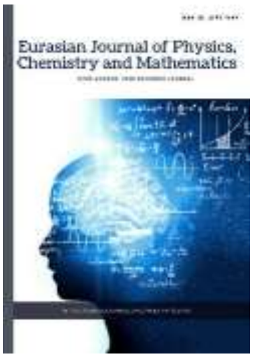

Technologies for Obtaining Modified Sulfur Concrete Based on Local Raw Materials

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ABSTRACT

In this article, the technology of obtaining modified sulfur and obtaining sulphurconcrete from the obtained product is studied.A variety of organic compounds have been used as elemental sulfur modifying additives, and almost all of them have been studied as polymeric polysulfides or, alternatively, olefinic hydrocarbons. As a result, sulfur can be used as an additive in construction materials such as concrete and asphalt. In this case, it was determined that the highest productivity and the degree of polymerization are higher than those obtained in a 1:1 mol ratio of the initial substances in the production of sulfur modification. Also, the effect of temperature on the modification was studied. The obtained results revealed their structure using IR spectra. Based on the research results, it was described that the obtained modified sulfur concrete gives strength and durability to sulfur concrete even in high concentrations of acids or salts with the help of unsaturated organic binders.

Keywords: modified sulfuric, sulphur, polymer modified sulfur, expanded clay, quartz sand, crushed stone and klinets.

Introduction

Sulfur is the tenth most abundant element on earth and has been considered a valuable chemical agent since ancient times. It has been used in medicine, fabric bleaching, lamp wicks, pistol powder, and more recently in the vulcanization of latex [1,2]. In developed industrial countries, highly reactive and toxic hydrogen sulfide (H_2S) diverges from oil refining residues. From crude oil gaseous mixture, elemental sulfur (S_8) is obtained with thermal expansion technologies [3]. With an annual production of approximately 70 million tons of by-product sulfur, oil refining by hydrodesulfurization is currently the largest source of sulfur production in the world [4]. A significant part of sulfur is used in the industrial production of sulfuric acid, rubber and fertilizers [5] in addition, modern synthetic chemistry has also benefited from the versatile chemical composition of elemental sulfur [6]. However, there is still a net surplus of sulfur that offers few economic applications, so finding large-scale applications of this sulfur, such as conversion to useful materials, would be an important advance [7].

Over the past few decades, numerous advances have been made in the synthesis of new types of sulfur-containing polymers and the modification of the properties of some important classes of polymers by adding sulfur or polysulfide fragments to polymer compositions [8, 9]. These new synthesis methods made it possible to obtain valuable polymeric materials and aroused great interest in this area, as evidenced by numerous studies of sulfur-containing polymers [10-14]. Recent research, both academic and applied, has focused on improving the properties and technological performance of these materials by introducing sulfur groups into the main chain to expand the technological application of these materials [15]. Historically, the term "polysulfide" referred to both the inorganic forms of sulfur-containing covalent solids of sulfur ($–S_n–$) chains. , ionic compounds (Sn_2-, n> 2), and to organosulfur compounds in which the sulfur chain ends with organic substituents. R ($R-S_n-R$). In accordance with this nomenclature, the name polysulfide was created to describe inorganic ionic compounds [16,17].

Phase transitions and the behavior of sulfur allotropes have been widely discussed in the following literatures [18,19]. The thermodynamically stable form of sulfur is orthorhombic sulfur, commonly referred to as α-S8, which is reported to convert to the monoclinic form β-S8 at 95°C and exhibit a predominant melt transition at 119°C [20]. With continued heating of molten sulfur to a temperature above 159 °C, homolysis of the S–S bond gives thiyl radicals, which attack and open the ring of another S_8 molecule [21]. The polymerization then propagates by reopening the ring and forming an S–S bond between S_8 and the growing polysulfide chain. Although high molar mass polymers are readily formed into polymers by S8, polymeric sulfur is chemically unstable at temperatures above the polymerization base temperature (Tf=159°C) because terminal sulfur radicals promote depolymerization back to cyclic monomeric sulfur [22].

