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BEHAVIOR OF TUVA CLAYS MIXTURES WITH SLIME AND CAKE OF DEARSENATION FROM KHOVU-AKSY DUMPS DURING ROASTING

Abstract: The article presents the data on the studies of phase transformations in the mixtures of clays from the Krasnoyarsk and Sukpak deposits of Tuva with the sludge of the Khovu-Aksy dump and the cake of its dearsenation. It is shown that when mixtures of clays with cake are heated, phase changes occur due to the gradual decomposition of silicates with the removal of various types of moisture, and also by decomposition of carbonates with CO_2 emission. In this case, active amorphous oxides are released which, at high temperatures, can form new structures such as spinel, mullite, and plagioclase. Some differences in the composition of clay from the Krasnoyarsk deposit in comparison with clay from the Sukpak deposit promote an enhancement of the technological properties of the former. Cake from dearsenation contains, along with silicate components, also sodium-magnesium silicate, which may promote the formation of readily melting structures in the formed multicomponent system. The cake is almost free from arsenic, which makes it possible to use it as an initial technogenic raw material for the production of various types of building materials and ceramic products. In the composition of sludge, an arsenic-containing compound of the group of vivianites was detected. It is parasimplesite, $Fe_3(AsO_4)\cdot 8H_2O$; it decomposes when the mixtures are heated, interacts with CaO and forms a new compound – johnbraumite $Ca_5(AsO_4)_3(OH)$. If this compound is present in rather high concentration (about 13 %) in the sludge, the use of the sludge in ceramic production may be decided only after special investigation.

Key words: clays, sludge, dearsenation cake, thermal analysis, X-ray phase analysis, silicates, aluminosilicates, amorphous oxides.

Introduction. For remote regions of our country, the availability of raw materials and their effective use seem to be the most important factor of social, economic and technological development. In particular, the availability of raw materials in the region can be the determining factor for the development of the construction industry in the region.

So, for example, the Republic of Sakha (Yakutia) fully provided its needs for solid bricks (porous ceramics) in the first half of the 20th century, producing up to 20 thousand pieces per year [1]. At present, the production of local raw materials and other types of ceramic building materials is being carried out, fully satisfying the requests of the Republic in this type of products [2].

At the same time, in the Republic of Tuva, until recently only full-bodied bricks of the M-75 brand in the amount of ~ 2-3 thousand pieces / year was produced. The needs of the Republic only in solid bricks are ~ 20-22 thousand pieces / year. The deficit is covered by revenues from other regions, which increases the cost of the material (due to transportation costs) by 1.5 to 1.7 times [3]. To get out of this situation, it is necessary to provide the industry with the necessary raw material basis, to conduct a complex of necessary studies of the properties of the raw materials to be produced, to develop the technologies for its processing with the expansion of existing works and organizing new ones to produce the required range of ceramic products.

An analysis of the geography of clay deposits in Tuva [3-5] showed that the existing clay deposits of the necessary group are located on the territory of Tuva in hard-to-reach areas and their extraction is still difficult. Therefore, montmorillonite clays are used as the main plastic raw material, and to obtain the necessary technological properties, pegmatites instead of natural melts are found in inaccessible places, various technogenic wastes are introduced into the charge, for example, quarry stone, asbestos, etc. Experiments were carried out to replace natural melts with the sludge of the Khovu-Aksy dumps (waste from the Tuvakobalt combine) [4-6]. These preliminary experiments have shown the possibility of obtaining a ceramic material of a dense shard with the use of local clays and dump slurry of the Tuvakobalt combine. However, in these experiments, the ecological factor was not taken into account - the presence of high levels of arsenic in the sludges used (~ 3.0 - 6.3 %). How will the arsenic compounds present in the sludge behave in the process of production and further exploitation of the products - this question remains open**.**

Therefore, in order to determine the possibility of maximizing the use of local raw materials for the development of the construction industry in Tuva, the Institute of Solid State Chemistry and Mechanochemistry of the RAS, Siberian Branch (SB RAS) is consistently working on the investigation of the properties of the mineral and secondary (technogenic) resources of the Tuva region. In accordance with the planned work program, thermal decomposition of the clays of the Krasnoyarsk and Sukpak deposits of Tuva and the dumping products of Khovu-Aksy (dump slurry and dearsenation cake) are being carried out.

