Mechano-Activation and SHS of Difficultly Taken Ore

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Abstract

Technological parameters of opening refractory ores by mechanical activation which determine remaining and the morphology of the samples after mechanical activation, SHS synthesis and the leaching process has been defined. Mechano-chemical activation of arsenopirita in different modes increases process have been defined. Optimal conditions for activation: time - 30 minutes at a ratio of grinding media and mineral 2:1. Leaching rate was higher for the activated samples the same amount of time than the original. Extraction of gold for the chosen optimum conditions is 93,2-95 %.

Introduction

Kazakhstan has rich mineral resource base but most of the gold deposit, more than 50% of these deposits are stubborn ores.

Important scientific and technological challenge for the gold mining industry is the problem of extracting gold from the technically hard materials. Such raw materials include gold-bearing ores and concentrate the processing of which under normal conditions of cyanide leaching does not provide a sufficiently high extract gold and accompanied by increased costs for the individual process steps [1]. The presence of such ores of sulfur, arsenic, cyanide and carbonaceous causes difficulties in the metallurgical processes.

Fine disseminations of gold is the most common cause persistence of gold ore, it took place mainly pyrite and arsenopyrite. Gold in these ores is in close mineral association [2, 3] in addition there is the so-called micro invisible gold [4]. Special persistence of gold is that it is part of the arsenopyrite replacing iron in it and getting the ionic form [5]. There are various tours: kiln technology opening the sulphide ores, autoclave, bacterial leaching. The most common way of opening refractory ores is kiln. Before firing after hydrometallurgical concentration slurry to thicken, dry, and after firing before cyanide leaching and re-grind moisten with water [1, 6].

As we know the rate of leaching depends on the nature of the solvent and the solid dispersion of the solid phase mixing intensity. Leaching rate and completeness of extraction of soluble cation depends not only on the degree of dispersion of the solid phase but also on the free surface. With the help of mechanochemical methods superfine grinding can dramatically influence the reactivity of solids, accelerate heterogeneous reactions to the synthesis and decomposition of substances, as well as to intensify the processes of dissolution and leaching [7].

The aim of the work done at this stage was to investigate the factors affecting the degree of opening of hard materials (arsenopyrite) and selection of optimal regimes of mechanical activation, providing a more complete extraction of gold leaching.

Results

Investigation of technological parameters autopsy refractory ores by mechanical activation

Most ore deposits of gold are due to persistent fine disseminations of gold in sulfides. Arsenopyrite in sulfide ores is the matrix material. Gold, part of the structure of arsenopyrite replaces the iron in it, takes the form of ions Au^{3+} [4, 5].

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Replacing Fe^{3+} on Au^{3+} in the lattice of arsenopyrite proved experimentally. From this it follows that this type of gold-bearing material in which the gold is chemically bound to the mineral matrix, cannot be processed in the usual way. As shown, without opening the mineral extraction of gold from refractory concentrates such is possible only in the range from 10-15 to 60-70%, depending on the composition of raw materials [3, 8, 9]. The most common method is the oxidative roasting followed by cyanidation of candle. Below is the overall reaction of oxidative roasting of arsenopyrite:

$$2\ FeAsS + 5\ O_2 \rightarrow Fe_2O_3 + 2\ SO_2\uparrow + As_2O_3\uparrow$$

With this opening of the sulfur and arsenic remain in the calcine (up to 1,21-1,8 %) [1].

For a more complete extraction of precious metals from refractory ores and intensify the process of opening the autoclave is used autopsy [10, 11]. Recently, biological methods have been developed expansions and the opening thrust of arsenic sulfide ores and concentrates [12, 13] in which gold-bearing sulfides are oxidized by oxygen.

Under the influence of mechanical activation, acting on the real structure of a rigid body, then its defects, that is part of the crystal lattice changes within the region of homogeneity of the compound [17]. A measure of the activity of a crystalline body which is in good condition and deficiency which is caused by disordering of the lattice of its own, which is a unique function of state parameters [17, 18] is the excess (ΔG_{exc}) free energy with respect to the phase of identical composition [19]:

$$\Delta G_{exc} = G_t^* - G_t,$$

where G_t^* and G_t – free energy, the phases in a normal and active states, respectively.

