2023, 20(6 Suppl.): 2414-2433
https://dx.doi.org/10.21123/bsj.2023.9038
P-ISSN: 2078-8665 - E-ISSN: 2411-7986
Baghdad Science Journal

Application of Sulfur-2,4-dinitrophenylhydrazine as Modifier for Producing an Advantageous Concrete

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Received 08/05/2023, Revised 07/07/2023, Accepted 09/07/2023, Published 05/12/2023

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Abstract

In this investigative endeavor, a novel concrete variety incorporating sulfur-2,4-dinitrophenylhydrazine modification was developed, and its diverse attributes were explored. This innovative concrete was produced using sulfur-2,4-dinitrophenylhydrazine modification and an array of components. The newly created sulfur-2,4-dinitrophenylhydrazine modifier was synthesized. The surface texture resulting from this modifier was examined using SEM and EDS techniques. The component ratios within concrete, chemical and physical traits derived from the sulfur-2,4-dinitrophenylhydrazine modifier, chemical and corrosion resistance of concrete, concrete stability against water absorption, concrete resilience against freezing, physical and mechanical properties, durability, elastic modulus, and thermal expansion coefficient of the examined sulfur-infused concrete were assessed. The acquired results also substantiated that the thermal expansion coefficient value for sulfur-2,4-dinitrophenylhydrazine modified concrete was 14.8×10-6/0C. The average deformation of the analyzed concrete was 0.0026-0.0051, indicating a superior deformation performance compared to conventional concretes. Concrete with smaller aggregate sizes exhibited greater density, specifically 2283 kg/m3. The concrete density decreased gradually with an increase in aggregate size. The stability of sulfur-2,4-dinitrophenylhydrazine modified concrete was remarkably high in various aggressive environments. EDS analysis revealed that carbon atoms constituted 56.63% of the total mass, while sulfur made up 33.91% of the total mass. The obtained SEM outcomes demonstrated that the sulfur-2,4-dinitrophenylhydrazine modifier exhibited a more porous structure, devoid of crystalline formations. The sulfur-2,4-dinitrophenylhydrazine modification experienced a single-stage thermal mass loss, with the mass loss events being endothermic in nature. The IR findings verified the presence of amino functional groups (connected melamine ring) and the establishment of polymer sulfur chains.

Keywords: Deformation, Elasticity, Sulfur concrete, Thermal expansion coefficient, 2,4-dinitrophenylhydrazine.

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Introduction

Initially developed in the United States, sulfur-based concrete has undergone extensive research to refine and enhance its properties. Studies have consistently demonstrated the safety and reliability of sulfur concrete as a building material. Sulfur, a compound found in crude oil and gas products, is an economical choice compared to other base materials due to its low cost [1-3].

In sulfur concrete, sulfur primarily functions as a binding agent. The composition also includes other components such as rock fragments, sand, fly ash, and stabilizing agents. With its low porosity and high-density mixture, sulfur concrete boasts superior strength compared to traditional cement concrete. The unique matrix structure of sulfur concrete can be attributed to the combination of sulfur and the incorporated aggregates [4-7].

Sulfur concrete is an innovative and eco-friendly building material that has gained significant attention in recent years. Developed as an alternative to traditional cement-based concrete, sulfur concrete offers unique properties and advantages that make it suitable for various construction applications [8-10].

Sulfur concrete is primarily composed of sulfur, which acts as a binding agent, along with aggregates such as rock fragments, sand, fly ash, and stabilizing materials. Sulfur, a byproduct of the oil and gas industry, is abundant and inexpensive, making it an appealing choice for use in construction materials. These types of concrete have following benefits [11-13]:

(i) Enhanced strength: Sulfur concrete exhibits superior strength compared to traditional cement concrete, thanks to its low porosity and high-density mixture. This results in a more durable and long-lasting building material [14-16].

(ii) Faster curing time: Unlike cement-based concrete, which can take weeks to cure, sulfur concrete hardens quickly, reducing construction time and labor costs [17-18].

(ii) Chemical and corrosion resistance: Sulfur concrete demonstrates excellent resistance to chemicals and corrosion, making it an ideal choice for structures exposed to harsh environments, such as wastewater treatment plants and coastal regions [19-22].

(iii) Environmental benefits: The use of sulfur, a waste product from the oil and gas industry, in concrete production helps to minimize waste and reduce the environmental impact associated with cement production, which is a significant contributor to CO_2 emissions [3, 7, 23-25].

(iv) Improved thermal properties: Sulfur concrete exhibits better thermal performance than traditional cement concrete, which can contribute to energy-efficient buildings [26-28].

While sulfur concrete offers several advantages, it also comes with some challenges and limitations. For example, the high melting point of sulfur can make the production process more energy-intensive. Additionally, the long-term performance of sulfur concrete under extreme temperature fluctuations is still being studied [29-31].

As the demand for sustainable and efficient building materials continues to grow, the potential for sulfur concrete in the construction industry is promising. With ongoing research and development, sulfur concrete could become a more widely adopted solution, contributing to a greener and more sustainable built environment [32-34].

Sulfur concrete has been primarily utilized in offshore structures, dams, and underground utility systems due to its high strength, density, and low porosity. In the construction industry, Portland cement concrete is the most common material. However, it has several drawbacks, such as increased porosity affecting the freezing properties, leading to concrete deterioration in winter or high humidity conditions. Furthermore, Portland cement concrete has poor chemical and corrosion resistance, high water adsorption performance, and subpar physical and mechanical properties, including durability, modulus of elasticity, and thermal expansion coefficient. In contrast, sulfur concrete demonstrates superior performance compared to Portland cement concrete [35-37].

In the current study, a sulfur-2,4-dinitrophenylhydrazine modifier was introduced for the fabrication of innovative concretes. A new sulfur-2,4-dinitrophenylhydrazine modified concrete was introduced and its various properties were examined. Its structure was confirmed by through IR spectroscopy and TG analysis. The surface morphology of the modifier was studied using SEM and EDS analysis. The thermal expansion coefficient, modulus of elasticity, durability, physical and mechanical properties, stability against water adsorption and freezing, chemical and corrosion resistance, component ratio in concrete, chemical and physical characteristics of sulfur-2,4-dinitrophenylhydrazine modified concrete of the newly developed sulfur concrete were studied.

Materials and Methods

Materials

Orthorhombic[32] sulfur, also known as alpha-sulfur or rhombic sulfur, is one of the various allotropes of elemental sulfur. It is characterized by its unique crystalline structure, which exhibits orthorhombic symmetry – a crystalline system defined by three unequal axes intersecting at right angles. This distinct structure sets orthorhombic sulfur apart from other sulfur allotropes, such as monoclinic sulfur (beta-sulfur) and amorphous sulfur. At room temperature and atmospheric pressure, orthorhombic sulfur is the most stable allotrope of sulfur, making it the most common form found in nature. It presents as a yellow, brittle solid that is odorless and tasteless. Owing to its stability, orthorhombic sulfur plays a crucial role in various industrial applications and chemical processes [14, 32].

Hydrazine (N_2H_4) is an inorganic compound and a powerful reducing agent characterized by its simple structure, consisting of two nitrogen atoms bonded together and each nitrogen atom connected to two hydrogen atoms.