This article is devoted to the next stage of the work: the study of the phase transformations occurring in mixtures of the clays of the Krasnoyarsk and Sukpak deposits with the products of the Khovu-Aksy dumps (sludge and cake of its dearsenation) during their roasting**.**

Experimental part. A study of possible phase transformations occurring during roasting of the mixtures of clays with the dumping products of Khovu-Aksy was carried out on clay samples from the Sukpak and Krasnoyarsk deposits of Tuva, the samples of the Khovu-Aksy dump and the cake of its dearsenation. Samples for the study of phase transformations during roasting in clay mixtures with dumping materials in a 1: 1 ratio were subjected to thermal analysis (DTGA) using a Pauliik Pauli-Erdei (Hungary) derivatograph of the MOM-1000 type. The process conditions are standard: heating rate ~ 10 deg/min, air environment, temperature limit - 950-1025 °C.

The initial materials and products of thermal analysis were studied for the mineralogical (phase) composition by X-ray diffraction (XRD) analysis using a powder X-ray diffractometer ARL XTRA from Thermo Scientific ARL Products (Switzerland). The samples were abraded in alcohol and applied to a glass substrate with a preparation thickness of ~20 mg/cm^2. The samples were scanned (Cu-Kα radiation) in the range from 2° to 65° (2Θ) in 0.05° increments, the scanning time at each point was 3 sec. The interpretation of X-ray diffraction patterns of minerals was compared with the reference data of the International powder database "Powder diffraction files" (PDF).

In interpreting the results of thermal analysis (DTGA) of the products studied, data on the chemical, physicochemical and thermochemical properties of individual compounds, minerals available in the reference and scientific literature were additionally used [7-13].

The data of the mineral composition of the starting products and after their thermal analysis, obtained using XRF, are presented in the table.

Table - Mineral composition of raw materials

N	Source materials	Mineral composition	
1	Sukpak clay		
	Initial sample	Dominate	quartz and calcite
		There are	plagioclase, kaolinite, potassium feldspar (kps), mica, smectite
		Traces of	illinite-smectite, hematite
	After DTGA	Dominate	quartz, plagioclase
		There are	potassium feldspar (kps), hematite
		Traces of	mica, illinite, smectite, anastase (?), Jarosite (?)
2	Krasnoyarsk clay		
	Initial sample	Dominate	quartz, kpsh, plagioclase, calcite
		There are	chloride, kaolinite, mica (muscovite type), Smectite
		Traces of	llinite-smectite, hematite, siderite, goethite
	After DTGA	Dominate	quartz, plagioclase
		There are	potassium feldspar (kps), hematite
		Traces of	mica, magnetite, goethite (?)
3	Sludge dump		
	Initial sample	Dominate	Magnesium calcite, Parasimplisite-$Fe_3(AsO_4)_2 8H_2O$ [PDFcard№350461]
		There are	Dolomite, calcite, smectite
		Traces of	Chloride, amphibole, mica, cps (?), D = 3.47 (?)
	After DTGA	There are	Quartz, anhydrite $CaSO_4$, aluminosilicate (neoplasm,?), Hematite, Jonbaomite $Ca_5(AsO_4)$ 3OH [PDFcard №330265], kapsh, plagioclase, portlandite $Ca(OH)_2$, goethite
		Traces of	Ca-Fe-Mg-garnet (?)
4	Leaching cake		
	Initial sample	There are	Silicate$Na_4Mg_2Si_3O_{10}$ [PDFcard№331265], Calcite, magnetite-hematite
		Traces of	Zeolite (zhismondin?), Quartz, d = 6.32 (?), 4.37 (?)
	After DTGA	Dominate	Silicate $Na_4Mg_2Si_3O_{10}$ [PDFcard№331265]
		There are	Magnetite Fe_3O_4, hematite Fe_2O_3, $NaAlSiO_4$ [PDFcard№110221 ?], Brediigite $Ca_{14}Mg_2(SiO_4)_8$ [PDFcard№360399 ?]
		Traces of	Vesuvéanite$Ca_3Al_2[SiO_4]_2(OH)_4$ [PDFcard№380474 ?], Mullite(?)

