Materials Engineering and Technologies for Production and Processing III

ICIE-2017

Edited by
Andrey Radionov

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Edited by

Andrey Radionov

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Preface

International Conference on Industrial Engineering took place on May 16-19, 2017 in Saint-Petersburg, Russian Federation. The conference was organized by 4 universities – Peter the Great Saint-Petersburg Polytechnic University, South Ural State University (national research university), Platov South-Russian State Polytechnic University and Far Eastern Federal University.

The conference was carried out under financial support of the South Ural State University (national research university), Peter the Great Saint-Petersburg Polytechnic University as well as at informational support of the Institute of Electrical and Electronics Engineers (South Ural IEEE Chapter).

The conference was really large-scaled and international. The international program committee has selected more than 1000 reports. The conferees represented 66 Russian cities and towns and 17 cities of 11 states such as Hungary, Egypt, India, Kazakhstan, China (including Taiwan), Iran, Kyrgyzstan, Poland, Tajikistan, Ukraine, Switzerland.

The conference participants submitted papers reflecting recent advances in the field of Industrial Engineering, in Russian and English. The conference was organized in 15 sections, including:

Part 1. Research and development of machines and mechanisms (Dynamics of machines and working processes; Friction, wear, and lubrication in machines; Design and manufacturing engineering of industrial facilities; Surface transport and technological machines);

Part 2. Materials engineering and technologies for production and processing (New functional materials and technologies; Innovation and cost-effective use of resources of metallurgy industry);

Part 3. Control and automation systems for manufacturing in the industrial production areas (Control systems and their industrial application; Industrial mechatronics, automation and robotics; Electric power systems and renewable energy sources; Power electronics, electrical machines and drives; Signal processing and real time embedded control; Modeling and computer technologies; Theory and applications of dynamical measurements);

Part 4. Sustainable development of industrial enterprises;

Part 5. Industrial and civil construction.

The international program committee has selected totally 200 papers for publishing in the Solid State Phenomena (Trans Tech Publications Ltd.).

The organizing committee would like to express our sincere appreciation to everybody who has contributed to the conference. Heartfelt thanks are due to authors, reviewers, participants and to all the team of organizers for their support and enthusiasm which granted success to the conference.

Conference Chair, prof. Andrey A. Radionov.

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CHAPTER 1:

New Functional and Structural Materials and Processing Technologies

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Physical-Chemical Properties of Molybdenum Films Prepared with Magnetron Sputtering

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Keywords: magnetron sputtering, molybdenum films, microelectromechanical sensors, accelerometers, quartz glass.

Abstract. The methods for evaluating the quality of the protective coating to the size etching of quartz glass with hydrofluoric acid were proposed. Molybdenum coating is generated with the installation NIKA 2012 TN by magnetron sputtering. Quartz glass with a roughness of Ra less than 1 nm was used. Discontinuity of coating was determined by the method of electron microscopy and energy dispersive analysis. Mathematical modeling of the hydrofluoric acid diffusion process performend via the molybdenum film was implemented. X-ray analysis of the coating was carried out to determine the residual internal stresses. We concluded that the studied phenomena affect the quality of the glass surface after etching.

Introduction

Quartz glass is one of the most used materials when developing and manufacturing devices based on the pinhole system (lab-on-a-chip) [1] which allow to transport, divide, and investigate small volumes of solutions as well as microelectromechanical sensors (MEMC) of accelerometers intended for measurement of linear accelerations [2]. Chemical inertness, hydrophilic nature of the surface, and a low coefficient of linear thermal expansion are the advantages of the quartz glass. To manufacture high-precision MEMC accelerometers, optical quartz glass plates of high-quality bilateral polishing are applied.

One of the most widespread ways of obtaining three-dimensional structures on a quartz glass plate is hydrofluoric acid (HF) pickling through protective coating. Quartz glass pickling can be presented by the reaction:

$$6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O.$$

Owing to the chemically aggressive nature of hydrofluoric acid, a number of requirements are imposed on the protective coating:

1. Covering quality (no cracks and punctures);
2. High adhesion to a substratum;
3. Chemical resistance to HF action.

Thus, the nature of a single-layer protective coating defines the quality of the structures generated on a quartz glass plate. The results of researches on dimensional pickling of quartz glass are given in [3].

The purpose of the paper was to establish how physical and chemical parameters of molybdenum films, generated on the glass surface by magnetron sputtering, influence the formation of dot defects when exposed to concentrated hydrofluoric acid for 1 hour. A molybdenum film received by magnetron dusting was used as a single-layer protective coating. Molybdenum was chosen because of its good adhesion to a quartz glass surface and chemical inertness to hydrofluoric acid [4-9].

Experimental Procedure

Plates of JGS-1 quartz glass with a diameter of 100 mm, produced by CQT-Group, China, were used as a substrate. Preliminarily surface treatment was carried out by means of ultrasonic processing in $NH_4OH:H_2O_2$ solution = 3:1 at 70 °C for 20 min and after-flush in the ultra clear deionized water. Immediately after drying with compressed air, the cleared plate was placed in a vacuum chamber for sputtering. All used agents were graded as especially clear and chemically pure.

Molybdenum films were received by DC magnetron sputtering with a pretreatment of the substrate surface in high frequency plasma of $Ar:O_2$ (1:1) gas mixture at power of 500 W for 20 min. The studies were conducted on the NIKA 2012 TN vacuum installation. The purity of the target material was not less than 99.99 %. The degree of argon purity, fed to the chamber during the coating deposition, was 99.99 %. The target-substrate distance was kept constant at 8 cm. The residual pressure before the deposition process in the vacuum chamber did not exceed 2×10^{-3} Pa.

The thickness of molybdenum films and roughness of the substrate surface were measured by the optical Zygo profilometer "New View 7300" (USA).

The examination of molybdenum film microstructure was conducted by Carl Zeiss "FE-SEM Sigma HD VP" (Germany) scanning electron microscope.

Morphology analysis of the glass surface after exposure to concentrated hydrofluoric acid (HF) for 1 hour on a molybdenum film was performed by MX61 (Olympus) optical microscope at magnification × 5. The relative area of the point defects which have appeared as a result of the HF penetration through the molybdenum film was calculated with the help of «Olympus Stream» software package.

"D8 Advance Eco" Bruker (US) X-ray diffractometer with the survey geometry by Bragg-Brentano, which provides for strictly parallel reflecting planes and substrate surfaces at all Bragg angles θ, has been used to determine the plane stress state of molybdenum coating. Processing of diffraction patterns was performed with the help of the "Fityk" software package using Voigt approximation.

Discussion

The development of technological processes of glass micro treatment has provided the increase in the use of glass substrates in the field of microelectromechanical systems. The most common and simple method in the technical aspect of glass plate treatment is liquid (wet) pickling [10]. The main problem of wet pickling is connected with dot defects (pinholes) that can be observed on the glass surface after a certain time of protective coating exposure to a pickling agent. Pinhole emergence is caused by the diffusion of HF molecules through molybdenum protective film formed on the surface of a quartz glass substrate [11-13].

The causes that lower protective properties of the coating and lead to the penetration of HF solution can be divided into the following groups:

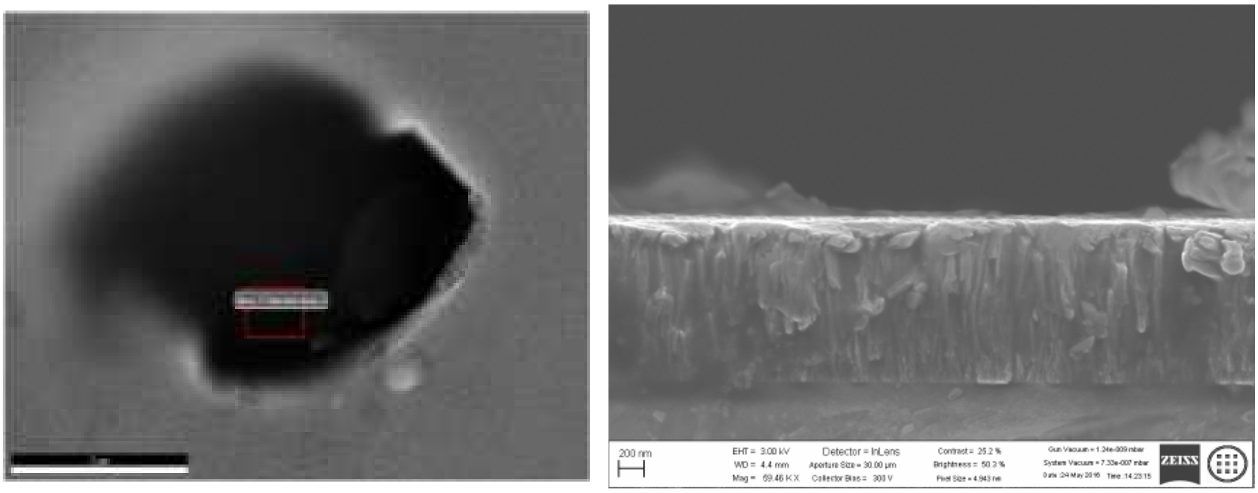
1) External factors (quality of the preparation and substrate roughness);

2) Physical and mechanical parameters of the film (especially the structure and thickness of the coating, mechanical stress).

The influence of substrate surface roughness to the number of pinholes was studied in [14]. To neutralize the influence of the substrate surface treatment purity, plates with a roughness of Ra<1 nm were used.

Among the reasons, leading to the appearance of coating defects, are particles that fall onto the substrate and retain on the surface due to van der Waals forces or electrostatic interaction. SEM-EDX method was used to detect the particles. Fig. 1a shows a through puncture in the molybdenum film, formed due to the particle, as indicated by the results of EDX analysis of the defect area. The average linear size of these defects is 1-2 microns. Henceforth, before sputtering and investigation of protective coatings durability (pinhole density), substrate preparation was carried out under the same conditions to produce the same amount of particles on the surface of all samples.

Protective coating properties also depend on its structure. The image of molybdenum film cross-section, obtained by scanning electron microscopy, shows a columnar microcrystalline structure of the coating (Fig. 1b). It should be noted that the formation of molybdenum columnar grains promotes efficient diffusion of hydrofluoric acid to the glass surface along the grain boundaries, extending continuously over the entire thickness of the film. The question of the coating thickness influence on its protective properties requires more detailed studies.



a b

Fig. 1. The point defect (a) and the cross-section (b) of the molybdenum coating.

A mathematical model has been developed to determine the change in the HF concentration along grain boundaries at various diffusion times and coating thickness. The model does not take into account the chemical reaction of HF with quartz glass; it is believed that the acid is accumulated in the surface area of glass. Fig. 2 shows the geometry of the system with parallel grain boundaries. On surface z = 0, there is hydrofluoric acid, which is distributed along the grain boundaries to glass surface z = h.

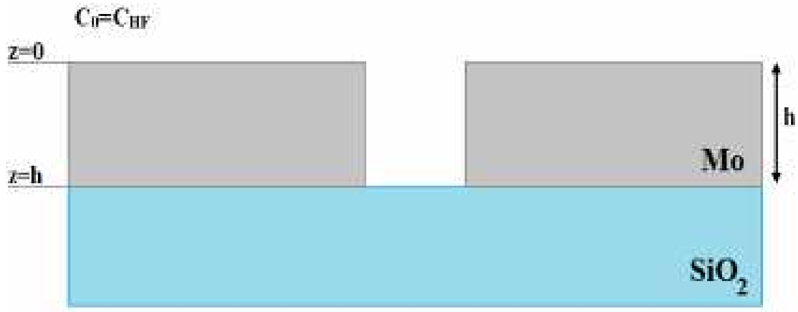


Fig. 2. The geometry of the system with parallel grain boundaries.

The diffusion process is described by Fick's equation, which is written as follows:

$$\frac{\partial C(z,t)}{\partial t} = D\frac{\partial^2 C(z,t)}{\partial z^2}. \qquad (1)$$

where C is the concentration of HF, and D is the diffusion coefficient of HF, equal to about 1×10^{-12} [cm^2/s], z is defined as the direction parallel to the grain boundaries. Since initially HF is absent in the film:

$$c(z,t=0)=0. \qquad (2)$$

The boundary conditions on surface z = 0, where the HF concentration is constant, equal to C_{HF} and surface z = h, where the flow is equal to zero, is written as follows:

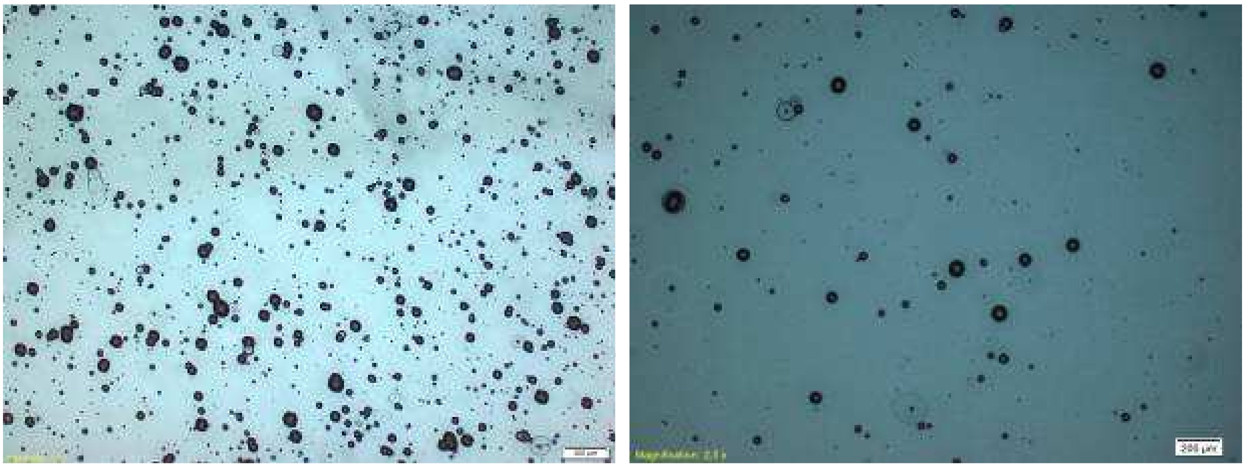
$$\begin{cases} C(z=0,t)=C_{HF} \\ \dfrac{\partial C(z=h,t)}{\partial z}=0 \end{cases} \tag{3}$$

Thus, it is necessary to find a solution to the differential equation with heterogeneous combined boundary conditions. The method of variables separation was applied to solve this problem; initially, the boundary conditions were transformed into zero ones. Relative acid concentration at depth *z* and coating thickness h at time t is calculated by:

$$\frac{C(z,t)}{C_{HF}}=1-\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{(2n-1)}\cdot e^{-\left(\frac{(2n-1)\pi}{2h}\right)^2 Dt}\cdot\sin\frac{(2n-1)\pi z}{2h} \tag{4}$$

By setting the thickness of molybdenum *h* coating and time *t*, during which HF acid affects the coating, we can construct the relative distribution of HF concentration across the film section. The depth of hydrofluoric acid penetration along the grain boundaries with the coating thickness of more than 1 micron during 1 hour is 0.8 microns. Thus, following the model and using protective films thicker than 1 micron, the diffusion along grain boundaries does not lead to pinhole formation on the glass surface during the exposure time of 1 hour.

