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Scientific Development and Creation Technologies of Directed Concentration of Copper from Aluminosilicate Raw Materials.

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ABSTRACT

A spatially-organized structure of aluminosilicates considered on account of self assembly and self-organization from silicon-oxygen-aluminum tetrahedron overlap of electron shell to form "Vernadsky`s kaolinite nucleus" undefined compositions. The variety of kaolin (clay) is determined by the content of basic cations that compensate the charge of final motifs $[SiO_4]^{4-}$ * $[AlO_4]^{5-}$, which impossible ascribe the specific chemical formula. It is shown that under the law of migration of elements, or rather, according to the law of inevitable polymerization of monomeric silicon-oxygen-aluminum tetrahedron in the framework structure reduces the amount of chemical traps that hold the transition, rare, radioactive and precious metals in silicates.The comprehensive technological scheme of directional concentration of copper, rhenium, rare earth and precious metals was developed by mechanical or chemical activating of polymerization process aluminosilicate raw material, with the release of metal concentrate and tailings of deactivated silica. The Hydrometallurgical process includes autopsy sludge with sulfuric acid, crystallization of potash alum (PA), the neutralization of the acid of collective solution of deactivated silica, extraction, electrowinning.

Keywords: aluminosilicates, kaolin nuclei, polymerization, extraction, electrowinning

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INTRODUCTION

Is long overdue need for a new universal approach to the recovery of copper, rhenium, rare and precious metals from aluminosilicate materials based on scientific advances of the last decades (thermonuclear fusion of elements, laser generation of light, the structure of water and silica, basaltic ocean phenomenon of the Earth, the chiral origin of oil and gas, directional concentration of transition, rare earth and radioactive and noble metals, etc.).

Hypergene aluminosilicate raw material, with a wide range of metals: non-ferrous (copper, zinc, lead, aluminum), rare refractory (titanium, zirconium, vanadium, niobium, tantalum, molybdenum, tungsten), radioactive (actinium, thorium, uranium), including rare earth (yttrium, scandium) and noble (silver, gold and PM) metals comprising them, usually in an amount of not more than 1%, while the mineral compounds of copper in sulfide and oxide forms subtly disseminated throughout the mass of clay-siliceous rocks. Aluminosilicates are a vast class of compounds of silicon, aluminum coordinated with oxygen. On presentation of D. Mendeleev the variety of aluminosilicates [1], related to the ability of silicon, aluminum interconnected by oxygen atoms to form "undetermined compounds" isomorphic composition depending on the ratio of the elements and not only the oxides of the same type, but different and capable of polymerization. Despite the extensive experimental data and extensive scientific generalizations concerning the nature of aluminosilicates, a number of hypotheses regarding the visionary role of oxygen radicals of silicon and aluminum, structure and properties of aluminosilicate are remained as a phantom mystery to the beginning of the XXI century.

The endless repetition of transformations of the Earth's crust was understanding for a long time. At the beginning of the XX century V. Vernadsky [2] formulated the postulates about the development of geo-bio-sphere of Earth systems and the law of migration of chemical elements. In his opinion the chemical composition of the lithosphere, "is not that - something still, but on the contrary, continuously changing over geological time". Aluminosilicates are derivatives complex aluminosilicate radicals "kaolin nuclei"$[SiO_4]_4^{4-} * [AlO_4]^{5-}$. The hypothesis about "kaolin nuclei" as a closed grouping of atoms O2, Si, Al is also actual today [3]. This is an ambiguous opinion, even James Hutton [4] wrote: "In the world device I could not find any tracks of start and end of any prospects". In fact, of course, there are probability of the beginning and the prospect of the ending. It is established [5] that the basic "building bricks" of aluminosilicates is tetrahedral of silicon (aluminum), surrounded by four oxygen atoms. If the formation of a silicate mantle of the Earth as a "beginning" to choose radical $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$, and as an "end» SiO^{2-} quartz and Al_2O_3- corundum, it is possible to draw a clear picture of its history, which will be used by the scientific substantiated facts and hypotheses.

