

*Research Article*

Valorization of Chrysotile Asbestos Waste into Hierarchically Porous Adsorbents for Thermal-Contact Demetallization of Heavy Oil: Mechanistic Insights and Process Optimization

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Abstract: The increasing use of heavy petroleum feedstocks necessitates the efficient removal of vanadium and nickel compounds that contribute to catalyst deactivation and coke formation. This study investigates the valorization of chrysotile-asbestos waste (CAW) as a porous adsorbent for the thermal-contact demetallization of heavy petroleum feedstock. The adsorbent was prepared by sequential magnetic separation, hydrochloric acid leaching (0.45 M HCl, 75 °C), and thermal activation at 650 °C. The treatment converted the original fibrous material into a predominantly amorphous silica-based matrix containing thermally stable forsterite, while increasing the specific surface area from 27.3 to 318.4 m²/g. The FTIR and EPR analyses indicated the formation of silanol-containing surface functionalities and paramagnetic defect centers that can contribute to the interaction with metal-containing petroleum species. Under thermal contact conditions at 360 °C and 8–10 atm, the resulting adsorbent achieved removal of vanadium and nickel, while sulfur removal remained substantially lower. The results demonstrate that controlled chemical-thermal transformation of chrysotile-asbestos waste can simultaneously reduce the hazardous fibrous morphology and produce a functional adsorbent suitable for pretreatment of heavy petroleum feedstocks.

Keywords: Chrysotile-asbestos waste; Demetallization; Guard-bed adsorbent; Heavy oil; Sustainability

1. Introduction

The progressive decline of conventional light crude reserves has inexorably steered the global refining industry toward heavier feedstocks derived from bituminous sands, shales, and extra-heavy oils (Aitkaliyeva et al., 2025; Marafi et al., 2019). These residues are inherently rich in

vanadium (V) and nickel (Ni), which are predominantly sequestered within metalloporphyrin structures embedded in asphaltene–resin matrices (Vishnyakov, 2023). The association of metalloporphyrins with high-molecular-weight petroleum fractions contributes to the formation and stabilization of nano- and supramolecular aggregates in heavy petroleum systems (Santos Silva et al., 2017). Upon thermal or catalytic processing, such metal species exert a cascade of deleterious effects: irreversible poisoning of hydrotreating and fluid catalytic cracking catalysts, accelerated coke formation, intensified high-temperature corrosion, and emission of toxic metal oxides (Chen et al., 2013). Thus, effective demetallization upstream of the reactor core has become an indispensable prerequisite for preserving catalyst longevity, ensuring process reliability, and complying with increasingly stringent environmental mandates in modern refining schemes (Ali & Abbas, 2006; Nguyen et al., 2022).

Conventional demetallization technologies are dominated by catalytic hydrotreating, which, despite its industrial maturity, incurs high hydrogen consumption, rapid catalyst deactivation under metal-laden feeds, and substantial operational expenditures (Rana et al., 2007). Solvent extraction using ionic liquids or deep eutectic solvents has demonstrated promising metal removal efficiencies at laboratory scale, yet practical implementation remains constrained by challenges associated with solvent recovery, regeneration economics, and scale-up feasibility (Baigenzhenov et al., 2015; Mohammed et al., 2023). Against this backdrop, adsorption-based methods present a compelling alternative. They offer operational simplicity, low energy intensity, hydrogen-free operation, and straightforward integration into existing refinery configurations—particularly as graded guard beds positioned upstream of hydroprocessing reactors, operating within the 320–360 °C pre-reactor window to protect downstream catalysts and stabilize pressure drop. However, the development of cost-effective adsorbents that simultaneously deliver thermal robustness and intrinsic chemisorption activity remains a persistent challenge (Okunev et al., 2015). A diverse array of adsorbents has been investigated, including activated carbons, zeolites, alumina, and templated mesoporous silicas such as SBA-15 and MCM-41. Yet their widespread adoption in guard-bed applications is frequently constrained by multiple interrelated factors. High production costs arise from multi-step syntheses and reliance on organic templates. Many materials exhibit limited thermal stability above ~350 °C, risking structural degradation or pore collapse under sustained operation. Moreover, intrinsic defect chemistry is often underdeveloped in as-synthesized states, necessitating post-synthetic functionalization to achieve strong, selective interactions with bulky metalloporphyrins—a step that adds manufacturing complexity and lifecycle cost. These considerations underscore the need for alternative, cost-effective adsorbents derived from waste precursors that can offer an optimal balance of thermal stability, surface reactivity, and process economics (Li et al., 2025; Marhoon et al., 2024).