Reactivity of real crystals is higher, the higher the energy of the lattice is different from the ideal crystal lattice energy [20]. For experimental studies of hard materials by opening the mechanical activation using planetary centrifugal mill (PCM), shown in Figure 1. Grinding bodies in the working drum PCM are in the field of action of three forces: the centrifugal force due to rotation of the carrier around the main axis of the planetary mechanism, the centrifugal force produced by rotation of the drum and its own forces of Kariolisa – the result of a relative and translational motion. Rotation of the carrier, which is working the drums around the main axis of the planetary mechanism, creates a centrifugal force, which replaces the PTM in the force of gravity to be used in conventional ball mills.

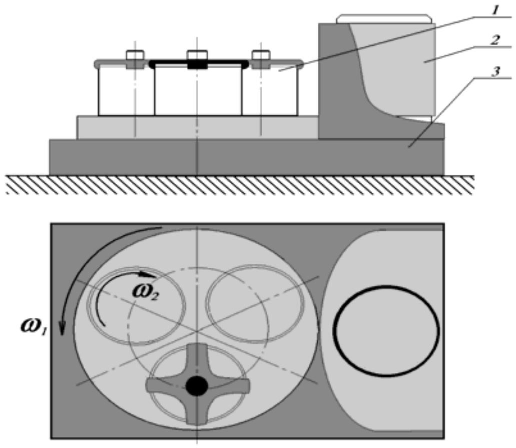

Fig. 1. General view of the planetary centrifugal mill:
1 - drum, 2 - motor, 3 - platform.

In the process of ultrafine grinding of the deformation and fracture of solids and the accumulation of defects of various kinds. The resulting defects, dispersion, and the associated formation of new surface, is the main factor causing changes in the reactivity of solids.

The main phases of the feedstock:

$FeAsS$, FeS_2, SiO_2.

To determine the changes arising in the studied minerals during mechanochemical treatment, samples of arsenopyrite was activated in PCM. The speed of rotation of the platform is 700 rev/min, the grinding vessels is 1200 rev/min. The volume of the grinding vessel is 300 ml, treatment was carried out in different modes from 5 to 35 minutes at various ratios of balls. The size of grinding balls is from 0.3 to 15 mm. The process of getting the finest powders is determined by a narrow notion is dispersion [7].

Parameters that characterize the degree of dispersion, are the specific surface area and particle size distribution of powder, which is defined generally as a function of the particle distribution by fractions. To characterize the specific surface area is the most convenient, since it is relatively easy to measure applied by different methods of gas adsorption. Granulometric composition is determined by sieving. The test arsenopyrite in the initial state is a polydisperse powder, mechanical activation contributes to the equalization of particle size.

Figure 2 shows a graphic representation of changes in dispersion of activation time. The most monodisperse sample is when you activate for 30 minutes. (83.1% particle size is of 12-23 μm).

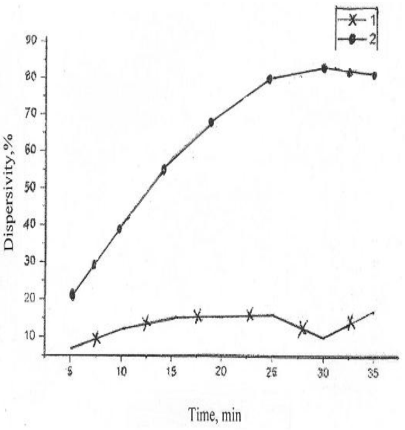

Fig. 2. Change the dispersion of activation time:
1 - Source arsenopyrite, 2 - MCA activation

Increasing the length of time over 30 minutes of mechanical treatment leads to adhesion of the particles due to the high dispersion, which leads to errors in the sieve analysis. Figure 3 shows the specific surface of samples after activation treated at the same time and loading. For mechanical activation of the specific surface of samples has increased dramatically, but it is refined more than 30 minutes is its decrease, due to the aggregation of particles of arsenopyrite.

