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# OBTAINING SULFUR CEMENT FROM WASTE HYDROCARBON RAW MATERIALS

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## ABSTRACT

The paper developed a technology for the production of sulfur cement from industrial sulfur waste. Fuel oil from the Atyrau oil refinery was used as a modifier. The filler is the local raw material, quartz sand of the West Kazakhstan region. It is shown that the resulting sulfur cement has improved performance properties: moisture resistance, chemical resistance, frost resistance, compressive strength, bending strength, and tensile strength. The use of technical sulfur waste allows for solving the problems of ecology and the construction industry.

**Keywords:** Sulfur, Cement, Strength, Frost Resistance, Water Permeability, Chemical Resistance.

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## INTRODUCTION

The accumulation of various types of wastes from human life and activities in the conditions of a rather complex today's environmental situation sets the requirement of finding new ways of their disposal.[1] The use of waste as secondary material resources allows for preventing environmental pollution to save basic raw materials.[2,3] Sulfur is one of the most common components of industrial waste generated during the processing of sulfurous oils, coking, copper smelting, and coal combustion.[4] In recent years, its reserves have been constantly increasing due to oil and gas production growth. A large amount of technical sulfur poses a serious environmental hazard to the environment. The excess sulfur formed as a by-product of oil and gas refining necessitates searching for new areas of its application.[5,6] Historically, the sulfur market has mainly depended on the demand for sulfuric acid and phosphate fertilizers as the main consumers of this product.[7] While there have been attempts to develop other large-scale sulfur markets in the past twenty years, these have been constrained by high sulfur prices during the 1980s.

The main areas of unconventional use of sulfur are:

- for solving the problems of radiation protection;
- in the production of building materials (sulfur cements and sulfur concrete) and road surfaces - sulfur asphalt[7]
- in the production of unconventional fertilizers (sulfur bentonite);
- for impregnation;
- for burying ash from waste processing enterprises.[8]

A significant improvement in the environmental situation can be facilitated by the use of sulfur obtained from waste in the production of building materials.[9] Sulfur is a good composite material and is used as a binder in building structures for various purposes, such as the production of sulfur cement.[10] The technology for the production of sulfur cement is obtaining copolymer sulfur (sulfur cement) using highly paraffinic fuel oil as a modifier.[11,12] The use of sulfur as a component of building materials is due to its properties, such as fast solidification, hydrophobicity, resistance to aggressive environments, and low thermal conductivity.[13–15] Sulfur-based building materials are distinguished by higher performance characteristics[16], such as mechanical strength, water resistance, frost resistance, resistance to aggressive environments, and service life.[17]

The use of sulfur as a binder in composite materials requires giving it a number of additional properties due to chemical modification.[18] This makes it possible to obtain a product with improved physical and mechanical characteristics, increased resistance to external factors, etc. In connection with the above, the goal of this work is to obtain sulfur cement using industrial sulfur waste.[19] In connection with the above, the goal of this work is to obtain sulfur cement using industrial sulfur waste.

## EXPERIMENTAL

Sulfur cement consists of a binder, a modifier, filler, and a fire retardant. For research, we took technical sulfur from the Atyrau Oil Refinery Factory (AORF), which is the main binding material. The characteristics of technical sulfur are given in Table-1.

Table-1: Characteristics of Technical Sulfur

| | |
|---|---|
| Purity, % | 99,99 |
| Color | bright yellow |
| The form | hemispherical tablets |
| Size, mm | 2-6 |
| Hydrogen sulfide content, ppm wt. Max | 10 |
| Acidity, ppm wt. Max | 40 |
| Organic/carbonaceous materials, ppm wt. Max | 1000 |

A heavy oil residue - fuel oil from the Atyrau oil refinery factory (AORF) - was used as a modifier. The use of the oil residue as a modifier is due to its chemical interaction with sulfur, which is expressed in its attachment to the ends of polymer sulfur, a saturation of its bonds, termination of the polymerization process, and stabilization in this state. The main role of the modifier is to stabilize the structure of sulfur and prevent the growth of its crystals. We have investigated the physical and chemical characteristics of fuel oil at the Atyrau refinery in accordance with Standard SanRaN 10585-2013. The data was given in Table-2.