In this research work, the orthorhombic sulfur and 2,4-dinitrophenylhydrazine were used to synthesis the sulfur modifier as sulfur based concrete.

Methods

Thermogravimetric Analysis

The objective of conducting the thermogravimetric analysis (TG) on the sulfur-2,4-dinitrophenylhydrazine modifier was to investigate its response to heat treatment. The TG analysis was executed using the Thermo Scientific GC1310 combined with Tsq 9000_TA Instruments STD 650 (USA). The temperature range for the analysis was set between 100-1000°C.

SEM and EDS Analysis

The EDS analysis for sulfur concrete is an essential tool for researchers and engineers seeking to understand and enhance the material's characteristics. By providing a detailed understanding of the elemental composition and distribution within the material, EDS analysis enables the development of improved sulfur concrete formulations, paving the way for more sustainable and durable construction materials [18-19, 38].

The surface properties of the sulfur-2,4-dinitrophenylhydrazine modifier were examined using scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) techniques. The SEM investigation focused on the surface morphology of the modifier, while the EDS method centered on the elemental analysis of the surface. Both SEM and EDS analyses were conducted using the Jeol JSM-IT200LA instrument.

IR Spectroscopy

Infrared (IR) spectroscopy was utilized to investigate the structural properties of the sulfur- hydrazine modifier. The IR analysis involved recording spectra using a Bruker Fourier spectrometer, Invenio S-2021, ATR, within the range of 4000 – 400 cm^{-1}. The observed IR shifts primarily correspond to the vibrations of various functional groups.

Evaluating the Thermal Expansion Coefficient

The thermal expansion coefficient is a valuable indicator of concrete efficiency under varying temperature conditions. The coefficient for sulfur-2,4-dinitrophenylhydrazine modified concrete was measured and compared with traditional concretes, such as Portland cement concrete. In this analysis, concrete samples were initially immersed in water for two days at various temperature ranges, spanning from 10°C to 50°C. Following immersion, the length of the concrete was measured. As the final step, changes in the length of the concrete at different temperatures were assessed using a differential transformer. The linear expansion of the samples was documented at a rate of 0.2°C/min [39-41].

Examining Elasticity, Deformation, and Durability

At the onset of evaluating elasticity, deformation, and durability, the sulfur-2,4-dinitrophenylhydrazine modified concrete samples were prepared in the form of cylindrical pieces, measuring 20 cm in height and 10 cm in width. These samples were stored for three days before assessing their elasticity and durability performances. A 1500 kN SATEC™ Series 1500 HDX (Norwood, MA, US) was utilized to measure these parameters effectively [42-46].

Assessing Concrete Stability Against Freezing

The stability of concrete under freezing conditions was investigated in an aquatic medium. Prismatic concrete specimens measuring 100x100x400 mm were prepared in accordance with the ASTM C666 procedure. The relative dynamic modulus of the samples was measured at intervals of 50, 100, and 300 cycles. Each cycle was four hours apart and conducted over a temperature range of 4°C to -18°C, repeating up to 300 times. The study concluded after 300 cycles, and consequently, the stability coefficient of the cycles was determined [47-49].

Assessing Concrete Stability against Water Adsorption

Assessing the water adsorption of concrete is crucial for determining its stability in aquatic and high humidity atmospheric environments. This study investigated the water adsorption stability of sulfur-2,4-dinitrophenylhydrazine modified concrete over a 30-day period by measuring the weight before and after immersion in water. The stability coefficient of the concrete against water adsorption was determined using Eq. 1. In the equation, W_A signifies the mass increase after water adsorption, M_b denotes the mass of water-adsorbed concrete (following water adsorption) and M_a represents the mass of dried concrete (prior to the experiment). The value of W_A is equivalent to the stability coefficient of concrete against water adsorption [26-27, 50].

$$W_A = \frac{M_b - M_a}{M_a} \times 100\% \qquad 1$$

Analyzing Chemical and Corrosion Resistance of Concrete

The stability of concrete when exposed to aggressive chemical and corrosive solutions is a crucial factor. This study examined the stability of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete in various harsh environments, including 10% acidic solutions (sulfate, chloride, nitrate, and phosphate acids), 3% saline solutions (sulfates, chlorides, and fluoride salts), 10% NaOH, pH-altering mediums (ranging from pH 4-10), and organic compounds (automotive oil, dichloroethane, and diesel fuel) [51].

Preparation of Sulfur Modifiers

Using a 100 ml heat-resistant chemical beaker, equipped with a mechanical stirrer, oil bath, and electric plate, 10 g of sulfur was heated with constant stirring to a temperature of 185°C for 30 minutes, forming a clear, viscous tangerine-colored liquid sulfur. Next, 0.6 g of 2,4-dinitrophenylhydrazine was added to the liquid sulfur solution with continuous stirring, maintaining a temperature of 185-190°C for 1 hour. Following the reaction, a slight decrease in viscosity and the formation of brown sulfur and 2,4-dinitrophenylhydrazine-derived comonomers were observed, Fig. 1.

Upon completion of the reaction process, the resulting product was transferred from the chemical beaker to a special container using a spatula and allowed to cool to room temperature. The produced sulfur copolymer was then heated to 180-190°C in a stainless steel reactor, equipped with a mechanical stirrer and a thermostated oil bath, until a liquid phase formed. As a result, the sulfur modifiers with 2,4-dinitrophenylhydrazine was obtained.

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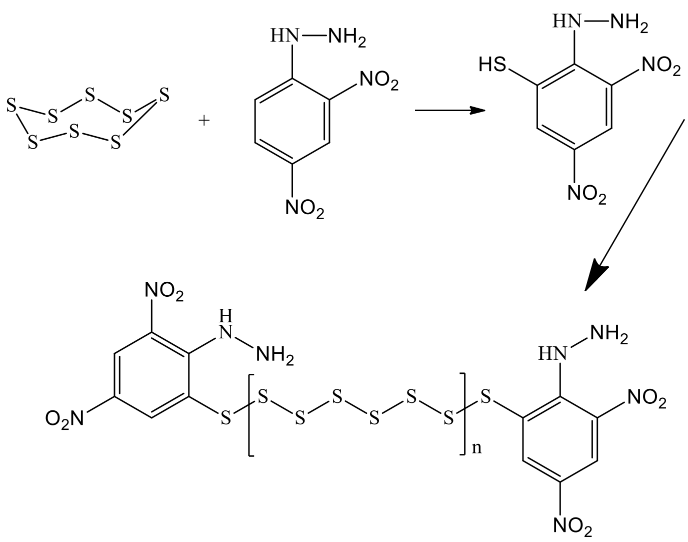


Figure 1. Sulfur Modifier Preparation Procedures.

Preparation of Sulfur-2,4-dinitrophenylhydrazine Modifier-based Concrete

At the onset of the sulfur-2,4-dinitrophenylhydrazine modified concrete preparation, the necessary components (crushed rocks, sands, and fly ash) were gathered and heated at 180°C for 6 hours. Subsequently, the liquid sulfur-2,4-dinitrophenylhydrazine modifier was combined with the prepared ingredients (crushed rocks, sands, and ash) using a 1:2.5 volume ratio. The resulting mixture was then heated at 140-160°C for 30 minutes. As the final step, the heated blend was allowed to cool to room temperature, yielding the desired sulfur-2,4-dinitrophenylhydrazine modified concrete. Following this, its mechanical and physical properties were evaluated, Fig. 2.

