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По представленной зависимости можно сделать вывод, что Ф – 4Д после термической деструкции имеет более низкий коэффициент трения качения, чем исходный, что может быть обусловлено наноразмерностью частиц УПТФЭ. Полученный продукт рекомендуется использовать как компонент твердых и консистентных смазок различного назначения.

Консистентная смазка может применяться для понижения коэффициента трения в системе ступица – вал или в качестве компонента при производстве смазывающих материалов.

Выводы.

Таким образом, нанотехнологии являются неотъемлемой частью современного мира. Применение отходов в качестве сырья для получения наноструктурных материалов экономически и экологически эффективный способ. Так при переработке отходов методом термической деструкции получен наноразмерный УПТФЭ. При изучении свойств выявлено, что УПТФЭ обладает высокими трибологическими характеристиками и может эффективно применяться для получения консистентных смазывающих материалов.

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THE USE OF WET MECHANICAL ACTIVATION FOR OPENING REFRACTORY ORES AND PRECIOUS METAL RECOVERY

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Abstract

The article describes the factors that influence the degree of fineness of arsenopyrite in various media. The effect of dry and wet thermal oxidation activation is sulfided. Found that activation of arsenopyrite in water leads to oxidative degradation with the formation of its trioxide iron, sulfur oxidation and transfer it to the water-soluble compounds.

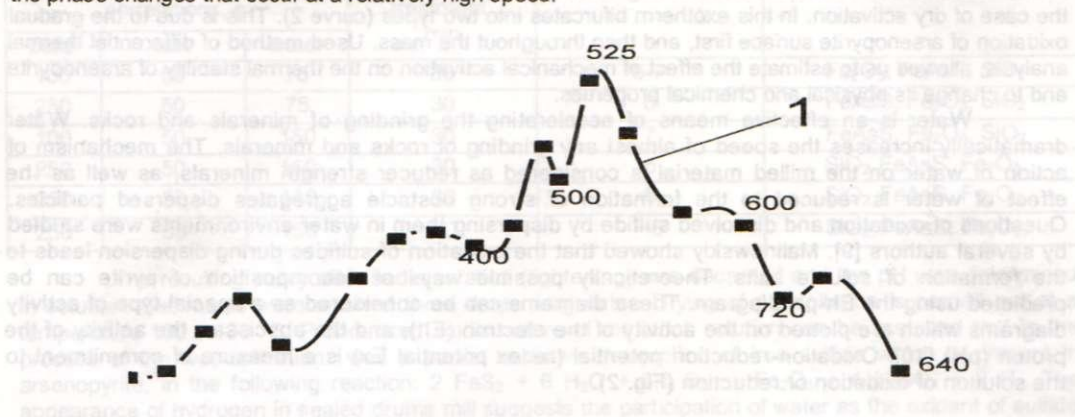
Keywords: arsenopyrite, thrust raw, mechanochemistry, activation, surface area, phase composition, sulfur.

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Kazakhstan is the most ancient gold-mining region. At present the country has more than two thousand deposits and gold occurrences, of which about 200 proven and in use for at least 60. Proven reserves of gold The Republic of Kazakhstan is the third largest among the CIS countries [1]. Important scientific and technical challenge for the gold mining industry is the problem of extracting gold from technically hard materials. According to experts, it is through involvement in the operation of refractory gold and complex gold ores in this century will be provided by the main increase in gold production in the world [2]. Most full mechanochemical effects occur when using modern devices for ultra-fine grinding. For the experiments the activation of arsenopyrite used planetary centrifugal mill. The quantitative composition of elements in arsenopyrite determined by XRD. The analysis was performed by three points, the following average values, %: Fe - 25.7, As -32.7, S -14.2, Cu - 0.2, Pb - 0.5, Ag-0.13, Tb -0.12, Al-0.05, Si -11.95, O - 14.5. Phase composition of the feedstock was determined by XRD. The main phases of raw materials and semi-quantitative composition, %: quartz (Si O₂) – 29.2, FeAsS₂ -71,4(including ~ 5 FeS₂). X-ray diffraction and X-ray analysis is not possible to determine with sufficient accuracy the quantitative content of precious metals. Therefore we conducted assay analysis method [3]. The basis of this method is put slight solubility of gold, silver and platinum group metals in the molten lead which gives you a lead to extract precious metals scattered in the sample. To remove sulfur and arsenic previously weighed sample was burned in a muffle furnace aluminum cups stirring occasionally. Studies have shown that the test materials, except arsenopyrite contains up to 30% quartz, sulphides, represented by pyrite.