Chrysotile asbestos waste (CAW), a globally stockpiled hazardous material accumulating to tens of millions of tons, presents an unexpected yet scientifically compelling opportunity. Despite its well-documented carcinogenicity in fibrous form, CAW is predominantly composed of magnesium silicate rich in MgO and SiO₂, making it amenable to controlled chemical and thermal transformation. Acid leaching selectively removes magnesium-rich layers, induces structural amorphization, and generates porosity. Subsequent calcination at elevated temperatures (≥ 600 °C) collapses the fibrous morphology, neutralizes toxicity, and produces a composite of amorphous silica reinforced by forsterite, a thermally stable magnesium silicate. This dual-purpose pathway—simultaneous detoxification and functional adsorbent synthesis—mitigates an environmental liability while circumventing the synthetic complexity and cost associated with conventional templated silicas (Baigenzhenov et al., 2022; Maletaškić et al., 2018). Achieving industrially relevant selectivity for metalloporphyrin removal requires chemisorption-active defect sites rather than purely physisorptive textures (Zhao et al., 2015). Despite the favorable chemistry and sustainability inherent to CAW upcycling, the application of processed CAW to heavy-oil demetallization remains largely unknown. A critical examination of the literature reveals two distinct gaps that the present study addresses. First, no prior work has established a direct, experimentally validated link between the controlled detoxification of asbestos waste,

the generation of a defect-rich silica matrix, and the efficacy of such materials for metalloporphyrin adsorption under industrially relevant thermal-contact demetallization (TCD) conditions (Maldybayev et al., 2024). Second, the potential role of intrinsic paramagnetic defects formed during thermal activation as active sites for selective metal binding has not been investigated, owing to the absence of EPR spectroscopy in this context (Djekoune et al., 2024; Maletaškić et al., 2018). This understanding is essential for translating material-level performance into a robust, industrially viable process design.

This study addresses three previously unresolved challenges through an integrated strategy that combines materials synthesis, mechanistic interrogation, and process engineering. A scalable, template-free route transforms chrysotile asbestos waste into a functional adsorbent. It employs magnetic separation, controlled acid leaching, and thermal activation to produce an amorphous silica matrix with well-developed mesoporosity and a high density of thermally stable paramagnetic centers. Complementary characterization techniques (XRD, BET, FTIR, EPR, TG-DTA) are used to establish the balance between amorphous and crystalline phases, define textural properties, assess surface chemistry, and confirm thermal resilience. Performance evaluation under thermal contact demetallization conditions across a relevant temperature window quantifies vanadium, nickel, and iron removal, confirming selectivity toward metal-bearing species.

The novelty of this study lies in integrating chrysotile-asbestos waste valorization with thermal-contact demetallization of heavy petroleum feedstock and in establishing a relationship between the chemical-thermal transformation of the waste, the development of a defect-rich porous surface, and the removal of metal-containing petroleum species. Unlike previous studies that focused primarily on asbestos-waste detoxification or silica recovery, this work combines magnetic separation, controlled acid leaching, and thermal activation to produce a silica-rich porous adsorbent containing thermally stable magnesium-silicate phases (Marian et al., 2021). Particular attention is given to the evolution of surface-active sites: EPR characterization is used together with XRD, FTIR, and textural analysis to examine the formation of paramagnetic defect centers and silanol-containing functionalities and their possible contribution to the adsorption of vanadium- and nickel-containing species. Thus, this study combines waste-derived adsorbent formation, physicochemical surface evolution, and demetallization performance within a single experimental framework. Accordingly, the aim of this study was to develop a porous adsorbent from chrysotile-asbestos waste through magnetic separation, acid leaching, and thermal activation; characterize the structural, textural, and electron-defect transformations occurring during treatment; and evaluate the resulting material for selective thermal-contact demetallization of heavy petroleum feedstock.