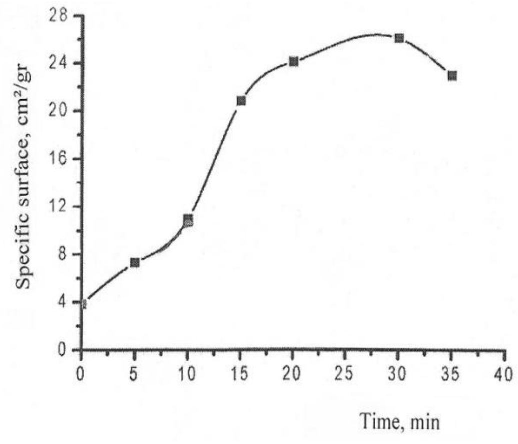

Fig. 3. Specific surface of arsenopyrite after mechanical activation.

Such behavior is typical for the activation of minerals with a layered structure [21]. The influence of mechanical activation on the properties of the samples. To change the properties of the samples allow us to judge the data of differential thermal analysis (DTA). Figure 4 shows the DTA data of the initial sample at 15 minutes of activation.

On the lines of the DTA is not activated and activated samples clearly shows a change in the properties of the activated samples. As a result of mechanical activation lowered the temperature threshold of the beginning of the oxidation of arsenopyrite and reduced the time of oxidation.

The temperature range in which the oxidation is not activated arsenopyrite 450-640°C (line 1, Figure 4).

Processing in a planetary mill leads to a change in the DTA data (line 2, Figure 4) in the initial section in the temperature range 160-320°C, which is related to the conversion of elemental sulfur formed during treatment [21].

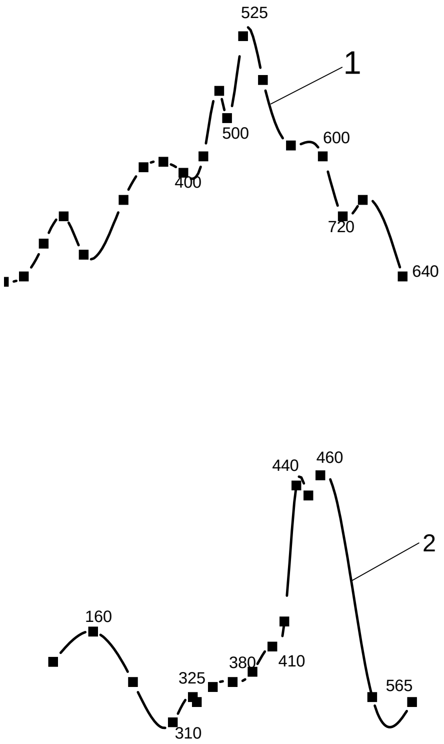

Fig. 4. DTA – curves of arsenopyrite and products of mechanical activation: 1 - not activated, 2 - activated in the air 15 minutes.

The study of the characteristics of the influence of preliminary mechanical activation on the properties of the samples was performed by XRF, XRD and DTA. Figures 5.6 X-ray source are arsenopyrite, arsenopyrite after mechanical activation. These phase composition of samples and the sulfur content in XRD data shown in Table 1.

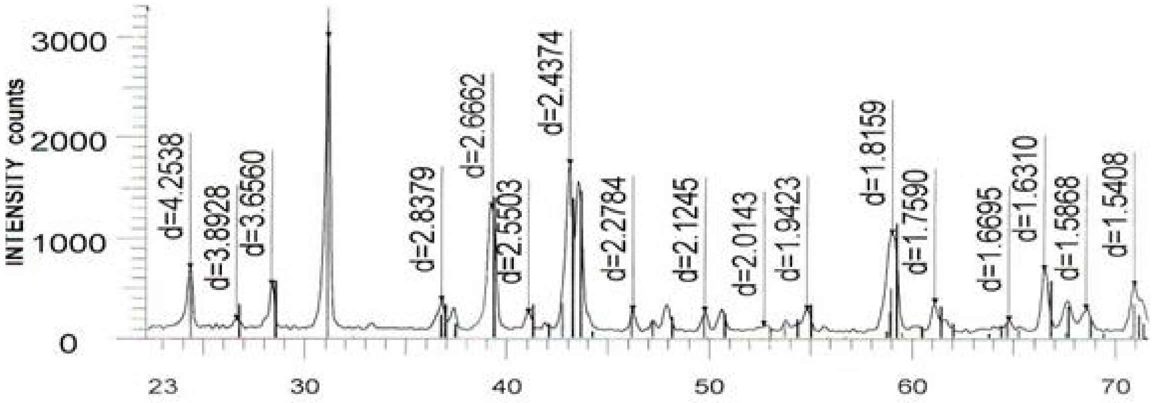

Fig. 5. X-ray of the original arsenopyrite (θ)