Analysis of the glass surface state after exposure to hydrofluoric acid for 1 hour (Fig. 3) on a molybdenum film, received at different working gas feed, showed.



a b

Fig. 3. Photo of the glass surface after exposure HF acid on the molybdenum film (1 hour), obtained by sputtering power of 350 W, the working gas feeding 6 l/h (a) and 7 l/h (b), the deposition time 20 min.

That despite the similar conditions of the substrate state before sputtering and close thickness values of protective coatings, pinholes density on the glass surface differs by ~ 5 times (Table 1, samples 1,2 and 3,4) at 6 l/h and 7 l/h working gas feeding. It is important to note that the treatment with HF during 1 hour of coatings with 1 µm 2 µm thickness (samples 1,3 and 2,4), pinhole density varies by ~ 3.5 times. The data indicate the existence of additional factors, which lead to pinhole formation on the glass surface.

In the work [15], it is noted that the occurrence of pinholes on the glass surface can be due to internal stresses and defects in the protective coating, which promote the penetration of hydrofluoric acid molecules.

To verify this hypothesis, the tests were conducted. Analysis of diffraction spectra of molybdenum films showed. Only two intense lines corresponding to reflections from crystallographic planes (110) and (211) are observed in the spectra. In case there are markedly position deviation of the diffraction peaks to the left side from the position, corresponding to the molybdenum unstressed state, the interplanar spacing decreases and tensile stresses are generated in the film. When the positions of the diffraction peaks decline to the right side, the interplanar spacing in the film increases and compressive stresses are generated. The shift of the diffraction peak (211) along 2θ allows to calculate the voltage in the coating.

Table 1. Pinhole density after exposure to hydrofluoric acid for 1 hour on a molybdenum film, obtained under different parameters of magnetron sputtering.

Sample	Sputtering power [W]	Working gas feeding [l/h]	Deposition time [min]	Coating thickness [μm]	Share pinhole [%]	Internal stresses [GN/m^2]
1	350	6	20	1.18	11.07	–
2	350	7	20	1.19	2.37	0.438
3	350	6	40	2.20	3.25	0.823
4	350	7	40	2.42	0.66	0.756

The quantity and nature of inner stresses σ is determined by the formula:

$$\sigma = \frac{-E(d-d_0)}{2\mu d_0}. \tag{5}$$

where E is the elasticity modulus equal to 3.36×10^{-11} [N/m^2], μ is Poisson factor (0.298), d is interplanar spacing for the plane system defined by the X-ray diffraction pattern of a test sample, d_0 is interplanar spacing of the same plane system in the absence of stresses .

Sputtering parameters have a significant influence on the voltage in a molybdenum film. The quantity and nature of the stress in the molybdenum films obtained by various parameters of magnetron sputtering is shown in Table 1.

Summary

1. EDX-SEM analysis of molybdenum film showed the presence of discontinuities. These discontinuities can cause damage to the quartz glass surface. It has been established that such films defects arise in cases when the surface area of the glass wafer greater or comparable with an area magnetron sputtering target. In our case, the sputtering target area ≈6361.7 mm^2 (Ø90 mm) and the area of the substrate ≈7853 mm^2 (Ø100 mm).
2. It found theoretically and experimentally confirmed that the thickness molybdenum film affects the quality of the protected glass surfaces after etching.
3. Stability of coating depends on the amount of residual internal stresses. It is shown that if the compressive residual internal stresses are small, the coating has a large stability.

Acknowledgements

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Optimization of Synthesis Mode for Hydro Silicate-Based Supplements Used for Lime Dry Construction Mixtures

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Keywords: calcium hydrosilicate, supplement, diatomite, dry mixes, compression strength.

Abstract. The following article presents information on the regularities of hardening of lime construction mixture samples, which were produced while adding the supplement based on calcium hydro silicate. Mathematical model of influence of the percentage of precipitation supplement and the quantity of diatomite used for synthesis upon the compression strength of the samples has been implemented.

Introduction

In previous studies the effectiveness of the introduction was confirmed in the formulation of finishing lime dry mixes of mineral supplements on the basis of synthesized calcium hydrosilicate that increase resistance lime coatings [1-3].

X-ray diffraction analysis revealed that the degree of crystallinity of the synthesized hydrosilicate is low, calcium hydrosilicate various basicity are formed [4-6].

The Research Results

Given that low-basic hydrosilicates have higher strength, in the continuation of further studies in order to obtain low-basic calcium hydrosilicate and efficiency we synthesized supplements introduced diatomite during synthesis. Supplement synthesis technology was as follows. To a solution of soluble glass with a module M = 2.8 was added a suspension of diatomite, after mixing $CaCl_2$ solution was injected. The resulting mixture was filtered and dried to constant weight at 100°C. The dried additive is pulverized to a specific surface area = 1,900 [m^2/kg]. In the synthesis of supplement ratio of the solid phase:liquid phase S:L has changed of 1:2.5 (0.4) to 1:1.66 (0.6) [7-9]. Diatomite of Inza field has been used.

The results of the studies showed that the supplement based on calcium hydrosilicate has high activity, which is determined by the value of solubility in a 20% KOH solution [10, 11].

Table 1. Impact of the synthesis mode on the activity of the synthesized hydrosilicate.

Supplement	Solubility M, [%]	Activity A, [mg/g]
The control mix (no supplement)	65	260
Precipitation in the presence of 10% $CaCl_2$ solution in an amount of 50% by weight of solution of soluble glass	68	350
Precipitation in the presence of 10% $CaCl_2$ solution in an amount of 50% by weight of solution of soluble glass with the addition of diatomite, wherein the ratio S:L = 1:2	70	370
Diatomite	61	299

The structure of the synthesized supplements has been explored by a scanning electron microscope Shanning Electron Microscope JSM - 6390 LV. Surveying was carried out in a low vacuum mode, pressure P = 50 Pa.

The structure of the supplement synthesized without diatomite represented by formations of different needle and plate shapes corresponding calcium hydrosilicate (Fig. 1) [12, 13].

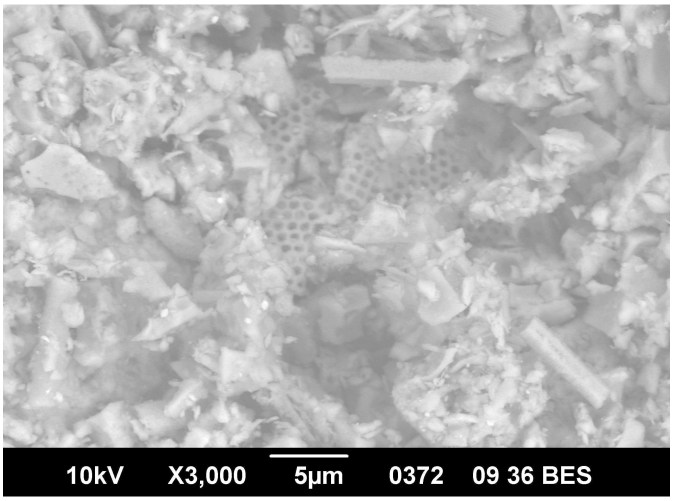

Fig. 1. Image of diatomite structure, x3000.

When studying supplement structure synthesized in the presence of diatomite it found that diatomite is a substrate on which the calcium hydrosilicate are formed (Fig. 2).

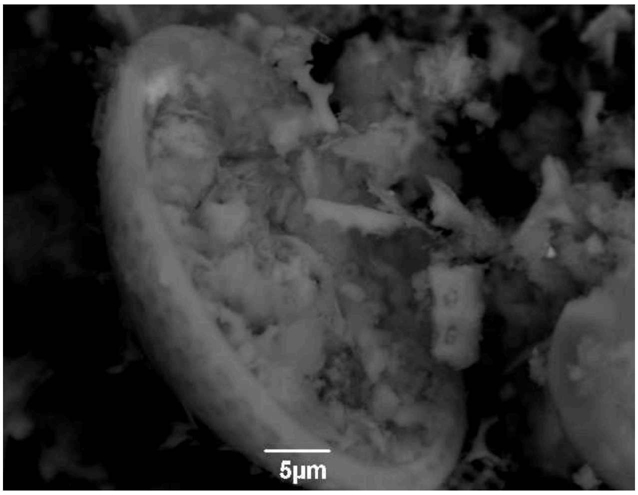

Fig. 2. Image of supplement structure synthesized in the presence of diatomite, x3000.

It is found that the amount of chemically free lime determined by titration with 1H hydrochloric acid [14-16], is 47.66 % of control samples after 28 days air-dry hardening, and 25.23-36.73 % with using synthesized supplements (Fig. 3).

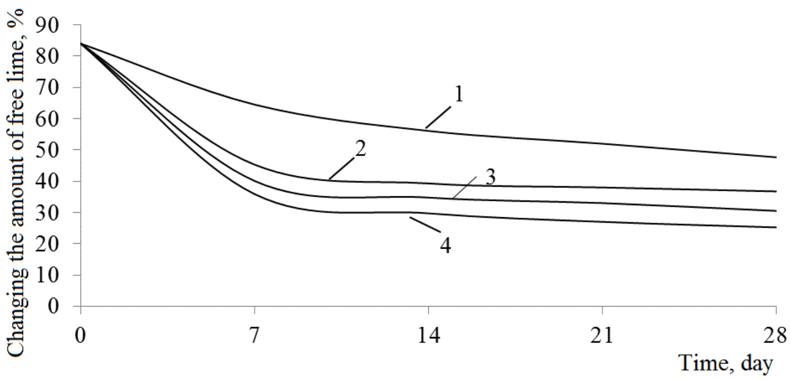

Fig. 3. Changing the amount of free lime during hardening.

In Figure 3: curve 1 is control sample; curve 2 is sample with diatomite (30% of mass of lime); curve 3 is sample with diatomite synthesized according to the 1st mode; curve 4 is sample with diatomite synthesized according to the 2nd mode; curve 5 is sample with diatomite synthesized according to the 3rd mode.

Synthesized supplement has been applied to the manufacture of lime samples, the content of supplement was 30 % by weight of lime. As the binder hydrated lime 2 grade with an activity of 86 % has been used. Mixes have been made with a water-lime ratio W/L = 1.2.

Compression strength of lime samples aged 28 days air-dry hardeninghas been estimated [17, 18]. For comparison, lime samples were made only using diatomite in an amount of 30 % by weight of lime.

It is found that the compression strength lime samples made with using calcium hydrosilicate supplement synthesized without diatomite is 4.7 MPa (Table 2), while at the lime samples made with using calcium hydrosilicate supplement synthesized in the presence of diatomite is 7.59 MPa (Table 2). Compression strength of control mix is 2.12 MPa.

Table 2. Compression strength of lime samples.

Supplement	Compression strength, [MPa]
The control mix (no supplement)	2.12
Precipitation in the presence of 10 % $CaCl_2$ solution in an amount of 50 % by weight of solution of soluble glass	4.7
Precipitation in the presence of 10 % $CaCl_2$ solution in an amount of 50 % by weight of solution of soluble glass with the addition of diatomite, wherein the ratio S:L = 1:2 (0.5)	7.59
Diatomite	3.25

To optimize synthesis mode of supplement based on calcium hydrosilicate the work was planned a full two-factor experiment. As optimization parameter, compression strength of limestone samples was taken.

As factorsthe percentage of $CaCl_2$ (x_2) and the ratio of the solid phase:liquid phase S:L(x_2) were taken. Table 3 presents the conditions of the variables.

Table 3.Terms of the variables.

Levels of factors	Factors	
	The percentage of $CaCl_2$ solution (x_1), [%]	The ratio of solid phase:liquid phase (x_2)
Top level	15	0.4
Bottom level	5	0.6
The interval of variation	5	0.1

As a result of processing experimental data the quadratic model was obtained:

$$R_s = -14.419 + 1.8716x_1 + 47.6x_2 - 0.0855x_1^2 - 47.6x_2^2, \quad (1)$$

The adequacy of the model was tested by Fisher's exact test. The selected model adequately describes the system under study, as a table-valued Fisher's exact test equal to 3.5, it was more than the estimated value of 3.1. The homogeneity of variances was assessed by Cochran's test. Estimated value of the criterion equal to 0.12, that less than the tabulated value of 0.63 [19].

The significance of the coefficients in the model (1) was tested by t-test at a significance level of 0.07. The significance of the coefficients of the regression equation (1) indicates a significant influence of the concentration of the supplement-precipitatorand the ratio S: L on parameter optimization [20].

Graphical interpretation of the resulting model is presented in Fig. 4.

