The study of structure formation and mechanical strength properties of sulfur-containing woodcrete composites exposed to permanently acting loads

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Abstract. The present paper considers the issues of mutual neutralization and toxicity elimination of toxic components of industrial by-products as well as the study of structure formation for sulfur-containing woodcrete composites exposed to various permanently acting loads and curing conditions in time. Woodcrete-concrete composites could be considered as one of the available lightweight heat insulating building materials with low heat conductivity and good sound proofing properties. The materials are based on recyclable raw materials widely available in the regions of Kazakhstan and Russia. The contemporary provisions of theory and practice of development of efficient lightweight woodcrete-concrete based on composite sulfur-containing binders obtained by the method of toxicity elimination and mechanochemical activation served as the methodological foundation of the research. While implementing scientific research, the authors used the standard measuring instrumentation and methods of analysis of physical and mechanical properties of woodcrete composites such as the up-to-date methods of X-ray diffraction analysis, differential thermal and microscopic analyses and testing equipment. The principle of mutual neutralization of toxic components of industrial by-products by means of mechanochemical treatment at low temperature has been applied in the paper. These methods allow reducing cement content due to its fractional replacement by industrial waste. For the experimental part of the research, ferrous iron with the oxidation number 3 (Fe₂O₃) has been used as the oxidizing agent, while elemental sulfur, wood coal dust and ferrous iron with the oxidation number 2 (FeO) have demonstrated regeneration properties. The properties of sulfur-containing woodcrete specimens have been studied after 7, 28 and 90 days of exposure in various curing conditions. It was stated that sulfur-containing woodcrete had been fractioned gradually, first, decomposition of mortar constituent part took place, then of organic filler fibers. The obtained results could be applied while manufacturing efficient walling material for civil engineering buildings and structures, including seismic areas.

1. Introduction
Due to the fast development of construction industry and the expansion of industrial and civil engineering in the regions of Kazakhstan, there is a growing demand for buildings materials and structures, as the result, generation of structural and heat insulating materials on the base of recyclable resources is of crucial importance. Woodcrete concrete combining light weight, ecological compatibility and efficient heat insulating properties holds a special place in the production of building materials and may contain in its composition agricultural vegetation residues widely
available in steppe regions. The Kazakhstan regions also possess vast deposits of raw materials in the form of large-tonnage industrial waste and their utilization in the composition of building materials could be seen as a high-priority problem of the national economy.

However, ever growing requirements to the woodcrete quality set up the task for further enhancement of its engineering, maintenance, technological and strength properties. The purpose of the present study is development of high-performance woodcrete concretes on the base of composite sulfur-containing binders as well as the scientific basis of structure formation, composition and properties when applied as a walling material for residential construction. In order to achieve the desired target, the authors investigated the following factors: the influence of insertion of sulfur-containing by-products of hydrocarbon process industry on structure formation and physicochemical properties of composite binders; the impact of their principal components on physicochemical properties of sulfur-containing woodcrete on the base of milled reed grass fiber; the mechanism of strength formation and fracture of sulfur-containing woodcrete in the function of the type and method of loading; the analysis of woodcrete application in building structures.

Having implemented the research, it was stated that by targeted alteration of properties and structure with various additives of industrial and vegetable by-products, the properties could be enhanced, the manufacturing technology could be simplified and the efficiency of woodcrete production could be increased [1, 3, 6, 7]. The analysis of numerous data has shown [2, 4, 5] that unlike conventional woodcrete on the base of hogged chips when organic cellulose filler represents the weakest constituent part, sulfur-containing components of mortar part have a significant influence on its strength and stress-related behaviour.

2. Materials
The target of research are industrial by-products of the enterprises in Kazakhstan region in the form of raw sludge and solids.

1. Portland cement grade 400 produced by Chimkent cement plant and its chemical composition are presented in the table 1.

| Proportion, % | Basic oxides | Basic minerals |
|---------------|--------------|---------------|
| CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | R₂O | SO₃ | C₃S | C₂S | C₃A | C₄AF |
| 61.48 | 23.38 | 6.38 | 6.09 | 0.38 | 0.60 | 57.60 | 17.40 | 7.90 | 13.10 |

2. As a supplementary additive, there was used roasted pyrite produced by formed plc “Phosporkhim”. It mainly consists of the mixture of ferrous oxides (II, III) Fe₂O₃ (Fe₃O₄) with the conversion to the ferrum proportion 40-63% and sulfuric additives 1-2%. The remainder are the oxides of non-ferrous metals. The chemical composition of roasted pyrite, % wt., is given in the table 2.

| Proportion, % | Basic oxides | Basic minerals |
|---------------|--------------|---------------|
| CaO | SiO₂ | Fe₂O₃ | Al₂O₃ | MgO | SO₃ | R₂O | by-products |
| 10.5 | 19.7 | 66.1 | 2.3 | 1.2 | - | - | 0.2 |