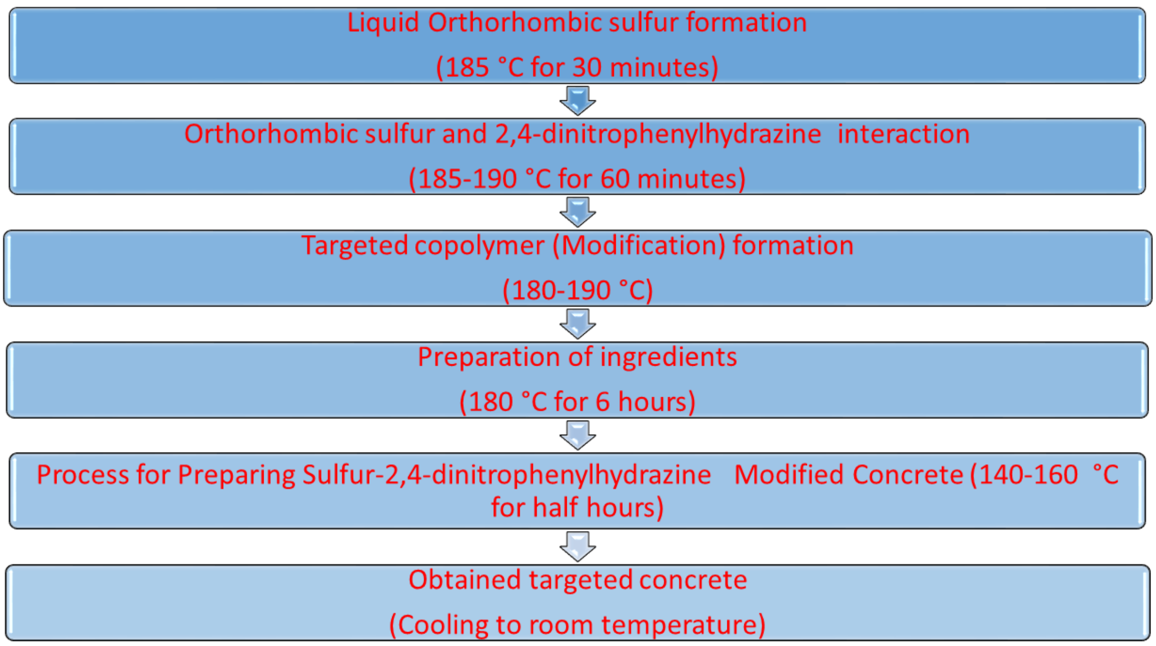


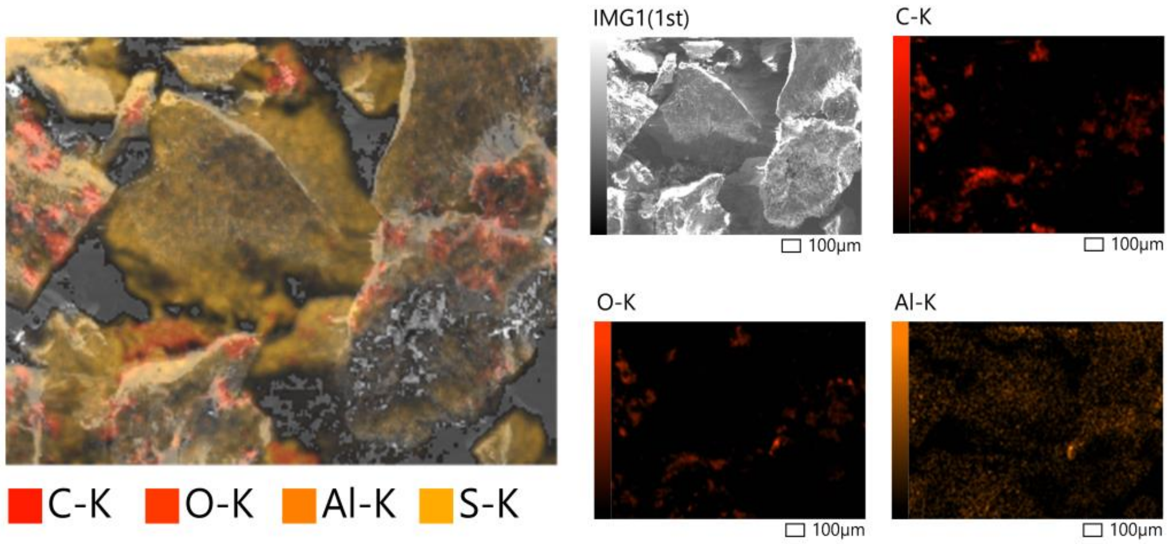
Figure 2. The outlined steps for preparing the intended sulfur-2,4-dinitrophenylhydrazine modified concrete.

Results and Discussion

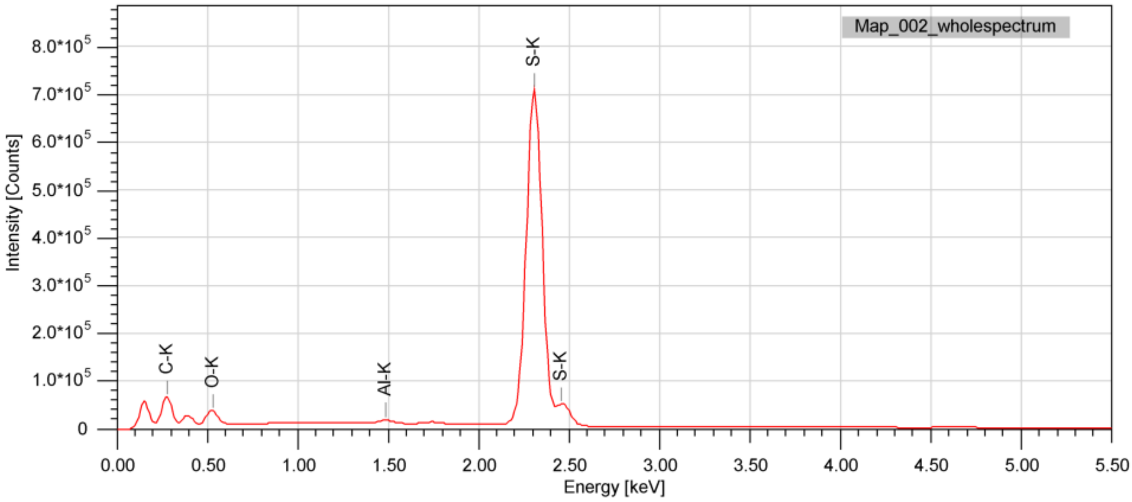
Element Mapping Exam

The EDS (Energy Dispersive Spectroscopy) analysis plays a crucial role in understanding the elemental composition of sulfur concrete. This advanced analytical technique provides essential information about the distribution and concentration of elements present within the material. By employing EDS analysis, researchers can gain valuable insights into the performance and characteristics of sulfur concrete and optimize its properties for various applications. Through the evaluation of EDS images and elemental maps, the presence of sulfur, along with other elements, can be confirmed, allowing for a more comprehensive understanding of the material's composition and performance.