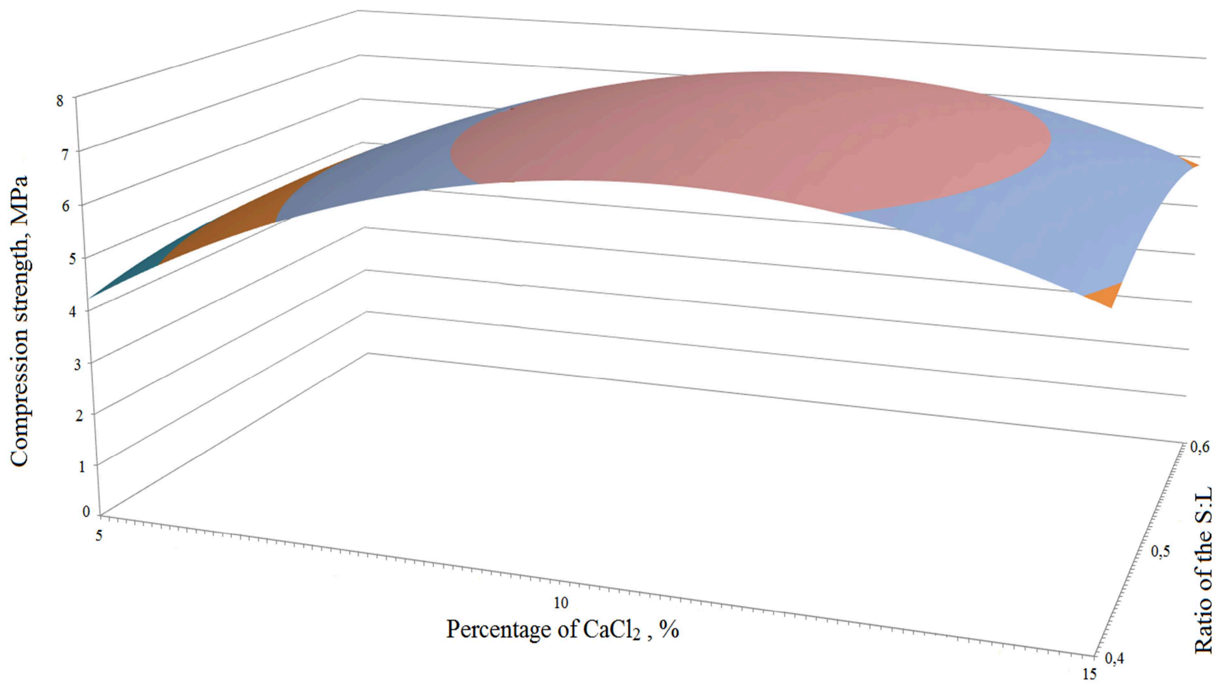

Fig. 4. Dependence of compression strength of lime samples from technological factors of calcium hydrosilicates upplement synthesis.

In the analysis of the obtained quadratic model, extremums were found. Optimal supplement synthesis mode corresponds to injection of $CaCl_2$ solution of 10 % and with a ratio S:L of 1:2 (0.5).

Conclusions

Thus, the model of the calcium hydrosilicates upplement synthesis parameters has been developed, which allowing to optimize the flow of calcium chloride and diatomite for supplements, used in the creation of lime mixes.

Lime mixes with synthesized supplement are characterized by high compression strength, vitality of 3-4 hours, adhesive strength of 0.9-1.1 MPa.

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Current State and Future Prospects for Improvement of Mineral Melt Production Technologies

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Abstract. The article outlines the production of fibrous materials, discloses energy production targets for mineral wool items production, scrutinizes specific features of cupola process. Besides, the article presents the experimental research of mineral wool cupola process. Thus, the article describes the design of a cupola furnace, principles of its operation, and its main performance indicators.

A summary of analytical and theoretical research of non-isothermal gas flow motion in shaft furnaces is presented herein. The results of the experimental studies of the patterns of change in gas-dynamic operation of the cupola furnace are also shown in the article.

To assess the development of solid fuel combustion in the furnace, the laws that govern the changes in gas composition at the level of stockline have been studied. The results are shown in the Table.

The analysis of the current state of thermal and gas-dynamic operation of the mineral wool cupola furnace yielded recommendations for optimization and performance enhancement of the operating cupola furnace.

Introduction

In modern conditions of the financial and energy crisis, the issues of efficient use of material resources, fuel and energy saving have become of major importance. Russia is of the countries leading the world in power production, nevertheless it lags significantly behind efficient use of energy resources demonstrated by developed economies.

One of the effective tendencies aimed at power saving and thermal energy saving is the use of high-performance building and industrial thermal insulation for additional heat insulation of cladding structures. Our estimates show that the demand for effective heat insulation materials in the housing sector may be equal to 30-35 [mln.m^3] by 2017. Current available production capacities for heat insulating materials in Russia are 17-18 [mln.m^3]. Economic estimates show that application of efficient heat insulating materials in construction is three or four times more effective than traditional use of dense construction materials. Thus, the payback on the investment in construction of new production premises for efficient heat insulating materials is 1.5-2 years [2].

Production of Fibrous Materials

Multistage production of fibrous thermal insulation involves high-temperature melting of mineral components, production of a liquid melt and its spraying by means of a centrifuge. The final stage is a mechanical formation of mineral wool into mats of specified thickness to which a liquid binder is added, and its heat treatment in a curing oven. These stages are characterized by high energy consumption (Table 1).

Current trends in the development of machinery and production technologies available for production of mineral wool items from smelter slag and rocks show that a mineral wool cupola furnace is the most efficient apparatus for production of a liquid melt (Table 2). However, despite its wide application in the industrial sector, its actual performance indicators are still low due to its suboptimal design and technological defects [3].

Table 1. Energy indicators in production of mineral wool items.

Stages of production	Method of production	Power consumption	
		[MJ/t]	[%] of total production costs
Production of mineral melt	Melting of mineral raw materials (slag, natural materials) in cupola furnaces	8-10	61-75
Production of fibers	Centrifugal blast spraying	2.0-2.5	16-18
Formation of the items and their heat treatment	Mechanical formation and convection heating in a curing oven	2.5-2.7	20-22

Table 2. Specific features of cupola process.

Advantages	- Simple design and easy maintenance - High specific capacity (up to 100-150 t/m^2 per 24 hours) - High efficiency of heat utilization (up to 60-80% of total heat input) - Continuous melting process and continuous tapping - Effectiveness, minor capital costs
Disadvantages	- Necessity to use lump material - Use of metallurgical coke

Current production of fiber heat insulation in Russia relies on wide application of domestic cupola furnaces with open cupola top and shaft furnaces with closed top, mostly imported.

Mineral wool cupola furnaces with open top are mainly characterized by distinctly peripheral gas motion in the furnace body due to application of inefficient gas-dynamic parameters (low speed of air blasts), caused by suboptimal supply and distribution of the air blast (unsatisfactory air supply, inefficient design of the tuyeres).

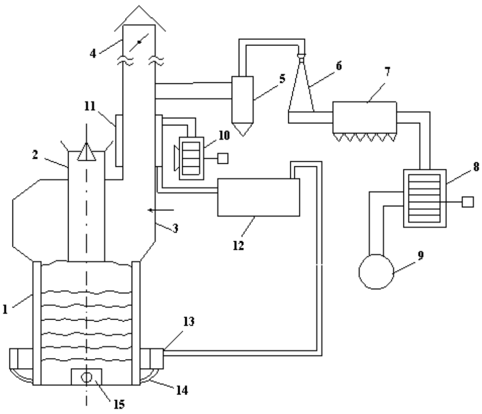
Circulating water supply is absolutely unacceptable for cooling the elements of a mineral wool cupola furnace. If this is the case, the entire heat coming from the cooled elements of the furnace, which can reach 20 % of the total heat consumption, is irretrievably lost in the environment.

Use of the air blast heated in a stand-alone air heater is an effective energy efficiency enhancement method for a cupola furnace [4].

Imported mineral wool cupola furnaces operated at some factories are characterized by availability of heated air blast, use of oxygen and additional amounts of natural gas. However, implementation of these technological measures in the production of a mineral melt is far from being perfect.

Experimental Research of Mineral Wool Cupola Furnace

The design of the cupola furnace under study differs from other cupolas in low height of the bed of charge materials (not more than 3.5 m), while at least 5.6 m is required to complete the heat-exchange process. This specific feature leads to increased incomplete combustion (CO=13-21 %) of gaseous products and their excess temperature of at least 300 ˚C. To decrease carbon monoxide content in the flue gases, the furnace is fitted with two additional burners above the charge. The combustion products and cupola gases are mixed outside the burners, and the total consumption of natural gas approximately equals to 300 [m^3/h] (Fig.1). However, application of such an approach showed that the amount of CO does not exceed 50-60 %, which weakens the effectiveness of use of the coke heat in the cupola furnace [5]. During secondary combustion of the cupola gases, the temperature in the combustion chamber increases to 800-1,000 ˚C. For the heat recovery, the furnace is fitted with an air blast radiation heater to heat the air blast to 300 ˚C. It is part of a flue that reduces the temperature of flue gases to 560 ˚C. [6] Dusty-bearing gases are sequentially cleaned in a battery cyclone and a vertical Venturi tube with a drop separator. They are cooled to 200 ˚C, and they are removed through a flue-gas pump and a 30-m-high pipe to the atmosphere [7].



1 – shaft furnace; 2 – fuel bell with sealing device; 3 – fume removal system with secondary combustion; 4 – emergency gas vent; 5 – cyclone; 6 – Venturi tube; 7 – drop separator; 8 – flue-gas pump; 9 – tube; 10 – blower; 11 – radiation recuperator; 12 – additional air preheater; 13 – distribution manifold; 14 – tuyeres; 15 – tap hole.

Fig. 1. Schematic plan view of a cupola furnace.

The air blast is supplied to the cupola furnace at a pressure of about 400 mm WG by a stand-alone airblower with rated capacity of up to 9,000 [m^3/h] through an air radiation recuperator for flue gases. It provides heating of the air blast up to 300 ˚C. To heat the air above this level, the furnace is fitted with an additional tube-type heater with external heat source in the form of the products from the natural gas combustion and maximum thermal efficiency 65 %. Hot air blast with final temperature not exceeding 600 ˚C is sent to the distribution manifold of variable cross-section. Its maximum cross-section is 1,200x1,200 mm near the air blast inlet. As the air moves through the manifold, its cross-section diminishes and reaches 800x800 mm at the side opposite to the air blast inlet. The air blast is directed over the perimeter of the cupola furnace through 12 tuyeres with inner diameter of 130 mm, which ensures that the average value of about 11 m/sec is achieved for the velocity at which the air blast leaves the tuyeres. The gas mainly moves in the periphery of the cupola furnace shaft [8].

The gas is collected from the cupola furnace in the upper part of the shaft at an angle of approximately 45˚ relative to the air blast inlet.

Initial cupola mixture consists of gabbro (67.35 %), dolomite (15.12 %), and coke (17.53 %). It is fed into the cupola as separate 800-kg, 180-kg and 155-kg charges respectively.

To assess thermal performance of the furnace, the following has been measured: total air blast consumption inside the furnace, air blast temperature and pressure, temperature of the melt at the outlet of the bottom gate, gas temperature and composition at the level of the stockline, as well as their distribution over the cupola cross-section.

Average temperature of the melt during the tests did not exceed 1,477 ˚C.

With average air blast rate of 6,300 [m^3/h] and preheating temperature of 494 ˚C, specific air blast consumption was equal to 33.43 [$m^3/(m^2 \cdot min)$]. As the experimental data shows, to assure efficient operation of the furnace, this parameter should be kept at the maximum level of 60-70 [$m^3/m^2 \cdot min$] [9]. Comparison of this data reveals that it is possible to improve cupola performance through increase in specific consumption. However, this measure is limited by the capacity of the flue-gas pump and gas-dynamic properties of the heated bed.

Analytical and theoretical research of non-isothermal gas flow motion in shaft furnaces [10] showed that the temperature fields of the gases and the bed of charge materials primarily depend on the gas flow distribution over the cross-section of the furnace. The changes in gas-dynamic operation of the cupola were subjected to experimental research on the basis of measurements of the temperature at the level of the stockline of the cupola mixture performed with the use of a butt-welded thermocouple type TXK(Fig. 2).

Analysis of this data demonstrates that the cupola cross-section is characterized by strongly pronounced nonuniformity of both temperature and velocity fields. The lowest gas filtration temperatures and velocities are reached in the region farthest from the air blast supply area. Maximum air blast supply is observed at the inlet nozzle of the distribution manifold. This is primarily attributed to its design: its cross-section diminishes towards the side opposite to the air blast inlet. Besides, vertical orientation of the spot where the gases are collected in the bed near the air blast inlet also attributes to such a nonuniformity. The opposite side of the cupola cross-section suffers from the shortage of the blast air, which leads to gasification of the coke carbon and formation of the increased amount of carbon monoxide [11]. Thus, for efficient performance of such a design, it is expedient to use a distribution manifold of uniform cross-section.

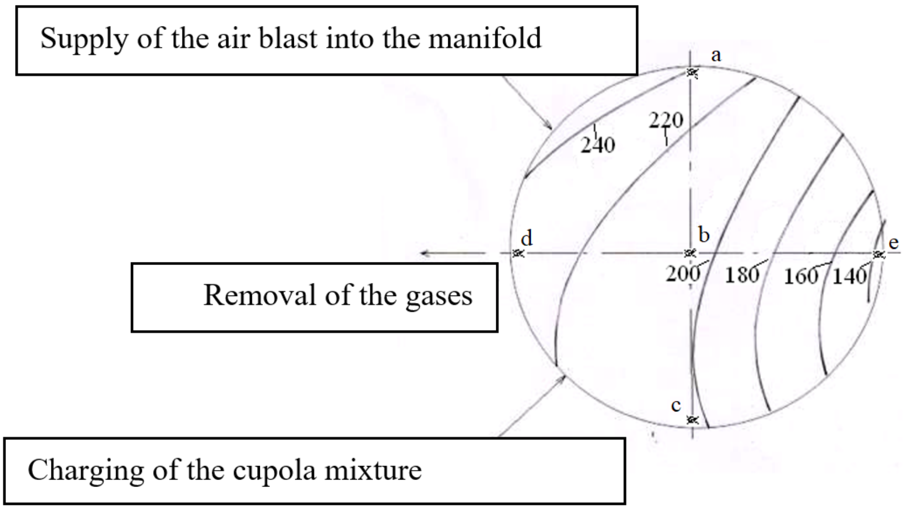


Fig. 2. Change in the temperature field of the charge bed at the level of the stockline
(figures near the curves, ˚C).

With an average temperature of the bed of 209 ˚C, circumferential nonuniformity of gas distribution over the horizontal cross-section of the furnace was found to be 27.94 % of the total, while its radial nonuniformity exceeded the value of 16.35 %, which indicates unsatisfactory distribution of the air blast in the cupola and requires its optimization. Such nonuniformity of the temperature and gas flow is an undesirable phenomenon as it stimulates the increase in the waste of coke, lowers the performance of the furnace, and increases the amount of solid particles and hazardous gas components that leave the furnace body [12].