*Thermal analysis (*DTGA) of a mixture of Krasnoyarsk clay + dearsenation cake. The product of a thermally analyzed sample of this mixture contains, in a given proportion, all mineral phases of the initial constituents of the mixture subjected to thermal analysis (see table). The results of the series of experiments (the thermogram of a separate experiment is shown in Figure 1 as an example) showed that when the mixture is heated, the same processes of thermal decomposition take place as in the samples of individual products. Interactions between the components of clay and cake are not noted. Some minor deviations, observed from the temperature limits and the loss of mass from one experiment to another, do not violate the general nature of the thermal decomposition of the material.

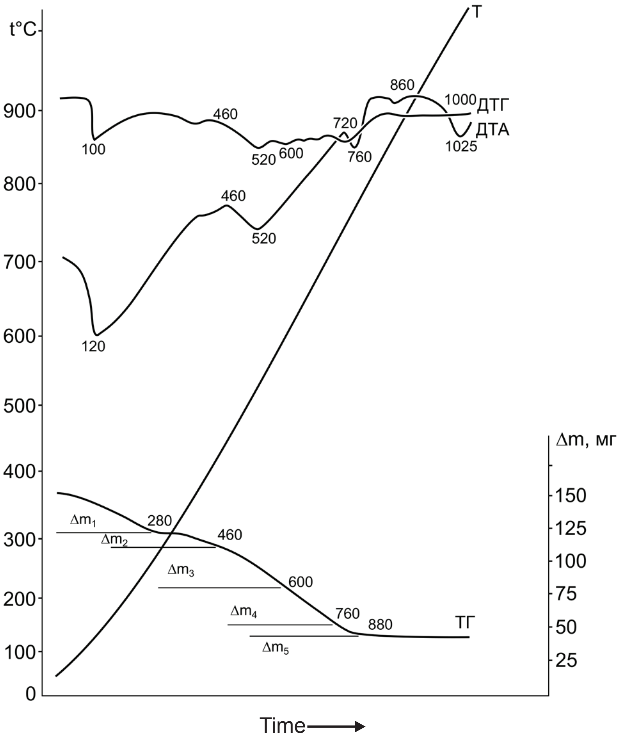

Figure 1 – DTGA of the sample composed from a mixture of the Krasnoyarsk clay with dearsenation cake

Thus, in the temperature range of ~ 80 - 300 °C, sorbed and hydrated moisture is removed; In the interval ~ 450-600 °C, the destruction of silicate phases containing bound water and hydrated groups (H_2O, $(OH)^-$, etc. in the structure) occurs. Within the range of 700-770 °C, decomposition of calcite begins with the removal of CO_2 and the formation of amorphous magnesium and calcium oxides, the decomposition proceeds up to temperatures of 850 ± 900 °C. Further, in the temperature range 860-1025 °C, after complete decomposition of calcite and destruction of chlorite and kaolinite with the formation of amorphous phases (Al_2O_3, SiO_2, CaO, etc.), their subsequent structuring begins in new crystalline phases such as mullite, spinels, plagioclase, etc.

At the initial stage of heating, in the temperature range up to 220 - 280 °C, the mass loss is 3.3 - 3.9 %; at subsequent heating up to 415-460 ° C - 1,1-1,7 %; up to 600 °C - 2,8-3,9 %; up to 720-760 °C - 2,2-4,4 % and up to 880 °C ~1,7 %. The total mass loss is within 13 %.

As a result of the thermal impact, the material in the crucible is heavily compacted and hardens without changing the volume. However, sintering does not occur. Under mechanical action, the material easily crumbles.

Thermal analysis (DTGA) of a mixture of Sukpak clay + dearsenation cake. The initial sample of this mixture also contains, in a predetermined proportion, both basic and impurity mineral phases present in the initial components of the mixture: quartz, sodium magnesium silicate, etc. (see table).

