у розчині на стадії подрібнення зросло з 16 до 48%. Виявлено, у процесі подрібнення часткове вилуговування золота утвореними із власної сірки реагентами. Встановлено, що перехід золота в розчин зумовлений утворенням у процесі подрібнення гідросульфідного водорозчинного комплексу золота (AuS). В результаті вилуговування реагентом вилучено додаткового близько 27% золота.

**Наукова новизна.** Встановлено фазові перетворення сульфідного золотовмісного продукту збагачення в результаті механохімічного активування. Цей процес здійснено вперше для інтенсифікації процесу вилуговування золотовмісної мінеральної сировини.

**Практична значимість.** Результати досліджень можуть бути використані в технологічних процесах переробки важкозбагачуваних золотовмісних руд та техногенної сировини.

**Ключові слова:** флотоконцентрат, золото, сірка, подрібнення, механохімічне активування, реагент, вилучення, розчин, окиснення, вилуговування