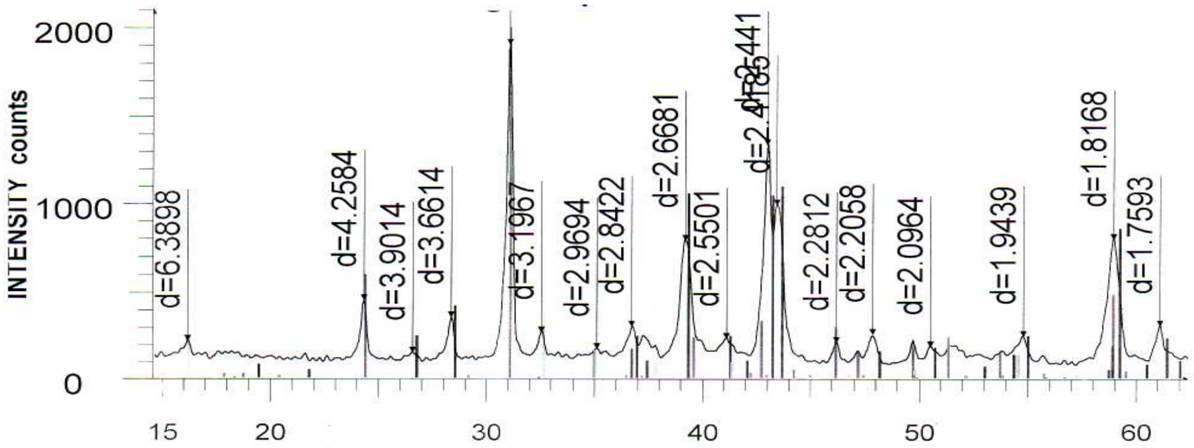

Fig. 6. X-ray arsenopyrite activated 30 min (θ)

Table 1

Phase composition of products of activation, the sulfur content in arsenopyrite

Environment Activation	Activation time, min	Phase composition, XRD data	Sulfur content,%, X-ray diffraction data
Initial	-	SiO_2 , FeAsS,	14,2
Mechanical activation	10	FeAsS, SiO_2	14,2
	20	FeS_2. FeAsS, As_2O_3, SiO_2	12,2
	30	FeAsS, Fe_2O_3, SiO_2, As_2O_3	11,8

Determination of the composition and morphology after mechanical activation, SHS synthesis and the leaching process

Influence of preliminary mechanical treatment on the reactivity of processed ores and concentrates sufficiently studied [14]. With the help of mechanochemical activation methods can dramatically affect the reactivity of solids, accelerate heterogeneous reactions to the synthesis and decomposition of solids, as well as intensify the processes of leaching.

Experiments were performed with the use of preliminary mechanical activation of arsenopyrite before firing, firing and subsequent leaching. In the traditional roasting of arsenopyrite oxidation in cinder remains to 1.5-1.8 % of arsenic and sulfur [1].

For removal of arsenic and sulfur were carried out repeated firing. Excess oxygen can cause oxidation of arsenic to As_2O_5 (nonvolatile) and the burning of sulfur can raise the temperature of the process at which the melting of the candle.

It is known that the mechanical activation lowers the melting point, sintering and thermal decomposition of minerals in the 100-2000 and may also change the phase composition [22].

In order to reduce the firing temperature, porous cinders and receive the maximum possible removal of arsenic and sulfur were carried out mechanical activation of arsenopyrite. To avoid the formation of arsenic pentoxide and of firing in oxidation-reduction mode, arsenopyrite activated before firing with a reducing agent. Activation of arsenopyrite was carried out at different time regimes during loading of 2:1 and 4:1 (ratio of balls and minerals).