The variety of aluminosilicates explained by sequential polymerization of the tetrahedra, in which a silicon or aluminum are being of peroxidation state and oxygen stable none quilibrium state with an excess of energy.

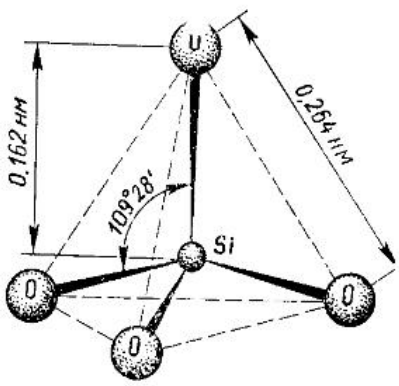

Figure 1: Average parameters of tetrahedral groups $[SiO_4]^{4-}$ in silica

Every act of polymerization is accompanied by the release of oxygen ions to forma bridge or siloxane bonds Si - O - Si, Al - O - Al. Process is accompanied by there lease of excess energy. There is impossible an attributed a specific chemical formula for aluminosilicate; their transformation takes place spontaneously by the internal energy of the crystal and strengthen by mechanical action, changing the nature of the chemical bond, and the degree of lattice imperfections at the atomic level.

Assessment of copper-containing aluminosilicates in a generalized form reviewed by the example of representative samples of deposits of Kazakhstan. **Table 1** shows the chemical composition of the copper-bearing aluminosilicate ore deposits occurring in the territory of Kazakhstan from western to eastern borders.

Table 1: Chemical composition of the copper-bearing aluminosilicate ore deposits of Kazakhstan arranged from west to east.

Elements and compounds	Deposits				
	Koskolskoe Priaralie	Dzheskazgan	Koktaszhal	Boschekul	Aktogai
Al_2O_3	12.0	13.0	15.0	20.0	22.0
SiO_2	75.0	70.0	65.0	55.0	55.0
Fe_2O_3	3.5	3.5	4.5	8.5	8.6
TiO_2	1.5	1.5	2.0	3.5	4.0
K_2O	4.0	3.5	2.3	1.6	1.5
Cu	0.9	0.9	0.48	0.42	0.35
∑ TReO	0.05	0.05	-	0.04	0.04
OB	2.5	3.0	2.5	6.0	-
Au	0.6 g/t	0.01 g/t	0.7 g/t	1.0 g/t	1.0 g/t
Ag	10.0 g/t	0.3 g/t	5.0 g/t	11.0 g/t	12.0 g/t
Re	1.0 g/t	0.9 g/t	0.3 g/t	0.3 g/t	0.2 g/t

As shown in the table the average content of basic components in the copper-containing aluminosilicate ore in wt.% Of SiO_2 (55-75), Al_2O_3 (8-22), Fe_2O_3 (3.5-8.6), K_2O (4.0-1.5), Cu (0.9-0.35), TiO_2 (1.5-4), TReO(0,05-0,04), Au (0.6- 1.0 g/t). The ratio SiO_2: Al_2O_3 ranges from 2: 1 to 6: 1, which corresponds to the composition of kaolin to feldspar. The system Fe-Ti-O represented: magnetite - $Fe_{2.5}$ [FeO_4], ilmenite - $FeTiO_3$, ortotitanat - $Fe_2[TiO_4]$. Copper in the ore is in the oxide and sulfide forms.

Aluminosilicate ore as shown in **Table 1** are always polymetallic low-target metals, difficult ore dressing and characterizes propensity host rocks to the sludge formation and the resulting resistant to autopsy. These features are defined not only by their material composition, as a mixture of carbonates, clay aluminosilicates and colloidal silica, riched with organic matter, but also the metals themselves are characterized by the completion of the internal electron orbits of atoms and thus has an enhanced reactivity properties capable of forming complex anions and double salt organic compounds with variable oxidation states, including iso- and polymorphic compounds. And all of decisions this problem are associated with the ultra-fine grinding of raw materials, to overlook the fundamental obstacles: incongruent multicomponent systems and colloidal ultrafine grinding materials.