This is primarily attributed to the design of the air supply elements (inefficient design of the distribution manifold, positioning of the tuyeres (diameter, inclination angle, their quantity, etc.). This leads to solid fuel combustion disturbance, ineffective heat generation in the bed, increase in specific fuel consumption, and lowers the productivity of the furnace.

To evaluate the dynamics of the solid fuel combustion in the furnace, the changes in gas composition at the level of the stockline were subjected to examination (Table 3).

The analysis demonstrated that melting of the cupola mixture in the shaft furnace occurs under different oxidation-reduction conditions. During the entire melting process, the initial components are heated in the furnace body in the reducing atmosphere that is created by the coke combustion products and is characterized by high concentration of carbon monoxide. This leads to the development of reduction reactions in the bed and formation of a metallic phase in the melt. This phase must be more frequently tapped, and as this process takes place, the furnace must be shut down. It was noticed that the change in the gas atmosphere composition over the cross-section of the furnace is characterized by pronounced nonuniformity, if compared with the composition in the middle of the furnace, with respect to oxygen in both radial (119.74%) and circumferential directions (119.74 %), carbon dioxide (65.41 % and 209.3 % respectively), carbon monoxide (18.89 % and 32.82 % respectively) and nitrogen (3.13 % and 2.85 % respectively, as it is not involved into the combustion process) [13].

Table 3. Changes in gas composition at the level of the cupola mixture stockline.

Point of measurement	Gas composition, [%]				Air consumption rate
	CO_2	O_2	CO	N_2	
a	4.0	4.0	20.2	71.8	0.76
b	8.4	0.1	21.9	69.6	0.63
c	12.0	2.6	14.4	71.0	0.80
d	9.0	1.2	13.8	76	0.77
e	13.0	1.6	14.4	71.0	0.77
Mean value	6.88	1.9	16.94	71.88	0.75
Circumferential nonuniformity, [%]	65.41	100.00	18.89	3.13	2.67
Radial nonuniformity, [%]	209.3	119.74	32.82	2.85	77.33

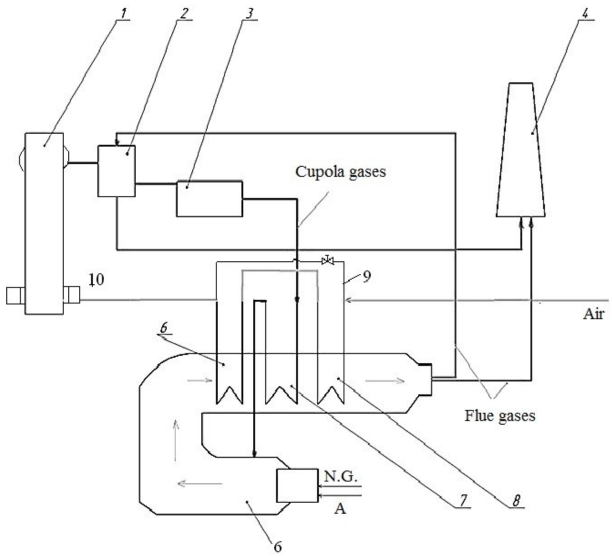
Significant radial distribution nonuniformity of the air consumption rate (77.33 %) is also noteworthy. Such gas distribution in the furnace shaft is primarily attributed to the specific features of the air blast supply that creates the conditions for layer-by-layer coke combustion in the upper part of the initial charge. At the same time, radial nonuniformity is mainly attributable to the distribution of the air blast over the cross-section of the furnace. Circumferential nonuniformity results from the design of the distribution manifold and the method of gas collection from the furnace body. Low values of the air consumption rate indicate the shortage of the air blast during melting process and coke overconsumption [14]. Attempts to increase total air blast consumption in the cupola are restricted by limited performance capabilities of the flue-gas pump, while the decrease in total coke consumption is accompanied by the temperature drop of the liquid melt. The analysis of the gas composition at the bed outlet showed that the highest carbon dioxide content and the best temperature conditions for melting of the mineral raw materials are observed to the left of air blast supply zone, while the worst conditions exist to the right of the air blast supply zone. The zone where the largest amount of molten material is formed at high temperatures is located in the furnace near the air blast supply area. The remaining space of the furnace body is characterized by low intensity of heat generation and formation of an extended reducing zone of coke combustion.

Gas composition in the cupola as a whole is characterized by practically total absence of excess oxygen in the flue gases (mean value of 1.9 %). Its lowest content is observed in the centre of the cupola where the air flow motion is restricted [15]. Such distribution of residual oxygen is mainly attributed to design features of the furnace and its tuyere area where the air flow is mainly restricted by the peripheral zone near the air supply.

If air blast heating is available, its implementation is far from being perfect. Thermal efficiency of the heat-exchanging device is lowered (not more than 50 % instead of 70-75 %). Sometimes coke is used as a heat source (as primary fuel), which is absolutely inadmissible due to its high cost. To assure such an air blast heating, operational efficiency of the furnace must be lowered at the expense of deterioration of heat exchange conditions in the upper part of the shaft and coke consumption increase. [16] Failure to implement efficient conditions of the heat transfer between the flue gases and heated air requires installation of an additional heat exchanger. The use of cupola gases and implementation of efficient conditions of their combustion in a separate air preheater enables reaching high temperatures of air blast heating (600-650°C) while reducing total natural gas consumption by more than ten times and having maximum total consumption of 50 [m^3/h] (Fig.3).

Due to design defects of the cupola gas collecting, cleaning and disposal system, an increase in power consumption is observed during operation of the air blowers. Application of a wet cleaning system leads to appearance of additional kinds of waste, i.e. wet slag, dirty water, and steam emission. This requires installation of additional equipment and leads to an increase in operating costs and power consumption. Dry cleaning method with fibrous filters requires their disposal [17].

Modern oxygen-enriched air systems are used only in emergencies. Their application for intensification of heat-mass exchange processes in the bed is restricted. Due to this reason, use of oxygen is accompanied by the increase in costs aimed at production of the main types of products, and thus it is not widely used [18].



1 – cupola; 2 – inertial dust-trapping unit; 3 – filter; 4 – flue gas stack; 5 – secondary combustion chamber; 6 – first section of recuperator; 7 – second section of recuperator; 8 – third section of recuperator. NG – natural gas; A – air

Fig. 3. Disposal of cupola gases.

The choice of alternative heat sources, other than coke, made by domestic plants is limited to coal and carbonaceous substitutes. However, it always lowers the performance of the cupola furnace.

Analysis of the heat exchange behaviour in the cupola shaft showed that steady-state heat capacity of the flow of molten materials is equal to the product of their heat capacity and their consumption W_m=5.024 [kJ/K], while heat capacity of the gas flow is equal to 6.083 [kJ/K]. Their ratio is W_m/W_g=0.83 [20]. Such a regime of the cupola operation is characterized by low intensity of coke combustion and relatively low final heating temperature of the materials. The flue gases leave the bed with excess temperature [21].

To assess the efficiency of thermal performance of the mineral wool cupola, an average heat balance chart has been drawn up (Table 4).

Table 4. Average heat balance chart for mineral wool cupola.

Input			Output		
Parameter	[kW]	[%]	Parameter	[kW]	[%]
Potential heat of coke	9666.1	73.95	Sensible heat of melt	1540.62	11.78
Sensible heat of air blast	1160.76	8.88	Sensible heat of flue gases	3336.48	25.53
Heat of melting heat-generating reaction	2243.77	17.17	Heat of incomplete combustion	7317.75	55.99
			External heat loss	875.78	6.70
Total	13070.63	100.0	Total	13070.63	100.0

As per the data represented, thermal efficiency of the cupola is only 11.78 %. Such a low efficiency of the furnace is primarily attributed to poorly organized coke combustion process that takes place with reduced air blast consumption and its unsatisfactory distribution over the cross-section of the furnace. This leads to a significant increase in carbon monoxide content and appearance of incomplete combustion (55.99 %), as well as an increase in flue gas temperature and in external heat losses (25.53 %).

Conclusions

Thus, analysis of the current thermal and gas-dynamic performance of the mineral wool cupola has revealed the following:

1. The mineral wool cupola under studies suffers from certain design defects that do not allow achieving high performance, i.e. insufficient bed depth, large diameter of the tuyeres, and narrow angle of their inclination relative to the horizon. These factors restrict the depth of gas penetration into the bed, thus causing the gas flow to move at the periphery of the furnace.
2. Existing air supply system is characterized by nonuniformity of air blast distribution over the cross-section of the furnace, which causes thermal performance of the bed to vary. The best operating conditions are observed in the layer of the bed near the area where the air blast is supplied to the furnace.
3. Thermal performance of the cupola is characterized by significant nonuniformity of gas flow distribution over the heated cupola mixture. The zone with insufficient air blow rate and low gas velocity is located at the side opposite to the air blast supply area. Here, the coke undergoes gasification and melting of the cupola mixture is slowed down. Such processes show that the design of the air manifold and gas collecting system is far from being perfect.
4. Coke combustion occurs whenever the development of the oxidizing zone is low, which leads to low intensity of coke combustion and cupola mixture melting with significant incomplete combustion and a relatively low temperature in the focus zone. Such property leads to fuel waste and lowers productivity of the furnace.
5. Thermal regime of cupola heat occurs at $W_m / W_g = 0,83$ and is characterized by low melting intensity with high-temperature flue gas flow generation and underheating of the melt.
6. Cupola thermal efficiency is 11.78 %, which indicates its unsatisfactory design and poorly organized melting process of mineral charging stock.

To enhance energy efficiency of mineral wool cupolas of any design

- It is important to pay due consideration to design features of both furnace body and air supply elements.
- Efforts should be made to achieve efficient distribution of the air blast with every element of the bed to be surrounded by a strictly defined amount of oxygen.
- It is important to utilize heat obtained from all available additional sources (air blast heating, natural gas, potential heat of cupola gases).
- It is necessary to implement efficient conditions of heat transfer from hot cupola gases to materials in order to make the most efficient possible use of the coke heat.
- It is expedient to scrutinize feasibility of application of external heat-mass exchange intensifiers in the bed through the use of acoustic field energy and pulsating air blast energy.

Implementation of these measures will allow setting environmentally friendly production of fibrous insulation with specified productivity and maximum specific coke consumption of 100-120 kg/t of melt.

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The Wear Resistance of Mottled Iron with Stabilized Carbide Phase

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Abstract. There is investigated the wear resistance of mottled irons with stabilized carbide phase, obtained by alloying iron with copper, chromium and sulfur. It is shown that during heat treatment the outer shell of the carbide phase inclusions, destabilized with copper, dissolves, leaving a core stabilized with chromium. Carbon from the carbide phase dissolution coats the surface of manganese sulphide inclusions, forming additional wear-resistant structural component of mottled iron. The resulting structures can be attributed to compositional structures, which morphology and phase composition can be controlled by alloying and heat treatment.

Introduction

For many years theoretical and practical researches in the field of friction, wear and metal cutting have been aimed at establishing formal and empirical relations between various parameters (surface roughness, dynamics and wear pattern, material properties, type of loading, contact geometry, type of lubricant etc.).

In theoretical studies there prevailed approaches limited, as a rule, within one field of knowledge. The most widely used in tribology were mechanistic models, which considered simplified types of interaction of friction surfaces excluding process energy and structural changes of the material. The fundamental drawback of this approach was just postulating of all kinds of friction bonds and fracture mechanisms in tribosystem without considering their interdependence and interdependence with the thermodynamic flows of energy and material causing inevitable structural transformation of materials, mainly in the surface layer of contacting bodies [1, 2].

So far the main goal of any hardening technology has been to achieve high hardness and therefore wear resistance, and the issue of possible structural changes in materials has been considered in general terms [1 – 4].

On the Nature of Friction

Thermodynamic nature of friction as a dissipative process has not found widespread occurrence as energy and thermodynamic criteria in it are not associated with the determining mechanism of wear and are considered only in general terms [3, 4].

Mechanistic and energetic approaches have not attempted to take into account in corpore structural or material factor, which has been considered only in the form of an empirical coefficient in calculations and models and has not been significant.

The fundamental framework, able to tie all the achievements of tribology involving material sciences, can be entropic and energetical or structural and energetical theory, opening the possibility of a quantitative description of tribosystems, as entropy is a quantitative way of violation of the material structure. This theory is based on modern achievements of material science and solid-state physics in the field of structural self-organization of materials and takes into account the specific features of structural and energetic adaptability of materials in friction. From the standpoint of entropic and energetical theory, friction is the process of transformation (dissipation) of external energy into internal energy, and the regularities of this transformation are due to the structural condition of the friction system materials and their structural self-organization [5 – 12].

It is shown [13] that the temperature of the friction part surfaces, depending on the friction conditions can vary from 200°C to 1000°C that's more than enough for the occurrence of various structural transformations. Account of phase transformations at high temperatures is realized in heat-resistant, high-temperature and other special steels, but in tribology this phenomenon is rarely taken into account [4].

Any process of friction is accompanied by a high level of specific pressures and contact stresses, and pressure and temperature are inextricably linked and have a joint effect on the material structure. It should be noted that the main contribution to the phase entropy, and hence the impact on the level of its stability is made by the uncertainty of atomic parameters, the level of order of the atomic and crystal structure and the degree of density of defects in the crystal [14]. In this case, pressure causing plastic deformation of metal grains in friction significantly increases the level of defective grains. This leads to an increase of entropy of phases and decrease of their stability at the macro level. The density of free electrons, radii and other characteristics of atoms change under pressure, i.e. the entropy factor increases at the micro level. This leads to a significant change in the interaction of elements at high pressures, the violation of stability conditions of the existing phases, and causes the appearance of new phases. It also changes the character of mutual solubility of the elements in each other and as a result, changes the configuration of constitution diagrams.

The most significant is the effect of pressure on diffusion processes [15], which determine the orientation of self-organization of material structure, especially considering the system temperature. In high pressure conditions the energy state of atoms in the crystal lattice and the state of the whole crystal change. Naturally, in this case, the conditions of implementing diffusive movement of atoms in the crystal lattice change too.

