Concrete based on sulfur binder being modified with inorganic additives

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Abstract. The sharply continental climate of the Irkutsk region is characterized by wide temperature intervals throughout the year. The repeated cyclicity of freezing and thawing of building materials in the water-saturated state influences the change in technical characteristics and the durability of concrete products and structures. The concrete products’ features in such climatic conditions create the need for the production of concretes with improved indicators of physical and mechanical properties. The effect of modifying additives on the technological characteristics of sulfur concrete is established. The effect of all elements of sulfur concrete on its strength and frost resistance. The composition of sulfuric concrete is obtained, which meets all the requirements and also has high strength and increased frost resistance. Formulations with a certain ratio of structural sulfuric concrete mixtures were developed. As a result of the use of technical sulfur in the composition of concrete products, the problem of utilizing annually accumulating reserves of technical sulfur is partially solved. The strength properties of sulfuric concretes easily compete with high-quality brands of concrete, special types of concretes that have in their composition additives.

1 Introduction

At present, the need to use concrete with increased strength indexes, resistance to aggressive media, and increased frost resistance has increased. The use of concrete with improved performance can solve several important problems:
- Ensuring the region’s construction market with high-strength products;
- Reducing costs of materials, structures, and products;
- Reducing building construction costs due to the durability of the structures;
- Reducing logistics costs due to existing waste of oil and gas industry in the region;
- Reducing a negative environmental impact through the utilization of industrial sulfur.

The sharply continental climate of the Irkutsk region is characterized by a wide temperature interval throughout the year. The repeated cyclicity of freezing and thawing of building materials in the water-saturated state influences the change in technical characteristics and reduces the durability of concrete products and structures. This forces each year to allocate financial resources for the repair of transport, industrial, and civil
construction objects. Applied methods of protection against premature destruction are ineffective.

Features of concrete products in such climatic conditions create the need for producing concretes with improved indicators of physical and mechanical properties.

Analysis of Russian and foreign literary sources shows that sulfur building materials are widely used in various areas of construction. Such materials are especially promising in the manufacture of structural parts and structures, during which the increased requirements for resistance to various aggressive environments, frost and atmospheric resistance, and water impermeability are required. The high quality of the products, the simplicity of the manufacturing process, and the low cost of consumable materials allow the sulfur building materials to be competitive with the building materials on cement binders [1-4].

Sulfur building materials are obtained by combining a melt of sulfur, fillers, aggregates, and modifying additives. As components, all known types of fillers can be used, which are used for the production of building materials based on cement. As modifying additives, both organic and inorganic substances can be used. Its physico-mechanical and operational properties depend on the content and properties of the components of sulfuric materials [5-8].

Studies have shown that sulfur building materials are characterized by relatively high strength, resistance to various aggressive environments, impermeability, frost resistance. In the shortest time, sulfuric concretes gain the given strength in comparison with concrete on cement binders (Fig. 1). In connection with this, the actual task today is the creation of high-density sulfur composites that can be used in any aggressive environment and retain their properties for a long time. Therefore, the main task of development is the selection of the composition of sulfur concrete, which retains technical characteristics during the entire period of its operation [9, 10].

![Fig. 1. Compression strength increase graph: 1 – heavy concrete on Portland cement of normal hardening in air-dry conditions; 2 – the same, 28 days hardening in wet conditions; 3 – the same, thermal treatment and subsequent hardening in air-dry conditions; 4 – sulfur concrete.]

2 Theory

One of the main criteria of the product, which further defines the field of application, is its strength. The strength of concrete based on sulfur binder depends on the strength of its components. Depending on the strength of its constituents, there are several types of destruction of products:
for the solution part: the aggregate strength is greater than the strength of the solution part;
for aggregate grains: the mortar strength is greater than the strength of the filler;
the equiprobable is reached both in aggregate grains and in the solution part.

The first and the third type of damage is typical for sulfur concrete using dense high-strength aggregates, and the second is for light gray concrete, obtained using porous aggregates [11-13].