Activation of dry materials in the different modes

Mechanochemical treatment is simple, convenient and effective method for modifying the physical and chemical properties and reactivity of solids [4]. The process of getting the finest of fine powders and suspensions defined a narrower concept - dispersion [5]. Some parameters characterize the degree of dispersion. The volume of the grinding vessel was 300 ml. Treatment was carried out at different time modes from 5 to 35 minutes and at different ratios of balls: arsenopyrite 2:1 4:1, 6:1. In dry grinding surface area of samples has increased dramatically, but the milling more than 30 minutes is reducing it, which is probably due to the aggregation of particles arsenopyrite. Such behavior is typical for the activation of minerals with a layered structure [6]. Autopsy sulfide raw materials by ultra-fine grinding is carried out both dry and wet. "Wet" mechanical activation involves processing of ores and concentrates in the aquatic environment. There is no aggregate and aggregate wet activation. Grinding media and other machine parts, contacted with refinable material in a liquid medium shredding directly affect the physical and chemical processes that occur during the activation. Effect of grinding media on refinable mineral substance in a liquid medium is known as an example of reactions of minerals with the evolution of hydrogen, the formation of which is due to the interaction of water with iron with wear steel or iron balls in a planetary mill [7]. In this process pH changes that may contribute to oxidative degradation of activated mineral. In order to determine the effect of wet mechanical activation to change the properties of arsenopyrite, experiments in planetary centrifugal mill in water. The activation time is 10 to 35 minutes, balls ratio: 4:1 is arsenopyrite, arsenopyrite: water - 1:2. After 30 minutes of activation turned monodisperse powder to 90.1% consisting of particles of 12-23 microns. About changing the properties of the samples after the activation of the dry and wet allow to judge the data of differential thermal analysis (DTA). Figure 1 shows the DTA curve of the original sample as well as samples obtained in different media activation, activation time 15 minutes. The method determines the phase changes that occur at a relatively high speed.



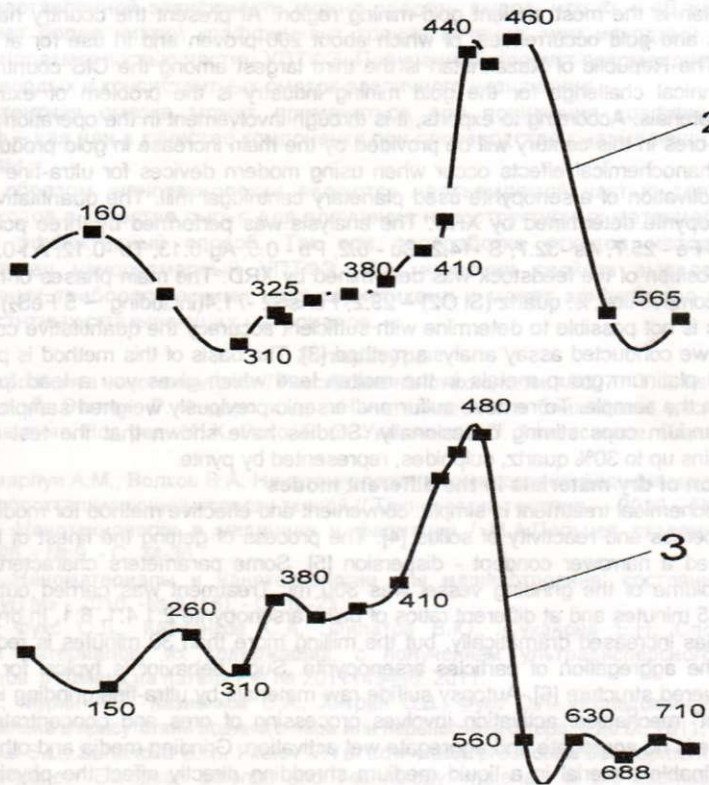


Fig 1. DTA - curves arsenopyrite and products of mechanical activation:

1 - not activated, 2 - activated in the air 15 minutes, 3 - activation in water 15 minutes

The temperature range in which the oxidation is not activated arsenopyrite 450 - 640 °C (curve 1, Fig. 1), which is close to the data in [8]. Processing of the sample in a planetary mill leads to a change in the DTA curve of the initial part of the temperature range 160 - 320 °C. It is associated with the transformation of elemental sulfur formed during processing. When activated arsenopyrite in water decreases its thermal stability. Position of the maximum exothermic cycle (Fig. 1 curve 3) is shifted to a lower temperature region from 525 °C to 480 °C and in the temperature range 160 - 350, a change in the character of the curve compared to the original model due to the transformation of elemental sulfur as in the case of dry activation. In this exotherm bifurcates into two types (curve 2). This is due to the gradual oxidation of arsenopyrite surface first, and then throughout the mass. Used method of differential thermal analysis, allowed us to estimate the effect of mechanical activation on the thermal stability of arsenopyrite and to change its physical and chemical properties.

Water is an effective means of accelerating the grinding of minerals and rocks. Water dramatically increases the speed of almost any grinding of rocks and minerals. The mechanism of action of water on the milled material is considered as reducer strength minerals, as well as the effect of water is reduced to the formation of strong obstacle aggregates dispersed particles. Questions of oxidation and dissolved sulfide by dispersing them in water environments were studied by several authors [9]. Malinowski showed that the oxidation of sulfides during dispersion leads to the formation of soluble salts. Theoretically possible ways of decomposition of pyrite can be predicted using the Eh-pH diagram. These diagrams can be considered as a special type of activity diagrams which are plotted on the activity of the electron (Eh), and the abscissa - the activity of the proton (pH) [10]. Oxidation-reduction potential (redox potential Ex) is a measure of commitment to the solution of oxidation or reduction (Fig. 2).

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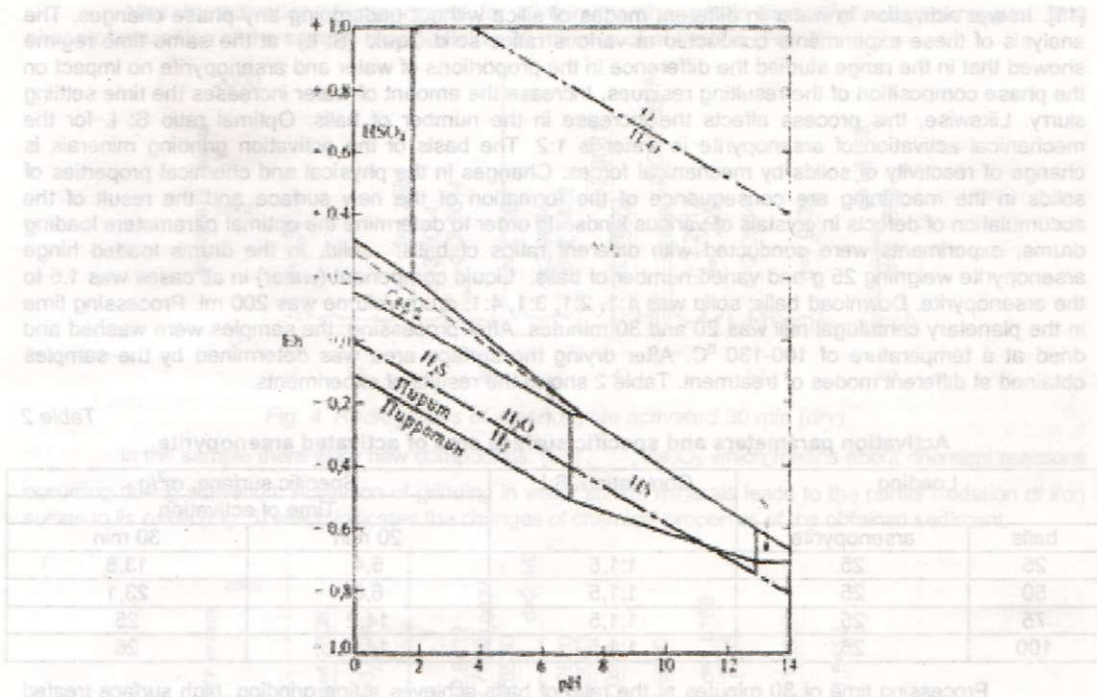