2. Materials and Methods

2.1 Materials

Chrysotile asbestos waste (CAW) was sourced from the tailings pond of the Zhitigara deposit in Kazakhstan. Its chemical composition, expressed in weight percent, was as follows: MgO, 39–40; SiO₂, 32–40; Fe₃O₄, 3.5–6.0; Al₂O₃, 0.7–0.9; CaO, 0.4–0.5; and NiO, 0.2–0.3. The waste was separated into different particle-size fractions and analyzed for chemical composition (Table 1). Hydrochloric acid (36%, chemically pure grade) was obtained from Sigmatec (Kazakhstan).

Tar sourced from the Pavlodar Petrochemical Plant LLP served as the model crude oil feedstock. Its key properties were as follows: vanadium content, 180–220 mg/kg; nickel, 50–70 mg/kg; iron, 50–70 mg/kg; sulfur, 1.7–2.5 wt%; density at 20 °C, approximately 1000 kg/m³; initial boiling point, 430 °C; and water content below 0.1 wt%.

2.2 Preparation of the Adsorbent

The adsorbent was prepared from chrysotile-asbestos waste (CAW) through a three-stage process; an adsorbent preparation method for the demetallization of oil residues is described in

Kazakhstan patent No. 38105 (Maldybaev et al., 2026). The non-magnetic fraction was isolated in the first stage using a dry magnetic separator operated at a field strength of 1500 oersteds (119 kA/m). This pretreatment step removed iron-bearing minerals, principally magnetite, thereby reducing the consumption of hydrochloric acid in the subsequent leaching stage. The second stage consisted of acid leaching in a mechanically stirred reactor under the following optimized conditions: HCl concentration, 0.45 M; solid-to-liquid ratio, 1:5 (w/v); temperature, 75 °C; and duration, 3 h. The solid residue was separated by filtration, washed repeatedly with deionized water until the filtrate reached neutral pH, and dried at 110 °C for 12 h. The third stage involved the thermal activation of the dried powder in a muffle furnace under air at 650 °C for 2 h, with a ramp rate of 10 °C min⁻¹. The resulting material was directly employed as a chemical adsorbent.

2.3 Characterization of the Adsorbent

The mineralogical composition of the initial and processed materials was determined by X-ray diffractometry (XRD) on a BRUKER D8 ADVANCE diffractometer (Cu-K α radiation, $\lambda = 1.5406$ Å, $2\theta = 5$ – 80° , 0.02° resolution). The chemical composition was analyzed by X-ray fluorescence (XRF) on a PANalytical Venus 200 spectrometer. Microelement analysis was performed using a PerkinElmer Optima 2000 DV inductively coupled plasma optical emission spectrometer. Elemental mapping and surface morphology were studied using a JEOL JXA-8230 electron probe microanalyzer and a Quanta 3D 200i scanning electron microscope at an accelerating voltage of 20 kV. Infrared spectra (IR) were recorded in the range of 4000 to 400 cm⁻¹ using a Fourier transform infrared (FTIR) spectrometer with a resolution of 4 cm⁻¹. The thermal behavior of the samples was studied using simultaneous thermal analysis (STA) on a NETZSCH Jupiter STA 449 F3 instrument in the range of 20 to 1000 °C at a heating rate of 10 °C/min under air. The specific surface area and pore-size parameters were determined by low-temperature nitrogen adsorption at 77 K on a SORBTOMETER-M analyzer, using the BET model. The micropore volume was calculated using the t-plot method, and the pore size distribution was calculated using the BJH model. The concentration of paramagnetic centers was estimated by the electron paramagnetic resonance (EPR) method on a JEOL JES-FA200 spectrometer (X-band, frequency 9.445 GHz, central field 340 mT, modulation amplitude 0.6 mT). Particle size distribution of the final adsorbent was analyzed by laser diffraction (Malvern Mastersizer 3000) after ultrasonic dispersion in deionized water.

2.4 Demetallization Tests

Demetallization experiments were conducted in a laboratory-scale setup employing a destructive-adsorption thermal contact process. Tar was continuously fed into a two-section reactor loaded with 10 g of the synthesized adsorbent. The operating conditions spanned a temperature range of 300–450 °C, a pressure of 8–10 atm, and a fixed contact time of 60 minutes. Hydrocarbon and water vapor were removed through a ventilation line and subsequently condensed. The vanadium, nickel, and iron in both the raw and treated tar were determined by inductively coupled plasma optical emission spectrometry. The demetallization efficiency, D (%), was calculated using Equation (1):

$$D (\%) = \left[\frac{C_0 - C}{C_0} \right] \times 100 \quad (1)$$

where C_0 is the initial concentration of metal in the untreated feedstock (mg/kg), and C is the metal concentration after treatment (mg/kg).