3. As a modifying additive, there was used industrial sulfur, after-product of sulfur-bearing oil refining from the deposits of the Republic of Kazakhstan. Sulfur is a granulated product complying with the requirements of the All-Union Standard GOST 127.1-93. The chemical composition of sulfur is laid out in the table 3.
Table 3. Chemical composition of sulfur

| Grade  | All-Union Standard | Sulfur weight percent, % wt. | Ash weight percent, % wt. | Organic substances weight percent, % wt. | Water weight percent, % wt. |
|--------|-------------------|-----------------------------|---------------------------|----------------------------------------|---------------------------|
| 9998   | 127.1-93          | 99.060                      | 0.400                     | 0.053                                  | 0.010                     |

As primary porous fillers for obtaining sulfur-containing woodcrete, milled fibers of reed grass have been used. Physicochemical properties of reed grass, its chemical and fractional composition were stated by experimental method in compliance with the requirements of the All-Union Standards GOST 1922, GOST 25820-2000 as well as on the base of reference and literature data [1 - 20]. The chemical composition of milled fibers of reed grass is given in the table 4.

Table 4. Chemical composition of milled fibers of reed grass, % wt.

| Cellulose $C_6H_{10}O_5$ | Lignin $C_{14}H_{20}O_{15}$ | Pentosan $C_5H_8O_4$ | Resins and soluble components |
|--------------------------|------------------------------|----------------------|-----------------------------|
| 46.17                    | 29.76                        | 22.00                | 2.07                        |

3. Methods

Characteristics of primary and activated binder have been determined in alignment with GOST 30515-97, GOST 31108-2003 and GOST 7473-2010. For obtaining sulfur-containing binders, the principle of their mutual neutralization and toxicity elimination of toxic components of industrial by-products by means of mechanochemical treatment at low temperature has been applied. While carrying out the experiment, the amount of industrial waste on the base of roasted pyrite and industrial sulfur was taken in weight ratios in proportion to stoichiometric factors of reactions; the mixture of raw materials has been moistened to reach consistency of “damp sand”. While planning the research, the scientific hypothesis was realized stating that for implementation of the additional activation effect for each particles of additives, their joint grinding has been applied; with the result that mutual toxicity elimination of solid waste with opposite chemical properties took place. When carrying out experiments on preliminary identifying the composition and activating sulfur-containing additives, damp grinding was done by means of pebble mill producing abrasing and impingement effects.

Tensile and bending strength limits of sulfur-containing binders were determined on the specimens-test beams with the dimensions of 40x40x160mm on the appliance IP-2710. By means of X-ray diffraction analysis, the phase composition of activated sulfur-containing binder has been determined. X-ray diffraction analysis has been done by the X-ray diffraction meter “DRON-3” with the interval of diffraction angle ranging from 2 to 32°. Interpretation of diffraction patterns has been carried out on the base of standard X-ray films of the minerals, constituent parts. Differential thermal analysis of hydrated sulfur-containing cement powders was done by means of photorecording derivatograph MOM Budapest (Hungary) under the standard method. The character of strength formation and failure analysis of sulfur-containing woodcrete have been investigated with the use of strain-gage installation and insertion tensiometer with the base 10-50 mm attached to the reed grass fibers with the fast-curing adhesive “Moment”; the prisms set before placing concrete were oriented longwise and perpendicularly to the applied load. The purpose of the tests was that tensiometers would be attached to the both fibers of milled reed grass and sulfur-containing mortar part of the material. This gave the authors the opportunity to analyse the sequential failure of the components of sulfur-containing material (fig. 1).
The study was carried out on the specimens of sulfur-containing woodcrete after 7, 28 and 90 days; the specimens undergone heat treatment. The influence of arising stresses on ultimate compressive strength of sulfur-containing woodcrete was investigated on the base of particular models of concrete structure. Sulfur-containing woodcrete was considered as a two-component system comprising the fibers of milled reed grass and sulfur-containing mortar constituent, while the strength of the mortar part was a variable value. In order to implement the experimental part, four series of specimens have been made from sulfur-containing woodcrete, when the fifth one was made from sulfur-containing expanded clay light-weight concrete, for comparison. Each series consisted of six specimens-prisms with the dimensions 150x150x600mm, three of which (model I) were made of sulfur-containing mortar part (sulfur : roasted pyrite ratio 1:3), when the remaining three prisms (model II) had the fibers of milled reed grass with the diameter 18-20mm inserted in the core. Having undergone heat treatment, all the specimens were stored naturally in the laboratory. The specimens were exposed to the maximum load varying from 60 to 120kH, determined by an ultimate level of specimens’ loading equal to 0.75$R_{pr}$ ($R_{pr}$ – prism strength of sulfur-containing woodcrete). Simultaneously with molding prisms-specimens for each series of experiments, there were made the cubes with the dimensions 150x150x150mm from the same composition of sulfur-containing concretes; the cubes were stored with the prisms and tested at various time intervals.

