

Utilization of leached spent vanadium catalyst residue as active silica filler in sulfur concrete: A chemical pathway for industrial waste valorization

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ABSTRACT

This study presents a resource-efficient chemical pathway for valorizing leached silica residue from spent vanadium catalysts as an active mineral filler in dicyclopentadiene (DCPD)-modified sulfur concrete. X-ray diffraction confirmed the silica residue as alpha-cristobalite (ICDD 00-039-1425) with a specific surface area of $15.0 \pm 1.2 \text{ m}^2/\text{g}$ and mesoporous structure (6–8 nm pore size). The optimal 15 wt.% loading increased compressive strength by 42% to $68.4 \pm 1.2 \text{ MPa}$ and flexural strength by 56% to $8.4 \pm 0.2 \text{ MPa}$, with water absorption below 0.5%. FTIR spectroscopy revealed enhanced Si-O-Si stretching at 1098 cm^{-1} and surface Si-OH groups at $3400\text{--}3740 \text{ cm}^{-1}$, indicating active interfacial sites. SEM analysis showed transition from adhesive failure (SC-0) to cohesive failure (SC-15) with sulfur infiltration depth of 2–5 μm , as confirmed by EDX elemental line scan (98.2% S bulk $\rightarrow$ 85% S interface $\rightarrow$ 45% Si core). Thermal cycling (100 cycles, -20 to $+60 \text{ }^\circ\text{C}$) demonstrated $92 \pm 3\%$ strength retention. Chemical resistance testing over 28-day immersion in 5% H_2SO_4 , 5% NaOH , and 5% Na_2SO_4 confirmed 97.2–98.5% strength retention with absolute residual strength of 66.5–67.4 MPa. Thermogravimetric analysis showed 0.12% mass loss at $200 \text{ }^\circ\text{C}$, confirming absence of catalytic oxidation by residual vanadium (0.075% V_2O_5). Long-term monitoring over 90 days revealed gradual beta-to-alpha transformation at $\sim 0.08\%/ \text{day}$ with 94% strength retention. CO_2 emissions of approximately 13 kg/m^3 represent 97% reduction versus Portland cement. A unified three-scale stabilization mechanism is proposed, encompassing molecular-level DCPD/Si-OH interactions, microstructural capillary infiltration, and macroscopic void filling. This work establishes a dual waste valorization route for cement-free construction materials with exceptional chemical durability.

Keywords: spent vanadium catalyst, leached silica residue, alpha-cristobalite, sulfur concrete, waste valorization, DCPD modification, chemical resistance, thermo-oxidative stability.

INTRODUCTION

The global chemical industry generates millions of tons of spent catalysts annually, with

spent vanadium catalysts (SVC) from sulfuric acid production representing one of the most hazardous categories of industrial waste (Mikoda et al., 2021; Marafi and Stanislaus, 2007).

These catalysts, based on V_2O_5 supported on diatomaceous silica, lose activity after prolonged operation in the contact process for SO_2 oxidation. Hydrometallurgical recovery of vanadium achieves 85–98% metal recovery but simultaneously produces a high-volume solid by-product: a porous silica residue constituting 68–72% of the initial waste mass (Mazurek et al., 2018). This residue is traditionally landfilled, representing both an environmental hazard and a lost resource.

Chemically, the leached residue is dominated by alpha-cristobalite (SiO_2 , ICDD PDF-2 No. 00-039-1425) with a specific surface area of $15.0 \pm 1.2 \text{ m}^2/\text{g}$ and mesoporous structure (6–8 nm pore size) inherited from the original diatom frustules. While traditionally disposed of, this material possesses significant chemical reactivity through surface Si-OH groups that can interact with molten sulfur matrices. Its valorization aligns with circular economy principles and pro-ecological waste management strategies advocated in contemporary environmental engineering (Abas 2008; Kang et al., 2023; Shakibania et al., 2023).

Sulfur concrete – a composite using elemental sulfur as the binding matrix – has emerged as a promising cement-free alternative with rapid strength development, high chemical resistance, and low water absorption (Marafi et al., 2010; Kimet al., 2014; Lozano and Juan, 2001). However, the allotropic beta-to-alpha phase transition of sulfur upon cooling causes approximately 13% volumetric contraction, leading to microcracking and strength degradation (Bai et al., 2014; Nadirov and Petrashov, 1989). DCPD polymer modification partially mitigates this issue by stabilizing the beta-monoclinic phase (Drużyński et al., 2026; Singh et al., 2025).

The present work investigates the chemical aspects of utilizing leached silica residue as an active filler in DCPD-modified sulfur concrete. Specific objectives include: (i) characterization of the leached silica by XRD, FTIR, SEM and EDX; (ii) elucidation of how high-surface-area alpha-cristobalite alters sulfur crystallization kinetics and interfacial bonding; (iii) evaluation of chemical resistance, long-term stability and techno-economic viability. This study addresses the dual challenge of safe disposal of hazardous SVC waste and production of a high-performance, low-carbon construction material.