Table-2: Research Results of physical and Chemical Attributes of Fuel Oil at Atyrau Refinery

| Indicator | Fuel AORF | Standard SanRaN 10585-2013 |
|---|---|---|
| Density, kg/m$^3$ | 980 | 980 |
| Viscosity (conditional), mm$^2$/s | 2,1 | 2,1 |
| Flashpoint, ºC | 158 | 158 |
| Pour point, ºC | 34 | 34 |
| The heat of combustion, ºC | 42099 | 42099 |
| Acidity, mg | 5 | 5 |

Cement and other binders can be mixed not only with chemically active substances (acidic hydraulic additives and blast furnace slags) but also with finely ground additives that are inert at normal temperatures, called fillers. Filler additives include quartz sand, limestone, dolomite, igneous rocks, natural pulverized quartz, clays, and a number of others. Fillers have a great influence on the ductility and water-holding capacity of the concrete mix. Heat generation and shrinkage deformations are reduced with the addition of filler. The addition of the filler accelerates the process of cement grains hydration. Filler grains are involved in the formation of the crystalline structure of the cement stone. On the surface of the filler grains, the gel-like phase becomes denser and crystallizes more intensively. In some cases, the filler has a modifying impact on the hydration products of cement grains, contributing to the development of individual crystalline forms of neoplasms. The introduction of filling additives, as well as hydraulic ones, reduces the consumption of electricity, fuel, and the cost of the final product. By correctly selecting the granulometric composition of the fillers, the density of the hardened cement and concrete can be increased. Based on this, in some cases, it is rational to add local cheap additives to high-grade cement, which are, for example, quartz sands and carbonate rocks. In our case, the filler is quartz sand from the West Kazakhstan region. The structural composition of quartz sand was studied using a scanning electron microscope. The experimental results are shown in Fig.-1 to 2 and in Table-3.

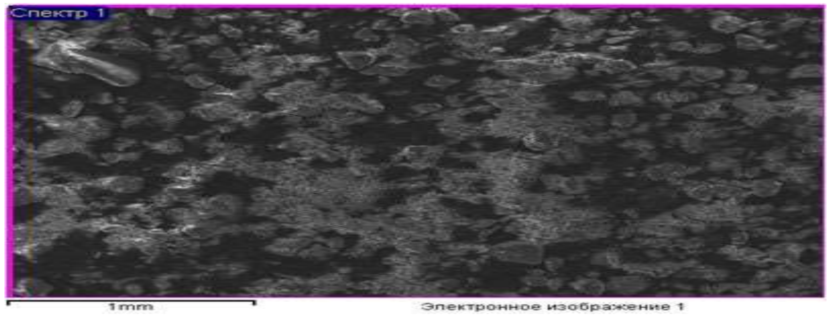

Fig.-1: Electronic Image of Quartz Sand of the West Kazakhstan Region

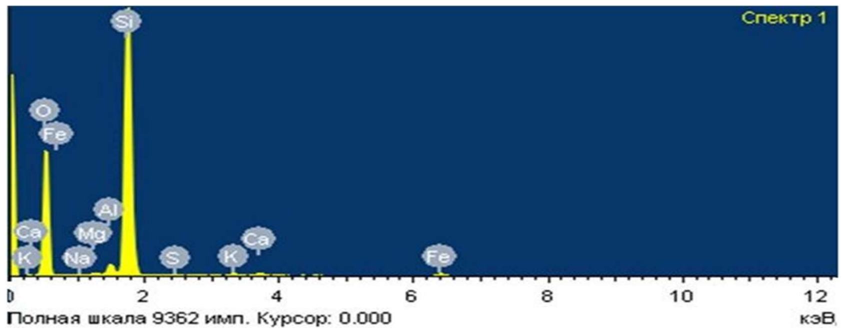

Fig.-2: Elemental Composition of Quartz Sand of the West Kazakhstan Region

Table-3: Elemental, Weight, and Atomic Compositions of Quartz Sand of the West Kazakhstan Region

| Element | Weight, % | Atomic, % |
|---|---|---|
| O | 54,80 | 68,56 |
| Na | 0,16 | 0,14 |
| Mg | 0,26 | 0,21 |
| Al | 1,52 | 1,13 |
| Si | 40,11 | 28,59 |
| S | 0,17 | 0,10 |
| K | 0,69 | 0,36 |
| Ca | 0,63 | 0,31 |
| Fe | 1,66 | 0,59 |
| Total | 100,00 | |