On the thermograms of samples of this mixture (Figure 2), clearly expressed endo-effects with maxima within the temperature range of 110-130 °C are due to the removal of sorbed moisture (introduced mainly by cake). In some experiments, their magnitude may differ somewhat, which may be due to the influence of external conditions in the preparation of samples (air humidity, storage time, etc.). In the temperature range of ~ 480-600 °C, hydrated silicates (for example, kaolinite) decompose with the removal of

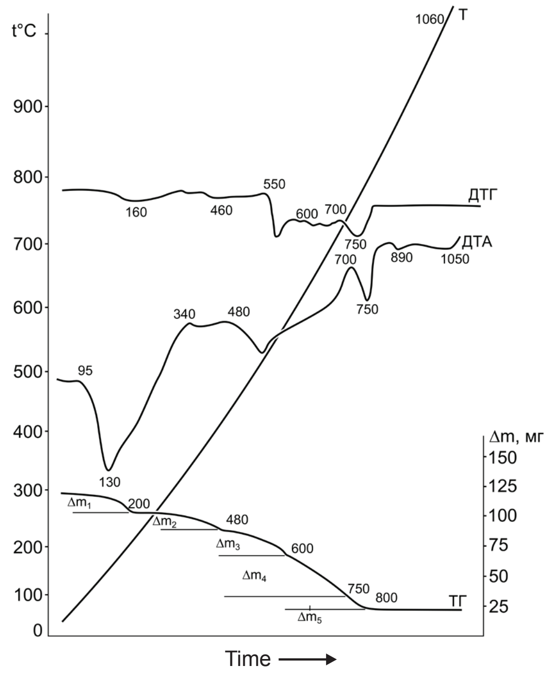

Figure 2 - DTGA samples of the mixture of Sukpak clay and dearsenation cake

structural water and other moisture relics and possible initiation of the formation of amorphous oxide phases. When heating is already in the temperature range ≤ 700 °C, decomposition of magnesium calcite begins with the separation of the amorphous phase of magnesium oxide. With a subsequent rise in temperature (within ~720-790 °C), the decomposition of calcite continues, but already with the formation of calcium oxide. At temperatures > 800 °C the processes of decomposition of calcite relics and hydrated aluminosilicate phases terminate and the process of formation (endo-effects at 850-890 and ~1000-1050 °C) of the new decomposition products (amorphous active oxides) of new crystal structures (spinels, mullite, plagioclase) take place.

The change in the mass of the samples during heating occurs within the framework of the thermal processes described above. Thus, within the limits of temperature up to 200-240 °C the mass of the sample decreases by 2.8-3.3 %. At the next stage, within the limits of temperature up to 425-480 °C, the mass loss is 2.4-3.3%. Further, when the temperature rises to 720-750 °C and 800 °C, the weight loss is 3.3-5.3 % and 1.1-1.7 %. The total weight loss is in the range of 12.8-13.3 %.

Depending on the maximum heating temperature, the cinder material acquires various mechanical qualities. So, if the experiment was finished at a temperature of ~ 1000 °C, the material in the crucible was somewhat compacted without changing the volume, but disintegrated under slight mechanical influence. At a higher final temperature of the experiment (1040-1060 °C), the material already has a strong cinder conglomerate with an unchanged volume of its mass and crumbles only when impacted.

Thermal analysis of mixture of Krasnoyarsk clay + sludge. The initial phase composition of the mixture is determined completely by the phase composition of the sludge and clay (table) and their proportions in this material. The mixture contains parasimplezite, magnesium calcite, quartz, kps (potassium feldspar), plagioclase, dolomite, kaolinite and a number of other components contained in the starting clay and sludge. It should be noted that parasimplezite - $Fe_3(AsO_4)_2 \cdot 8H_2O$ (according to PDF card №350461) differs from the natural speed of $FeAsO_4 \cdot 2H_2O$ in that it is ferrous and contains not two but eight molecules of crystallization water, characteristic for the whole group of Vevianites [9]. When the mixture is heated, a number of phase transformations occur in the material, fixed as endo-effects on the DTA curve (Figure 3) with maxima at 100, 176, ~370, 565, and 800 °C. These transformations are accompanied by a phased mass loss, roughly determined by the final temperatures: 176, 460, 650 and 800 °C. It should be noted that the endothermic course of the DTA curve from the diffuse exo-peak 890 °C to 1010 °C is not accompanied by a change in the mass of the sample. This course of the DTA curve can be determined by structural transformations, the formation of new high-temperature structures based on amorphous oxides: plagioclase and other high-temperature aluminosilicates such as spinels, mullite, etc.

