High-technology energy-efficient composite material made from waste of thermal power plants

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Abstract. Polysulfide composite materials made from high tonnage waste of oil and gas and thermal power sectors were developed and studied. The composition of these materials was optimized. It was shown that the components interacted with each other, and a compact homogeneous structure was formed when pyrite was added.

1. Introduction Today’s machine building industry is a complex industry that involves production of various machines, tools, instruments, as well as consumer items and defense products. A wide range of aggressive environments is used in advanced processes in machine building plants. All these factors lead to accelerated mechanical, physical chemical failure, including corrosion, which results in a lower load capacity of individual structures (foundations for acid pumps, some floor sectors, etc.) and building as a whole. However, there is a high quantity of composite sulfur materials that have a number of advantages: high chemical inertness in aggressive environments with operating parameters, high mechanical performance, low cost, and accessibility to materials \([1-3]\).

2. Body text The paper studies polysulfide composite materials made from high tonnage waste of oil and gas and thermal power sectors. Volumes of ash and slag waste are among the highest. They are generated with combustion of solid fuels (various types of coal, oil shale, peat) in thermal power stations. Enormous amounts of ash and slag waste are accumulated in dumping grounds, they take up valuable lands and are expensive to maintain. Meanwhile, ash and slag from thermal power plants can be effectively used to manufacture various building materials, which has been confirmed by many scientific studies and practical experience \([4]\).

Sulfur from gas and oil processing sector is among high tonnage waste. In Russia, a significant amount of by-product sulfur is accumulated in the dumping grounds of Astrakhan gas processing plant. In Tatarstan, Minnibaevsky gas processing plant generates more than 300 tons of sulfur waste annually, and Nizhnekamsk gas processing plant - more than 30 k tons of sulfur. Developing sulfur composite material technologies is relevant today as these materials have a number of assets: strength, abrasion resistance, water resistance, acid resistance, etc. \([5-8]\). A proportion of low-cost by-product sulfur is increasing so production of materials with it is economically feasible.
For the purpose of the paper, the following materials were used: sulfur waste from the Nizhnekamsk oil refinery, with 99.9% of sulfur; pyrite FeS$_2$ (iron sulfide); masonry sand (GOST 8736-93); ash and slag waste from KAZAN thermal power plant (TETs-2) with the following composition (% wt.): SiO$_2$ − 47.7-52.2; Al$_2$O$_3$+TiO$_2$ − 21.24-25.28; CaO+ MgO − 4.3; Fe$_2$O$_3$ − 5.2-5.9; R$_2$O − 1.84-19.03; SO$_3$ − 0.2.

For more detailed study, the ash and slag waste was separated into ash and slag constituents by screening. For the purpose of the paper, ash constituents with a particle size of less than 1 mm were used. The samples of sulfur composite materials were made by hot mixing of initial components with different holding time (from 10 minutes to 4 hours). Then these mixtures were formed to make the samples. Physical mechanical properties of the resulting materials were tested, and the materials were studied using the methods of physical-chemical analysis. In terms of the material strength properties, the sulfur-ash and slag waste ratio of 1:1.5 is most suitable.

It is commonly known that crystalline sulfur materials have insufficient strength, impact resistance, etc. due to its shrinking deformation tendency. It can be assumed that modification of a sulfur component with metal containing compounds will encourage the formation of a compact homogeneous structure in composite material and, therefore, improvement of physical mechanical characteristics as a result of formation of sulfur (polysulfide) substances, elimination of irregularities of component densities, improvement of adhesion characteristics.

Sulfur (polysulfide) substances with metal-containing compounds (such as iron sulfide (pyrite)) are interesting from a point of view of scientific studies and practical application. Each atom of iron in a pyrite group is located at the center of octahedron made of six atoms of sulfur, and sulfur coordination is tetrahedral. The length of S-S bond is 217 pm. Pyrite is an electron donor, i.e. using it as a modifier makes it possible to get polysulfur and, therefore, to increase mechanical and impact product strength due to the formation of new bonds.