In the materials of rubbing bodies, thermodynamic processes of different nature occur under external stresses, substance flows and energy flows and they are directed to their structural self-organization [5 – 10]. The material is more wear-resistant if its structural components are more thermodynamically stable and sustainable, regardless of the density degree of matter and energy flows in friction. If the density of matter and energy flows exceeds a certain level, then structural self-organization begins in the material, i.e. at the atom-molecule level there are processes aimed at compensation or neutralization of external energy flows. In the structural components, which in the given circumstances do not possess sufficient thermodynamic stability, quasiinvertible or irreversible phase transformations begin to occur (the product of such irreversible phase transformations is, in particular, the so-called "white layer" formed in the surface steel contents in friction), and friction energy dissipates in these transformations [7 – 12].

The heavier the wear is, the further from equilibrium thermodynamic state the friction system is. In this case, the structural components of the material cannot dissipate friction energy. As a result of energy accumulation in friction process, the system discharges its surplus due to the structure destruction, i.e. in the form of wear.

To the greatest extent the conditions of thermodynamic and kinetic stability, both of the structure and properties in a wide range of temperatures and pressures are met by the following substances: graphite, copper and carbides of various elements, in particular, iron carbide (cementite) and carbides of refractory metals (tungsten, chromium, vanadium, molybdenum, titanium and others).

Experimental Studies of Alloyed Cast Irons

As an object of research we selected pearlite mottled iron, which structure consists of graphite, cementite and pearlite. Taking into account that plain cementite is metastable at high temperatures; cast iron was additionally alloyed with copper and chromium.

Alloying of cast iron with copper is carried out for multiple purposes. Firstly, it is known that copper in cast iron increases its conductivity and the majority of tribotechnical properties. Secondly, copper, unlike silicon, destabilizes cementite, due to the fact, that it is partly included in its composition, replacing some iron atoms: $(Fe_{2-n}Cu_n)C$. Destabilization of cementite is a direct manifestation of forming copper with fullerenes cuprous endohedrals. This means that first portions of crystallizing cementite are enriched with chromium (inner core of cementite inclusions), and with copper — the last portions, which are also enriched with silicon, although to small degree due to the low solubility of this element in cementite. There is a kind of polarization of the carbide phase that is one part of it gains increased tendency towards graphitization, and the other part (inclusion core) - dramatically reduced one.

To achieve guaranteed chilling cast iron was additionally alloyed with sulfur, bismuth and tellurium. High sulfur content in cast iron (and low manganese content to prevent a loss of too large amount of manganese sulphides from melt, reducing metal fluidity) guarantees full chill of cast iron and graphitization only during annealing. Chemical composition of cast iron is given in Table 1.

Adding chromium at the rate of 2.0% to iron (Table 1) dramatically stabilized iron cementitious structure. Full pearlitizing of the structure was only completed after 3 hours when heated to 980^{0}C (Fig. 1). Iron structure consists of ledeburite frame (Fig. 1a) and a large number of sulfide inclusions (Fig. 1b). Additional 8 hours of soaking is needed for the dissociation of the ledeburite frame of some cementite inclusions (Fig. 2), while perlite ferritizing did not happen because of the stabilizing effect of copper and chromium.

Table 1. Typical chemical composition on mottled iron alloyed with copper, chromium and sulphur.

Chemical composition, [% mass percent]							Additive *
C	Si	Mn	S	P	Cu	Cr	
2.91	2.24	0.44	0.377	0.31	1.20	2.10	12% sulphur ferro-copper+0.01% (Bi+Te)

* sulphur ferro-copper is a product of additional recovery of copper from copper-smelting wastes with the composition: 11.6%Cu; 2.7%S; 0.44%C; 0.07%Si.

In the iron the effect of graphitization on manganese sulphides is first detected (Fig. 1b and Fig. 2c). Each annealing graphite inclusion has a non-metallic inclusion (Fig. 3a, 3b, 3c). Adsorption of ferrocarbide fullerene complexes [16] activates surfaces of nonmetallic inclusions (Fig. 3c, 3d), crystallizing with cementite, only from the perlite side, where the decay process of destabilized cementite shell begins. Sulfide surface inside cementite is not activated and the decay process of the complexes does not occur. During graphitization not only the outer shell of cementite decays, which is destabilized by endohedrals based on bismuth, tellurium and copper.

Central nuclei of cementite, stabilized by chrome form cementite grain structure of mottled iron (Fig. 2a). Table 2 gives the results of testing mechanical and tribotechnical properties of stable mottled irons.

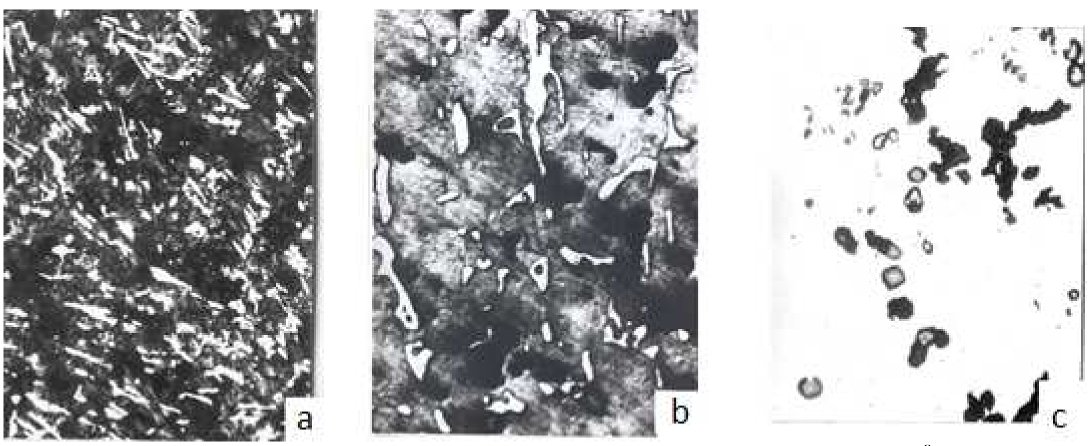

Fig. 2. Microstructure of iron, subjected to graphitizing annealing at 980^{0}C during 8h:
a – x100; b, c – x400, nickel etching.

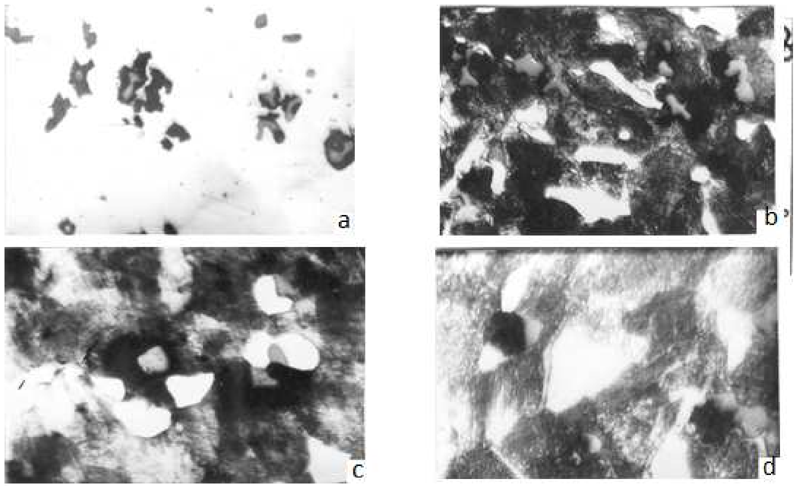

Fig. 3. Influence of sulfide-manganese phase on graphitization of stable mottled iron, x630 (nickel etching).

Table 2. Tribotechnical and mechanical properties of stable mottled irons.

№ iron	Chemical composition **, [% mass percent]				Wear*, [mg/cm^{2}km]	Friction coefficient *	σ_B, [MPa]	HB, [MPa]
	C	Si	S	Cu				
1	2.22	3.41	1.11	3.02	5.4	0.07	382	2260
2	2.17	3.37	1.12	3.22	6.1	0.10	390	2010
3	1.85	2.41	1.40	4.96	6.6	0.08	578	1970
4	1.80	4.40	0.92	4.99	6.7	0.09	490	2400

* triboengineering testings were carried out according to standard technique on friction machine SMC-2 with a counterbody, made of hardened steel 40X, with shoe pressure on the roller 120 MPa in distilled water, simulating the conditions of half-floating condition;

** P no more 0.3%; Mn no more 0.45%; Cr = (1.8…2.1)%.

Discussion of the Results

The data obtained for mottled iron wear are comparable to bronze wear in the same conditions for which friction coefficient with lubricant in the pair of steel – bronze is 0.07 to 0.10.

In fact, the obtained structure of mottled iron is a composite structure consisting of the matrix alloyed with copper - perlite, and reinforcing wear-resistant compact phases of high dispersion – stabilized with chromium cementite and sulfide inclusions in a graphite shell.

Similar studies of thermodynamically stable structures were carried out in the study of wear resistant surface layers with implanted nanodiamonds of detonation synthesis [18].

The obtained results enable to draw the following conclusion. To create a universal wear-resistant material is impractical. A wear-resistant material must be created in accordance with the applicable working conditions of the tribological system, which are determined by the processes forming and stimulating the formation of respective wear-resistant structures in the material.

Summary

Thus, the present task is to create materials with specific structure for the given working conditions of a tribotechnical unit. The solution of this problem is possible in the following areas:

1. The creation of alloys with metastable structures that undergo a reversible phase transformation upon reaching a certain power-energy level in the friction zone.
2. The creation of alloys with dissipative structures able to dissipate the frictional energy to a safe level, at which structural changes in the material do not occur.

3. The creation of alloys with thermodynamically stable structures that retain their tribotechnical properties in a wide range of variation of thermal and mechanical energy in the friction zone.

4. Optimization of parameters of surface layer with various technological methods creating a particular type of structural organization of a material for the specified operating conditions of the tribological system.

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Research of Activity of Natural Radionuclides in Construction Raw Materials of the Volgograd Region

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Keywords: Natural radionuclides, gamma background, absorbed dose rate, radon, affiliated products of disintegration, natural radionuclides, ionizing radiation sources.

Abstract. In article results of a complex research of activity of natural radionuclides in construction raw materials of the Volgograd region are stated. The analysis of frequency distribution of effective specific activity of natural radionuclides in construction materials was carried out. It was revealed that the population of the Volgograd region is more exposed to radiation from construction materials, than on average across Russia. The radiation control while developing and marketing of construction materials to is a possible way to decrease a dosage power in premises.

Intorduction

Naturally occurring radionuclides, forming background radiation areas lead among all sources of ionizing radiation (SIR). As the populations of the industrialized countries in the world spend most of the time in residential and public buildings, natural radionuclides (NRN), contained in building materials significantly affect on radiation exposure from natural sources of ionizing radiation. Because NRN content in building materials varies widely, individual doses to the public in buildings and in various regions differ from values lower than twice the average values of up to 100 times more than the average [1]. Therefore, the study of the radiation characteristics of building materials and the development of methods for reducing the exposure of the population are urgent tasks.

It is now established that the average dose to the population due to natural background radiation and the radiation dose during medical procedures are 0.1 – 0.2 Sv over fifty years. Thus, the yield of somatic long-term outcomes is 1-2% of all deaths from malignant tumors [2]. Early diagnosis and prevention of diseases become possible for health care facilities only by implementation of modern information technologies in health care process, in particular, the developing of automated differential diagnosis medical systems [3, 4]. A special place is given to systems which help to improve the quality of medical services [5]. Medical expert systems of differential diagnosis seem to be the most relevant approach to implementation of medical knowledge software.

The set of various factors negatively influencing on psychological status of people in certain regions of Russia [6, 7] has been accumulated for the last decades. One of these factors is the radiation background in rooms [8]. Now the doses received by the population in rooms can be very high that is connected with use of waste of the industry in production of construction materials [9].

Natural sources of ionizing radiation affect people, both in municipal, and in production spheres. The greatest share in radiation of the population is contributed by construction materials and designs, as well as radon and affiliated products of its disintegration from soils. Millions of tons of construction raw materials are taken from a subsoil of the earth and are gone to construction production where effective specific activity of minerals [10, 11] is sharply deformed.

The increasing population of the planet requires constant increase in scales of construction calling for need of research of new, economically more profitable construction materials. Now industrial waste is successfully applied in the construction process. But in some cases it contains the increased activities of natural radio nuclides.

The solution of the problem of dose loadings decreasing in premises can be reached by complex researches of radiation characteristics of construction raw materials and power of a dose in buildings under construction as well as already operated, depending on territories. During the conducted researches problems of detection of a gamma background changing regularities of construction raw materials depending on the district of the Volgograd region, and on a type of breed and geological age were solved.

Methods of researches included: analytical generalization of the known scientific and technical results; standard techniques of a research of properties of construction materials and gamma and spectrometer analysis of effective specific activity of NRN; dosimetric and radiometric methods of determination of dose loadings and handling of experimental data by methods of mathematical statistics.

Gamma Radiation Dose Assessment in Rooms

The radiation background in rooms is considered as one of main types of ray impact of the environment on the population as the person spends the most part of the time in rooms [12]. The dispersion of γ-background values in rooms depends on many factors from which it is possible to allocate the following: type of material of which the building is built and concentration of NRN in it; geometry of the building (architectural planning solution); housing unit density; γ-background of nearby territories and buildings.

As inside, and out of rooms the dose of external radiation is estimated taking into account of stay inside of 80% of time (coefficient 0.8) and the ratio of the absorbed dose power (ADR) in rooms to dose power out of rooms, equal to 1.2. Then 50 * 1.2 = 60 nGy / h, and the exposure dose rate (EDR) will be:

$$H_{eff} = 60 * 0.7 * 8760 * 0.8 = 290mkSv. \quad (1)$$

The dose of space radiation on the open area depends on its height above sea level and geographic latitude. The highest levels of radiation are characteristic to Kyrgyzstan (377 mkSv) and Armenia (350 mkSv), the considerable part of the population of which lives in mountainous areas. In Russia the average level of space radiation almost doesn't differ from a dose above sea level for 43° of NL (292 mkSv / year). The dose of space radiation is weakened indoors by plates of overlappings. Weakening coefficients in modern brick or concrete houses, depending on number of storeys are equal from 0.89 (on 1 floor) to 0.54 (on the 20th floor). At the same time the conditional thickness of plates of overlappings is accepted equal 40 g/cm2.