After the activation phase of the investigated samples, Table 2. When you activate the 10-minute loading and 2:1 there is no change in phase composition.

Increasing the intensity of the impact on work patterns leads to the formation of new phases of $Fe_{1-x}S$ and As_2O_3. Before activating the charge injected reductant for firing in oxidation-reduction mode.

In carrying out the oxidation- reconstruct - activated samples fired indeed, the heat liberated in the system when the chemical reaction can cause a transition from the regime of the mechanical mode of synthesis in the self-propagating high synthesis (SHS) [22].

When using mechanical activation of initial charge it is possible for IFOR. In carrying out the process in this regime can be achieved to address such adverse effects as a combustion sintering and melting [23], which affects the subsequent calcine leaching process of arsenopyrite.

Table 2

Conditions of activation and the phase composition is not activated
and activated arsenopyrite

Weight loaded, g		Activation time	Phase composition of samples,%				
balls	arsenopyrite		FeAsS	FeS_2	$Fe_{1-x}S$	SiO_2	As_2O_3
30	15	10	69.0	0,9	-	30,1	-
30	15	20		-	0,9	29,0	0,7
30	15	30		-	14,3	29,1	1,4
60	15	10		0,8	0,7	28,7	0,5
60	15	20		-	8,2	28,9	1,2
60	15	30		-	12,1	30	1,6
60	15	40	42,1	-	17,4	32,0	1,8

During the experiments as a reducing agent used aluminum grade -4 and powdered coal technology. Selection of the composition of the charge carried by experiment, as predicted amount of peroxide formed arsenic is not possible, it depends on various factors that affect the burning process (amount of oxygen, the process rate, temperature, etc.). The optimum content of the reducing agent must ensure the flow of the oxidation-reduction burning in a temperature- time regime in which the oxidation of arsenic to volatile compounds and to obtain a porous cinder. Excess aluminum in the charge could lead to the restoration of iron trioxide to the metal and silicon oxide to silicon.

Activation of the charge carried by the relation of balls and arsenopyrite 2-1. Charge composition and phase composition of the activated samples are shown in Table 3.

Table 3

Compositions of activated mixtures and the phase composition after activation

Composition of the charge , %			Phase composition after activation
Arsenopyrite	Carbon	Aluminum	
96	2	2	FeAsS, SiO_2, Fe_7S_8, Al, C
92	6	2	FeAsS, SiO_2, $Fe_{1-x}S$, Al, FeAs
90	4	6	FeAsS, SiO_2, Fe_7S_8, Al, C
88	6	6	FeAsS, SiO_2, $Fe_{1-x}S$, Al, FeAs
90	10	-	FeAsS, SiO_2, $Fe_{1-x}S$, Al, FeAs
90	-	10	FeAsS, SiO_2, Al, FeAs

The activation time is 20-30 minutes, it is chosen from the results of the activation of arsenopyrite with no additives. XRD data showed the change of phase composition in comparison with the initial sample. Activated samples without the reducing agent, with a reducing agent and is not activated, the samples were fired. To commit changes in temperature using a thermocouple and oscilloscope mode P-0716m, the relative error in determining the temperature of – 5% [24]. Macrokinetic combustion characteristics of the system FeAsS-Al-C at different ratios of the components is shown in Table 4. Kinetic characteristics which are obtained by roasting arsenopyrite mechanoactivated additives vary greatly with the characteristics of the activated samples without the reducing agent. The heat in the system during a chemical reaction as well as due to relaxation of the stress field in mechanical activation may be the cause of the transition process in SHS [25, 26]. When the firing decreases the induction period of ignition of the samples activated with a reducing agent as well as decreasing the temperature of the process (in particular the content of components in the system). The nature of the combustion mode is not activated and activated samples without additives and with additions of the reducing agent can be judged from the temperature profiles of combustion (Figure 7). The temperature profiles are not activated and activated samples without additives are observed endothermic areas. For samples with reducing agents such processes are not typical. The system burns in the SHS mode. The resulting cinders were analyzed for phase composition by XRD (Table 5).