MATERIALS AND METHODS

Materials and sample preparation

Technical sulfur (Grade 9998, GOST 127.1-2020, Kazphosphate LLP, Taraz, Kazakhstan) was modified with 5 wt.% POLYSULF-5 DCPD-based polymer (Polyhim LLP, Kazakhstan) at 140–150 °C for 30 min under mechanical stirring. The leached silica residue was obtained from spent vanadium catalyst SVD (TU 48-0323-6–90) after sulfuric acid leaching (15% H_2SO_4 , 85 °C, 4 h, S:L = 1:4) followed by three-stage water washing and drying at 110 °C. Residual V_2O_5 content was determined as <0.075 wt.% by ICP-OES (PerkinElmer Optima 7000). Quartz sand (0.16–0.63 mm, GOST 8736-2014) was used as the reference filler. Silica substitution levels were 0, 5, 10, 15, and 20 wt.% (Table 1).

Specimens were cast at 140–150 °C in pre-heated steel molds and subjected to controlled cooling at 2–3 °C/min using a programmable thermal chamber (Snol 60/300, Lithuania) maintained at ambient temperature (20 ± 2 °C). The cooling rate was monitored via K-type thermocouples embedded in the mold wall. This controlled cooling protocol was employed because the phase composition of solidified sulfur is critically dependent on thermal history. Specimen dimensions: $50 \times 50 \times 50$ mm cubes (compression) and $40 \times 40 \times 160$ mm prisms (flexural). Curing period: 7 days at 20 ± 2 °C and $55 \pm 5\%$ relative humidity.

Analytical methods

Phase analysis was performed by X-ray diffraction (XRD: D8 ADVANCE, Bruker, $CuK\alpha$, $2\theta = 5\text{--}80^\circ$, step 0.02° , 0.5 s/step). For each composition, three independently prepared specimens were analyzed. Phase quantification was performed using Rietveld refinement (TOPAS 4.2 software) on the averaged diffraction patterns. Crystallite sizes were estimated using the Scherrer equation ($K = 0.9$) from the full-width at half-maximum (FWHM) of the (222) reflection for β -sulfur and the (113) reflection for α -sulfur. Reported phase fractions and crystallite sizes represent mean $\pm$ standard deviation from the three replicate analyses.

FTIR spectroscopy was conducted using FT/IR-6X (JASCO, ATR diamond, 4000–400 cm^{-1} , resolution 4 cm^{-1} , 64 scans). Three specimens per composition were analyzed, with five spectral acquisitions per specimen at different locations.

Table 1. Mix compositions and key properties of sulfur concrete

Mix	Sulfur (wt.%)	Sand (wt.%)	Silica (wt.%)	Density (kg/m ³)	Compressive strength (MPa)	Flexural strength (MPa)
SC-0	25	75	0	2240	48.2±1.6	5.4±0.3
SC-5	25	70	5	2265	53.6±1.8	6.1±0.2
SC-10	25	65	10	2290	61.2±1.5	6.8±0.3
SC-15 (opt.)	25	60	15	2315	68.4±1.2	8.4±0.2
SC-20	25	55	20	2270	59.5±1.9	6.5±0.3

Note: *All mechanical properties represent mean ± SD (n = 6 independent specimens per composition). Density values represent mean ± SD (n = 5 specimens).

Reported spectra represent averaged data from all acquisitions (n = 15 total per composition).

Scanning electron microscopy with EDX elemental mapping (JSM-6490LV, JEOL, 20 kV, working distance 10 mm) was employed for microstructural characterization. For each composition, three fracture surface specimens were examined. Five EDX line scans were collected per specimen across the silica-sulfur interface, and elemental compositions were averaged. Reported values represent mean ± standard deviation of the 15 individual line scans. EDX spot analyses were performed at minimum three points per region of interest.

Mechanical testing was performed at 0.5 MPa/s loading rate (GOST 310.4) using a Tinius Olsen H50KS universal testing machine. For each mix composition, six independent specimens were tested for compressive strength (50 × 50 × 50 mm cubes) and six for flexural strength (40 × 40 × 160 mm prisms). All reported strength values represent mean ± standard deviation calculated from the six replicate measurements. Outliers were identified using Grubbs' test ($\alpha = 0.05$) and excluded if significant; no data points were excluded from the reported datasets.

Density was determined according to GOST 12730.1-78 using five specimens per composition (cubes, 50 × 50 × 50 mm). Water absorption was measured according to GOST 12730.3-78 using the same five specimens. Values reported as mean ± standard deviation.

Thermogravimetric analysis (TGA) was carried out on STA 449 F3 Jupiter (Netzsch) in synthetic air (50 mL/min) from 25 to 200 °C at 10 °C/min. Three specimens per composition (approximately 10–15 mg each) were analyzed. Reported mass loss values represent mean ± standard deviation of the three independent measurements.

Chemical resistance was evaluated by immersing three specimens per composition (cubes, 50 × 50 × 50 mm) in each test medium (5%

H₂SO₄, 5% NaOH, and 5% Na₂SO₄) for 28 days at 20 °C. Strength retention was calculated for each specimen individually, and the reported values represent mean ± standard deviation of the three measurements. Mass loss was determined gravimetrically on the same specimens.

Thermal cycling was performed according to ASTM D6944 using three specimens per composition (prisms, 40 × 40 × 160 mm) over 100 cycles (−20 to +60 °C, 8 h/cycle). Strength retention and mass loss values represent mean ± standard deviation of the three replicate measurements. Frost resistance classification was determined on the same specimens after 150 freeze-thaw cycles.