The degree of desulfurization, DS (%), was calculated according to Equation (2):

$$DS (\%) = \left[\frac{S_0 - S}{S_0} \right] \times 100 \quad (2)$$

where S_0 and S are the sulfur contents (wt.%) of the initial and treated feedstocks, respectively. The sulfur content was determined by X-ray fluorescence analysis. All experiments were performed in triplicate, and the measurement error did not exceed $\pm 2\%$.

3. Results and Discussions

3.1 Intact Chrysotile Asbestos Waste

Chrysotile asbestos waste (CAW) from the Zhitigara deposit (Kazakhstan) is a technogenic mineralogical conglomerate generated during serpentinite ore enrichment. The waste is dominated by serpentine-group minerals, primarily lizardite $[\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]$. In current industrial practice, over 90 % of the processed ore is discarded into tailings dams, leading to low resource efficiency and the accumulation of substantial volumes of potentially hazardous materials. Nevertheless, this waste stream contains up to 40 % MgO and 32–40 % SiO_2 , rendering it a promising raw material for the production of functional adsorbents provided that controlled chemical and thermal processing is applied.

The representativeness and technological suitability of the feedstock, the particle size distribution was first analyzed, followed by chemical analysis of the isolated fractions. The material was separated into three size fractions: 1.25–0.5 mm, 0.5–0.25 mm, and >0.25 mm. This fractionation allowed the assessment of how the specific surface area and accessibility of reaction sites influence the efficiency of subsequent processing steps—namely magnetic separation, acid leaching, and thermal activation. As shown in Table 1, the contents of the major components—MgO (39.0–40.0 %), SiO_2 (36.1–36.6 %), Fe_3O_4 (3.39–5.70 %), and NiO (0.22–0.25 %)—are virtually independent of particle size. The standard deviation for MgO does not exceed 0.4 %, indicating high mineralogical and chemical homogeneity throughout the waste mass. This uniformity has significant technological implications: it eliminates the need for preliminary granulometric classification on an industrial scale, thereby reducing both capital and operating costs.

Table 1 Chemical composition of the products by fractions

Fraction size (mm)	MgO	SiO_2	Al_2O_3	CaO	Fe_3O_4	NiO
1.25–0.5	39.0	36.5	0.79	0.46	3.39	0.22
0.5–0.25	40.0	36.6	0.72	0.49	4.87	0.25
>0.25	39.1	36.1	0.75	0.44	5.70	0.25

X-ray diffraction (XRD) analysis of the initial material (Figure 1) confirmed that lizardite-1T $[\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]$ is the dominant crystalline phase, accounting for approximately 88.2 wt.% of the identified crystalline phases. Greenalite $[\text{Fe}_6\text{Si}_4\text{O}_{10}(\text{OH})_8]$ and brucite $[\text{Mg}(\text{OH})_2]$ were also identified at approximately 7.9 and 3.8 wt.%, respectively (Table 2). Phase identification was performed by comparison with the ICDD Powder Diffraction File (PDF) reference cards: PDF 00-062-0393 for lizardite-1T, PDF 01-072-0177 for greenalite, and PDF 01-071-5972 for brucite. The corresponding reference diffraction peak positions are included in Figure 1 to facilitate direct comparison with the experimental XRD pattern and support the phase assignments. The predominance of lizardite-1T confirms that the characteristic crystalline serpentine structure of the original chrysotile-asbestos waste was preserved before chemical treatment.

Table 2 X-ray phase composition of the original chrysotile-asbestos waste

Compound name	Chemical formula	Content, wt.%
Lizardite-1T	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$	88.2
Greenalite	$\text{Fe}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$	7.9
Brucite	$\text{Mg}(\text{OH})_2$	3.8

The microstructure of the CAW particles was examined by SEM. As illustrated in Figures 2a and 2b, the original material comprises aggregates of diverse morphologies: fine-needle fibers

with diameters of 0.1–0.3 μm (typical of chrysotile), plate-like formations up to 5 μm in size (talc), and bulky amorphous aggregates likely containing iron and magnesium oxides. The preservation of a fibrous texture is consistent with the XRD data and indicates that the natural serpentine structure remains intact, an essential prerequisite for its targeted disruption during subsequent acid treatment.