2. Experimental part

2.1. *Modification of sulfur with gossypol resin or pyrolysis distillate and production of sulfur concrete*

Sulfur (200 g) was heated in a 500 ml reactor to 185°C in an oil bath with a thermostat with vigorous stirring until a viscous orange molten mass of sulfur was formed. Thereafter, 20 g of gossypol resin (or pyrolysis distillate) was directly added to the molten sulfur phase. The resulting mixture was mixed at 185–190°C for 60–70 min, which led to some decrease in the viscosity of this reaction medium. After completion of the process, the resulting modified polymeric sulfur was taken from the reactor and allowed to cool down to a temperature of 20–25°C. [23].

Polymer modified sulfur (PMS, sulfur binder) was prepared from elemental sulfur and pyrolysis distillate: mixed mixture, in a weighted ratio of 1:1. A certain amount of sulfur, placed in a cylindrical tube with an inner diameter of 2 cm, was straightened in a glycerol bath, heated to 1400 C and intensively stirred with a mechanical stirrer. At this temperature, the modifying agent (pyrolysis distillate) was added to the molten sulfur at about 2,4,6 or 8% by weight of sulfur. After completion of the addition of modifiers, the resulting PMS melt was stirred at a temperature of 150-1800C for another 20-30 minutes. The viscous mass was placed in a mold to improve adhesive properties, then held for an hour to form, and cooled to room temperature. [24].

2.2. Obtaining sulfur-polymer concrete and its composites from TPP waste

Sulfur polymer concrete (SPB, sulfur binder) was prepared from elemental sulfur and polymerization modifiers: pyrolysis distillate (PD) and gossypol resin (GS) in a ratio of 1:1. A certain amount of sulfur placed in a cylindrical tube with an inner diameter of 2 cm was melted in a glycerol bath, heated to 140 °C, and stirred vigorously with a mechanical stirrer. At this temperature, the modifying agent (PD) or (HS) was added to the molten sulfur at a rate of 5 ml/min per 1 μg 1 to final doses of approximately 2, 4, 6, or 8% by weight of sulfur. After completion of the addition of modifiers, the resulting SPB melt was stirred at a temperature of 135–140°C for another 20–30 min. The composite with waste was obtained by additional addition of ash and slag to the molten SPB in the form of a powder. The final content of ash and slag was 25 or 50% by weight of the composite, respectively. Continuous homogenization by mixing was carried out during the addition of waste and lasted approximately 10–20 min. SPB based on pyrolysis distillate with the addition of waste (at 135–140 °C), the formation of a gel-like (slightly rubber-like) consistency was observed. This prevented the uniform distribution of ash and slag over the entire volume of the prepared samples. They were then degassed by vibration on a vibrating table for about 5 minutes, after which the tubes were cooled to room temperature. The thus obtained monoliths of the hardened SPB and its composites in the form of cylindrical discs 2 cm in diameter and 4 cm high were used to evaluate their properties and the effectiveness of the obtained samples of sulfur concrete [25].

Determining water absorption capacity involved stepwise immersion of the cured monoliths in water at room temperature and monitoring water absorption (wet weight) and weight loss (dry weight) at regular intervals. In this method, the monoliths were placed in a container and filled with water to a quarter of their height. The samples were kept in this state for 2 h. Then the water level was raised to half the height of the sample. After another three hours the water level had risen to three-quarters of the height of the hardened specimens. The submerged samples were left for another 19 hours. Finally, the samples were completely immersed in water. The upper surface of the samples was located approximately 2 cm below the water level. Over time, every 24 h of immersion of the samples in water, they were removed from the container and weighed on an electronic balance with an accuracy of 0.01 g. The weighing was repeated until a constant wet weight of the sample was reached. Water absorption (WA) was calculated as the percentage increase in the mass of the monolith according to the formula. (1):