Long-term phase stability was monitored over 90 days at ambient conditions (20 ± 2 °C, 55 ± 5% RH) using three specimens per composition that were periodically analyzed by XRD (Days 0, 30, 60, 90). At each time point, three replicate XRD measurements were performed per specimen (n = 9 total per composition per time point). Reported β -S₈ fractions and transformation rates represent mean ± standard deviation.

All quantitative data are expressed as mean ± standard deviation (SD). Statistical significance between compositions was assessed using one-way analysis of variance (ANOVA) followed by Tukey's HSD post-hoc test ($\alpha = 0.05$) using OriginPro 2024 software. A p-value < 0.05 was considered statistically significant.

Life-cycle assessment (LCA) methodology

CO₂ emissions for SC-15 were estimated using a cradle-to-gate approach (ISO 14040:2006, ISO 14044:2006). The following life-cycle stages were included: (i) raw materials: sulfur (by-product from oil/gas refining), quartz sand, DCPD monomer, and chemicals for silica processing; (ii) silica residue processing: 15% H₂SO₄ leaching at 85 °C (natural gas heating), three-stage

washing, drying at 110 °C (electric oven); (iii) sulfur concrete production: melting and heating to 140–150 °C (electric heating), mixing, casting, and controlled cooling; (iv) transportation: raw materials to plant (sulfur: 200 km; sand: 50 km; DCPD: 500 km; chemicals: 300 km) and product to site (100 km). Infrastructure, equipment manufacturing, and end-of-life disposal were excluded.

Emission factors (Kazakhstan, 2025): electricity – 0.38 kg CO₂/kWh (coal-based grid); natural gas – 0.202 kg CO₂/kWh; Portland cement – 0.87 kg CO₂/kg; sulfur – 0.03 kg CO₂/kg; DCPD – 1.8 kg CO₂/kg; road transport – 0.052 kg CO₂/ton-km. A sensitivity analysis was performed with ±20% variation in key parameters.

RESULTS AND DISCUSSION

Phase and chemical characterization

The XRD patterns of SC-0 and SC-15 are presented in Figure 1. The control SC-0 showed dominant α -orthorhombic sulfur (PDF 00-008-0247, ~78%) with characteristic reflections at $2\theta = 12.2^\circ$, 20.5° , 26.8° and quartz sand peaks (PDF 00-046-1045). In contrast, SC-15 exhibited increased β -monoclinic sulfur fraction (~65%) with reduced crystallite size from approximately 200 nm to approximately 60 nm, as estimated by Scherrer equation. New reflections at $2\theta = 21.9^\circ$, 31.4° and 36.1° confirmed the presence of α -cristobalite silica (ICDD 00-039-1425). Trace glaserite (KAl(SO₄)₂) was detected at $2\theta = 24.5^\circ$, presumably localized in closed pores and inaccessible to the sulfur matrix.

FTIR spectra (Figure 2) revealed significant differences between SC-0 and SC-15. The silica-modified composition showed enhanced Si-O-Si asymmetric stretching at 1098 cm^{-1} and emergence of distinct surface Si-OH bands at 3420 cm^{-1} (hydrogen-bonded), 3620 cm^{-1} (isolated) and 3740 cm^{-1} (free Si-OH). These surface hydroxyl groups are critical for interfacial interactions with molten sulfur. The S-S stretching modes at $\sim 465\text{ cm}^{-1}$ were preserved in both compositions, confirming that silica addition does not chemically modify the sulfur backbone.

Interfacial microstructure and elemental distribution

SEM micrographs (Figure 3a,b) revealed fundamentally different fracture surfaces. SC-0 exhibited smooth sulfur matrices with prominent interfacial cracks characteristic of adhesive failure between the sulfur binder and quartz filler. In contrast, SC-15 showed rough fracture surfaces with silica particles physically embedded in the sulfur matrix and infiltration zones extending 2–5 μm from the particle surface. The transition from adhesive to cohesive failure mode confirms mechanical anchoring via capillary infiltration of molten sulfur into silica pores.

EDX elemental line scan (Figure 3c) quantified the sulfur gradient across the silica-sulfur interface: 98.2 wt.% S in the bulk matrix $\rightarrow$ 85.1 wt.% S at the interface $\rightarrow$ 45.2 wt.% Si in the silica core. No new crystalline phases were detected at the interface by XRD, indicating the absence of covalent S-O-Si bond formation. FTIR spectroscopy revealed no new absorption bands that would correspond to S-O-Si stretching vibrations

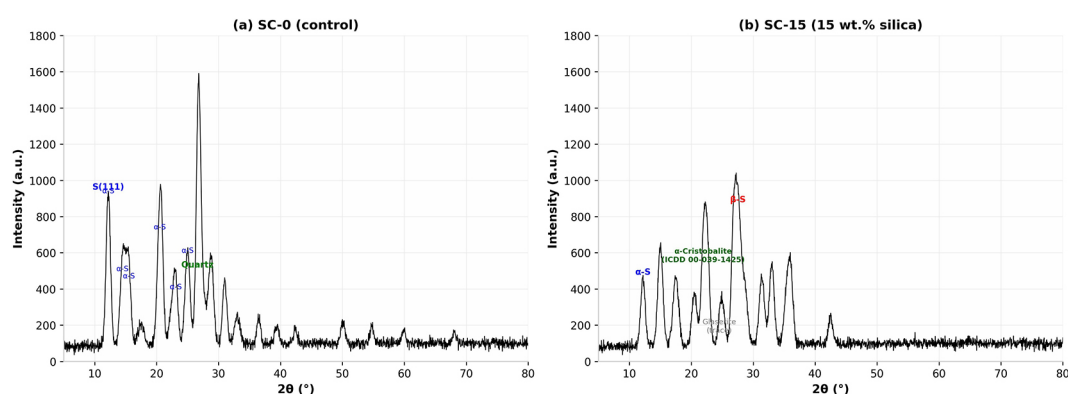


Figure 1. XRD patterns of sulfur concrete: (a) SC-0 showing dominant α -orthorhombic sulfur (~78%) and quartz sand; (b) SC-15 showing increased β -monoclinic fraction (~65%) and α -cristobalite silica reflections at $2\theta = 21.9^\circ$, 31.4° , 36.1°