Fig. 2. Eh-pH diagram showing (1 atm) and lower (= 1 atm), the limits of stability of the water and the prevalence of various forms of sulfur. The dashed lines are the boundaries between the areas of water ions in the field of sulfur [15]

Sulfur contained in arsenopyrite is in the form of iron sulfide and depending on environmental conditions (pH) can interact with the environment (salt solution, alkali, water). Natural pyrite usually does not react with water, hydrochloric acid and alkali. Used to determine the physical and chemical properties of the resulting sludge varied the ratio of water to the arsenopyrite. The works were carried out in sealed vessels in planetary centrifugal mill. This eliminates the possibility of dust (Table 1). Loading balls and arsenopyrite was 2:1. As activator we used planetary centrifugal mill.

Table 1

Activation conditions

Mass correlations, g			Time of treatment, min	pH in basic solution	Phase composition
balls	test	water			
100	50	75	30	6-7	Fe ₂ O ₃ , FeAsS, SiO ₂
250	50	75	30	6	FeAsS, Fe ₂ O ₃ , SiO ₂
100	50	150	30	7	FeAsS, Fe ₂ O ₃ , SiO ₂
250	50	150	30	6	SiO ₂ , FeAsS, Fe ₂ O ₃ ,
250	50	100	30	5	SiO ₂ , FeAsS, Fe ₂ O ₃ ,
250	50	150	30	~6	SiO ₂ , FeAsS, Fe ₂ O ₃ ,

The resulting slurry after sedimentation (lightening) was decanted and the pH was determined in solution. Sediments were washed three times with water. Drying of precipitation is carried out at a temperature 100 - 130 °C. Pronounced acidic nature of the stock solution can be assumed that in the process of the wet activation was a partial oxidative destruction of iron sulfide which is present in arsenopyrite, in the following reaction: $2 \text{FeS}_2 + 6 \text{H}_2\text{O} + 6,5 \text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + 4 \text{H}_2\text{SO}_4 + 2 \text{H}_2$. The appearance of hydrogen in sealed drums mill suggests the participation of water as the oxidant of sulfide

[11]. In wet activation in water in different modes of silica without undergoing any phase changes. The analysis of these experiments conducted at various ratios solid: liquid (S: L) at the same time regime showed that in the range studied the difference in the proportions of water and arsenopyrite no impact on the phase composition of the resulting residues. Increase the amount of water increases the time settling slurry. Likewise, this process affects the increase in the number of balls. Optimal ratio S: L for the mechanical activation of arsenopyrite in water is 1:2. The basis of the activation grinding minerals is change of reactivity of solids by mechanical forces. Changes in the physical and chemical properties of solids in the machining are consequence of the formation of the new surface and the result of the accumulation of defects in crystals of various kinds. In order to determine the optimal parameters loading drums, experiments were conducted with different ratios of balls: solid. In the drums loaded hinge arsenopyrite weighing 25 g and varied number of balls. Liquid component (water) in all cases was 1.5 to the arsenopyrite. Download balls: solid was 1:1, 2:1, 3:1, 4:1, drum volume was 200 ml. Processing time in the planetary centrifugal mill was 20 and 30 minutes. After processing, the samples were washed and dried at a temperature of 100-130 °C. After drying the surface area was determined by the samples obtained at different modes of treatment. Table 2 shows the results of experiments.