Mineral formations (sulfides, phosphates, spinels) of transition, rare, radioactive and native precious metals are subtly embedded in the clay-siliceous-carbonate formation and genetically related to the organic matter. Interpenetration of rare and rare earth metals in the host rocks are so scale, that gradually and effectively separate their existing methods is almost impossible, as confirmed by the inapplicability of modern methods of enrichment (gravity, magnetic separation, flotation, mixed methods) to this type of ore.

Extraction of target metals depends on the structural and textural characteristics of aluminosilicate raw material, as well as the properties of chemical bound and free silica. The high content of chemically bound silica and alumina in the raw materials in the ore preparation process causes forming of sludge layered aluminosilicate which formed colloidal micro-dispersion with an organic substance not amenable neither magnetic separation, nor gravitation, nor flotation to obtain the selective or collective concentrates. Classical methods of enrichment do not allow to achieve the effective concentration of the transition, rare, radioactive and precious metals from the layered aluminosilicate material. Developed methods for seperation transition, rare earth, radioactive and noble metals of aluminosilicate raw material, which provides for direct processing with mineral acids not found industrial application. The reason for this is the high consumption of acid for extraction from silicates of compatible metals (aluminum and iron) and to maintain a high pH for retention in solution transition, rare earth and radioactive metals, and also is not solved, the problem of recycling of alumina and silica. Thereby, logical decision is directional formation the structure of aluminosilicates.

The formation perfect of structure achieves at the stage of ore preparation aluminosilicates, due to the transition of monomeric and final motifs in endless polymer aluminosilicate structure with a high proportion of siloxane bonds. Results of separation layered aluminosilicate and the formation of their polymeric structures realized on ore deposits Boschekul, Koktaszhal and Dzhezkazgan. Methodology of experiments for selected ore was carried out under the same conditions.

EXPERIMENTS

The ore was ground to a particle size of 0.2 mm - 100% with content of fraction 74 microns - 60% and separated in cycles. In the first cycle ground ore is mixed with liquid mass at S: L = 1: 1, the pulp was stirred for 3 hours, classified in a hydrocyclone with siphon height of 1 m water column, and the sand was subjected to in second cycle of polymerization, stirring the thick pulp prior to classification at the regime first phase. The low yield of layered aluminosilicates was got in the third and fourth stage polymerization and classification. Layered aluminosilicates was combined and made control of classification on the hydrocyclone with siphon height of 10 m water column. The results are summarized in **table 2**.

Table 2: Results of separation of layered and polymer structures copper-containing aluminosilicate

Cycles of separation	Deposits											
	Boschekul				Koktaszhal				Dzheskazgan			
	Layered aluminosilicates		Al_2O_3		Layered aluminosilicates		Al_2O_3		Layered aluminosilicates		Al_2O_3	
	weight	%	%	g	weight	%	%	g	weight	%	%	g
1	385,0	25,6	27,2	104,7	318,0	21,2	19,4	61,7	187,5	12,5	18,1	32,6
2	234,0	15,6	27,3	63,9	203,0	13,5	18,0	36,5	106,5	7,1	17,2	17,3
3	28,5	1,9	26,8	7,6	24,0	1,6	16,8	4,0	16,5	1,1	15,8	2,4
4	16,9	1,1	17,8	3,0	20,0	1,3	15,3	3,0	13,5	0,9	14,3	1,7
Total	**664,4**	44.3	27,0	179,4	**565,0**	37,7	18,7	105,6	**324,0**	21,6	17,8	57,7
control classification of sludge	**596,0**	**39,7**	**30,2**	**180,5**	**500,0**	**33,3**	**20,5**	**102,5**	**307,5**	**20,5**	**19,3**	**59,3**