Studies show that the strength of concretes based on sulfur binder depends on several factors, including the quantitative content of all the constituents in concrete. To produce sulfur concrete with high strength indicators, the required amount of sulfur in the product ranges from 10 to 15% by weight. As the sulfur increases above the optimum, the strength of the product would decrease. When a load is applied, sulfur, which has low strength and low modulus of elasticity, changes and transfers the external load to the filler and aggregate, with a higher modulus of elasticity and strength, which increases the strength of the product. Consequently, when using sulfur in the optimum amount, an increase in strength is inherent. But with an increase in the optimal amount of sulfur, the amount of deformation of the structure increases, and so does strength. Fraction of inert aggregate also affects the strength of the product of gray concrete in general [14, 15].

In addition to the above factors, the strength of sulfur-concrete products is affected by the content and small fractions of the aggregate, the process of preparation, molding, etc.

Strength of products made of sulfuric concrete can be improved by accurately following the process of their manufacture. Studies have established that the optimal conditions after the formation of a concrete mixture are a cooling rate of 10-15°C per hour, up to a temperature of 96°C over the entire product’s surface. Further cooling can continue in natural conditions. Gradual cooling promotes redistribution of internal stresses, reduction of cracking. It was found that the strength of sulfur concrete increases by 13-28% under these conditions [16, 17].

In the manufacture of products from sulfur composite of large sizes within the construction, shrinkage cracks can form, because of the uneven cooling, in the body of concrete, and under the influence of different temperatures.

On the basis of the foregoing, it follows that in order to obtain high strength concrete based on sulfur binder, it is necessary to follow the process clearly, as well as take into account all the properties and characteristics of the materials used.

The results of various studies on the frost resistance of sulfuric concrete vary. For example, according to some studies, it is found that sulfuric materials, due to their hydrophobicity, are frost-resistant, and, depending on the type of filler and aggregate, the frost resistance grade reaches 500 cycles. Such a high frost-resistance is due to the presence of closed pores in the body of the product, water penetration is difficult due to hydrophobicity of sulfur. Consequently, when being exposed to negative temperatures, namely the amount of pressure exerted by freezing water on concrete products with a sulfur binder, their influence would be minimal. Therefore, with cyclical sequential freezing and thawing, the structure of concrete undergoes minimal exposure to freezing water, which means that such materials are considered to be frost-resistant.

3 Research results

Selecting the composition for the manufacture of sulfur composites, as well as for traditional concrete, is carried out in determining the most optimal content of all constituents in the mixture in order to achieve the specified technological requirements, the mixture layability, as well as all physical and mechanical characteristics.
Selecting the composition was developed experimentally with an analysis of the indices of the samples obtained, which makes it possible to determine the dependences of the obtained physicomechanical characteristics.

Samples of sulfur composites were prepared according to the following technology: a previously dried and suspended mixture of aggregates of crushed stone and sand, mixed and heated at a temperature of 150-160 °C. Then sulfur was mixed with a modifying additive. Further, a mixture of sulfur with a modifying agent was introduced into the heated mixture of aggregate. It was held for 45-60 minutes at 135-140°C. Each 10-15 minutes, the mixture was stirred to make it homogeneous. Compositions of sulfur composites were selected taking into account the porosity of the mineral part of the composition, the workability and mobility of the mixture, if necessary taking into account the vibration compaction. The movement of the concrete mixture was no more than 15 cm. The hot sulfur-concrete mixture was molded in preheated shapes of 100x100x100 mm, followed by a bayonet filling to 50% of the total volume of the mold. After the end of molding, the molds were subjected to vibration-compacting for 10-15 seconds on the vibrating plate. The stripping of the samples was carried out after one day to further determine the samples’ strength. Table 1 shows the recommended composition of the structural sulfuric concrete.

Table 1. Recommended composition of the structural sulfuric concrete.

| Components     | Mass, % |
|----------------|---------|
| Sulfur technical | 16      |
| Crushed stone   | 55      |
| Sand            | 27      |
| Modifier        | 2       |

The selected sulfur binder composition and its quantity in sulfuric concrete (16%) provides high strength concrete to sulfur concrete (up to 43 MPa), sufficient motion (cone sediment more than 15 cm). Concrete with such strength corresponds to the B35 and M450 class.