Table 2

Activation parameters and specific surface area of activated arsenopyrite

Loading		Correlation S:L	Specific surface, m ² /g	
balls	arsenopyrite		Time of activation	
			20 min	30 min
25	25	1:1,5	5,4	13,8
50	25	1:1,5	6,8	23,1
75	25	1:1,5	14,2	25
100	25	1:1,5	14,8	26

Processing time of 30 minutes at the ratio of balls achieves a fine grinding, high surface treated arsenopyrite, with a ratio of Balls: Solid 2:1 and 3:1. When the ratio of balls: Solid = 4:1 there is a slight increase in the specific surface area. Mechanical activation for 30 minutes at a ratio of 3:1 and 4:1 turns arsenopyrite in a finely dispersed state. This complicates the process of settling and filtration (pulp bleaching increases the time) which may require the use of special equipment to speed up the process. Effect of mechanical pre-treatment on the physical properties and reactivity of solids is well known. In the process of mechanical activation is an increase in supply of free energy of a solid. The increase in activity due to mechanical treatment always leads to an increase in the deviation from equilibrium, and thus to increase the rate of reaction [12]. Increase in the stock of excess energy affects the properties of the samples can be determined calorimetric measurements by establishing a value of the heat of solution or by DTA. Increase in the stock of excess energy affects the properties of the samples can be determined calorimetric measurements by establishing a value of the heat of solution or method - differential thermal analysis (DTA). The nature of the DTA curve changes as compared with the curve of non-activated and activated dry. Temperature peaks are more diffuse profile and oxidation occurs over a shorter period of time (Fig. 1). X-ray analysis of the activated samples (XRF) gives an indication of phase transformations during its processing. Non- activated original sample has a weight composition, %: 71,4 – FeAsS, 28,6 – SiO₂ (Fig.3)

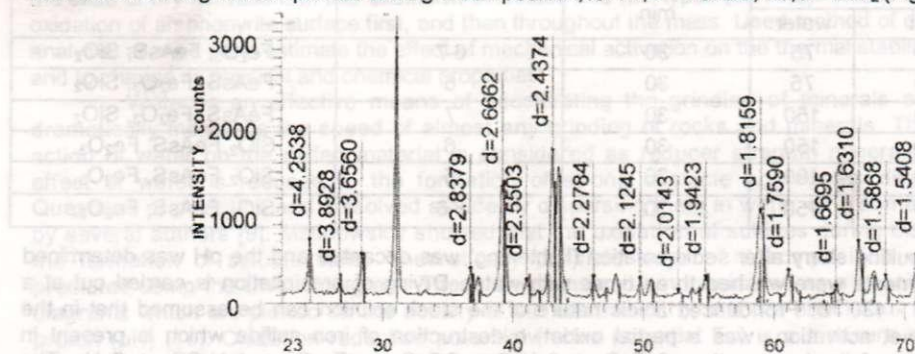


Fig. 3. X-ray of the original arsenopyrite

After dry activation of arsenopyrite for 10 minutes changes in the sample did not happen. The phase composition of the sample changed after 30 minutes of activation (Fig. 4).

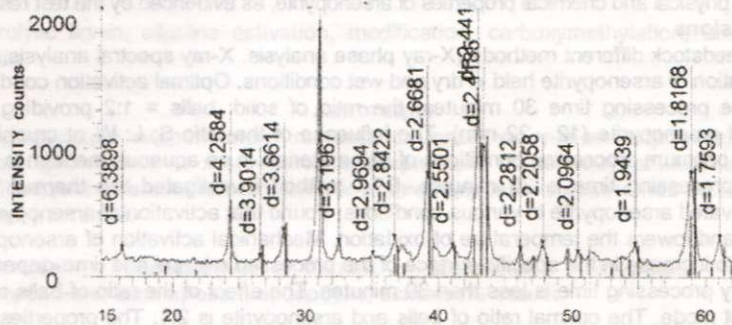


Fig. 4. Radiographs of arsenopyrite activated 30 min (dry)

In the sample there were new compounds: $(Fe)_{1-x}As_2O_3$, As_2O_3 which means about chemical reactions occurring during activation. Activation of grinding in water sulfide minerals leads to the partial oxidation of iron sulfide to its oxide (Fig. 5) which indicates the changes of chemical properties of the obtained sediment.