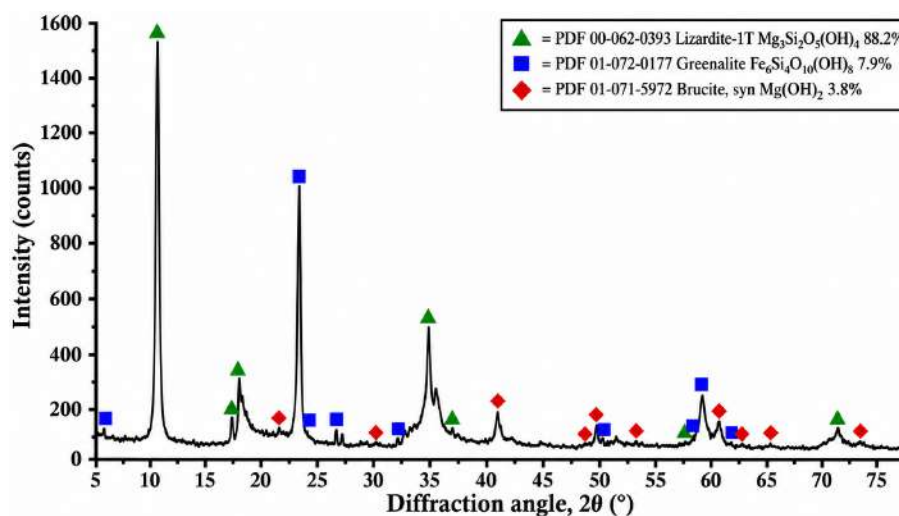


Figure 1 Experimental XRD pattern of the original chrysotile-asbestos waste with phase assignments based on ICDD PDF reference cards: lizardite-1T (PDF 00-062-0393), greenalite (PDF 01-072-0177), and brucite (PDF 01-071-5972)

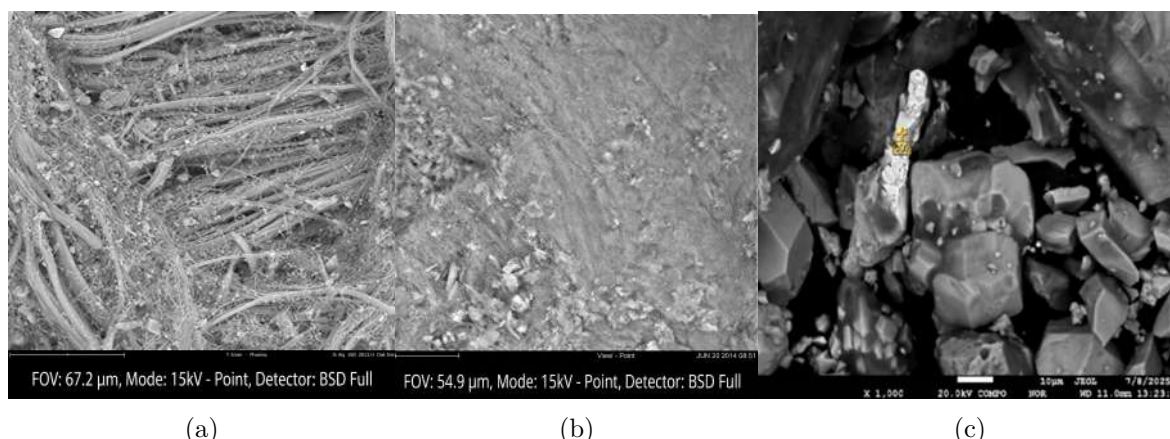


Figure 2 SEM micrographs showing the morphological transformation of chrysotile-asbestos waste: (a) and (b) original CAW, FOV = 67.2 and 54.9 μm , respectively, accelerating voltage = 15 kV; (c) adsorbent after thermal activation at 650 $^{\circ}\text{C}$, magnification = 1000 $\times$, scale bar = 10 μm

FTIR spectroscopy further confirmed the high degree of crystallinity and the presence of characteristic functional groups in the pristine material (Figure 3). The spectrum displays an intense absorption band at approximately 3680 cm^{-1} , assigned to the stretching vibrations of structural OH groups associated with the Mg-containing octahedral layers of chrysotile, which is in agreement with the spectroscopic characteristics of natural chrysotile (Anbalagan et al., 2010). The region between 1020 and 1100 cm^{-1} is dominated by Si–O stretching vibrations originating from the serpentine structure's tetrahedral layers. The bands observed at 650 – 700 cm^{-1} are attributed to the deformation vibrations of the Mg–O–Si linkages, reflecting the ordered arrangement of the octahedral–tetrahedral framework.