Fig. 3 presents the EDS images and the corresponding EDS element map of the sulfur-2,4-dinitrophenylhydrazine modifier. An in-depth surface elemental analysis was performed on the sulfur-2,4-dinitrophenylhydrazine modifier to ascertain the elemental composition of the selected modification substance. It is noted that the sulfur content was determined to be 33.91 % of the total mass, verifying the presence of sulfur in the modifier being examined. The analysis revealed that oxygen atoms constituted 9.2 % of the total mass, while carbon comprised 56.63 % of the total mass. These findings confirmed the existence of 2,4-dinitrophenylhydrazine within the sulfur-2,4-dinitrophenylhydrazine modifier. As a result, the EDS images and EDS element map outcomes demonstrated that the sulfur-2,4-dinitrophenylhydrazine modifier was composed of nitrogen, carbon, and sulfur elements, with sulfur serving as a connecting component in the modifier.



(a)



(b)

Figure 3. EDS analysis results of sulfur-2,4-dinitrophenylhydrazine, with (a) an element map and (b) the EDS data.

Surface Morphology Exam

In recent years, there has been a growing interest in developing novel concrete modifiers to enhance its mechanical properties, durability, and sustainability. Among these modifiers, sulfur-2,4-dinitrophenylhydrazine-based additives have shown promising results in improving the overall performance of concrete. This study presents a detailed Scanning Electron Microscopy (SEM) analysis of sulfur-2,4-dinitrophenylhydrazine modified concrete to better understand its microstructural characteristics and the effects of the modifier on the concrete matrix.

The surface morphology of the sulfur-2,4-dinitrophenylhydrazine modifier was investigated using Scanning Electron Microscopy (SEM) analysis. Fig. 4 presents SEM images of the sulfur-2,4-dinitrophenylhydrazine modifier at various sizes: (a) 100 µm and (b) 50 µm. The results clearly demonstrate that the sulfur-2,4-dinitrophenylhydrazine modification introduces a structure with increased porosity and no detectable crystalline forms, indicating an amorphous nature of the modifier.

The sulfur-2,4-dinitrophenylhydrazine modification powder plays a fundamental role in concrete composition. The enhanced porosity and amorphous characteristics of the sulfur-2,4-dinitrophenylhydrazine modifier contribute to the increased efficiency of sulfur-based concrete. Additionally, the absence of oxidation products on the surface of the sulfur-2,4-dinitrophenylhydrazine modifier confirms that the sulfur-based concrete does not undergo oxidation and that no oxidation products are formed. If oxidation processes had occurred, the resulting concrete would be unstable when exposed to atmospheric conditions.

The SEM analysis of sulfur-2,4-dinitrophenylhydrazine modified concrete revealed promising microstructural improvements in the cement paste and interfacial transition zone. These improvements can be correlated with the observed enhancements in mechanical properties and durability. This study highlights the potential of sulfur-2,4-dinitrophenylhydrazine as an effective modifier for concrete, paving the way for further research and optimization of this novel additive in concrete technology.

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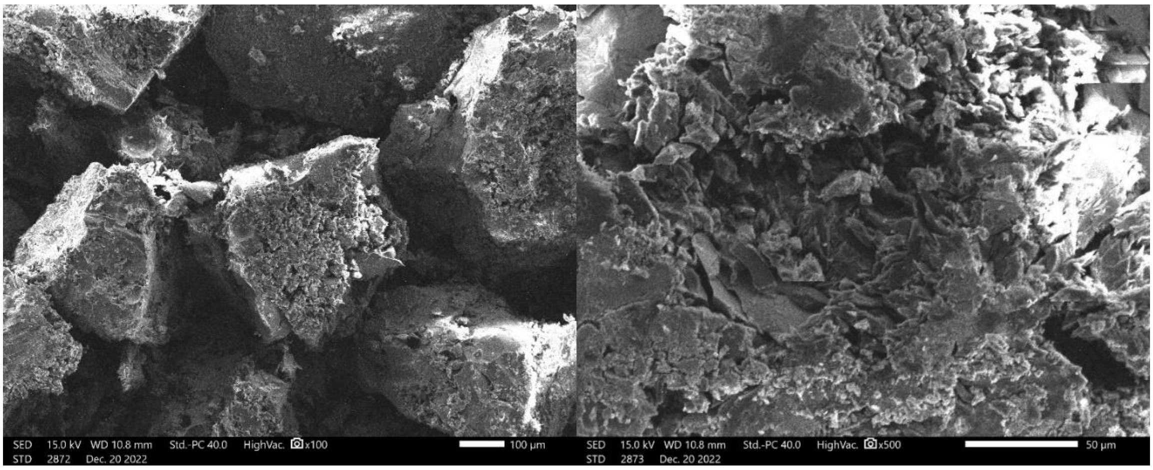

(a) **(b)**

Figure 4. SEM images of concrete modified with sulfur-2,4-dinitrophenylhydrazine at various magnifications: (a) 100 µm and (b) 50 µm.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) has proven to be an essential tool for understanding the thermal stability and compositional changes of sulfur-2,4-dinitrophenylhydrazine concrete. This technique allows researchers and industry professionals to assess the impact of incorporating sulfur modifiers in concrete, leading to enhanced performance characteristics and material longevity. Sulfur-modified concrete has gained significant attention due to its improved properties, such as increased resistance to chemical attack, enhanced strength, and shorter setting times. However, understanding the thermal behavior of these modifications is crucial for optimizing the concrete's performance and ensuring long-term durability. The TGA process involves monitoring the mass changes of a sample as it is subjected to a controlled temperature program. In the case of sulfur-modified concrete, TGA helps to identify the thermal decomposition stages of the sulfur modifier, as well as the interactions between the sulfur and cementitious components in the mixture. By analyzing the obtained thermogravimetric data, researchers can determine the optimal amount of sulfur modifier to be used and the ideal curing conditions for the concrete.

The analysis of the thermal performance of the selected modification method was carried out through thermogravimetric (TGA) testing of the sulfur-2,4-dinitrophenylhydrazine modifier. The TGA curves for the sulfur-2,4-dinitrophenylhydrazine modifier, Fig. 5 and its thermogravimetric properties Table 1 were obtained. The TGA testing involved measuring the consumed energy (µV*s/mg), weight loss percentage (%), and weight loss (mg) for the sulfur-2,4-dinitrophenylhydrazine modifier as the temperature changed from 100 ^{0}C to 1000 ^{0}C.

The results show that the weight loss of the sulfur-2,4-dinitrophenylhydrazine modifier was stable up to 215 ^{0}C, as this was the liquefaction temperature of the modifier. The mass loss of the sulfur-2,4-dinitrophenylhydrazine modifier began after 220 ^{0}C and slowly decreased until 230 ^{0}C. Then, it experienced a dramatic decrease until 309.91 ^{0}C, where the mass loss was 82.636% and the residue was 7.624 mg. The next heat peak was cited at 393.44 ^{0}C. This confirms that:

(i) The modifier concrete remained stable up to 210 ^{0}C.

(ii) The sulfur-2,4-dinitrophenylhydrazine modifier exhibited one-step thermal mass loss.

(iii) The mass loss processes of this modifier are endothermic processes since all peaks are endothermic, indicating that the mass loss of this concrete required extra energy.