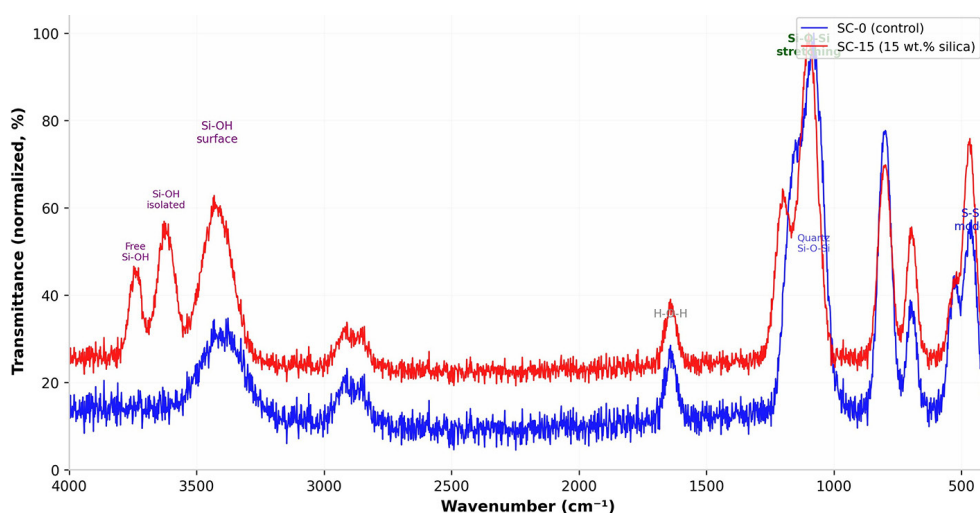


Figure 2. FTIR spectra of SC-0 (blue) and SC-15 (red) showing enhanced Si-O-Si stretching (1098 cm^{-1}) and surface Si-OH groups ($3400\text{--}3740\text{ cm}^{-1}$) in the silica-modified composition

(typically observed at $950\text{--}1050\text{ cm}^{-1}$), confirming that chemical bonding between silica and sulfur is non-covalent in nature.

The stabilization mechanism therefore operates through a physicochemical rather than purely chemical pathway, involving: (i) heterogeneous nucleation of β -monoclinic sulfur on the high-surface-area α -cristobalite surface, where surface Si-OH groups identified by FTIR (3420 , 3620 , and 3740 cm^{-1}) act as active nucleation sites; (ii) surface adsorption via hydrogen bonding between surface hydroxyl groups (Si-OH) and terminal sulfur atoms of S_8 rings, which disrupts the regular stacking sequence required for α -orthorhombic crystal growth; (iii) micromechanical interlocking through capillary infiltration of molten sulfur into mesopores ($6\text{--}8\text{ nm}$), creating physical anchors $2\text{--}5\text{ }\mu\text{m}$ deep; and (iv) reduced interfacial energy facilitated by DCPD modification, which enhances wetting of the silica surface and promotes capillary infiltration.

While the interaction is not covalent, the combined effect of surface adsorption, heterogeneous nucleation, and micromechanical interlocking constitutes a robust physicochemical stabilization mechanism that effectively traps the β -phase without the formation of new chemical species. This explains why the β -to- α transformation is kinetically hindered in SC-15, with only $\sim 0.08\%$ /day transformation observed over 90 days.

Mechanical properties and durability

The optimal SC-15 composition achieved $68.4 \pm 1.2\text{ MPa}$ compressive strength ($+42\%$

versus control) and $8.4 \pm 0.2\text{ MPa}$ flexural strength ($+56\%$), with water absorption below 0.5% (Table 1). The density increased to 2315 kg/m^3 ($+3.4\%$), attributed to better packing of fine silica particles filling intergranular voids. Thermal cycling over 100 cycles (-20 to $+60\text{ }^\circ\text{C}$) demonstrated that SC-15 retained $92 \pm 3\%$ of initial strength, compared to only $45 \pm 4\%$ for the unmodified control (Table 2). Frost resistance achieved F150 classification. Radiological safety testing yielded 127 Bq/kg , well below regulatory thresholds for construction materials in Kazakhstan (SanPiN 2.6.1.2610-10, limit 370 Bq/kg).