It is possible to estimate the maximum power of a dose in premises by means of a formula for calculation of ADR γ-radiation (nGy / h) in an air cavity of infinite space with evenly distributed NRN in it. However, the executed researches show that ADR created in an air cavity of infinite space is possible to determine precisely by specific effective activity (A_{eff}) of NRN in material:

$$P_{max} = 1.04 * A_{eff}. \quad (2)$$

With a margin error no more than 10% it is possible to accept ADR in modern stone buildings (P_{build}), nGy / h:

$$P_{build} = 0.76 * P_{max} = 0.79 * A_{eff}. \quad (3)$$

The transition coefficient from ADR to an equivalent dose is equal 0.72 Sv / Gy.

By direct researches it is established that ADR in wooden, brick and concrete buildings of a number of the states are respectively in limits 44-104, 26-217, 26-304 nGy / h. Average EDE is equal to 411 mkSv/year at average A_{eff} = 93 Bq / kg for the population of Russia living in stone houses. The gamma radiation dose power ratios P_{build} created in the buildings built of various construction materials to dose power P_{str} on the open area are given in table 1.

Table 1. The relation of capacities of a dose of gamma radiation in buildings and on the open area

Building material	P_{build} / P_{str}	Building material	P_{build} / P_{str}
Pumice	1.50	Limestone	1.24
Slag	1.47	Heavy concrete	1.84
Brick and stone	1.36	The blown-up concrete	1.18
Clay	1.45	Tree	0.95

These data allow to judge on influence of the construction material used at a building construction at a gamma background size indoors. Wooden and easy prefabricated houses can't significantly influence a gamma background of the open area.

NRN Activity in Construction Raw Materials of the Volgograd Region

The natural radionuclides included in objects of the external environment are the main sources of radiation for humans. Its radiation creates a natural radiation background, and a dose of radiation for humans due to practically all components of a natural radiation background depends on activity of people. These components called the technologically strengthened background (TSB) are subject to rationing and control on an equal basis with natural radionuclides.

Many components of TSB create dangerous conditions and influence the big contingents of people, making the significant contribution to a collective dose of radiation of the population at rather small individual doses of radiation. As consequences of radiation are defined by the size of a collective dose, the importance of this TSB components needs to be estimated on it contribution to a collective dose of radiation of the population.

In the housing and industrial sphere the dose of external radiation of people is determined by concentration of NRN in construction materials. According to regulations an effective dose of 1 mSv per year on average for any consecutive five years, but no more than 5 mSv per year are established for the population. These main dose limits of radiation of the population don't include a dose from natural, medical sources of ionizing radiation and a dose due to radiation accidents. On these types of radiation special restrictions are set. To calculate a contribution to the general (external and internal) radiation of an organism due to radionuclides intake the sum of products of each radionuclide intake per year into its dose coefficient should be estimated. The annual effective dose of radiation is equal to the effective dose of external radiation per calendar year, and expected effective dose of internal radiation caused by radionuclides intake for the same period. Time interval for determination of the expected dose established for the population is 70 years.

At design of new buildings of housing and public appointment it should be provided that the average annual equivalent equilibrium volumetric activity (EEVA) of isotopes of radon and toron in air of rooms shouldn't exceed 100 Bq / m^3, and the power of a dose of gamma radiation didn't exceed dose power on the open area more than on 0.2 mkSv / h (20 mkR / h). In the operated buildings average annual EEVA of isotopes of radon in air of premises shouldn't exceed 200 Bq / m^3. For providing normal (on a radiation sign) conditions indoors, the first class construction materials should provide effective specific activity no more than 370 Bq / kg. For the materials used in road construction within the territory of settlements and zones of perspective building and also in case of construction of factory buildings the second class is established at which effective specific activity shouldn't exceed 740 Bq / kg. In case of effective specific activity more than 740 Bq / kg, materials are not applicable for buildings.

Features of a geological structure of the Volgograd region define availability of natural minerals. There are 101 operated fields determined by geological exploration for December, 2015, including: different types of clay raw materials - 24; sandstones - 29; limestones and dolomite - 12; swept - 11; sands - 20; a molding - 3; mineral paints - 2. The rocks extracted and developed in the territory of the area for needs of the construction industry are provided by exclusively sedimentary breeds.

A Research of Specific Activity of NRN in the Industrial Waste Applied for Production of Construction Materials

The materials made of industry waste are of special interest. The wasteless technology stimulates use of industrial waste for production of construction materials. Such practice promotes preserving natural resources, prevents pollution of the land surface, the rivers, and also cuts down expenses on production of building materials. In table 2 results of researches of specific activities of NRN in the waste of the industry used for production of building materials are given.

Table 2. Average specific activities of NRN in the waste of the industry applied for production of construction materials

Name of material	Sampling point	Specific activity of NRN, [Bq / kg]			
		^{40}K	^{226}Ra	^{232}Th	A_{eff}
Blast-furnace slag	JSC VGTZ	36.0	9.9	10.8	27.1
Mould waste	JSC VGTZ	59.8	13.7	9.6	31.4
Ash slag	JSC Serebryakovtsement	1079	119.7	83.6	320.9
Cinder	JSC Serebryakovtsement	98.3	14.8	8.0	33.6
Granulated slag	JSC Serebryakovtsement	143.3	85.1	37.1	145.9
Thermo-phosphorus slag	Chimkent	173.9	224.9	21.8	268.2
Cinder	Chimkent	156.3	6.1	5.6	26.7
Ash slag	Chimkent	1002	106.4	60.6	270.9
Blast-furnace slag	CJSC WKP	37.3	39.2	13.1	59.5

From table 2 one can see that specific activity in the industrial waste corresponds to the NRN average values in the materials received in pits or by traditional conversion. While analyzing A_{eff} of the industrial waste of the Volgograd region used for production of construction materials it should be noted high A_{eff} of the ash slag mixes compared to slags. Thus, the studied materials in the Volgograd region have raised A_{eff} in comparison with other countries, but lower, than on average across Russia corresponding to 1st class construction materials.

Researches of a Gamma Background of Territories and Premises of the Volgograd Region

The Volgograd region is located in the southeast of the European territory of Russia in lower reaches of the Volga River and middle reaches of the Don river. Its area makes 113900 sq. km. The geographical location and the considerable sizes of area have caused a big variety and specificity of natural minerals. The long geological history has led to formation of sharp contrasts in a structure of the Right bank of the Volga and Zavolzhye (Left bank). The right coast is occupied with the southern termination of Volga Upland forming Volga-Don watershed. Its eastern slope is abrupt downward and scarred through by the long branching gulches, and the western slope gradually merges with the valley of the Don river.

The left bank of the area is occupied with equal, slightly sloping Caspian lowland located in a zone of the hollow of the same name. Numerous approaches of the sea have created the powerful thickness of sedimentary breeds reaching sometimes 10-15 km and have formed exclusively plain surface of Caspian lowland. The western part of Caspian lowland to the south of Volgograd is called Sarpinskaya (with system of hollows, estuaries and lakes).

In the northwest the Kalachevskaya Upland comes into borders of the area. Don bend is formed by the Don ridge with heights to 250 m and is strongly damaged by erosion. Aeration processes, plane washout, have bared radical breeds, chalk and marls. Local sands are gray-haired from cretaceous dust. Between the Average-Russian and Volga Uplands the Khopyor and Buzuluk plain with flat watersheds, wide valleys and extensive flood plains of the rivers lay down.

The results of large-scale researches of a dosage power of the Volgograd region area, (see tab. 3) are close to data in [13] and lay beyween 50 - 120 nGy / h (5 - 12 mkR / h). All measured values don't exceed admissible level of a dose power. In places of a bedding of primary rocks where works on extraction of the main construction materials are conducted, the power of a dose fluctuates from 128 to 374 nGy / h on a surface, and from 187 to 460 nGy / h at a depth from 3 to 5 meters.

Table 3. Average territorial power of absorbed dose values and A_{eff} of the Volgograd region soils

Name of the area	Area of the area, [sq.km]	ADR indicators, [nGy / h]		A_{eff} of the soil, [Bq / kg]
		averages	variations	
Alekseevsky	3100	117	70 – 140	148
Bykovsky	3160	87	50 – 120	114
Gorodishchensky	2450	118	60 – 150	147
Danilovsky	2400	61	30 – 100	98
Elansky	3400	93	50 – 130	138
Ilovlinsky	5500	113	70 – 130	149
Kalachevsky	3400	109	60 – 140	142
Kamyshinsky	3150	114	70 – 150	148
Leninsky	4900	96	50 – 130	134
Mikhaylovsky	4130	101	60 – 140	132
Nekhayevsky	1900	93	50 – 130	130
Nikolaevsky	2910	50	30 – 90	96
Octyabrsky	2350	51	50 – 120	98
Olkhovsky	3200	82	60 – 130	124
Pallasovsky	12600	104	70 – 140	132
Serafimovichesky	4500	83	40 – 120	106
Sredneakhtubinsky	1900	119	70 – 160	164
Surovikinsky	3640	87	50 – 130	120
Uryupinsky	2900	106	60 – 140	132
Frolovsky	3000	108	70 – 140	136
Volgograd city	300	113	70 – 130	184
Volzhsky city	85	116	80 – 140	170

Based on the results of conducted researches (see tab. 3), "Normative of admissible levels of gamma radiation, radon on sites of building and sampling" have been developed and accepted to execution for the Volgograd region, which establish the ADR limiting level of gamma radiation on open sites of the territory of the area, equal 200 nGy / h (0.2 mkSv / h). Also the map of distribution of a dosage power in the territory of the area has been made for carrying out the analysis of territorial dose loadings allocated under building.

Conclusion

In the course of this study, the problem was solved, which has significant practical value - reducing dose loads from natural radionuclides contained in construction materials in residential and public buildings. For the first time extensive radiological studies (more than 7000 measurements) of residential, public and industrial buildings, built from a variety of building materials has been conducted in the Volgograd region. It was established that the ADR in production facilities of construction companies is an average of 15 - 20% higher than in residential areas. The regularities of changes in territorial dose power, as well as dose power for deposits of building materials and premises, depending on the influence of various factors (time of year, the building materials used, the number of storeys of the building, etc.) were revealed.

The map of radiation dose distribution was made up for the first time in Volgograd region, allowing engineer design organizations to navigate during radiation-ecological survey and designated areas for development. The dependence of NRN on effective specific activity of the used building material in premises for the first time was experimentally found on.

"Normative of admissible levels of gamma radiation, radon in the areas of development and sampling" was developed and accepted for execution in order to ensure radiation safety of the population of the Volgograd region. "Handbook of radiation monitoring in the construction industry of the Volgograd region" was developed and released, allowing consumers to focus on radiation parameters in mineral raw materials, and designers in the selection of areas for development.

Results of the executed researches are implemented at the entities of building industry of the Volgograd region in case of development of fields and production of construction raw and finished materials, withdrawal of sites for and construction of buildings, and are also used in case of annual creation of the radiation and hygienic passport of the Volgograd region.

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Sulfur Composite Materials Based on Sulfide Containing Industrial Waste

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Keywords: calcium sulfide, silicon dioxide, sulfides, quantum chemical calculations.

Abstract. A technology for the production of sulfur composite materials based on waste from $BaCl_2$ at Karpov Mendeleyevsk Plant (Russia) was developed. The physical chemical and quantum chemical studies were performed for the “sulfur – sulfide containing industrial waste–filler” system. The usage of sulfide ion CaS enables sulfur activation to promote the chemical interaction between the components and synthesis of sulfides and sulfur materials with high physical mechanical properties from them.

Introduction

One of the key aspects of resource efficiency is the effective use of production waste. Rehabilitationofman-madedepositswillsolvetheimportantproblemsinthe Russian mineral resources sector and improve the ecological situation.

Thesustainablemultipurposeuseoffeedstockreducesthequantityofunderused substances, increases a range of end products, makes it possible to manufacture new products from the portion of the feedstock which has been gone to waste earlier. All the above indicates the urgency and importance of the disposal and recycling problem for waste from the different industry sectors [1-8].

About the Problem

This paper discusses the possibility of producing calcium sulfide using silicon containing waste from Karpov Mendeleyevsk Plant. This waste contains 20.5% of silicon dioxide and up to 14.7% of calcium sulfide. Sulfide ions are known to be nucleophilic activators for sulfur ring cleavage. The presence of sulfide ions CaS may help in increasing the chemical activation of sulfur, and producing calcium sulfide and sulfur composite materials with high physical mechanical properties on its basis [9-13].

By being nucleophilic agents the sulfide ions activate sulfur to promote the chemical interaction between the components and synthesis of sulfur materials with high physical mechanical properties from them. The samples were made using the proposed formula, and with optimum component ratio they have high coefficient of resistance to HCl, H_2SO_4, $CaCl_2$, NaCl, $MgSO_4$solutions, high impact resistance (52 MPa), freeze resistance (280 cycles) [14-20].

The physical chemical and quantum chemical studies in the “sulfur – sulfide containing industrial waste – filler” system.

The mechanism of component interaction in the “calcium sulfide - sulfur” system was studied using the quantum chemical calculations.

The physical chemical and quantum chemical studies were performed in order to explain changes in the properties in the structure of the samples.

X-ray diffraction studies of the samples of sulfur concrete with sand-and-gravel material and fine-ground filler (waste from barium chloride production in Karpov Mendeleyevsk Plant)showed that there were orthorhombic sulfur (1.621; 1.698; 1.726; 1.781; 2.21; 2.37; 2.43; 2.50; 2.62; 2.84; 3.21; 3.57; 3.86; 4.06; 5.75 7.7), α-quartz (1.818; 1.981; 2.28; 2.46; 3.34; 4.2), barite, calcium sulfide (CaS – 2.84; 2.04, pm) in the crystalline phase (Fig. 1).