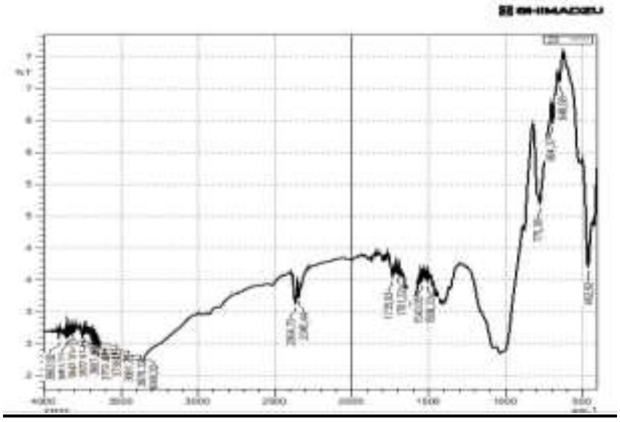
$$W_A = \frac{M_b - M_a}{M_a} \times 100\%$$

where: Ma is the mass of the dry monolith, Mb is the mass of the monolith with absorbed water.

The compressive strength of SPB and its monoliths with ash and slag was determined after 24 hours of their preparation. The cylindrical specimens used for this purpose (20 mm in diameter and 40 mm high) were much smaller than those required in the standard for such materials. This was due to the limited amount of galvanic waste available for testing. Compressive strength results for non-standard SPB monoliths based on the PD modifier and its waste composite show comparative value when compared with the results for similarly shaped monoliths based on the conventional DCPD sulfur polymerization modifier. The results obtained are the average of two measurements for the corresponding monolith.

Result and its discussion

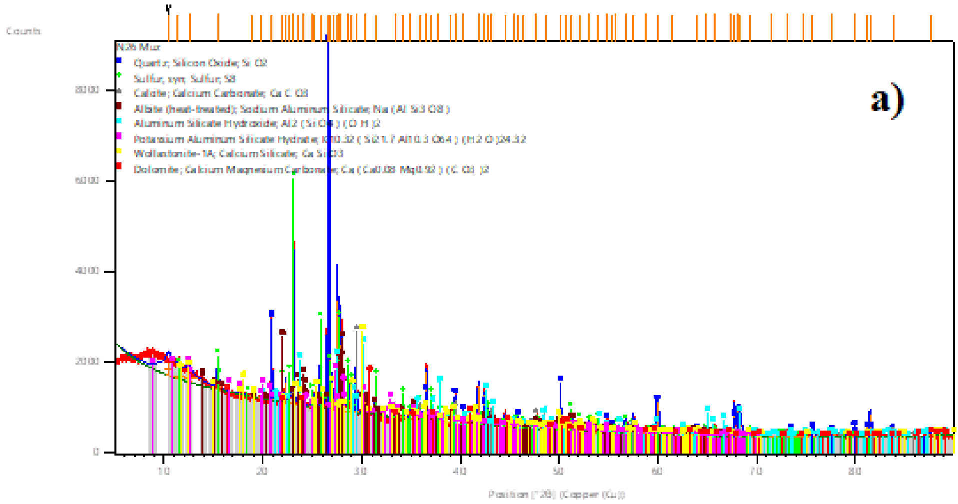
In the IR spectroscopic analysis, intense peaks appear in the region of 649-3753 cm^{-1}, related to the hydroxyl groups -OH of the gossypol resin, peaks are also observed in the region of 1701 and 1735 cm^{-1}, proving the carbonyl groups -CO- in naphthenic derivatives. The IR spectrum of a low-intensity absorption band in the region of 3676 cm^{-1} reflects the bound hydroxyl –OH groups. According to the IR spectroscopy data, one can assume a conclusion about a complex structure. Quaternary ammonium–NH_4 groups of some compounds of the sample are observed in the region of 2364-2345 cm^{-1}. The remaining functionally active groups correspond to the deformation vibrations of organic compounds; these peaks reflect new bonds of bound sulfur with functional groups contained in modifiers. In the region of 1508 - 1543 cm^{-1}, bound carbonyl groups –CH_2–CO– are observed. There is also a new peak at 1701 and 1735 cm^{-1} related to the cyclic compounds of the naphthal radical that exists in the modifier. Sulfur compounds with organic functional groups related to -S-O- and S-C groups. These compounds appear as a wide intense band at 1000, 1050 and 1100 cm^{-1}, these peaks are explained by the presence of new sulfur-containing compounds. Also associated sulfur compounds are observed in the region of 462.92 and 775.38 cm^{-1}, 1000-1050 cm^{-1} and 1100-900 cm^{-1}. In this regard, one can observe low-intensity peaks in the region of 1420 cm^{-1} and 648-674 cm^{-1}, these peaks also belong to new bonds of sulfur with organic compounds. The analysis of sulfur concrete differs from modified sulfur, in these there are completely new peaks in the region of 1400-1440 cm^{-1}, attributing dimeric compounds -CH_2-S- groups.