It can be seen from **table 2** The scale of separation of layered aluminosilicates depends on the content of alumina in the raw material. At content of 20% Al_2O_3 allocated 40%, 15% Al_2O_3 allocated 33%, 13% Al_2O_3 allocated 20% of layered aluminosilicates. The process of mechanical polymerization finished effectively in two cycles. Polymerized framework silicates is sent to process of flotation and gravity. Flotation of concentrate of copper sulfides is carried out on deoxygenated pulp at pH 7.0. To the pulp was mixed sodium sulfide - 35 g/t, butyl xanthate - 35 g/t, diesel fuel - 10 g/t, frother T-80 - 20 g/t. Main flotation is performed for 5 minutes to obtain a coarse flotation concentrate and the control flotation is performed for 7 minutes, to get a trade concentrate. The sodium sulfide - 15 g/t and xanthate - 15 g/ t were added into the pulp control flotation before.

Further polymerization of layered aluminosilicates is carried out by high-temperature sulfidation in excess sulfuric acid. Hydrometallurgical process of directed extraction of copper, rare-earth metals, aluminum, potassium is tested in ore deposit Dzhezkazgan, Koktaszhal, Boschekul. Results of the study, the material flows and balance by Cu and Al_2O_3 in processing aluminosilicate polymetallic ores summarized in Table 3.

The sample was taken in an amount of 1 kg of crushed and out magnetized product to each experience. Layered aluminosilicates was sulfated with sulfuric acid in excess of 140% of the stoichiometry by reaction to dissolve the alumina at a temperature 170-200^{0}C and leached with water at S: L = 1: 2 to produce a solution of aluminum sulphate, transition, rare earth and radioactive metals. The potassium sulfate was entered to solution from calculated on the binding of aluminum sulphate by reaction of 100% to double salt of aluminum and potassium sulphate. Synthesis of normal salts was carried out under temperature of 70-90^{0}C.

The process of crystallization of a double salt of sulphate aluminum and potassium from hot solutions were at forced cooling to a temperature of 15 ^{0}C for 8 hours. The mother liquors with high acidity directed to the operation of the flotation tailings neutralization and gravitation.

Copper from productive solution were recovered by liquid-liquid extraction reagent company Cytec "ACORGA". Extraction was performed in two steps with 7% solution in kerosene ACORGA reagent at a ratio of the phases O:W=1: 1. The extract copper was reextracted with spent electrolyte containing 35g / l copper and a sulfuric acid concentration of 180 g / l. When re-extraction of copper with spent electrolyte the ratio O:W is supported to those that would be the concentration of copper in the reextract were at 45g / l. As shown in Table 3, the extraction of copper by combined technology from aluminosilicate raw material is 95-97%, in flotation stage of framework aluminosilicates 51-68%, in hydrometallurgical process 30-40%.

The polymer product obtained after neutralization and the siliceous kek from atmospheric leaching is sent to a gravitation. Gravitation Au, Ag and PM, Re is carried out on hydrocyclone with siphon height of 10 meters. Thus obtained a concentrate with the content g / t: Au 2,73, Ag 500, PM 55 – 80, Re 1.2.