The changes in the derivate weight d(weight)/dT (%/^{0}C) indicated that the sulfur-2,4-dinitrophenylhydrazine modifier has one volatilization temperature (peak) at 309.91 ^{0}C. The

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P-ISSN: 2078-8665 - E-ISSN: 2411-7986
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heat flow was fluctuated to 260 ^{0}C, then it suddenly decreased to 309.91 ^{0}C due to the volatilization of the sulfur-2,4-dinitrophenylhydrazine modifier. After this temperature, the heat flow increased rapidly to 400 ^{0}C and experienced a roughly stable increasing trend.

Therefore, the use of thermogravimetric analysis for the evaluation of sulfur modifiers in concrete provides valuable information regarding the material's thermal stability, decomposition, and interactions with other components. This knowledge contributes to the development of high-performance, durable, and sustainable sulfur-modified concrete solutions for the construction industry.

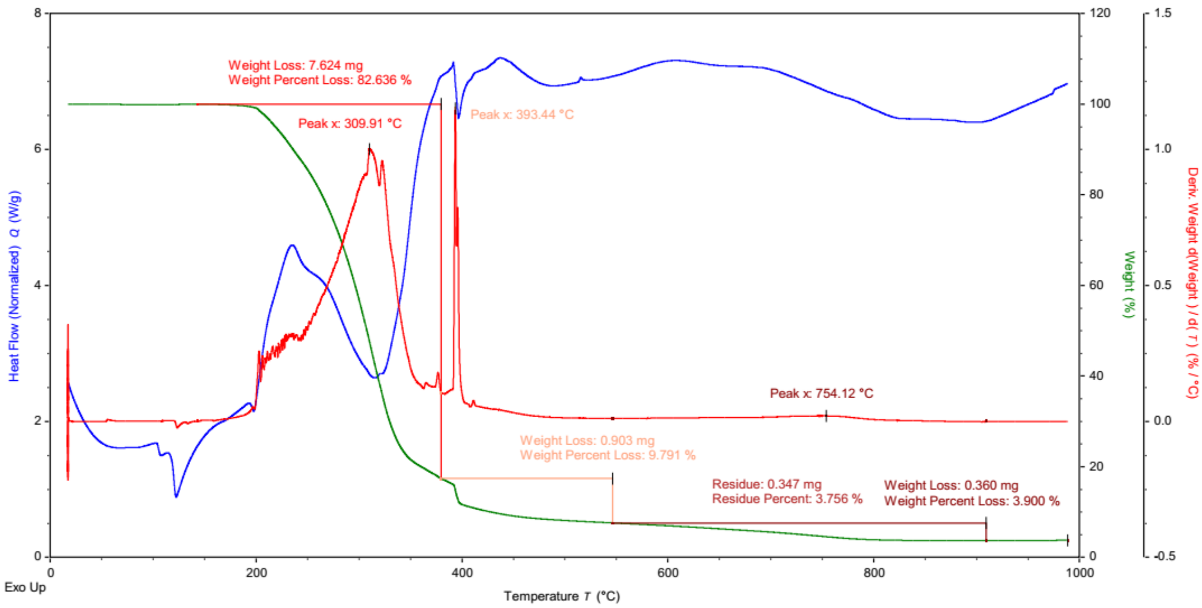

Figure 5. Thermogravimetric curves of sulfur-2,4-dinitrophenylhydrazine modifier.

Table 1. Thermogravimetric results of sulfur-2,4-dinitrophenylhydrazine modifier.

№	Temperature, ^{0}C	Values in consumed energy, μV	Weight loss, %	Weight loss rate, mg/min
1	100	-0,00105	0.075	0.0155
2	200	-0.09585	0.84	0.6452
3	300	-0.856	43.206	0.688
4	400	-0.101	88.338	0.0538
5	500	-0.01322	91.855	0.018
6	600	-0.0125	93.022	0.0212
7	700	-0.0159	94.425	0.0258
8	800	-0.00725	96.114	0.0032
9	900	0.0109	96.312	0.00315
10	1000	0.00056	96.44	0.0031

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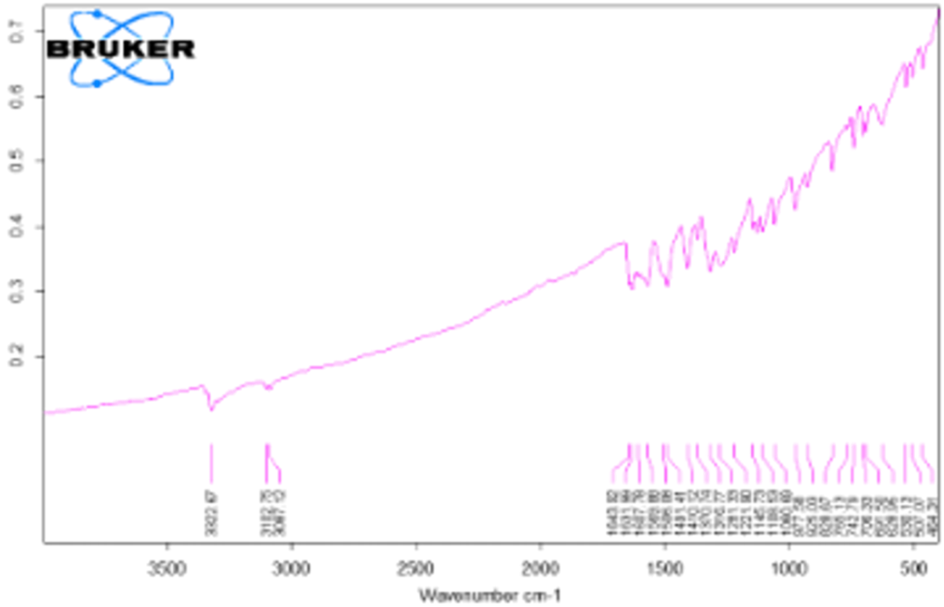

Figure 6. IR results of sulfur-2,4-dinitrophenylhydrazine modifier.

IR Test

The structural characterization of the sulfur-2,4-dinitrophenylhydrazine modifier was validated through infrared (IR) analysis. The derived IR results for the sulfur-2,4-dinitrophenylhydrazine modifier are depicted in Fig.6. From the resulting spectrum, it is evident that the valence vibrations of amino functional groups (associated with the phenyl ring) appeared at 3322 cm^{-1}. These signals verify the presence of amino functional groups, which are connected to the aliphatic ring of melamine.

The IR spectrum of sulfur-2,4-dinitrophenylhydrazine typically shows characteristic peaks that correspond to specific functional groups. For example, the peak at around 3102 cm^{-1} is associated with the N-H stretching vibration of the hydrazine functional group. The peak at around 3087 cm^{-1} is associated with the C-H stretching vibration of the phenyl group. The peak at around 1631 cm^{-1} is associated with the C=O stretching vibration of the 2,4-dinitrophenyl group. The peak at around 1607 cm^{-1} is associated with the C-N stretching vibration of the hydrazine group. The peak at around 1370 cm^{-1} is associated with the NO_2 bending mode of the 2,4-dinitrophenyl group.