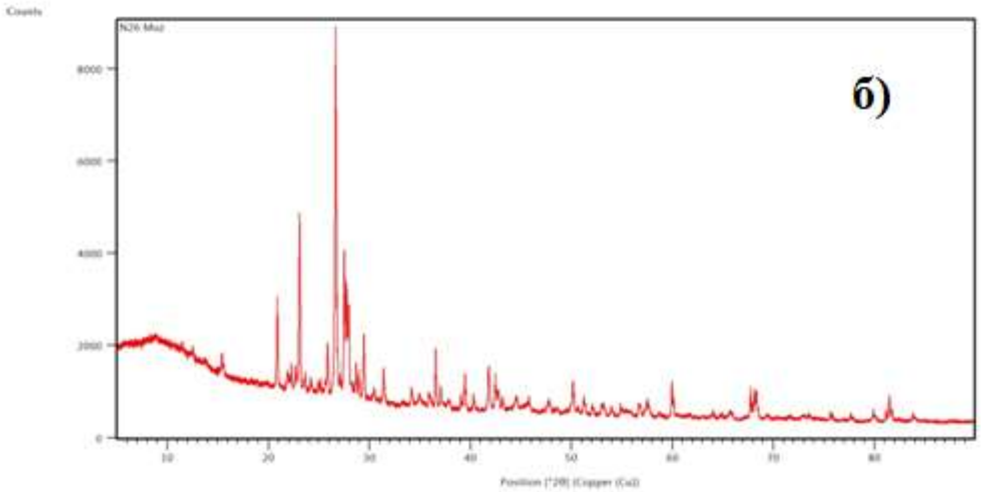


Picture.3.1. IR spectrum of modified sulfur concrete.

When studying the composition and structure of sulfur concrete by X-ray phase analysis (Pic. 3.2), it showed that the reaction between sulfur and fillers proceeds solid-phase chemical reactions with the formation of compounds of complex composition, polysulfide compounds of various types are formed when sulfur interacts with filler.

In the reaction system, the modified sulfur reacts with alkali metals, fly ash and sand to cause complex chemical changes, the modified sulfur solidifies in the system through preheating. Since active sulfur is present in the reaction system, and during the reaction they combine with the iron phase and aluminum silicate to form a solid solution, and other phases present without a solid solution are easily packed by these intermediate layers.





Pic. 3.2. a and b. Diffractogram of sulfur concrete

The study shows that sulfur concrete in terms of phase and oxide compositions meet the stated characteristics and meet the requirements of regulatory documents.

Conclusion

It has been established that modified sulfur, when prepared from elemental sulfur and from pyrolysis distillate, is mixed in a weighted ratio of 1:1. The amount of sulfur placed in a cylindrical tube with an inner diameter of 2 cm, which is straightened in a glycerin bath, heated to 1400 C and intensively mixed with a mechanical stirrer, was determined.

The composition and structure of the modified sulfur of sulfur concrete was studied by IR spectrometry, differential thermogravimetric analysis, scanning electron microscopy, X-ray phase and elemental analysis.