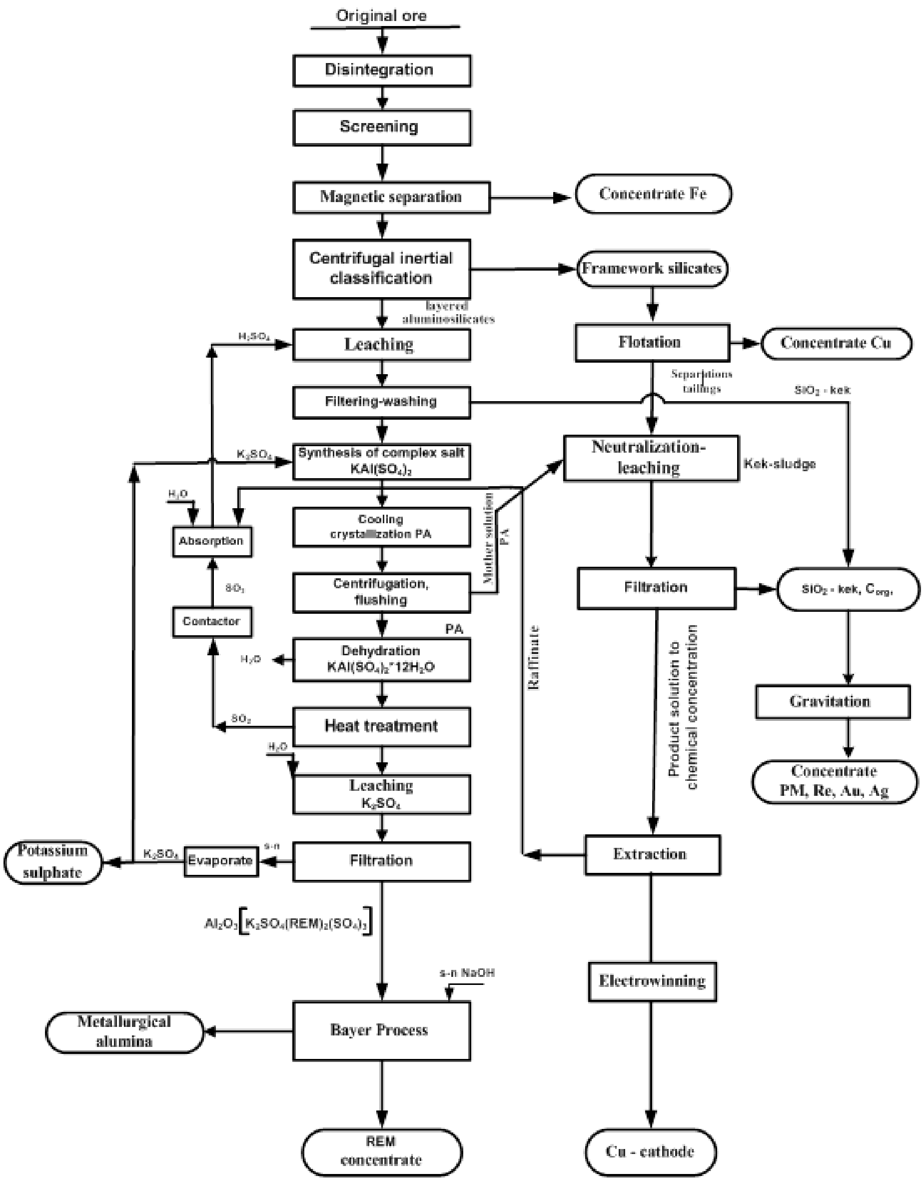

Figure 2: The technological scheme of complex processing for copper-aluminosilicate ores of Kazakhstan

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Table 3: The material flows and balance for Cu and Al_2O_3 in the processing of silicate polymetallic ores of Kazakhstan

Deposits	Original ore				Classification										Flotation									
					Sludge					Sand					Tailings					Concentrate				
	Al_2O_3		Cu		Weight, %	Al_2O_3 %	%	Cu %	%	Weight, %	Al_2O_3 %	%	Cu %	%	Weight, %	Al_2O_3 %	%	Cu %	%	Weight, %	Al_2O_3 %	%	Cu %	%
	%	g	%	g																				
Dzhezkazgan	13	130	0,9	9,0	20	17,8	27,4	1,0	22,0	80	11,8	72,6	0,87	78,0	72	11,8	65,6	0,125	10,0	8,0	11,4	7,0	7,65	**68**
Koktaszhal	15	150	0,48	4,8	34	18,7	42,4	0,5	35,4	66	13,1	57,6	0,47	64,6	61	11,7	47,6	0,06	8,6	5,0	10,0	10,0	5,3	**56**
Boschekul	20	200	0,42	4,2	40	27,3	54,6	0,43	41,0	60	15,1	45,4	0,41	59,0	53	14,6	38,7	0,06	8,0	8,0	19,2	6,7	3,06	**51**