The IR spectrum of sulfur-2,4-dinitrophenylhydrazine also provides information about the sulfur linkage in the sample. The peak at around 507 cm^{-1} is associated with the S-S stretching vibration, which is a characteristic feature of the sulfur linkage. Additionally, the IR spectrum of sulfur-2,4-dinitrophenylhydrazine can be used to assess the purity of the sample. The absence of impurities or other functional groups in the spectrum confirms the purity of the sample.

Conversely, the connection of melamine with sulfur polymer chains was substantiated by the presence of N-S bonds. The IR signals corresponding to N-S bonds were identified at 1643 cm^{-1}. The formation of polymer sulfur chains is facilitated by S-S bonds, with IR signals in the 628 cm^{-1} range responsible for these bonds. Consequently, the acquired IR signals confirm the structure of the sulfur-2,4-dinitrophenylhydrazine modifier.

Thermal Expansion Coefficient

The thermal expansion coefficient is significant when considering the design of structures subjected to extreme temperature variations, such as bridges, pavements, and buildings in regions with significant seasonal temperature differences. Properly accounting for the thermal expansion coefficient in the design and construction of these structures can minimize the risk of thermal-induced stresses, cracks, and other forms of deterioration.

The thermal expansion coefficient value indicates the effectiveness of concrete under varying

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temperature conditions. The obtained data reveals that the thermal expansion coefficient for concrete incorporating a sulfur-2,4-dinitrophenylhydrazine modifier is $14.8\times10^{-6}/^{0}C$. This low value suggests that the chosen sulfur concrete demonstrates increased efficiency in response to heat changes. It is also worth noting that the thermal expansion coefficient for sulfur-2,4-dinitrophenylhydrazine modifier-based concrete surpasses that of conventional concretes, as the thermal expansion coefficient of Portland cement concrete falls within the range of $10.0\times10^{-6}/^{0}C$ to $13.0\times10^{-6}/^{0}C$. However, advances in concrete technology have led to the development of innovative concrete mixtures with modified thermal expansion coefficients. For instance, concrete incorporating sulfur-2,4-dinitrophenylhydrazine modifiers exhibits a lower thermal expansion coefficient of around $14.8\times10^{-6}/^{0}C$, which indicates increased efficiency in response to temperature changes.

Physical and Mechanical Properties and Durability of Concrete

In the formulation of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete, recycled coarse aggregate, natural coarse aggregate, and fine aggregate were incorporated. The fundamental physical and mechanical properties of these aggregates were determined, and the findings are presented in Table 2. The analysis reveals that the utilized recycled coarse aggregates possess a lower density and increased water absorption compared to natural coarse aggregates. Natural coarse aggregates consist of crushed aggregates with maximum dimensions of 25, 19, and 13 mm. The maximum sizes for recycled coarse aggregate and natural fine aggregate are 25 and 10 mm, respectively.

Table 2. Properties of aggregates used in tests.

Properties		Used aggregates		
		Recycled coarse aggregate	Natural coarse aggregate	Fine aggregate
Absolute density in dry form (g/mm^3)		1.64	2.32	1.26
Absorption (%)		3.28	0.45	1.16
Abrasion (%)		16.2	12.4	-
Absolute volume (%)		35	38	34
Passage through a 0.08 mm sieve (%)		0.4	0.1	1.2
Alkaline Aggregate Reaction		Harmless	-	-
The amount of clay mass (%)		0.12	0.08	0.4
Stability (%)		4.6	2.6	3.8
Impurity content (%)	Organic impurity	Less than 1.0 (volume)	-	-
	Inorganic impurity	Less than 1.0 (weight)	-	-

The tensile strength, in compression, and splitting for the sulfur-2,4-dinitrophenylhydrazine modifier-based concrete were investigated, and the findings are presented in Table 3. In this analysis, seven variations of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete related to aggregate size were assessed. The observations revealed that:

(i) Concrete sample 5 demonstrated superior compressive strength, 85 MPa, and enhanced splitting tensile strength, 5.9 MPa, in comparison to the other specimens. This specific concrete sample was prepared using a 25 mm aggregate size.

(ii) The smaller aggregate size in sulfur-2,4-dinitrophenylhydrazine modifier-based concrete contributes to a higher density, 2283 kg/m3. The concrete density gradually decreased as the aggregate size increased.

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https://dx.doi.org/10.21123/bsj.2023.9038
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Table 3. Tensile strength in compression and splitting for the sulfur-2,4-dinitrophenylhydrazine modifier-based concrete.

Samples	Density (kg/m^3)	Compressive strength (MPa)	Splitting tensile strength (MPa)
№ 1	2117	45	-
№ 2	2289	55	-
№ 3	2274	66	-
№ 4	2265	75	4.4
№ 5	2283	85	5.9
№ 6	2248	80	4.2
№ 7	2292	72	4.4

The modulus of elasticity for the sulfur-2,4-dinitrophenylhydrazine modifier-based concrete was also examined, and the acquired data is displayed in Table 4. The results showcase the modulus of elasticity and deformation at peak stress for the sulfur-2,4-dinitrophenylhydrazine modifier-based concrete. The findings revealed that the average deformation of the analyzed concrete ranged between 0.0022 and 0.0051, indicating that the deformation performance of this concrete surpassed that of conventional concretes.

Table 4. Modulus of elasticity of the sulfur-2,4-dinitrophenylhydrazine modifier-based concrete.

Samples	Deformation at maximum stress	E_{exp} (GPa)	E_{code} (GPa)	E_{exp}/E_{code} (%)
№ 1	-	-	-	-
№ 2	0.0051	21.2	31.2	**60**
№ 3	0.0022	48.6	38.4	120
№ 4	0.0032	34.4	40.0	84
№ 5	0.0031	35.4	42.1	82
№ 6	0.0026	35.6	42.8	83
№ 7	0.0024	36.9	39.1	92

Stability of Concrete against Freezing

The freezing of concrete is a crucial aspect in determining concrete efficiency. The stability values of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete against freezing were evaluated for 50, 100, and 300 cycles, and the gathered information is presented in Table 5. As observed from the results, the stability values of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete against freezing were close to 1.0, confirming the high resistance to freezing temperatures for this concrete. Consequently, it is recommended that the examined concrete be employed in low-temperature environments. The low porosity and elevated sulfur content of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete contribute to its exceptional hydrophobic performance. As a consequence, interactions with water molecules were significantly reduced. The minuscule pores on this concrete's surface were minimal, a factor that also leads to increased stability. It is disclosed that the freezing stability of concrete relies on various aspects, such as the sample size, the type and quantity of filler, the water saturation conditions, the cycle duration, the

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type and amount of the modifier, the freezing temperature, and other factors.

Table 5. Values of stability of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete against freezing.

Freezing temperature, T	Medium	Stability coefficient of cycles		
		50	100	300
-18 ^{0}C	Water	0.98	0.96	0.91

Stability of Concrete against Water Adsorption

Water absorption in concrete is a crucial aspect when evaluating the stability of concrete in aquatic settings and high humidity atmospheric conditions. In this research, the stability of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete against water absorption was examined over a 30-day period by comparing the weight differences before and after immersion in water. The compiled data can be found in Table 6. The results indicated that:

(i) The reduced porosity of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete plays a role in affecting the stability values of concrete against water absorption.

(i) The presence of sulfur in the concrete influences its water resistance properties. As sulfur levels rise, the water resistance also increases. This is attributed to the enhancement of the concrete's hydrophobic characteristics with the increase in sulfur content.