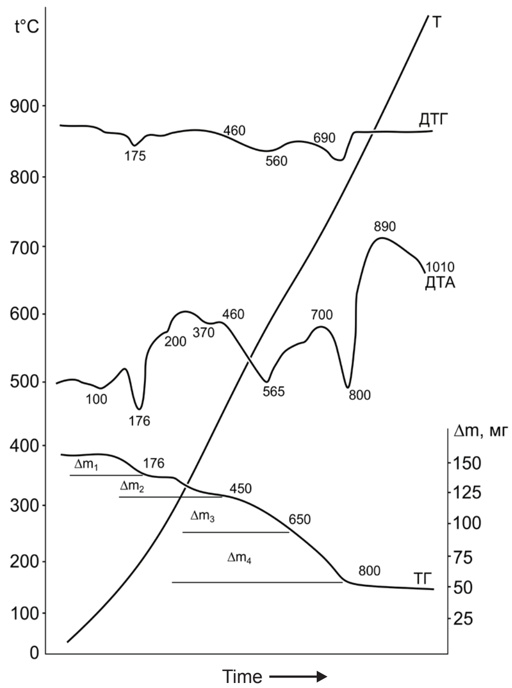

Figure 3 - DTGA samples of the mixture of Krasnoyarsk clay and sludge

Based on the data of DTGA, RFA and literature sources, it is possible to represent the dynamics of the phase transformations occurring when the mixture is heated. In the temperature range of ~ 100 °C, the sorbed moisture is removed. A pronounced effect on DTGA with a maximum at 176 °C, accompanied by a sharp loss of mass, corresponds to the decomposition of parasimplisite. According to XRF data in the sample, after initial heating to 300 °C, the initial parasimplezite is completely absent, and a new phase, johnbraumite, $Ca_5(AsO_4)_3 \cdot (OH)$. appears. Probably, the process occurs according to the reaction:

$$3Fe_3(AsO_4)_2 8(H_2O) + 10CaCO_3 + 2O_2 = \\ = 2Ca_5(AsO_4)_3(OH) + 2Fe_2O_3 + Fe_3O_4 + \\ + 2\,FeOOH + 10CO_2 + 22H_2O.$$

Further, up to temperatures of ~ 450 °C, the residual hydrate and crystallization moisture of the mineral phases can possibly be removed: chlorite, mica, etc. Within the temperature range of 450 to 650 °C, aluminosilicates (kaolinite, smectite, etc.) decompose, with the loss of structural (molecular) water. At subsequent heating up to ~ 800 °C, an intense decomposition of dolomite and calcite occurs to form amorphous magnesium and calcium oxides, and the removal of CO_2.

Thermal process is accompanied by heating with the following loss of material mass: up to 176 °C - 2,2 %; Up to ~ 450 °C - 2,2 %; Up to ~ 650 °C - 3,9 % and up to ~ 800 °C - 5,0 %. The total weight loss is 13.3 %.

Thermal analysis of the mixture of Sukpak clay + sludge. The mineralogical composition of this mixture includes a corresponding proportion (1: 1) of the constituent components of the mixture. The constituent phases in it are: parasimplezite, calcite, dolomite, quartz, kaolinite, plagioclase, possibly feldspar and other aluminosilicates. Thermal analysis showed rather good similarity of the position of the thermal curves of the DTGA of this material to temperatures of ~ 700 °C (Figure 4) with the position of these DTGA curves of the samples of the sludge mixture with Krasnoyarsk clay (Figure 3). Although, it is noted that the endo-effect on DTA, corresponding to the removal of sorbed water (at 120 °C), is more pronounced than the analogous endo-effect on DTA samples of the mixture with Krasnoyarsk clay, and the endo-effect of decomposition of aluminosilicates with a minimum at 560 °C is somewhat blurred and less in area. Upon subsequent heating on the DTA curve, a sharp bifurcation of the endo-effect is noted at ~ 750 °C with an increase in the sparing of the subsequent part of the endo-effect peak, while on the DTG curve the line segment broadens, characterizing the change in the rates of the phase changes occurring at these temperatures in the sample. On the DTA curve, endo-effects at 900 and 1000 °C are more clearly detected. All this is due to some difference in the phase composition of the Sukpak clay from that of the Krasnoyarsk clay (Table). Thus, quartz and calcite are dominant in the composition of the Sukpak clay, and in the composition of the Krasnoyarsk clay, the list of dominant constituents contains, in addition to calcite, also potassium feldspar and plagioclase. This indicates that during the thermolysis of the mixture with Sukpak clay, the decomposition of magnesium calcite proceeds more intensively, and subsequent reactions of the formation of new phases with more active participation of calcium and magnesium oxides take place.