Leaching										Excretion PA		Neutralization								
	Original solution					SiO_2 - kek						Productive solution					Tailings of neutralization			
H_2SO_4, кg/т	pH	Al_2O_3, g/l	%	Cu, g/l	%	Al_2O_3, %	%	Cu, %	%	PA, g	%	pH	Al_2O_3 g/l	Al_2O_3 %	Cu g/l	Cu %	Al_2O_3, %	%	Cu, %	%
28.7	-0,2	26,0	10,0	3,68	20,5	12,6	17,4	0,07	1,55	116	**11,0**	1,6	14,0	2,4	6,42	**27,1**	11,5	62,2	0,04	3,4
70.0	-0,12	30,0	15,6	2,1	34,2	13,0	26,8	0,02	1,25	228	**16,5**	1,5	13,5	2,54	3,8	**40,4**	11,3	44,2	0,01	1,25
129.0	-0,15	67,0	30,2	1,86	40,0	14,8	24,5	0,01	0,83	537	**30,5**	1,3	17,0	3,87	3,16	**46,7**	13,5	34,5	0,01	0,71

Productive solution				Extraction				Re-extraction				
Cu		pH	O:W	Water phase		Organic phase		O:W	Organic phase		Water phase	
ml	g/l			g/l	Educ. %	g/l	Educ. %		g/l	Educ. %	g/l	Educ. %
380	6,42	1,6	1:1	0,06	1,0	6,35	99,0	2:1	0,10	1,5	47,5	**98,5**
510	3,8	1,5	1:1	0,06	1,5	3,74	98,5	2,7:1	0,04	1,0	45,0	**99,0**
620	3,16	1,3	1:1	0,08	2,5	3,08	97,5	3:1	0,02	0,8	44,2	**99,2**

Based on the investigations the technological scheme was developed for the extraction of copper, rhenium, TReO, aluminum and potassium from mixed aluminosilicate copper-containing ores. The technology of complex processing of polymetallic aluminosilicate materials is presented in Fig.1. and includes the division into layered and framework silicates, layered silicates is leached with sulfuric acid to a residual acidity of 80-180 g /l , separated by filtration siliceous product , and the received sulfuric acid solution of aluminum, copper, rare-earth metals and potassium synthesized double salt of aluminum and potassium sulfate, potassium alum and double salt of rare-earth metals crystallized and centrifuged them from the mother liquor, potassium alum dried and treated thermally with the release of sulfur dioxide and technical alumina, from which the potassium sulphate is leached with water, and the insoluble residue was treated with a solution sodium hydroxide according to the Bayer Process of obtaining metallurgical alumina concentrate and rare earth metals, framework silicates is subjected to flotation, gravity separation with heavy metals and noble metals in concentrate forms, tailings of gravity fed to the leaching – neutralizing the mother liquor, siliceous kek filter out. The ratio of layered and frame silicates in the sample should be such that in the final stages of technology acidity productive solutions was in the range of pH 1.0-1.5.

CONCLUSION

- It was found that copper, rare earth and noble metals are genetically related to organic matter and finely are distributed in supergene aluminosilicate rocks applies to the system: Si - Al - O and Fe -Ti - O.
- It is shown that the existing technological schemes of extraction of target metals from aluminosilicate materials exhausted technological resource profitable production. And the only way to solve this problem so far has been linked ultrafine grinding of raw materials, not taking into account the fundamental obstacles incongruent, colloidal particulate materials.
- It was found that the chemical and the mechanical energy for polymerization and improvement random structure from monomeric tetrahedral and final of aluminosilicate motives to framework structures with an increase proportion siloxane bond and reduction of crystal lattice defects are used in ore preparation of aluminosilicate materials.
- A combined technology directed concentration of copper, rare and noble metals from aluminosilicate raw materials including the formation of structure on redivision of ore preparation by mechanical and hydrometallurgical process followed by flotation and gravity enrichment concentrate of copper sulfide and platinum metals from polymerized aluminosilicate material.
- A technological scheme of complex extraction of the target component in the form of metals and concentrates is offered. It is shown that copper is recovered in greater than 95%, 72% iron, REM 55%, Al_2O_3 about 30%, potassium 93%.

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