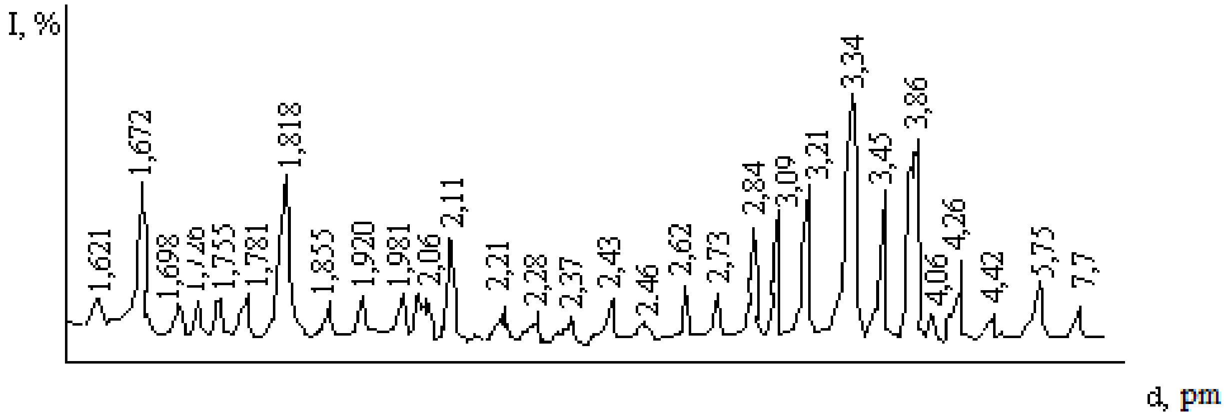

Fig. 1. XRD pattern of sulfur concrete based on $BaCl_2$ production waste with sand-and-gravel material.

The thermal gravimetric studies of $BaCl_2$ production waste revealed the endothermic processes which occurred in the temperature range 140-250 °C (endothermic effect at 180 °C). They were accompanied by a loss of the sample mass (3.3%), which was related to removal of hygroscopic and crystalhydrate water (Fig. 2).

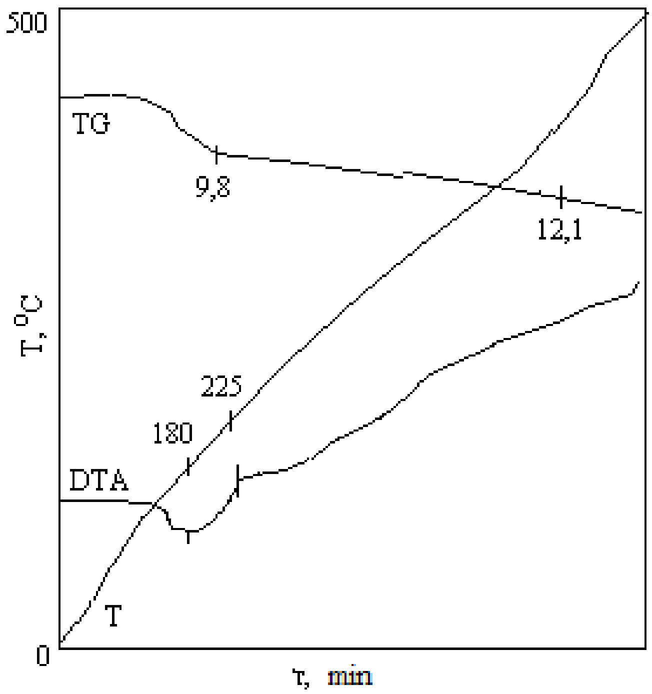

Fig. 2. Thermogram of $BaCl_2$ production waste.

With further temperature rise the system heat content is observed to increase, which appears to be associated with oxidation of the mixture components (possibly, calcium sulfide).

When heated to 500 °C the total loss of the sample mass is equal to 5% wt. Based on the results of the differential thermogravimetric curve the initial filler – waste – was subjected to drying in the drying cabinet for several hours to prevent gas formation and blowout of the sulfur concrete.

The IR spectroscopic studies established that the sample of sulfur concrete with fine-ground filler ($BaCl_2$ production waste) had no absorption peaks in the range of 3400-3600 cm^{-1} and 1621 cm^{-1}, which correspond to water deformation vibrations (Fig. 3).

No new absorption bands responsible to sulfide bonds and change in their intensities are observed in the range of 450-550 cm^{-1}.

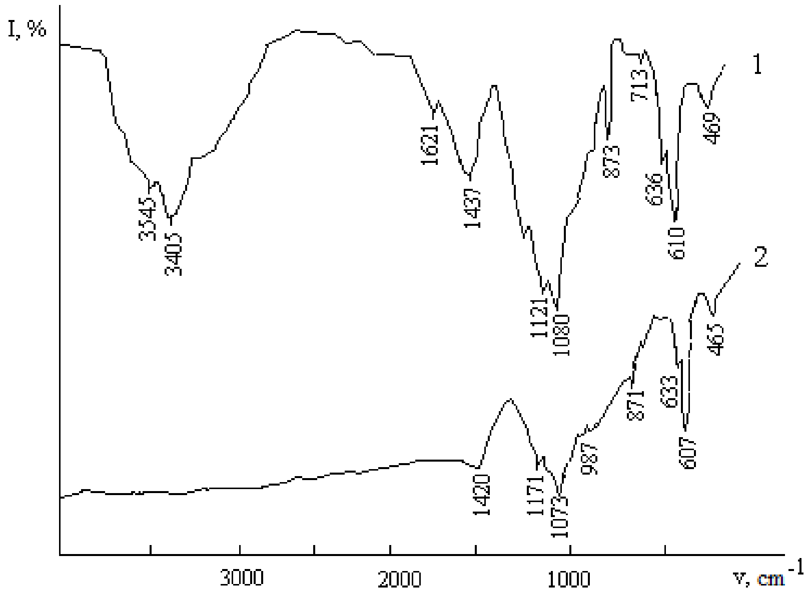

Fig. 3. IR spectra of samples of $BaCl_2$ production waste (1) and sulfur concrete with waste (2).

Electron paramagnetic resonance spectroscopy showed that the heat-treated sulfur had a lot of paramagnetic centers (15502 standard units).

The presence of active centers in the heat-treated sulfur is indicative of a rupture of the sulfur rings and occurrence of the biradicals in the system, and interaction between sulfur and $BaCl_2$ waste results in sharp decrease in paramagnetic centers in the system (7 standard units).The "quenching" of paramagnetic centers after mixing sulfur with calcium sulfide containing waste indicates the chemical interaction in the system.

The quantum chemical studies were performed in the "sulfur – calcium sulfide" system to evaluate the influence of calcium sulfide on the activation of sulfur ring rupture. The calculations were made using density functional method by Priroda software with basis 3z.bas that includes p and d orbitals in the atoms.

As the calculations show, addition of CaStoS$_6$results in significant decrease in bond energy in the cycle by 67.36 kJ/mol and stretching from 210.5 pm to 243.9 pm (Fig. 4). The reaction is exothermic (-302.21 kJ/mol). The addition is likely to occur by means of s-orbitals with the formation of valence bonds (Ca–S(7) – 277.7 pm, Ca–S(2) – 277.8) and vacant p-orbitals of calcium with the formation of donor-acceptor bonds (Ca–S(3), Ca–S(5), Ca–S(1)) (Fig. 5).

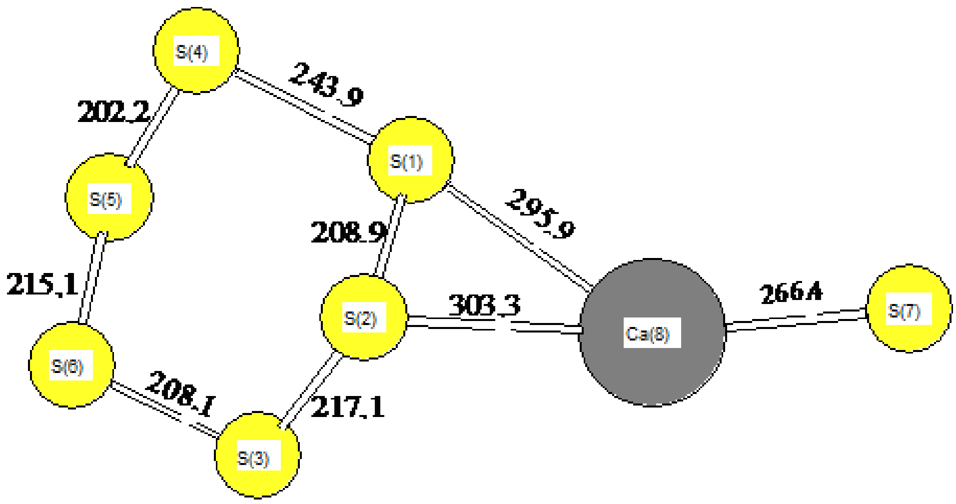

Fig. 4. Scheme of addition of CaS to S_6 cycle.

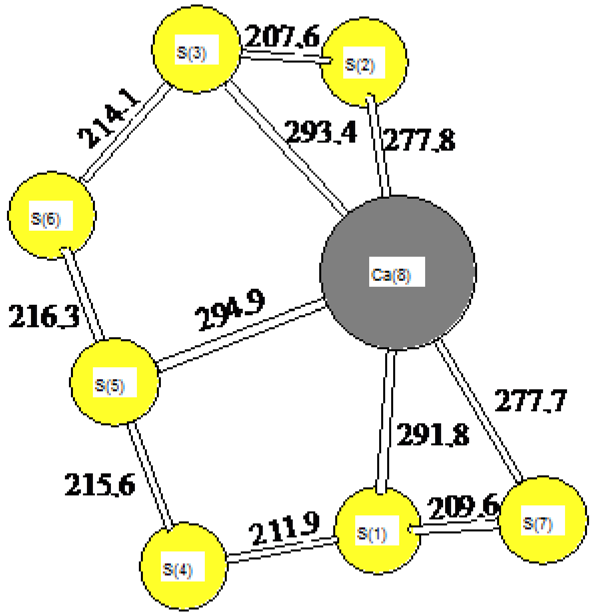

Fig. 5. CaS_7 geometry.

The energy of Ca – S bond in the compound $Ca(SH)_2$ is equal to 304.14 kJ/mol. According to the calculations we made it takes 369.51 kJ/molto break two bonds Ca–S(2) (valence) and Ca–S(3) (donor-acceptor) in CaS_7 (Fig. 5). Thus, the energy of donor-acceptor bond Ca – S(3) is ≈ 60 kJ/mol, and of valence bond Ca –S(2) is ≈ 300 kJ/mol. Then, the reaction between calcium sulfide and sulfur occurs by means of s- and p-orbitals of calcium with the formation of valence and donor-acceptor bonds.

The addition of CaS to S_8 is also exothermic (-267.27 kJ/mol), and forms similar valence and donor-acceptor bonds (Fig. 6). When heat effects of the formation reactions for CaS_7 (-302.21 kJ/mol) andCaS_9 (-267.27 kJ/mol), and molecule geometries (Fig. 5 and Fig. 6) were compared, CaS_7compound was revealed to be more stable from the thermodynamic point of view.

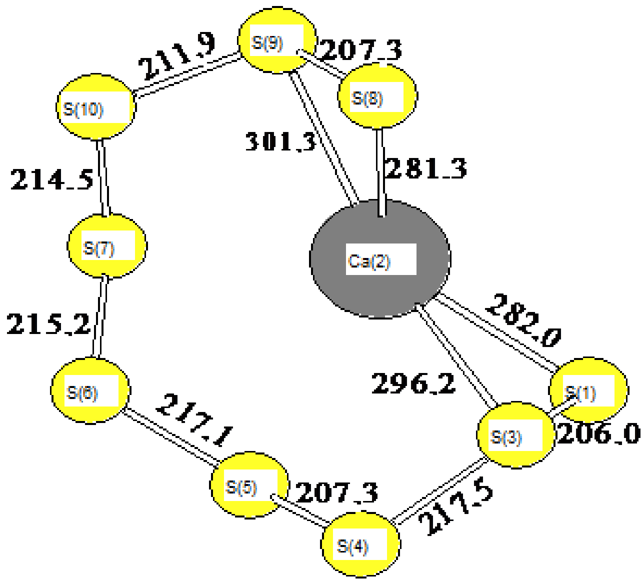

Fig. 6. CaS_9 geometry.

Then, as the quantum chemical calculations show, the presence of calcium sulfide conduces to weakening of the bonds in the sulfur cycles, opening of a sulfur ring and formation of calcium polysulfides with strong valence bonds. These factors govern production of durable and chemically stable material. Clearly, from thermodynamic point of view CaS_7 is the most stable structure (Fig. 5).

The properties of sulfur composites are much influenced by the filler geometry: first of all, it is powder fineness. Fine fillers are suitable enough to fill the interfacial space between the sulfur binder particles. According to the studies, as the filler fineness increases the ultimate strength of the material improves. The reason for that is higher reactivity of the ground silicon containing filler where the particles have higher surface activity after grinding as a result of partial breaking of bonds Si–O–Si in the crystal lattice.

The effect of filler loading capacity and fineness cannot be considered in isolation. In fact, this is about the area of common interface, more specifically, contact between the filler – binder phases per a unit binder volume.

The microscopy analysis of the sample showed that the smaller sulfur crystals were responsible for not only higher strength of the sulfur binder, optimum film thickness around the filler, but strong adhesive bonds between sulfur and filler surface (Si–O–S). Much higher strength of the sample with sand (binder-filler ratio is 40–60 % wt.) can be explained by the formation of more compact structure where the fine filler particles (fraction of less than 0.5 mm) fill the intergranular aggregate space in the sample evenly and provide additional intermolecular bonds in the binder-filler phase boundary. A higher sand ratio in the filler (more than 20%) makes the composite density decrease by 0.3 g/cm^3, which is likely due to the lower intensity of the bond between binder and filler [11-14].

As one of the disadvantages of sulfur and sulfur materials is its propensity to burn the resulting samples were tested for burning behavior. The studies showed that the samples of sulfur concrete based on sulfur and sand-and-gravel material were burnable. When the waste from $BaCl_2$ production in Mendeleyevsk Chemical Plant is added to sulfur concrete it significantly reduces burnability of sulfur composite materials based on industrial waste, which are self-extinguishing. Flame chilling time is 5-6 seconds.

X-ray transmissivity of the samples with the waste from $BaCl_2$ production in Mendeleyevsk Chemical Plant was analyzed according to the known procedure. This analysis showed that the presence of barium sulfate in the waste (13% wt.) decreased X-ray transmissivity of the samples two times.

Conclusions

1. The technology for synthesis of calcium sulfides and sulfur composite materials on their basis using silicon containing waste from barium chloride production was developed; the compositions and operating practices were improved.
2. The quantum chemical studies confirmed that calcium sulfide has an activating effect on sulfur melt. It manifests itself in lower rupture energy of sulfur rings, formation of reactive sulfur radicals, interaction between the latter and calcium sulfide, and formation of polysulfides.
3. The physical chemical studies established the chemical interaction between sulfur and silicon containing waste with the formation of sulfides, which dictates the formation of compact uniform structure and high physical mechanical properties of sulfur composite materials made from them.
4. It was established that addition of $BaCl_2$ production waste to sulfur composite materials decreased the composite burnability significantly.
5. The presence of barium sulfate in the waste (13% wt.) decreases X-ray transmissivity of the sulfur composite samples two times.