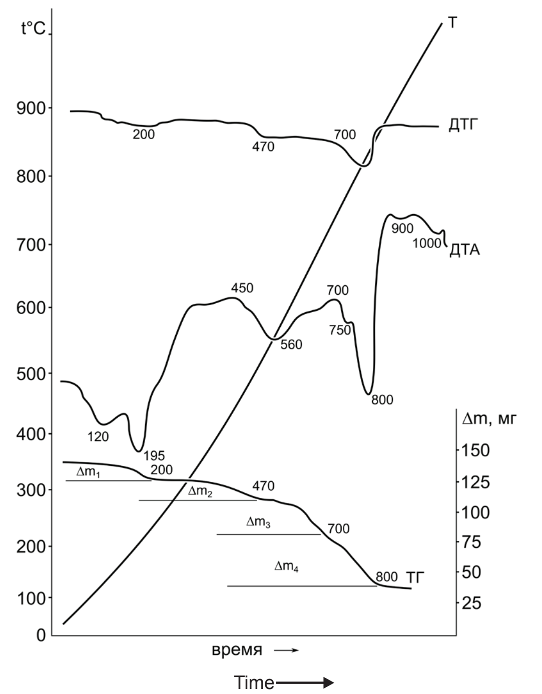

Figure 4 - DGTA samples of a mix of Sukpak clay and sludge

Thermal decomposition of the mixture is accompanied by a step-by-step decrease in the mass when heated in the following sequence: up to 200 °C - 2.2 %, to 470 °C - 2.8 %; Up to 700 °C - 3.9 %; Up to 750 °C - 2.5%; Up to 800 °C - 3,1 %. The total mass loss of the mixture when the mixture is heated up to 1025 °C is 14.5 %.

Discussion of results. In the thermal treatment of the products considered, with the exception of the waste sludge, the phase transformations accompanied by the loss of mass proceed by the gradual removal of various types of moisture from the silicate mineral components: sorbed, hydrated, crystallization, structural (molecular) water, and also by decomposition of carbonates with the emission of CO_2 and the release of active amorphous oxides of calcium, magnesium and iron. When the structural moisture is removed from the silicates, the silicate structure decomposes with the formation of active oxides (SiO_2, Al_2O_3 etc.), which upon further rise in temperature are able to react with other oxides to form new high-temperature structures such as spinels, mullite, plagioclase.

A certain difference in the phase composition of the Krasnoyarsk clay from the Sukpak clay (the presence of a greater amount of potassium feldspar and plagioclase) contributes to an improvement in its technological properties.

Dearsenation cake, along with other silicate phases, contains sodium-magnesium silicate $Na_4Mg_2Si_3O_{10}$ (or $2Na_2O{\cdot}2MgO{\cdot}3SiO_2$), which can contribute to the formation of low-melting structures in the resulting multicomponent system. The cake material is practically free of arsenic. According to the chemical analysis, its residual content after dearsenation is about 0.4 % by weight.

The arsenic compound of the vivianite group of parasimplesite $Fe_3(AsO_4)·8H_2O$ contained in the sludge of the dumps is decomposed and, upon interaction with calcium carbonate, forms a new johnbraumite compound $Ca_5(AsO_4)_3(OH)$. If there is a high content of parasimplezite (~ 13 %) in the sludge, the use of the latter in ceramic production can be decided only after additional studies.

Conclusions. Based on the studies carried out, the following conclusions can be drawn.

The sludge and dearsenation cake contain, in practical terms, the background levels of arsenic (at a level ≤ 0.4 %), which in the final ceramic-silicate material will be in an impurity form in the composition of stable silicate phases. The presence of sodium-magnesium silicate $Na_4Mg_2Si_3O_{10}$ in the cake can promote the formation of low-melting eutectic structures in this complex aluminosilicate system. This points to the possibility of using dearsenation cake as a technogenic raw material for the production of ceramic materials.