Frost resistance of building composites is one of the main indicators characterizing the ability of a material in a water-saturated state to resist alternating exposure to negative temperatures. In this paper, samples based on sulfur binder were used with a modifying additive.

As is known, the main reason for the destruction of concrete in the water-saturated state, subjected to cyclical action of negative temperatures, is the pressure exerted by the blasting water on the pores of concrete. The expansion of water is preceded by a solid skeleton of concrete, in which high internal stresses arise. These stresses in the area of contact between the filler grain and the matrix reach a maximum value and can lead to the formation of microcracks. Gradually, micro-crackles join together, forming more extensive cracks, which leads to a significant decrease in the strength of concrete and its destruction. From the above, we can conclude that the frost resistance of concrete, under all other equal conditions, depends on the structure of the material, the concentration and the physico-mechanical properties of the components.

For the tests, samples were made on the basis of a sulfur binder in the size of 100x100x100 mm. As the saturation medium, a 5% solution NaC1 is used [18].

As a result of the frost-resistance test, the standard method is based on the normative documentation [19], samples based on the sulfur binder correspond to the F400 frost resistance grade, and therefore have a very high resistance to cement in comparison with cement based on the same grade strength (Table 2).

Table 2. Comparison of the obtained characteristics of frost resistance with concrete on the basis of cement.

| Characteristics | Concrete based on cement | Concrete based on sulfur |
|-----------------|--------------------------|--------------------------|

4
Concrete grade for compressive strength (grade)

| Grade | Value |
|-------|-------|
| В 35  | М450  |

Frost resistance

| Resistance | Value |
|------------|-------|
| F200       | F400  |

4 Conclusion

The cost of sulfur concrete is now much lower than all known concrete with additives that improve their properties. This is due to the fact that the world market of sulfur in recent years (and also in the forecasted future until 2020-2025) will have a steady tendency to exceed the production of sulfur over its consumption. This is due to the production of associated sulfur, with the processing of ever-increasing volumes of sulfur-containing hydrocarbon feedstocks, deeper purification of sulfur products of oil refining, exhaust and flue gases of enterprises. As a result of using technical sulfur in the composition of concrete products, the problem of utilizing the annually accumulating reserves of industrial sulfur is to be gradually addressed [20].

Sulfuric concretes in relation to concrete based on cement binder with each year increase their competitiveness.

The use of sulfur concrete in various types of construction is promising, since they have the best physical and mechanical characteristics for construction on the territory of the Irkutsk region.

Sulfur concretes can be used in structures of buildings and structures, in the period of operation of which there are increased requirements for resistance to aggressive environments, frost, and weather resistance, water impermeability. The strength properties of sulfuric concretes easily compete with high-quality concrete classes, special types of concretes, which contain expensive organosilicon and epoxy additives.

Sulfur concretes can be used for engineering structures in the construction of highways in a wide range of environmental conditions, since they are resistant to stresses caused by temperature changes and do not form such potholes and cracks as on roads from asphalt concrete or cement-concrete.

Pipes made of sulfuric concrete are not exposed to bacteria, mold and fungi, and these microorganisms cannot reproduce on their surface. Such pipes are resistant to blockage, clogging, and deposition of salts on the inner surface, which is a common problem for the standard concrete, reinforced, or metal pipes [21].

Sulfuric concretes are cheaper than other pipe materials, such as cement, asbestos cement, reinforced concrete, or various metals. These materials are not only more expensive for manufacturing, installation and operation, but also do not provide all the advantages of sulfuric concretes.

Sulfuric concretes may not be suitable for transporting materials with temperatures above 120°C. However, for most applications that require low-cost, easy, easy-to-get and operate pipes, they are an ideal material.

The lower cost of materials, greater durability, and faster strength of the product make sulfuric concrete an ideal material for the construction of dams and other hydraulic structures.

Sea ports and related structures can also successfully use sulfuric concrete, because they are resistant to corrosion and salt water. Structural deterioration, which is a common problem for offshore structures from standard structural materials, does not take place in this case.

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