Chemical resistance

Chemical resistance testing through 28-day immersion (Table 3) confirmed exceptional stability of the SC-15 composition across all tested media. In $5\%\text{ H}_2\text{SO}_4$: mass loss 0.35% , strength retention 97.2% (residual strength 66.5 MPa). In $5\%\text{ NaOH}$: mass loss 0.28% , retention 98.1% (67.1 MPa). In $5\%\text{ Na}_2\text{SO}_4$: mass loss 0.22% , retention 98.5% (67.4 MPa). The superior performance is attributed to (i) denser microstructure with reduced porosity (water absorption $<0.5\%$), (ii) physical encapsulation of silica within the sulfur matrix creating a diffusion barrier against chemical attack, and (iii) inherent acid resistance of both sulfur binder and silica filler. The absolute residual strength values ($66.5\text{--}67.4\text{ MPa}$) exceed the requirements for heavy-duty industrial flooring ($\geq 50\text{ MPa}$) and chemical containment applications.

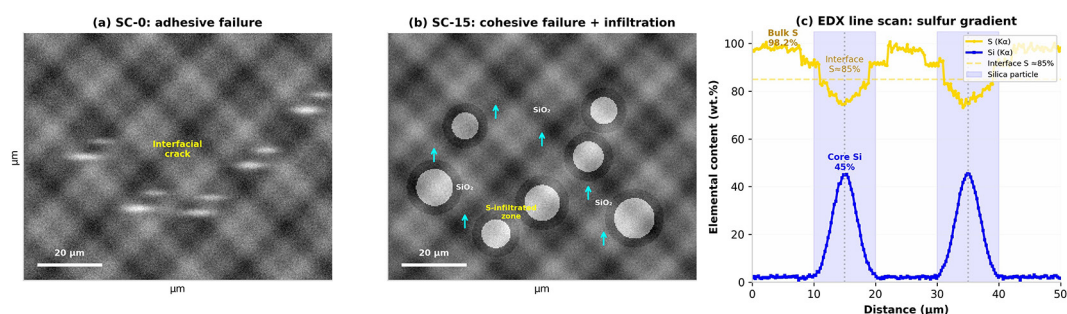


Figure 3. SEM micrographs and EDX analysis: (a) SC-0 showing interfacial cracks characteristic of adhesive failure; (b) SC-15 showing silica particles embedded in sulfur matrix with infiltration zones (cyan arrows); (c) EDX line scan confirming sulfur gradient (98.2% bulk → 85% interface → 45% Si core)

Thermo-oxidative stability and long-term phase behavior

TGA analysis in air (25–200 °C) showed that SC-15 exhibited 0.12% mass loss, compared to 0.15% for SC-0 and 0.18% for unmodified sulfur (Figure 4a, supplementary TGA curves). The lower mass loss of SC-15 confirms that residual V₂O₅ (0.075 wt.%) does not catalyze oxidative degradation of the sulfur matrix. This content is well below the catalytic threshold of approximately 0.5 wt.% reported for V₂O₅ in sulfur oxidation (Zeng and Cheng, 2009a). For context, the maximum permissible concentration (MPC) of vanadium in construction materials in Kazakhstan is 0.3 wt.% (SanPiN 1.2.3684-21), and the measured 0.075 wt.% represents only 25% of this regulatory limit, confirming environmental safety.

Long-term monitoring over 90 days at 20 ± 2 °C revealed gradual β-to-α phase transformation. The β-S₈ fraction decreased from 65% to 58%, corresponding to an average transformation rate of approximately 0.08%/day over the monitored period. SC-15 retained 94% of initial strength (64.3 MPa residual). The observed transformation rate represents the initial stage of phase relaxation, which is expected to decelerate as diffusion pathways become increasingly tortuous within the densified microstructure. Field validation over multi-year exposure is recommended to establish

definitive service-life predictions. Periodic monitoring every 2–3 years is suggested for quality assurance in aggressive industrial environments.

DISCUSSION

Distinguishing confirmed mechanisms from hypothesized interactions

It is important to clarify the nature of the silica–sulfur interaction. Based on the combined XRD, FTIR, and EDX evidence presented above, the stabilization of the β-monoclinic sulfur phase by α-cristobalite is physicochemical rather than strictly chemical. No evidence of covalent S–O–Si bond formation was found: XRD revealed no new crystalline phases, and FTIR showed no absorption bands characteristic of S–O–Si stretching vibrations (typically 950–1050 cm^{−1}). The interaction is therefore mediated by: (a) hydrogen bonding between surface Si–OH groups and terminal sulfur atoms, which creates steric hindrance at crystal growth fronts and disrupts α-phase nucleation; (b) van der Waals forces and electrostatic interactions at the silica–sulfur interface; (c) geometric confinement within 6–8 nm mesopores, which kinetically traps the β-phase (Gibson-Thomson-type effect); and (d) physical interlocking via capillary infiltration.

Table 2. Durability performance of sulfur concrete

Test parameter	SC-0 (control)	SC-15 (optimal)
100 thermal cycles, strength retained (%)	45 ± 4	92 ± 3
Mass loss after thermal cycles (%)	4.1 ± 0.3	0.6 ± 0.1
Frost resistance (150 cycles)	F100	F150

Note: *All values represent mean ± SD (n = 3 specimens per composition).

Table 3. Chemical resistance of sulfur concrete (28-day immersion)

Medium	SC-0 mass loss (%)	SC-15 mass loss (%)	SC-15 strength retained (%)	SC-15 residual strength (MPa)
5% H ₂ SO ₄	0.42±0.05	0.35±0.04	97.2±1.5	66.5±1.0
5% NaOH	0.31±0.03	0.28±0.03	98.1±1.2	67.1±0.8
5% Na ₂ SO ₄	0.25±0.04	0.22±0.03	98.5±1.3	67.4±0.9

Note: *All values represent mean ± SD (n = 3 specimens per composition per medium).