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Environmental and Technical Possibilities of Marble Waste Recycling in Bricks and Sorbents Production

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Keywords: waste recycling, marble waste, facing ceramic brick, volumetric colouring.

Abstract. The article considers the environmental, technological, and economic problems of recycling at application fine marble waste in the production of facing ceramic bricks by the volumetric coloring method. The environmental and economic feasibility of using fine marble waste is proved. Also the problem of obtaining ceramic sorbents is raised.

Introduction

Facing ceramic bricks are used in cities of Russia, Europe, Asia and America not one century. They create a unique architectural appearance of many buildings due to various colours and shapes [1-3]. Ceramic sorbents are used for water purification.

Relevance

According to the authors [4-6], ecological effect of interaction of buildings and materials with the environment can be assessed by independent methods. The method of analysis of human and environmental loads allows to place products in order of ecological series and to classify for environmental quality. System analysis calculates the ecological balance of influences of the material and products, sorbents on the environment. It assesses the consequences of this influence. Other methods are also used.

Currently, environmental assessment of building materials and products is carried out most often through life cycles [4-10]. It includes [5]:

- raw material extraction, elaboration of composition of the material and products, definition of the life cycle, including maintenance, repairs, the durability of the products, the ultimate recycling;
- assessment of impacts during the life cycle;
- optimization of composition and technology of production, increasing the quality of material and products, sorbents;
- environmental classification and cataloguing of material and products, sorbents.

The elaboration of the foundations of such an integrated analysis is the actual task from the point of view of ecology, technology and economy of construction, production of building materials and products, sorbents.

Problem Statement

The aim of this article is to consider the environmental and technical problems of recycling of fine marble waste in the production of facing ceramic bricks by the method of volumetric colouring.

The main raw material for the manufacture of ceramic bricks is fusible clay. After firing the colour of the brick turns into red [1-3, 5, 11-19]. Also mineral wastes are applied [3, 5, 9, 11-20]. It is possible to produce ceramic bricks of different colours by several ways:

- by the method of volumetric colouring;
- by the method of surface colouring.

In the first case, different ferrous pigments are entered in to the raw mixture. After firing bricks become the required colour throughout of their volumes.

At the method of surface colouring dried adobes are covered by angobe in the thickness 1-2 mm. Angobes are the colored clay. They have mat lustre after firing [1, 2].

The method of volumetric colouring is the most expensive way of producing facing ceramic bricks. This is due to the large consumption of ferrous pigments. However, these bricks have a uniform colour throughout the volumes [1, 2, 3, 5, 13-15].

To obtain ceramic bricks of dark brown colour it is necessary to enter the ferrous pigment - manganese oxide (MnO_2) in the composition of the blend. In the manufacture of facing bricks the number of ferrous pigments can be from 2 to 15% by weight of clay rock.

Theoretical Part

In the researches to obtain bricks of the same colour at the roasting temperature 950° C it was found that it is necessary to add 3.5% ferrous pigment MnO2 or 22.5% fine marble waste from the mass of clay rock into composition of blend. Microstructure of firing ceramic bricks with 22.5% fine marble wastes is presented in Fig. 1.

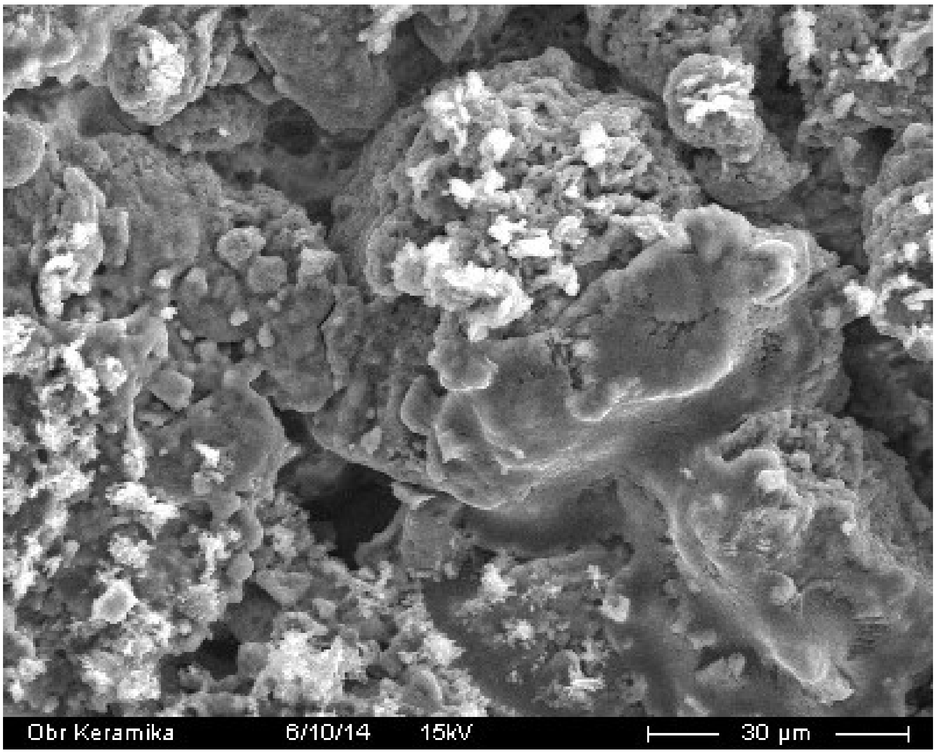

Fig. 1. Microstructure of firing ceramic bricks with 22.5% fine marble wastes.

Production of ferrous pigments has a high cost, requires a lot of energy. It exerts an adverse effect on the environment. Fine marble wastes are obtained when processing marble rocks. They do not require energy for their production and their cost is minimal. Application of fine marble waste is environmentally and economically beneficial [5].

The danger degree of ferrous pigments belongs to class 4 and fine marble waste - to danger class 3 [5].

The Results of Experimental Researches

In Table 1 the consumptions of components of the raw mix for the production of 1000 pieces of ceramic bricks by the method of volumetric colouring using MnO_2 and waste marble- $CaCO_3$ present.

Table 1. Consumptions of components of the raw mix on 1000 ps. of bricks, [kg].

№	The number of components of the mixture	
1	Clay rock	Ferrous pigment - MnO_2
	2556	92
2	Clay rock	Waste of marble - $CaCO_3$
	2649	596

In Russia, the average price per ferrous pigment MnO_2 is equal to 120 rubles per 1 kg. A ton of fine marble waste costs an average 630 rubles. The results are shown in Table 2.

Table 2. The cost of raw material components on 1000 ps. of bricks.

Component	Number of component, [kg]	Cost of 1 kg, [rub]	Total, [rub]
Pigment MnO_2	92	120	11040
Marble waste $CaCO_3$	596	0.63	375.48

From table 2 it is visible that the cost of the components of the mixture at 1000 pieces of facing bricks with a ferrous pigment compared to the cost of a mixture with marble waste is higher more than in 20 times.

For the production of ceramic sorbents for water purification the granules from adobes are formed and then their firing is done at a temperature of 700^{o} C.

Conclusions

Thus, it was determined the reduction of the cost of bricks due to introduction fine marble waste into the blend. Such wastes exert a positive impact on intensification of the process of drying and firing of adobes, which improves production efficiency. When using fine marble wastes their disposal occurs. At the same time, it is possible to obtain environmentally safe building material of danger class 4. The energy cost of production is considerably reduced. Also the area of dumps and environmental load in the territories of extraction and processing of marble are reduced. When replacing ferrous pigments on fine marble wastes the cost of bricks is significantly decreased. It is possible to produce a facing ceramic bricks of different colours - from dark brown to light yellow.

For the purification of industrial waters, it is possible to obtain ceramic sorbents in the form of granules with a large porosity.

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Improvement of Environmental Safety due to Utilization of Industrial Wastes in Refractory Concretes Production

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Abstract. The article suggests recycling aluminium and pipe industry wastes in the production of refractory materials. New compositions of light fibrous concrete are developed, compared to the known structures they have improved physical and mechanical properties and a low cost. This is achieved due to the lack of heat treatment and utilization of industrial waste. Aluminous slag and sulphate sludge are stored in open landfills. Recycling of slag and sludge helps to improve the ecological state of environment. This article describes the chemical composition of the waste and suggests the optimal ratio of the mixture components. The properties of refractory fibrous concretes were defined at hardening of mixture in the natural conditions in the absence of heat treatment.

Introduction

In the manufacture of aluminum products waste is generated - aluminous slag. They are stored in open landfills. At the manufacture of steel pipes texnogenic waste formed in the form of sulphate sludge. This sludge is disposed in dumps. This causes environmental damage in the region. During the construction of oil wells large quantities of drilling sludge produce. Such dumps are in the amounts in millions of tones. Drilling sludge and particulate waste of thermal units have a negative impact on the environment [1-8].

Relevance

Recycling of sludge waste is an actual scientific problem. Industrial slag and sludge have a high melting point, so they can be used in the production of refractory concretes [9-13]. As is known, high temperatures lead to a reduction of strength, crack resistance and durability of concrete of thermal structures. So far, the selection of compositions of refractory concretes was carried out based on the residual compressive strength of concrete. It should be not less than 30 % after its heating at temperature 800°C. In this case, the concretes with the same compressive strength can have varying bending strength. Crack resistance and durability will also be different. It should be considered when choosing the type and composition of the concrete.

Problem Statement

In the manufacture of lightweight refractory concretes the ratio between strength and average density while maintaining high refractory properties is important.

With a view to increase the indicators of compressive strength and bending strength the composition of light refractory concrete was developed [9] which does not require thermal processing. The comparison with concretes used in thermal plants was carried out. The new composition of the concrete has high refractory property, low average density and high bending strength. Porous structure of concrete is solid partitions between pores. They are formed by the interaction of aluminous slag and sulphate sludge with orthophosphoric acid and aluminium powder. Sulphate sludge is formed during etching of steel pipes with sulfuric acid, with subsequent liming. Chemical composition of sludge includes: Fe_2O_3 – (10-15) %; MgO – (3-5) %; SiO_2 – (7.0-

7.3) %; $CaSO_4$ – (25-30) %; Cr_2O_3 – 1 %; CaF_2 – (25-30) % etc. Content in the sludge of oxides Si, Cr, Mg и Fe is a positive factor for use in refractory mixtures. In the system with H_3PO_4 these components give high strength and heat-resistant properties. Calcium sulphate (till 30 %) from sludge interacts with orthophosphoric acid with the formation of sulfuric acid H_2SO_4. Sulfuric acid interacts in concrete mixed with aluminum powder. As a result, combinations are formed - $Al_2(SO_4)_3$, $Al(OH)_3$, and also - $Al(H_2PO_4)_3$. They provide quick strength generation of system. Reduction of average density produced products occurs due to release of hydrogen and use of expanded vermiculite sand (fractions 0...5 мм). Vermiculite sand has a low average density and high heat resistant properties.

Theoretical Part

Known raw material mixture for the production of lightweight refractory concrete [9] has the following composition (mass, %): aluminium powder 3-4; orthophosphoric acid 60 % of concentration 22-25; aluminous slag 40-42; sulphate sludge 12-14; vermiculite 15-23. The disadvantage of this composition is a low compressive and bending strength.

There is also a raw mixture for the production of lightweight refractory fibrous concrete [10]. It includes aluminium powder, orthophosphoric acid with concentration 60 %, aluminous slag, sulphate sludge, vermiculite, as well as the fiber wire «Xromel T» [10].

Alloy wires NX 9,5 «Xromel T» use for the manufacture of thermocouples. It consists of 8-10 % of chromium and 90-92 % of nickel, has great tensile strength (till 500 MPa) and high refractory properties. This mixture can be used only at the temperature 800 ^{0}C. It has a low compressive strength and tensile, and fiber from the wire « Xromel T » increases the cost of mix.

The purpose of researches in the article was to reduce the average density, increasing the compressive strength and tensile of refractory concrete. This can be obtained by increasing the resistance to compression and tensile stresses and temperatures up to 1100° C while maintaining the curing time of mixture.

The raw material mixture for the production of lightweight refractory gas fibrous concrete with operating temperature up to 1100° C was developed. The mixture includes, mass, %: aluminium powder: 3-4; orthophosphoric acid: 24-26; aluminous slag: 32.5-34.5; sulphate sludge: 13-15; vermiculite fractions: 0-5 мм 20.3-27.4; basalt fiber with diameter of 12-14 mkm, length 6-10 mm: 0.1-0.2.

The offered lightweight refractory fibre concrete is operated at temperatures up to 1100° C and corresponds to I-11 class on the maximum temperature limit of application according to GOST 20910 "Heat-resistant concretes. Technical conditions". The obtained values of compressive strength and tensile strength were determined after heating at a temperature of 1100° C.

To increase the resistance to compression and stretching the basalt fiber with diameter 12-14 μm and length 6-10 mm was injected into the raw material mixture [14-22]. Basalt fiber at temperatures over 800° C will not deform and lightweight concrete is not destroyed. This affects on the increase in strength while maintaining curing time. Basalt fiber produces from basalt [18]. It increases the resistance to mechanical stress during tensile strength up to 2000 MPa. This blocks the development of cracks in light concrete. In addition, basalt fiber has a high refractoriness, low bulk density (no more 35 kg/m^3) and low cost.

Decrease in density and increasing the strength of the received goods in comparison with known structures [9-13] are provided by the increasing amount of vermiculite. More durable and not expensive basalt fibers are used instead of expensive metal fibers.

Thus, the introduction into the raw mix of the light and high-strength basalt fibers, as well as increasing flow of vermiculite provide getting the fast hardening mixture. Concrete from this mixture has the higher durability while reducing density with persistent high fire resistance and curing time. New material withstands the temperatures up to 1100° C, the harden for 30 minutes, has small density. Concrete retains high levels of durability and fire resistance after heating. This is due to the complex influence of aluminum powder, phosphoric acid, alumina slag, sulphate sludge, vermiculite and basalt fiber.