Table 4

Macrokinetic combustion characteristics of the system FeAsS, Al, C

The composition of the harge			Processing, time, min.	The parameters of combustion		
FeAsS	Al	C		Flash point, °C	Burning time, sec	The maximum combustion temperature, °C
100	-	-	-	450	380	800
100	-	-	30	330	340	750
96	2	2	30	280	360	760
96	2	2	-	400	370	800
92	4	4	30		180	820
92	4	4	-	410	340	800
90	6	4	30	280	90	820
90	4	6	30	300	180	810
88	6	6	30	280	120	780
88	6	6	-	360	300	800
88	12		30	290	85	850
88		12	30		340	780

Table 5

Phase composition stubs

№	The composition of the charge, %			Phase composition
	FeAsS	Al	C	
1	100	-	-	FeAsS, FeS, Fe_3O_4, γ-Fe_2O_3 SiO_2,
2	90	6	4	Fe_2 S, , γ-Fe_2 O_3, FeS_2 , SiO_2
3	90	4	6	Al_2 O_3, Fe_3O_4, SiO_2, γ-Fe_2O_3
4	92	4	4	Al_2O_3, Fe_3O_4, SiO_2, γ-Fe_2O_3- traces arsenate

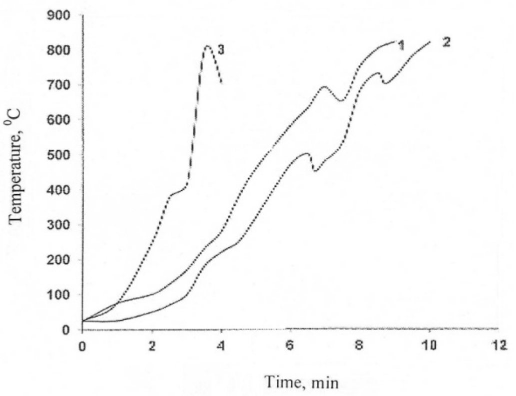

Fig. 7. Temperature profiles of combustion of arsenopyrite: 1 - Activated; 2 - not activated; 3 - activated with 6 % Al and 4% carbon.

Cinders turned porous are fairly loose. In figure 8 shows the cinder obtained from the activated sample 4.

This spectral analysis of this sample (Table 6) show almost complete removal of arsenic and sulfur in the calcine. Table 7 shows the composition of the feedstock and cinders.

The use of activated before firing contributes to the intensification of the firing process (process temperature, time of firing) and enhances the removal of sulfur and arsenic from the candle.

Cyanidation is the primary method of extraction of fine gold [1, 5].

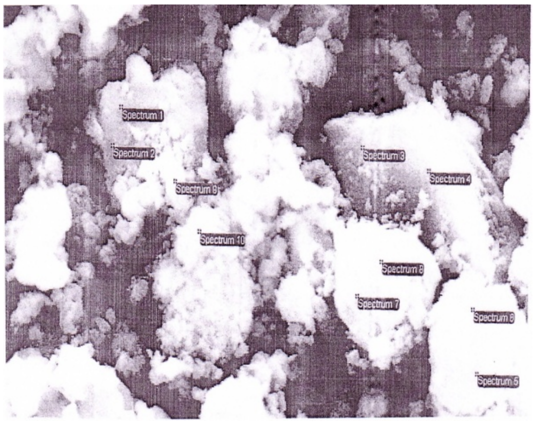

Fig. 8. The calcine samples (4), arsenopyrite.

Table 6

Analysis of the resulting calcine (4),%

spectrum	O	Al	Si	S	Fe	As	Pd	Tb	total
spectrum 1	54,77	2,12	36,98	0,10	3,90	0,10	1,41	0,64	100,0
spectrum 2	59,48	1,80	33,87	0,40	4,54	0,60	0,21	0,36	100,0
spectrum 3	37,69	2,60	45,61	0,29	8,44	0,55	3,42	2,49	100,0
spectrum 4	55,05	2,53	38,27	0,09	2,73	0,29	1,45	0,17	100,0
spectrum 5	53,52	1,76	37,90	0,30	4,14	0,11	1,59	0,89	100,0
spectrum 6	49,82	3,21	27,20	0,55	15,99	0,45	2,41	1,28	100,0
spectrum 7	42,00	1,86	6,33	0,96	43,72	0,36	1,78	2,99	100,0
spectrum 8	37,38	2,74	2,90	0,79	47,97	0,60	2,78	4,73	100,0
spectrum 9	53,75	5,68	26,01	1,46	10,39	0,89	1,84	0,03	100,0
spectrum 10	47,87	5,53	13,89	0,88	26,61	0,18	2,95	2,45	100,0