Formation of a mixture of clays with slag of the basic calcium arsenate $Ca_5(AsO_4)_3(OH)$ during roasting indicates the need for additional toxicity studies of the resulting materials on the basis of these mixtures, using arsenic-containing sludge as a flux.

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ТҮЙІНДЕМЕ

Мақалада Туваның Красноярск және Сукпакск кенорындары балшықтарының Хову-Аксы үйінді шламымен және оның деарсинизацияланған қоқымдарымен қоспасындағы фазалық өзгерістердің мәліметтері келтірілген. Балшықпен қоқым қоспасын қыздырғанда фазалық өзгерістер – әртүрлі ылғалдар шығарылатын силикаттардың кезең-кезеңімен айырылу нәтежесінде, сондай-ақ карбонаттардың CO_2 возгонымен айырылу есебінен болатыны көрсетілген. Бұл ретте белсенді аморфты оксидтер босатылады, олар жоғары температурада шпинел, муллит, плагиоклаза түріндегі құрылымдарды түзуге икемді келеді. Красноярск балшығының бастапқы құрамының Сукпакск балшығынан біршама айырмашылығы оның технологиялық қасиеттерінің артуына мүмкіндік тудырады. Деарсинизация қоқымында силикат құрамдастарымен қатар натрий-магнийлі силикат болады, ол түзілетін көп компонентті жүйеде жеңіл балқитын құрылымдардың түзілуіне себепкер болады. Қоқымда іс жүзінде күшән (мышьяк) болмайды, бұл оны әртүрлі құрылыс материалдары мен керамикалық бұйымдарды жасауға бастапқы техногенді шикізат ретінде қолдануға мүмкіндік береді. Шламның құрамында вивианит тобының күшәнді қосылысы – парасимплезит $Fe_3(AsO_4)·8H_2O$ болатыны анықталды, ол қоспалар қыздырылғанда айырылып және CaO-мен жаңа қосылыс – джонбраумит $Ca_5(AsO_4)_3(OH)$ түзеді. Шламда бұл қосылыстың мөлшері жоғары (~13 %) болса, соңғыны керамика өндірісінде қолдану үшін арнайы зерттеулерді жүргізгеннен кейін ғана рұқсат берілуі мүмкін.

Түйінді сөздер: балшық, шлам, деарсенизация қоқымы, термиялық талдау, рентгенфазалық талдау, силикаттар, алюмосиликаттар, аморфты оксидтер

РЕЗЮМЕ

В статье приведены данные изучения фазовых преобразований в смесях глин Красноярского и Сукпакского месторождений Тувы со шламом отвала Хову-Аксы и кеком его деарсенизации. Показано, что при нагреве смесей глин с кеком фазовые изменения происходят за счёт поэтапного разложения силикатов с удалением различного типа влаги, а также за счёт разложения карбонатов с возгоном CO_2. При этом происходит высвобождение активных аморфных оксидов, которые в области высоких температур способны образовывать новые структуры типа шпинели, муллита, плагиоклаза. Некоторые отличия исходного состава красноярской глины от сукпакской способствуют повышению её технологических свойств. Кек деарсенизации наряду с силикатными составляющими содержит натриево-магниевый силикат, который в образующейся многокомпонентной системе может способствовать образованию легкоплавких структур. Кек практически не содержит мышьяк, что позволяет использовать его как исходное техногенное сырьё для производства различного рода строительных материалов и керамических изделий. В составе шлама было обнаружено мышьяковое соединение группы вивианитов – парасимплезит $Fe_3(AsO_4)·8H_2O$, которое при нагреве смесей подвергается разложению и, взаимодействуя с CaO, образует новое соединение – джонбраумит $Ca_5(AsO_4)_3(OH)$. При наличии высокого содержания данного соединения (~13 %) в шламе, использование последнего в керамическом производстве может быть возможным только после проведения специальных исследований.

Ключевые слова: глины, шлам, кек деарсенизации, термический анализ, рентгенофазовый анализ, силикаты, алюмосиликаты, аморфные оксиды

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