Also, research is currently underway to select a fire retardant that will remove the main and, perhaps, the only drawback of sulfur-containing binders - low fire resistance. Compositions that make it possible to identify the best fire retardant have already been created. Aluminum hydroxide, sodium tetraborate, ammonium sulfate, etc. are used as fire retardants. In this work, sodium tetraborate was used to increase the fire resistance of sulfur cement.

**Sulfur Cement Production Method**

In a 200 ml metal container, load no more than 2⁄3 of the volume of crushed industrial sulfur (the piece with a diameter of not more than 100 mm). The contents are evenly heated at a temperature of 140-150 ° C, preventing local overheating and sulfur ignition. At a temperature of 120 ° C, sulfur begins to melt. After its complete melting, fuel oil (preheated) is gradually introduced with continuous stirring using a magnetic stirrer. Sulfur with fuel oil is boiled until fully cooked (until the volatiles are completely removed). Quartz sand is added to the resulting mixture and thoroughly mixed with a mixer. Then sodium tetraborate (fire retardant) is injected. The resulting sulfur cement is poured into molds and left to cool.

## RESULTS AND DISCUSSION

Sulfur cement was obtained at various concentrations of the components. The most optimal composition of sulfur cement that meets the requirements of GOST is the following, % technical sulfur -50; fuel oil - 10; quartz sand - 40. The study of the exploitative characteristics of sulfur cement determines the purpose of the areas of their practical application. The main indicator of cement is strength, which determines its reliable operation in structures. The obtained sulfur cement can be considered as a special-purpose building material designed for operation under conditions of variable temperatures and in aggressive environments. The data are presented in Table-4.

Table-4: Exploitative Attributes of Sulfur Cement of Sulfur Cement

| Indicator | Unit measure ments | Test method | Indicator value in age 28 days | |
|---|---|---|---|---|
| | | | Concrete based on Portland cement PC 500 | Modified Sulfur Concrete |
| Compressive tensilestrength | MPA | Standard SanRaN 10180 | 59,8 | 64,5 |
| Flexural tensile strength | | | 7,3 | 11,8 |
| Frost resistance | cycle | Standard SanRaN 10060-2012 | F 200 | F 1000 |
| Water permeability | ati | | W 12 | W 20 |
| Chemical resistance (toacids) | % | | 23 | 84 |

As shown in Table-4, the properties of sulfur cement obtained on the basis of modified sulfur are higher in comparison with concrete based on Portland cement. The results of testing cement samples based on modified sulfur are characterized by high parameters in terms of frost resistance, water resistance, and chemical resistance in acidic environments. The obtained sulfur cement can be considered a special-purpose construction material intended for operation in conditions of variable temperatures and corrosive environments.

## CONCLUSION

The main purpose of the study is the modification of technical sulfur in order to obtain cement with improved properties. In the given study, the modifier is fuel oil, which mainly consists of unsaturated hydrocarbon compounds with reactive double bonds (arenes), boiling point 300-350$^0$C. Sulfur can react with both -CH=CH- and C=O bonds, which also makes it possible to form cross-linked polymers. Probably, the shape of the polymer fraction is determined by the number of cross-links between macromolecules. Crosslinking of macromolecules can occur due to the formation of polysulfide bridges, similar to the process of vulcanization of rubbers. Due to the instability of the S-S polysulfide bond, the bridges are gradually destroyed, and the proportion of rare cross-linked and linear polymers increases. The resulting polymers are a variety of sulfur compounds with a modifier (polysulfides), which are evenly distributed in the composition, forming a spatial network structure, which provides the strength advantages of the material. Thus, the conducted studies allowed us to conclude that the development of the technology for the production of sulfur cement will significantly reduce the extraction of natural resources and determine the ability to maximize the use of technological waste products, including sulfur-containing waste. The production of sulfur cement does not only solve technical and economic problems, but also environmental ones, and above all environmental protection.

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## CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

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All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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