Table 7

Composition of the feedstock and cinders

sample	Content of elements,%									g/t	
	SiO_2	Cu	Pb	Fe	FeO_3	Al	S	As	Zn	Ag	Au
initial	30,1	0,2	0,5	22,25	-	-	13,1	31,18	0,29	15	2,3
activated	30,1	0,2	0,5	22,25	-	-	13,1	31,18	0,29	15	2,3
activated annealed	60	0,2	0,1	-	34,4	1,5	-	0,130	0,32	90	20
Activated annealed with a reducing agent	60,5	0,3	0,1	-	37,0	1,5	-	0,128	0,38	90	20

The process of dissolution of noble metals in cyanide solutions is diffusive in nature [5, 6]. In this regard, factors that accelerate the diffusion should be considered as possible ways to intensify the process of cyanidation.

One way of intensifying the process of refractory ores is cyanidation hyperfine blending which allows more in-depth dissection of hard materials [27], resulting in significantly increased surface area of raw materials thus increasing contact with the gold cyanide solution.

Leaching of gold from cinders were carried out by conventional cyanide method of mixing with all the technological requirements: mixing, aeration, pH 11, the ratio of M: T-4: 1, cyanide concentration 0.05%. Time cyanide is 2, 4, 6, 8 hours. Figure 9 shows the kinetics of extraction of gold depending on the methods of preparing samples for cyanide leaching. Gold recovery from a pre- activated samples above – 94,4-95,0 %. Data on the degree of extraction of gold from cinders, activated with additives and without additives, for 8 hours of leaching, are no different. An indicator of autopsy materials is hard to extract gold in the fullness of cyanidation.

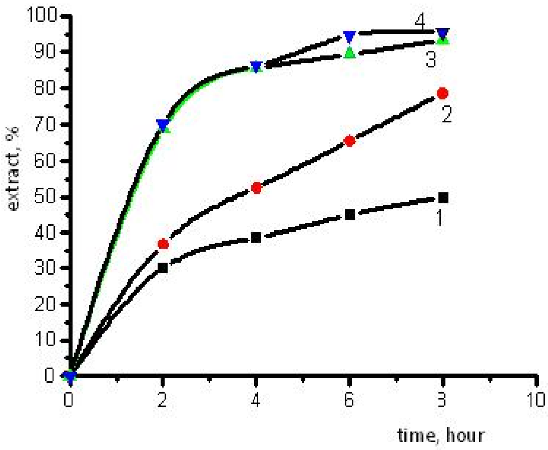

Fig. 9. The kinetics of gold extraction depending on the method of preparation for cyanidation of arsenopyrite:
1 - source, 2 - annealed non-activated, 3 - annealed activated, 4- annealed activated with a reducing agent

Conclusion

Mechanochemical activation of arsenopyrite in various modes leads to an increase in specific surface area of the mineral being processed, and hence to increase the reactivity of arsenopyrite and its value depends on the time of activation. Optimal conditions for activation: time - 30 minutes at a ratio of grinding media and mineral 2:1. Increasing the mechanical activation leads to adhesion of the particles of the mineral which reduces the rate of the specific surface.

It is established that the activation of the sample leads to an increase in the reactivity of the mineral, which is expressed in the temperature of thermal oxidation.

As a result of preliminary mechanochemical activation to obtain new phases Fe_xS_{x-1}, FeS, and As_2O_3, and the firing of redox SHS mode reduces the firing temperature. Arsenic and sulfur in the calcine – 0,10-0,39 %. Cinder obtained friable and porous.

On increasing the chemical activity of the samples obtained by mechanical activation of said kinetics and extent of cyanide leaching gold recovery. Leaching rate was higher for the activated samples as compared to original ones. Extraction of gold for the chosen optimum conditions of 93,2 - 95 %.

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