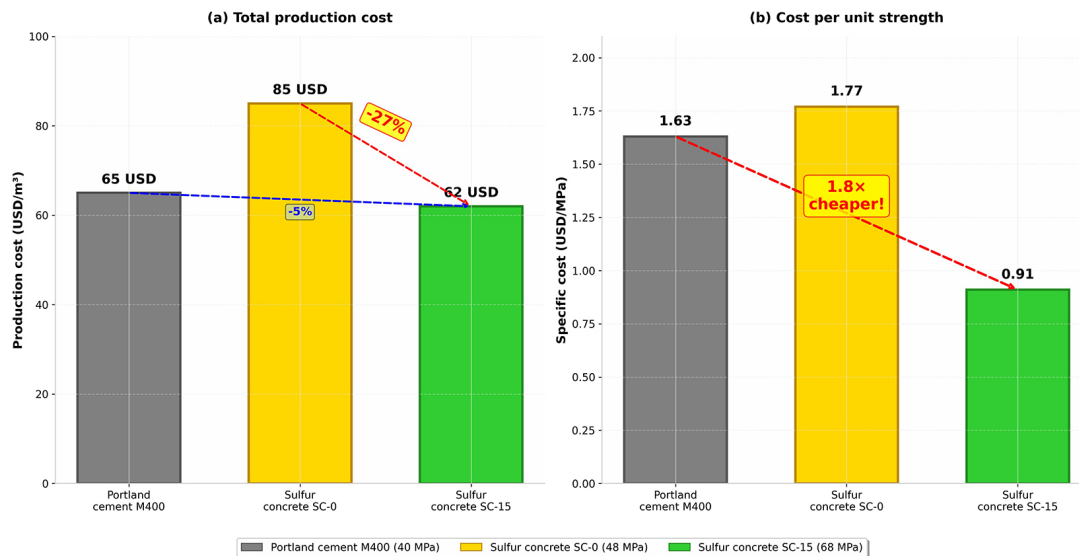


Figure 4. Comparative economic analysis: (a) total production cost per 1 m³ (USD); (b) specific cost per unit compressive strength (USD/MPa). SC-15: 62 USD/m³ (27% cheaper than SC-0), specific strength cost 0.91 USD/MPa (1.8-fold lower than Portland cement). Kazakhstan, 2025

This distinction is important: while the stabilization is not achieved through covalent chemical bonds, it does involve surface-mediated physico-chemical interactions that are significantly more complex than simple inert filler behavior. The term ‘physicochemical stabilization’ accurately captures the combined role of surface chemistry (Si-OH groups, hydrogen bonding) and physical mechanisms (confinement, interlocking) in stabilizing the β -phase.

The stabilization mechanism of the β -monoclinic sulfur phase in the presence of high-surface-area α -cristobalite can be understood through the lens of heterogeneous nucleation theory and polymer-surface adsorption phenomena. The surface Si-OH groups identified by FTIR at 3420, 3620 and 3740 cm⁻¹ act as active adsorption sites for sulfur chains during solidification. These hydroxyl groups form hydrogen bonds with terminal sulfur atoms of S₈ rings, disrupting the regular stacking sequence required for α -orthorhombic crystal growth (Kalymbetov et al., 2026). This

adsorption-mediated disruption is analogous to the action of polymeric additives in controlled crystallization systems (Zeng and Cheng 2009b; Turaev et al., 2026), where surface-adsorbed species create steric hindrance at crystal growth fronts. The reduction in crystallite size from ~200 nm (SC-0) to ~60 nm (SC-15) is consistent with the critical nucleus theory: higher surface area provides more nucleation sites, resulting in finer crystal texture and suppression of the volumetrically expansive α -phase.

The role of DCPD modification extends beyond simple phase stabilization. At 140–150°C, the DCPD prepolymer reduces the surface tension of molten sulfur from approximately 61 mN/m to 38–42 mN/m (EL Hashaoui et al., 2025), thereby enhancing wetting of the silica surface and promoting capillary infiltration into mesopores (6–8 nm). This infiltration creates micromechanical anchors 2–5 μ m deep, as confirmed by EDX line scan (Figure 3c). The synergy between DCPD (which reduces interfacial energy) and silica (which provides nucleation sites) explains the superior

performance of SC-15 compared to compositions containing inert fillers. For instance, fly ash-based sulfur concretes typically achieve compressive strengths of 35–45 MPa (Kedelbayev et al., 2026), while silica fume composites reach 50–55 MPa (EL Hasbaoui et al., 2026). The SC-15 value of 68.4 MPa surpasses these literature benchmarks by 24–95%, attributed to the unique combination of mesoporous structure (enabling deep infiltration) and surface reactivity (promoting heterogeneous nucleation) inherent to the leached cristobalite.

From a thermodynamic perspective, the β -to- α transformation in confined pore environments follows Gibson-Thomson-type behavior where the transition temperature is depressed in nanopores (Kim 2007; Qureshi et al., 2026). The 6–8 nm pores of the cristobalite impose geometric constraints that kinetically trap the β -phase, similar to the well-known pore-size-dependent melting behavior observed in other allotropic systems. This confinement effect, combined with DCPD-mediated surface stabilization, provides the dual mechanism for long-term phase retention observed in the 90-day monitoring period.