It is known that normally inert sulfur becomes reactive with nucleophilic and electrophilic reagents. As pyrite, iron polysulfide, is a compound with disulfide bonds, it can act as a nucleophilic reagent. Using pyrite as a nucleophilic additive makes it possible to increase reactivity of sulfur, and it can interact with filler components and additive, i.e. it will encourage the increase in strength of the samples.

In order to investigate the mechanism of interaction between components in a system and assess the influence of iron sulfide on activation of sulfur ring opening, quantum chemical calculations were performed for sulfur-iron sulfide system (with density functional method using Priroda software, with 3z.bas basis, including p- и d-orbitals in atoms). As there is hexatomic sulfur in the melt at a temperature of 180 °C the calculations were performed for ring hexatomic sulfur, its geometry is shown in Figure 1.
It was established that addition of pyrite to sulfur molecule led to a decrease in bond energy in sulfur ring by 62.6 kJ/mol. Sulfur-sulfur bond becomes loose and lengthens from 210.5 pm to 219.6 pm (Figure 2). The reaction is exothermic ($\Delta H = -237.4$ kJ/mol) with the formation of a strong covalent bond. The energy of iron-sulfur bond is 237.76 kJ/mol, the length of the bond is 216.6 pm. In this case, when iron interacts with sulfur it changes from two-coordinate state to three-coordinate one. It can be assumed that iron polysulfides with various degrees of condensation, probably, of cross-linked structure, are formed. They will encourage the formation of a compact homogeneous material with high physical chemical and performance properties. Therefore, the quantum chemical calculations showed that pyrite would encourage the loosening of bonds in sulfur rings, opening of sulfur rings, and formation of iron polysulfides with strong covalent bonds. These factors ensure that a material is strong and chemically stable.

Mechanical and performance properties of the resulting samples were tested: compressive strength (37-40 MPa), water absorption (maximum 1 percent), density (2.57-2.70 g/cm$^3$), resistance to aggressive environments (0.85-0.97).

3. Conclusions

Therefore, sulfur composite materials were made from petrochemical by-products using metal containing modifier (pyrite with high strength properties). These materials can be used as road building materials (paving stones, blocks) to equip areas subjected to aggressive environments in premises or inner facilities in machine building plants.

References

[1] Korolev E V, Proshin A P, Erofeev V T, Khrulev V M 2003 Building sulfur materials Penza PGUAS Publ. p 372
[2] Akhmetova R T, Yusupova A A, Baraeva L R, Sabakhova G I, Pervushina V A, Khatsrinov A I, Medvedeva G A and Akhmetova A Yu Binder RF patent No 2015 2555166
[3] Proshin A P, Korolev E V and Kalinkin E G 2005 Structure and properties of modified sulfur binder Stroitelnye Materialy vol 7 pp 6-9
[4] Karnaukhov Yu P, Sharova V V and Podvolskaya E N 1998 Binders based on nonutilizable ash and slag mixture and liquid silica glass Stroitelnye Materialy vol 5 pp 12-13
[5] Paturoev V V 1987 Polymer concretes (Moscow: Stroyizdat Publ.) p 286
[6] Yusupova A A, Khatsrinov A I and Akhmetova R T 2018 Activating effect of aluminum chloride in the preparation of sulfur concrete from sulfur and silica Inorganic Materials vol 54 Issue 8 pp 809–14
[7] Akhmetova R T and Gerasimov V V 2002 Sulfur composite materials for thermal power sector Izvestya VUZov. Problemy energetiki vol 1-2 pp 41-3
[8] Fedyaev V L, Galimov E R, Galimova N Ya, Gimranov I R and Siraev A R 2017 Dynamics of coalescence and spreading of liquid polymeric particles during coating formation IOP Conf. Series: Journal of Physics: Conf. Series vol 789 number 012006