(iii) The deformation of the concrete maintained relative stability following water absorption. The sulfur-2,4-dinitrophenylhydrazine modifier is chiefly responsible for the increased deformation.

(iv) The water absorption on the surface of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete varied between 0.1 and 0.34%, and the coefficient of concrete against water absorption stood at 0.85, indicating that the selected concrete displays higher stability in aquatic and high humidity environments. The sulfur-2,4-dinitrophenylhydrazine modifier, fillers, and other constituents of the concrete also contribute to its heightened water resistance.

Table 6. Stability values of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete in relation to water adsorption resistance.

Deformation, MPa		Water adsorption, %	Coefficient of concrete against water absorption
Dried	With water adsorption		
54.6	45.3	0.1-0.34	0.85

Chemical and Corrosion Resistance of Concrete

The chemical and corrosion resistance properties of the developed sulfur-2,4-dinitrophenylhydrazine modified concrete were examined, and the acquired information is displayed in Table 7. The chemical and corrosion stability of this concrete was assessed in various aggressive chemical and corrosion environments. Prior to the experiment, the formulated concrete was immersed in the chosen aggressive chemical and corrosion solutions for 60 days. The stability coefficient values were determined in this test, with the maximum value being 1.0. The experiments were conducted after the 60-day period. A stability coefficient above 0.5-0.6 signifies increased stability, while a value above 0.7-0.8 indicates excellent stability. The findings showed that:

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(i) Organic substances, such as car oil, dichloroethane, and diesel fuel, do not impact the stability of the examined concrete.

(ii) The chemical and corrosion stability of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete was average in alkaline solutions. Highly concentrated alkaline ions exhibit strong corrosiveness. The stability coefficient of this concrete is 0.5, signifying that it maintains normal stability in harsh alkaline environments.

(iii) The aggressive salts do not affect the stability of this concrete. This is attributed to the molecular structure of the sulfur-2,4-dinitrophenylhydrazine modifier, which does not interact with the anodic and cathodic salt ions.

(iv) The chemical and corrosion stability of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete in sulfate, chloride, nitrate, and phosphate acid solutions remained average over a period of two months.

Table 7. Impacts on stability of sulfur-2,4-dinitrophenylhydrazine modifier-based concrete in chemical and corrosive environments.

Aggressive chemical and corrosion solution	Stability coefficient (60 days)
Organic compounds:	
- Car oil	0.68-0.92
- Dichloroethane	0.60
- Diesel fuel	0.67
Medium, pH = 4-10	0.69-0.73
10% NaOH	0.48
3% Saline solutions:	
- Sulfates salts	0.70-0.80
- Chlorides salts	0.70-0.80
- Fluorides salts	0.89-0.96
10% Acidic solutions:	
- Sulfate acid	0.30-0.48
- Chloride acid	0.51-0.60
- Nitrate acid	0.52-0.61
- Phosphate acid	0.70-0.77

Proportions of Elements in Concrete

In this study, an effective concrete utilizing sulfur-2,4-dinitrophenylhydrazine modification was developed. This copolymer serves as the primary foundation for sulfur-concrete, which is widely employed in the construction sector. Sulfur-2,4-dinitrophenylhydrazine modified material represents a novel addition to conventional concretes.

The proportion of components in the concrete influences the alteration of various chemical and physical attributes. The ratio between sulfur-2,4-dinitrophenylhydrazine modified concrete ingredients was determined using the centripetal force method. The component ratio analysis of concrete revealed that:

(i) A 18.1%:13.9% volume ratio of modified sulfur-2,4-dinitrophenylhydrazine to fly ash was optimal for superior concrete preparation.

(ii) The incorporation of fly ash enhanced ease of formability and strength. Replacing 20% of modified sulfur-2,4-dinitrophenylhydrazine with fly ash resulted in easily formable and high-strength concrete.

(iii) A 35.2%:30% ratio of large fillers to lower fillers was more efficient for concrete formation.

(iv) A 54%:46% (sand: filler) ratio proved more effective for creating sulfur-2,4-dinitrophenylhydrazine modified concrete.

(v) A more efficient concrete was achieved with a 2:1 ratio (fillers: chosen copolymer), resulting in a high-strength and compressive material.

In the subsequent phase of the study, the selection of concrete preparation was based on various ingredient ratios (Table 8). The investigation was conducted after three days. Five sulfur-2,4-

dinitrophenylhydrazine modified concretes with different ingredient ratios were prepared, and their properties were measured. Consequently, it was discovered that:

(i) The humidity was extremely low at 0.09%. The comparable surface area measured 3330 cm^2/g, with a specific gravity of 1.93 g/cm^3. The loss on ignition was 3%. These fly ash properties contributed to the successful creation of high-quality sulfur-2,4-dinitrophenylhydrazine modified concrete.

(ii) Fly ash properties also play a crucial role in producing high-quality sulfur-2,4-dinitrophenylhydrazine modified concrete. Table 9 displays various fly ash properties used in the preparation of sulfur-2,4-dinitrophenylhydrazine modified concrete. The silicon oxide content was 49%, significantly contributing to concrete strength enhancement.

(iii) Alterations in fly ash and sulfur-2,4-dinitrophenylhydrazine modification volumes impacted aggregate size. A 12.6:15.2 volume ratio between fly ash and sulfur-2,4-dinitrophenylhydrazine modification was deemed the best choice.

(iv) Sample 4 outperformed the others. Its maximum large aggregate size was 25 mm, and this type of large aggregate is recyclable.

Table 8. Choosing the appropriate ingredient proportions when preparing concrete.

Example	Large aggregate, (%)		Little aggregate, (%)		Modifier, (%)		Fly ash (%)		Size of large aggregate (mm)	Type of large aggregate	Duration (days)
	Volume	Mass	Volume	Mass	Volume	Mass	Volume	Mass			
№.1	35.2	39.7	30.0	32.1	27.4	22.1	5.8	5.3	19	Natural	3
№.2	35.2	39.6	30.0	32.1	27.4	22.1	5.8	5.3	19	Natural	3
№.3	35.2	38.8	30.0	31.9	18.2	15.2	13.9	12.6	19	Natural	3
№.4	35.2	33.0	30.0	33.6	18.1	15.3	13.9	14.9	25	Recycled	3
№.5	35.2	38.7	30.0	31.5	13.2	12.0	18.1	16.1	19	Natural	3

Table 9. Diverse properties of fly ash in the creation of sulfur-2,4-dinitrophenylhydrazine modified concrete.

Comparable surface, (cm^2/g)	Specific gravity, (g/sm^3)	Loss on fire, (%)	Humidity, (%)	SiO_2, (%)
3330	1.93	3.0	0.09	46

The chemical and physical traits resulting from sulfur-2,4-dinitrophenylhydrazine modification Table 10 affect the concrete's effectiveness. The fundamental qualities of the chosen modified concrete were evaluated. The sulfur-2,4-dinitrophenylhydrazine modifier acquired was a dark-brown powder with excellent solubility in CCl_4. This modifier did not dissolve in water-based solutions but demonstrated increased stability in the aqueous stage. The high viscosity of this modifier confirmed its ability to contribute to the creation of superior concrete. Additionally, the density and melting temperature of the sulfur-2,4-dinitrophenylhydrazine modifier further supported the production of efficient concrete.