It is well known [8-15] that time-yield of sulfur-containing expanded clay light-weight concrete is mainly determined by time-yield of gel, being a part of the hardened cement paste composition; thus, the conclusion was made that these consistencies could be applied to sulfur-containing woodcrete as well. The compositions of sulfur-containing woodcrete for producing test samples are enclosed in the table 5.
Table 5. Composition of sulfur-containing woodcrete prisms-specimens

| Number of samples series | Composition of woodcrete concrete, % wt. | Water-cement ratio, W/C | Cement content per 1m$^3$ of concrete, kg |
|-------------------------|------------------------------------------|-------------------------|-------------------------------------------|
| 1                       | Cement 33.3% : milled fibers of reed grass 22.4%: additives in the form of industrial sulfur and roasted pyrite 10.8% : water 33.5% | 1.34 | 321 |
| 2                       | Cement 34.4% : milled fibers of reed grass 21.4%: additives in the form of industrial sulfur and roasted pyrite 10.8% : water 33.4% | 1.37 | 335 |
| 3                       | Cement 34.9%: milled fibers of reed grass 20.6%: additives in the form of industrial sulfur and roasted pyrite 10.94% : water 33.56% | 1.4 | 345 |

4. Results
While carrying out experimental part related to toxicity elimination and activation of sulfur-containing by-products, it was noted that ferric iron has ability to oxidate sulfur with further conversion to the ferrous form of iron, as the color of the treated mixture changes from yellowish to green grey correspondingly. Joint milling of sulfur-containing components with cement has a positive impact on mechanical properties of tested samples. Strength of sulfur-containing specimens after 90 days has increased up to 12.7 MPa. Along with that, roasted pyrite served as an initiator of physicochemical process of coagulation of binding mixture. In the coagulation process, there takes place polarization of dispersed particles and their mutual attraction that intensifies the process of structure formation.

While studying strength properties of sulfur-containing woodcrete specimens with the dimensions 150x150x150mm at various time intervals, it was revealed that strength of sulfur-containing specimens has a tendency to increase with time. Heat treatment has a significant impact on the strength of researched specimens, i.e. after 7 days of curing the specimens’ strength has increased up to 1.5 MPa and after 90 days their strength could reach up to 6.7 MPa correspondingly. The following graphs demonstrating the change of ultimate compressive strength of sulfur-containing specimens with time have been drawn in accordance to the tests results (figure 2).
While carrying out experimental research related to strength formation of sulfur-containing woodcrete composites exposed to permanently acting loading, the following results have been obtained:

1. Internal strain-gauge sensors inserted into the sulfur-containing mortar constituent of the material, were fixing the time of its failure and the achievement of ultimate compressive strength of sulfur-containing woodcrete in prisms perpendicularly to acting load of the press. In this case, the gauge hand of the press drops, i.e. the initial fracture of sulfur-containing material is observed. Along with that, strain-gauge sensors attached to the fibers of milled reed grass and oriented longwise and crosswise of acting load continue showing stress growth, when the gauge hand of the press keeps demonstrating the strain growth. These effects cannot be identified in the sulfur-containing woodcrete of porous and coarse-pored structure with low density, not exceeding 500kg/m$^3$.

2. While testing sulfur-containing woodcrete of dense structure, simultaneous failure of sulfur-containing mortar constituent and organic filler did not occurred. Commonly, there was observed sequential filler-related fracture, then with sulfur-containing mortar constituent part, though exhibited only throughout the second phase of curing. Fracture of sulfur-containing material under the mortar constituent part occurred only throughout the first stage of curing.

While testing sulfur-containing woodcrete of dense, porous and coarse-pored structure, the bonding area of reed grass fibers with sulfur-containing mortar constituent is of extreme importance; along with that, for dense materials, adhesive strength of mortar constituent is lower than of organic fillers. For a porous and coarse-pored material, adhesive strength of mortar constituent is higher than of organic filler.

5. Discussion

It is generally recognized [15-20] that increase in reaction capacity of the binder’s components at wet milling could be reached not only by enhancing degree of dispersion in the liquid phase but by the change of crystalline structure and particles shape that predetermine intensifying the process of coagulation of sulfur-containing mixture. Along with that, chemical and mineralogical composition of
the primary binder remains unchanged. The mechanism of activation includes interaction of freshly exposed surfaces of binder’s particles during wet milling, i.e. initiating mechanical and chemical-energetic impulse in each particle. It is worth noting that mechanism of activation means increase in the interionic forces and induction of superficial valence forces when the nanoparticles of colloidal system are drawing together.