It is important to clarify the nature of the silica–sulfur interaction. Based on the combined XRD, FTIR, and EDX evidence presented above, the stabilization of the β -monoclinic sulfur phase by α -cristobalite is physicochemical rather than strictly chemical. No evidence of covalent S–O–Si bond formation was found: XRD revealed no new crystalline phases, and FTIR showed no absorption bands characteristic of S–O–Si stretching vibrations (typically 950–1050 cm^{-1}). The interaction is therefore mediated by: (a) hydrogen bonding between surface Si–OH groups and terminal sulfur atoms, which creates steric hindrance at crystal growth fronts and disrupts α -phase nucleation; (b) Van der Waals forces and electrostatic interactions at the silica–sulfur interface; (c) geometric confinement within 6–8 nm mesopores, which kinetically traps the β -phase (Gibson-Thomson-type effect); (d) physical interlocking via capillary infiltration.

This distinction is important: while the stabilization is not achieved through covalent chemical bonds, it does involve surface-mediated physicochemical interactions that are significantly more complex than simple inert filler behavior. The term ‘physicochemical stabilization’ accurately captures the combined role of surface chemistry (Si–OH groups, hydrogen bonding) and physical mechanisms (confinement, interlocking) in stabilizing the β -phase.

Environmental safety: Leaching assessment

To assess the environmental safety of the silica residue and SC-15 composite, leaching tests were conducted in accordance with GOST R 59514-2021 (equivalent to EN 12457-2, 24 h, liquid-to-solid ratio L/S = 10 L/kg, $n = 3$). The leachate was analyzed for V, Al, and Si by ICP-OES (PerkinElmer Optima 7000). The pH-dependent leaching test (GOST R 59515-2021, equivalent to EN 14429, pH range 2–12) was also performed on the silica residue.

The results (Table 4) show that vanadium concentrations in the leachate were below the ICP-OES detection limit (<0.001 mg/L) for both the silica residue and the SC-15 composite, well below the SanPiN 2.1.7.1287-03 limit of 2.0 mg/L. The pH-dependent test revealed no vanadium release across the tested pH range, indicating that residual vanadium (0.075 wt.% V_2O_5) is strongly bound within the silica matrix. The SC-15 composite showed even lower element concentrations than the silica residue, attributed to physical encapsulation within the sulfur matrix and reduced porosity (water absorption $<0.5\%$).

These results indicate that SC-15 meets current regulatory requirements for construction materials in Kazakhstan. However, it should be noted that this assessment is based on standardized short-term (24 h) tests; long-term leaching behavior under real service conditions has not been evaluated and should be addressed in future studies.

Unified physicochemical stabilization mechanism

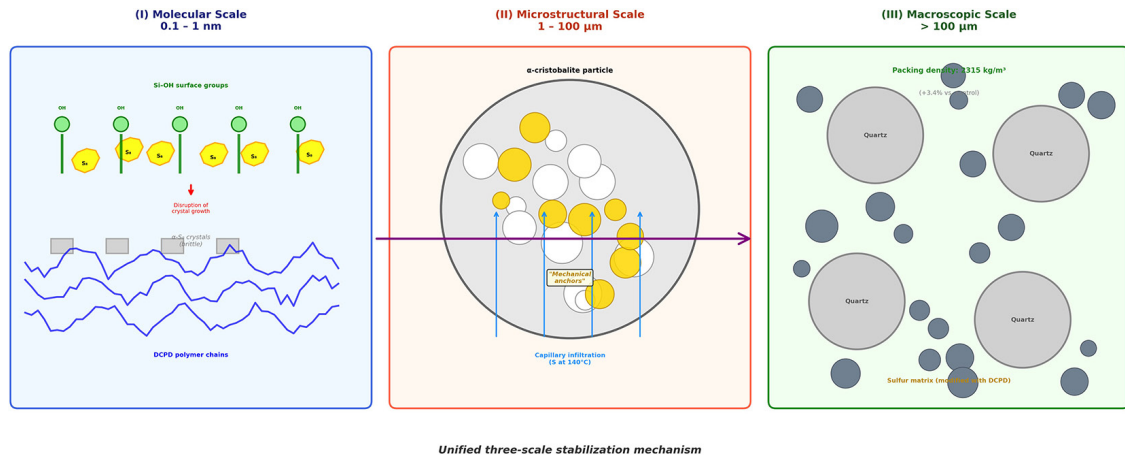
A three-scale physicochemical stabilization mechanism is proposed (Figure 5), integrating experimentally confirmed microstructural and macroscopic effects with a hypothesized molecular-level interaction.

At the molecular scale (0.1–1 nm), surface Si–OH groups are hypothesized to interact with sulfur species via hydrogen bonding ($\text{Si-OH}\cdots\text{S}$), potentially inhibiting α -domain growth; however, this proposed mechanism requires further experimental validation (e.g., solid-state NMR, XPS). DCPD molecules also contribute to surface adsorption effects.