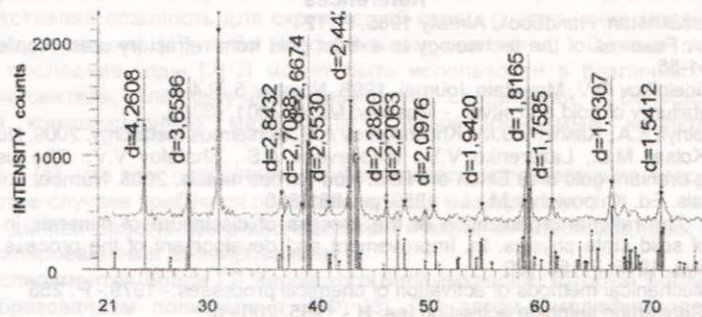


Fig. 5. Radiographs of activated water arsenopyrite, the activation time is 30 minutes

In precipitate Fe_2O_3 formed when activated 10 minutes. Further activation does not lead to the formation of new phases and only increases the iron content (Table 3).

Table 3

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

Environment of activation	Time of activation, min	Phase composition, XRD data	% Sulfur content, data of X-ray spectral analysis
original	-	$SiO_2, FeAsS,$	14,2
dry 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
wet activation	10	$FeAsS, SiO_2, Fe_2O_3,$	3,54
	20	$FeAsS, SiO_2, Fe_2O_3,$	3,42
	30	$FeAsS, SiO_2, Fe_2O_3,$	2,99

Original and activated samples were examined by XRD arsenopyrite. X-ray analysis method determines the dynamics of changes in the concentration of elements with different activation conditions. The source of sulfur arsenopyrite was 14.2%. There was a slight decrease in the number of sulfur When dry activation within 20 and 30 minutes. In residues derived after wet activation there was a sharp decrease in the amount of sulfur (data from X-ray spectral analysis, Table 3). The reason for this change is the oxidation of sulfur to water-soluble compounds which are then washed into the filtrate [13, 14]. On the change in the physical

properties of the activated samples (surface area) can be judged by the considerable increase after mechanical treatment (Table 2). Analysis of the properties of the samples leads to the conclusion: mechanical activation led to a change in the physical and chemical properties of arsenopyrite, as evidenced by the test results.

Conclusions

Study feedstock different methods (X-ray phase analysis, X-ray spectral analysis, assay method). Mechanical activation of arsenopyrite held in dry and wet conditions. Optimal activation conditions are set for dry activation: the processing time 30 minutes, the ratio of solid: balls = 1:2 providing the production monodispersity of arsenopyrite (12 - 22 mm). The influence of the ratio S: L: W at crushing arsenopyrite investigated. The optimum processing conditions of raw materials in an aqueous medium is the ratio S: L: B = 1:1.5:2:2, the processing time is 30 minutes. DTA method investigated the thermal stability is non-activated and activated arsenopyrite in various conditions. Found that activation of arsenopyrite increases its chemical activity and lowers the temperature of oxidation. Mechanical activation of arsenopyrite in wet and dry modes leads to increase in the specific surface of the processed mineral and time-dependent activation. To activate the dry processing time is less than 30 minutes. The effect of the ratio of balls and arsenopyrite is activated in wet mode. The optimal ratio of balls and arsenopyrite is 2:1. The properties of the samples obtained in the wet mode activated by X-ray phase analysis and X-ray spectral analysis. As a result of the activation changed the phase composition, the balance of a new phase is Fe_2O_3 . According to the results of X-ray spectral analysis has been a significant reduction in the sulfur content of the obtained samples: 14.4% in the original sample and 2,99 + 3,5% in the resulting residue. This indicates an increase in the reactivity of the treated arsenopyrite and led to oxidation of sulphides.

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MODIFICATION OF HYDROLYSIS LIGNIN

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Abstract

Modification of hydrolytic lignin for the purpose of receiving sorbent is carried out. It is shown that different types of physical and chemical modification differently influence sorption ability.

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