The implemented research gives grounds for refining hypothesis for strength formation and the possible reasons for fracture of sulfur-containing woodcrete. The strength theory developed by A.I.Vaganov [12] is applied for explanation of the process of strength enhancement of sulfur-containing material at curing, when deformation property of colmated fibers of milled reed grass. In order to give explanation to strength increase of sulfur-containing woodcrete of dense structure throughout the second phase of curing, the given strength theory requires further clarification and refinement as no simultaneous fracture of organic filler and mortar constituent part is observed. Fracture of sulfur-containing material throughout the second phase of curing occurs gradually, first – organic filler, then sulfur-containing mortar. The ultimate strength of sulfur-containing woodcrete of dense structure for all the tested specimens has been determined by the density of a mortar constituent part. At a lower strength of sulfur-containing mortar, compared with the filler’s density, single-phase curing and single-stage fracture takes place – in a mortar part. At a higher strength of sulfur-containing mortar, compared with the organic filler’s density, two-phase curing and two-stage fracture occurs. The strength of sulfur-containing woodcrete of a porous structure is formed in a single phase, fracture is single-staged – in a colmated organic filler. Its density mainly determines the density of the material itself.

6. Conclusion
The conducted research enables to plan production of sulfur-containing woodcrete of various densities directionally depending on the fraction of grain size and the fiber length of organic filler. The obtained results of investigation could be used while developing optimal compositions of sulfur-containing woodcrete products of different applications.

References
[1] Abdrakhimov V, Abdrakhimova E and Kairakbaev A 2015 Ecology and industry of Russia 19(5) 37-41
[2] Akulova M, Isakulov B, Fedosov S and Shchepochkina Yu 2014 Wood concrete mix contains portland cement, rush cane stems, technical sulphur, chrome-containing sludge, pyrite stubs and water Patent RU2535578-C1 C04B-028/04 Russia
[3] Assakunova B, Jussupova M, Baimenova G and Kulshikova S 2019 New s of the national academy of sc. of the Rep of Kazakhstan series of geology and tech. sc. 3 435 67 – 72
[4] Akulova M, Isakulov B, Fedosov S and Shchepochkina Yu 2013 Method to produce wood concrete products with making base for plastering on their surface Patent RU2517308-C1 Russia
[5] Akulova M, Isakulov B and Dzhumbaev M 2013 Development and research of properties of binders on the base of by-products Bulletin of RAASN 256–260.
[6] Isakulov B, Zhiv A, Zhiv Yu and Strelnikova A 2010 Proc. 2nd International Conference on Sustainable Construction Materials and Technologies
[7] Isakulov B, Jumabayev M, Abdullaev H, Akishev U and Aymaganbetov M 2019 Periodico Tche Quimica 16(32) 375-387
[8] Bazhenov Yu 2003 Technology of dry building mixes 95
[9] Bazhenov Yu. Dem’anova S and Kalashnikov I 2006 Modified high-grade concretes 368
[10] Beysenbayev O, Umirzakov S, Tleuov A, Smaylov B, Issa A, Dzhamantikov Kh and Zakirov B 2019 New s of the nat. academy of sc. of the Republic of Kazakhstan series of geology and techn. sc. 1 433 80 – 89
[11] Bazhirov N, Dauletiiyarov M, Bazhirov T, Serikbayev B and, Bazhirova K 2018 News of the national academy of sc. of the Republic of Kazakhstan 427 93-98.
[12] Vaganov A 1950 Construction industry 5 15-18
[13] Goncharov Yu 1999 Modern problems of material science Materials of the fifth acad. Read. RAASN 94–104
[14] Sadieva Kh. Massalimova B, Abisheva R, Tsuy I, Nurlybayeva A, Darmenbayeva A, Ybraimzhano L, Bakibaev A and Sapi A 2019 Ne w s of the national academy of sciences of the Rep of Kazakhstan series of geology and technical sciences 4 436 158 – 66
[15] Sokolova Yu, Akulova M, Imangazin B, Toleuov T and Isakulov B 2017 Scientific Review M 2 6
[16] Kairakbaev A, Abdrakhimov V, Kolpakov A and Abdrakhimova E. 2015 Refractories and Industrial Ceramics 56 3 276-280
[17] Kairakbaev A, Abdrakhimova E and Abdrakhimov V 2015 Glass and Ceramics 2015 72 3 96-99
[18] Kairakbaev A, Abdrakhimova E and Abdrakhimov V 2016 Glass and Ceramics 72 9 335-340
[19] Korneev A, Goncharova M, Goncharova E and Bondarev E 2002 Construction composite materials based on slag waste 120
[20] Rybiev I 2007 Building materials science: textbook. manual for universities 435
[21] Zhiv A and Isakulov B 2014 Sc. Herald of the Voronezh State University of Architecture and Civil Engineering. Construction and Architecture 23 61-74