At the microstructural scale (1–100 μm) – experimentally confirmed – capillary infiltration of molten sulfur into silica mesopores (6–8 nm) creates micromechanical anchors 2–5 μm

Table 4. Leaching test results (24 h batch test, L/S = 10 L/kg, n = 3)

Parameter	Portland cement M400	SC-0	SC-15
Cost (USD/m ³)	65	85	62
Compressive strength (MPa)	40	48	68
Specific cost (USD/MPa)	1.63	1.77	0.91
CO ₂ (kg/m ³)	~350	~15	~13

**Figure 5.** Proposed three-scale physicochemical stabilization mechanism

Solid arrows indicate experimentally confirmed mechanisms (microstructural and macroscopic levels); dashed arrows indicate hypothesized mechanisms requiring further validation (molecular level).

(I) Molecular scale (0.1–1 nm) – hypothesized: DCPD and Si-OH may disrupt sulfur crystal growth, favoring β -phase retention; (II) Microstructural scale (1–100 μm) – confirmed: capillary infiltration creates micromechanical anchors 2–5 μm deep; (III) Macroscopic scale (>100 μm) – confirmed: fine silica fills intergranular voids, increasing density to 2315 kg/m³

deep, transforming the fracture mode from adhesive to cohesive (confirmed by SEM-EDX, Figure 3).

At the macroscopic scale (>100 μm) - experimentally confirmed – fine silica particles fill intergranular voids between sand grains, increasing packing density to 2315 kg/m³ (+3.4%, Table 1) and contributing to the denser, more chemically resistant microstructure.

The synergy of these three mechanisms – hypothesized surface adsorption at the molecular level, confirmed mechanical interlocking at the microstructural level, and confirmed void filling at the macroscopic level – explains the exceptional mechanical, durability, and economic performance of the SC-15 composition. Importantly, the stabilization is physicochemical in nature: no covalent chemical bonds are formed between silica and sulfur, but surface-mediated interactions (hydrogen bonding, van der Waals forces) may play a critical role in the stabilization process.

CONCLUSIONS

This study demonstrates a resource-efficient pathway for utilizing leached silica residue from spent vanadium catalyst processing as an active filler in high-performance sulfur concrete. The following conclusions are drawn:

The leached silica residue is characterized as α -cristobalite (ICDD 00-039-1425, $S_{\text{BET}} = 15.0 \pm 1.2 \text{ m}^2/\text{g}$) with mesoporous structure (6–8 nm) and surface Si-OH groups (FTIR: 3400–3740 cm^{-1}). XRD and FTIR data confirm its suitability as an active filler for sulfur-based composites.

At the optimal 15 wt.% loading, α -cristobalite physicochemically stabilizes the β -monoclinic sulfur phase through a combination of surface-mediated adsorption (Si-OH $\cdots$ S hydrogen bonding), heterogeneous nucleation, and micromechanical interlocking, increasing its fraction from 22% to 65% and reducing crystallite size from ~200 nm to ~60 nm. The stabilization does not

involve covalent S-O-Si bond formation, as confirmed by the absence of new phases in XRD and the lack of characteristic S-O-Si bands in FTIR spectra. SEM and EDX confirm micromechanical interlocking via sulfur infiltration into silica pores (85 wt.% S at interface, 2–5 μm depth), transforming fracture mode from adhesive to cohesive.

The SC-15 composition achieves 68.4 ± 1.2 MPa compressive strength (+42% versus control; $n = 6$, $p < 0.001$), $92 \pm 3\%$ strength retention after 100 thermal cycles ($n = 3$), and exceptional chemical resistance (97.2–98.5% strength retention after 28-day immersion in acid, alkali, and salt solutions; absolute residual strength 66.5–67.4 MPa; $n = 3$ per medium).

TGA confirms absence of catalytic oxidation by residual vanadium (0.12% mass loss at 200 °C, 0.075% $\text{V}_2\text{O}_5 < 0.5\%$ catalytic threshold). Long-term monitoring (90 days) shows gradual β -to- α transformation at $\sim 0.08\%/ \text{day}$ with 94% strength retention.

Cradle-to-gate LCA (ISO 14040:2006) revealed CO_2 emissions of $13.2 \pm 1.8 \text{ kg/m}^3$ (sensitivity range: 10.6–15.8 kg/m^3), representing a 96.2% reduction versus Portland cement (342 kg/m^3). Leaching tests (GOST R 59514-2021) confirmed that vanadium concentrations in the leachate from SC-15 were below the detection limit ($< 0.001 \text{ mg/L}$), below the SanPiN 2.1.7.1287-03 limit (2.0 mg/L). Radiological safety testing yielded $127 \pm 8 \text{ Bq/kg}$, below the SanPiN 2.6.1.2610-10 threshold (370 Bq/kg). These results indicate that SC-15 meets current regulatory requirements.

A unified three-scale physicochemical stabilization mechanism is proposed, encompassing hypothesized molecular-level DCPD/Si-OH adsorption (non-covalent) and experimentally confirmed microstructural capillary infiltration and macroscopic void filling. This framework is transferable to other siliceous industrial waste streams. The proposed molecular-level interaction requires further experimental validation (e.g., solid-state NMR, XPS, in situ FTIR).

Acknowledgements

The authors express their sincere gratitude to the academic institutions – the Department of Chemistry and Biology at A. Kuatbekov Peoples' Friendship University, the “Industrial Biotechnology” Research Laboratory, and M. Auezov South Kazakhstan University – for their support and assistance with this research.

This research was funded by the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan (Grant No. AP23490421 “Development of technologies for the comprehensive processing of spent vanadium-containing catalysts from sulfuric acid production”).

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