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https://dx.doi.org/10.21123/bsj.2023.9038
P-ISSN: 2078-8665 - E-ISSN: 2411-7986
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Table 10. The chemical and physical attributes of sulfur-2,4-dinitrophenylhydrazine modifier.

Characteristics	Sulfur-2,4-dinitrophenylhydrazine modifier
Color and appearance	Yellow-brown powder
Solubility	Toluene
Viscosity	0.070
Liquefaction temperature, ^0C	130
Density, g/sm^3	2.140

Conclusion

In this study, a novel concrete type utilizing sulfur-2,4-dinitrophenylhydrazine modification was introduced, and its diverse characteristics were examined. A new sulfur-2,4-dinitrophenylhydrazine modifier was developed, and its structure was validated using IR spectroscopy and TG analysis. The surface texture of this modification was explored through SEM and EDS analyses. The innovative concrete was formulated with sulfur-2,4-dinitrophenylhydrazine modification and various components. This concrete's properties were determined, leading to the following key findings:

(i) Results demonstrated that the thermal expansion coefficient value for sulfur-2,4-dinitrophenylhydrazine modified concrete was $14.8\times10^{-6}/^0C$.

(ii) Smaller aggregate sizes led to denser concrete, measuring 2283 kg/m^3. Concrete density decreased gradually with increasing aggregate size. The average deformation of the examined concrete was 0.0026-0.0051, indicating superior deformation performance compared to traditional concretes.

(iii) The stability coefficient of sulfur-2,4-dinitrophenylhydrazine modified concrete against freezing was approximately 1.0.

(iv) Water absorption on the surface of sulfur-2,4-dinitrophenylhydrazine modified concrete ranged from 0.1-0.34%, and the concrete's water absorption coefficient was 0.85, signifying increased stability in aquatic and high-humidity settings.

(v) Sulfur-2,4-dinitrophenylhydrazine modified concrete displayed exceptional stability in various aggressive solutions.

(vi) SEM outcomes revealed a porous structure for the sulfur-2,4-dinitrophenylhydrazine modifier. EDS analysis showed carbon atoms accounting for 56.63% of the total mass, while sulfur composed 33.91% of the total mass.

(vii) The sulfur-2,4-dinitrophenylhydrazine modification experienced a one-step thermal mass loss, with the mass loss process being endothermic.

(viii) The valence vibrations of amino functional groups (associated with the phenyl ring) appeared at 3322 cm^{-1}. The peak at around 1607 cm^{-1} is associated with the C-N stretching vibration of the hydrazine group. The peak at around 1370 cm^{-1} is associated with the NO_2 bending mode of the 2,4-dinitrophenyl group. The IR signals corresponding to N-S bonds were identified at 1643 cm^{-1}. The formation of polymer sulfur chains is facilitated by S-S bonds, with IR signals in the 628 cm^{-1} range responsible for these bonds.

(i) Incorporating fly ash enhanced formability and strength. When 20% of the modified sulfur-2,4-dinitrophenylhydrazine was replaced with fly ash, the desired concrete exhibited easy formability and superior strength.

(ii) Larger and smaller fillers at a 35.2%:30% proportion were more effective in concrete formation.

In summary, the extensive investigations in this research signify the potential of sulfur-2,4-dinitrophenylhydrazine as a viable modifier for concrete.

Acknowledgment

Authors thanks Karshi Institute of Engineering Economics and Termez State University, Uzbekistan

Authors' Declaration

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any Figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in Karshi Institute of Engineering Economics and Termez State University, Uzbekistan.

Authors' Contribution Statement

K.T: Drafting the MS; D.Sh.: Conception, design, drafting the MS; N.A.: Acquisition of data; M.H.Sh.: Interpretation; E.B.: Conception, design, drafting the MS, revision and proofreading; N.B.: Revision and Proofreading; A.H.-B.: Revision and Proofreading

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2023, 20(6 Suppl.): 2414-2433
https://dx.doi.org/10.21123/bsj.2023.9038
P-ISSN: 2078-8665 - E-ISSN: 2411-7986
Baghdad Science Journal

استخدام الكبريت -2.4-دينيتروفينيل هيدرازين كمادة معدلة لإنتاج خرسانة مفيدة جديدة

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الخلاصة

في هذا المسعى الاستقصائي ، تم تطوير نوع جديد من الخرسانة يشتمل على تعديل الكبريت -2.4-ثنائي نيتروفينيل هيدرازين ، وتم استكشاف خصائصه المتنوعة. تم إنتاج هذه الخرسانة المبتكرة عن طريق تعديل الكبريت -2.4-ثنائي نيتروفينيل هيدرازين ومجموعة من المكونات. تم تصنيع الكبريت -4،2-دينيتروفينيل هيدرازين المعدّل والذي تم إنشاؤه حديثًا . تم فحص نسيج السطح الناتج باستخدام تقنيات SEM و EDS. تم احتساب نسب المكونات و الصفات الخرسانية والكيميائية والفيزيائية المشتقة من الكبريت -2.4-ثنائي نيتروفينيل هيدرازين المعدل ، المقاومة الكيميائية ومقاومة التآكل للخرسانة ، ثبات الخرسانة ضد امتصاص الماء ، مقاومة الخرسانة ضد التجمد ، الخصائص الفيزيائية والميكانيكية ، المتانة ، معامل المرونة ، وتم تقييم معامل التمدد الحراري للخرسانة المشبعة بالكبريت. أثبتت النتائج أن قيمة معامل التمدد الحراري للخرسانة المعدلة للكبريت -2.4-دينيتروفينيل هيدرازين كانت 14.8 × 10-6.0 درجة مئوية. كان متوسط التشوه للخرسانة التي تم تحليلها 0.0026-0.0051 ، مما يشير إلى أداء تشوه متفوق مقارنة بالخرسانة التقليدية. أظهرت الخرسانة ذات الأحجام التراكمية الأصغر كثافة أكبر، 2283 كجم / م 3. تناقصت كثافة الخرسانة تدريجياً مع زيادة حجم الركام. كان ثبات الخرسانة المعدلة الكبريت -2 ، 4-دينيتروفينيل هيدرازين مرتفعًا بشكل ملحوظ في مختلف البيئات غير المناسبة . كشف تحليل EDS أن ذرات الكربون شكلت 56.63٪ من الكتلة الكلية ، بينما شكل الكبريت 33.91٪ من الكتلة الكلية. أظهرت نتائج SEMالتي تم الحصول عليها أن معدل الكبريت -2.4-ثنائي نيتروفينيل هيدرازين أظهر بنية مسامية أكثر ، خالية من التكوينات البلورية. شهد تعديل الكبريت -2 ، 4-دينيتروفينيل هيدرازين خسارة الكتلة الحرارية على مرحلة واحدة ، مع فقدان الكتلة التي تكون ماصة للحرارة بطبيعتها. تحققت نتائج الأشعة تحت الحمراء من وجود مجموعات وظيفية أمينية (حلقة ميلامين متصلة) وإنشاء سلاسل كبريت بوليمر.

الكلمات المفتاحية: التشوه ، المرونة ، الخرسانة الكبريتية ، معامل التمدد الحراري ، 4،2-دينيتروفينيل هيدرازين.