References

1. F. Seel, Sulfur in History: The Role of Sulfur in “Black Powder”, in Sulfur - Its Significance for Chemistry, for the Geo-, Bio- and Cosmosphere and Technology, ed. A. Müller and B. Krebs, Elsevier, 1984, vol. 5, pp. 55–66.
2. K. H. Wedepohl, Sulfur in the Earth’s Crust, its Origin and Natural Cycle, in Sulfur - Its Significance for Chemistry, for the Geo-, Bio- and Cosmosphere and Technology, ed. A. Müller and B. Krebs, Elsevier, 1984, vol. 5, pp. 39–54.
3. R. J. Angelici, Acc. Chem. Res., 1988, 21(11), 387–394.
4. L. A. Apodoca, Sulfur: US Geological Survey, mineral commodity summaries, 2014, pp. 156–157.
5. E.P.A. Reregistration, eligibility document facts: Sulfur, Office of Pesticide and Toxic Substances, Washington D.C., 1991.
6. N. T. Binh, Adv. Synth. Catal., 2017, 359(7), 1066–1130.
7. J. A. Ober, Materials flow of sulfur–, 2002, 2002–298.
8. S. R. Rafikov, The characteristic features of sulphur containing polymers. A review. // Polym. Sci. U.S.S.R., 1979, 21(11), 2780–2792.
9. A. Duda and S. Penczek, Sulfur-containing polymers, in Encyclopedia of Polymer Science and Engineering, ed. J. I. Kroschwitz, John Wiley & Sons, Inc, New York, 1989, vol. 16, pp. 246–368.
10. D. Vietti, Polysulfides, in Encyclopedia of Polymer Science and Technology, 2001.
11. P. T. Dirlam, R. S. Glass, K. Char and J. Pyun, J. Polym. Sci., Part A: Polym. Chem., 2017, 55(10), 1635–1668.
12. J. J. Griebel, R. S. Glass, K. Char and J. Pyun, Prog. Polym. Sci., 2016, 58, 90–125.
13. J. Lee, J. Pyun and K. Char, Angew. Chem., Int. Ed., 2015, 54, 3249–3258.

14. A. Kultys, in Sulfur-containing polymers, John Wiley & Sons, Inc., 2014, pp. 286–352.
15. H. Mutlu, E. B. Ceper, X. Li, J. Yang, W. Dong, M. M. Ozmen and P. Theato, Macromol. Rapid Commun., 2019, 40(1), 1800650.
16. C. P. Tsonis, Polysulfides, in Advances in Engineering Fluid Mechanics: Multiphase Reactor and Polymerization System Hydrodynamics, ed. N. P. Cheremisinoff, Gulf Professional Publishing, Burlington, 1996, pp. 737–746.
17. R. Steudel, Inorganic Polysulfides Sn 2− and Radical Anions Sn·−, in Topic in Current Chemistry, ed. R. Steudel, Springer Berlin Heidelberg, Berlin, Heidelberg, 2003, pp. 127–152.
18. R. Steudel, Sulfur: Organic Polysulfanes, in Encyclopedia of Inorganic Chemistry, 2007.
19. E.-K. Bang, M. Lista, G. Sforazzini, N. Sakai and S. Matile, Chem. Sci., 2012, 3(6), 1752–1763.
20. Y. Zhang, J. J. Griebel, P. T. Dirlam, N. A. Nguyen, R. S. Glass, M. E. Mackay, K. Char and J. Pyun, J. Polym. Sci., Part A: Polym. Chem., 2017, 55(1), 107–116.
21. Bencowitz I. Effect of sulfur upon some of the properties of asphalts / I. Bencowitz, E.S. Boe // Proceedings of the American Society of Testing Materials – 1938 – vol. 38 – pp. 539-550
22. Książek, M. The experimental investigations of propriety and applies in the building special coating – Sulfur polymer composite as the industrial waste material // Composites Part B: Engineering, 2014. – vol. 58, Issue null – pp. 378-385
23. Хайитова Ж.М., Бекназаров Х.С., Тураев Х.Х. Модификация серы с промышленными отходами для получения серного бетона // Universum: технические науки: электрон. научн. журн. 2021. 1(82). – С. 94-97. URL: https://7universum.com/ru/tech/archive/item/11204 (02.00.00 №1)
24. 24.Хайитова Ж.М., Тўраев Х.Х., Бекназаров Х.С. Исследование модификации серы диамидофосфатом кальция и золошлаком Ново-Ангренский ТЭС // Развитие науки и технологии, -Buхара, -2021, №3, -С.119- 125. (02.00.00. №14)
25. J.M.Khayitova , Kh.S.Beknazarov. Modification of sulfur with pyrolysis distillate and gossypol resin Study of properties of initial and modified sulfur samples // Actual problems of modern science and innovation in the Central Asian region: collection of articles of the international conference. -Jizzakh, -2020. -p.76.