Altogether, the spectroscopic features confirm the crystalline and functional architecture integrity of the mineral before any chemical modification. The well-defined positions and rela-

tively sharp profiles of the characteristic absorption bands confirm that the ordered serpentine structure was preserved before chemical modification. These properties render the starting material a predictable and controllable substrate for targeted chemical transformation. Moreover, the presence of structural hydroxyl groups creates favorable requirements for the formation of sorption sites during subsequent acid and thermal treatment steps.

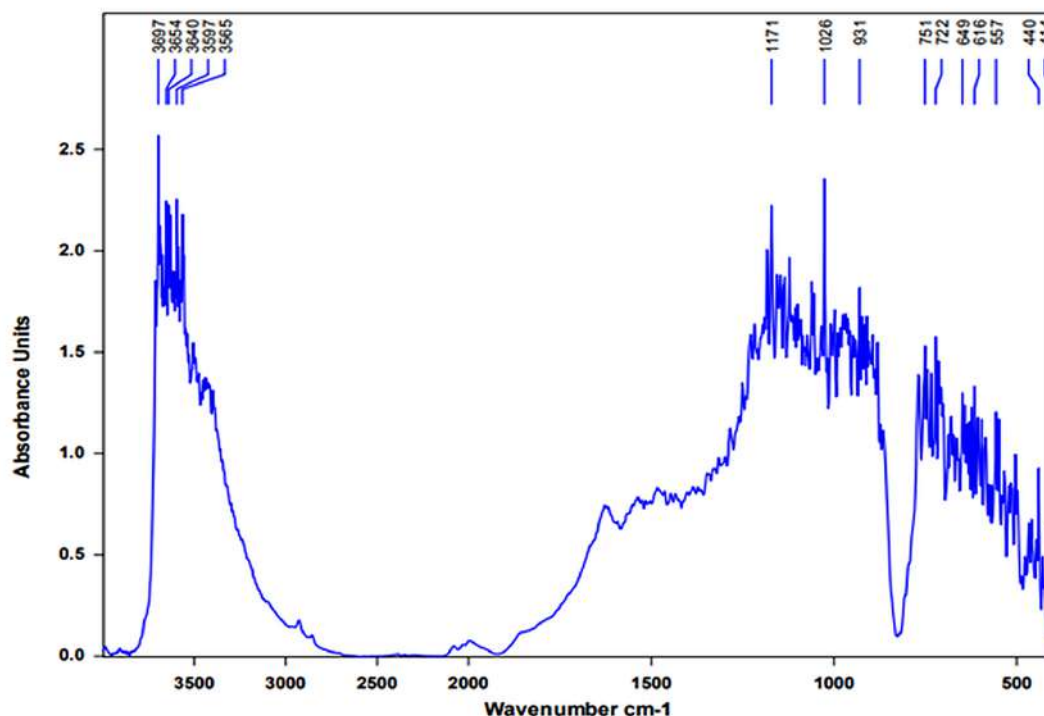


Figure 3 FTIR spectrum of the original serpentine

3.2 CAW Transformation during Chemical-Thermal Activation and Functional Adsorbent Formation

3.2.1 Magnetic preconcentration and acid leaching

The raw chrysotile asbestos waste contains iron-bearing phases in addition to the dominant serpentine minerals. Dry magnetic separation at 1500 Oe yielded a magnetic fraction representing 17.5–18.0 wt.% of the feed and containing 26–28 wt.% Fe_3O_4 (Table 3). In the non-magnetic fraction, the reported iron content decreased to 3.5–3.9 wt.%, whereas MgO and SiO_2 increased to 42.6–43.1 and 40.3–41.0 wt.%, respectively. The non-magnetic fraction was subsequently leached with HCl to remove Mg and residual Fe and produce a silica-rich solid. The effects of solid-to-liquid ratio, acid concentration, temperature, and time are summarized in Table 4. A ratio of 1:5, 0.45 M HCl, 75 °C, and 3 h were selected because increasing the acid concentration to 0.50 M or the temperature to 95 °C provided only limited additional enrichment in SiO_2 .

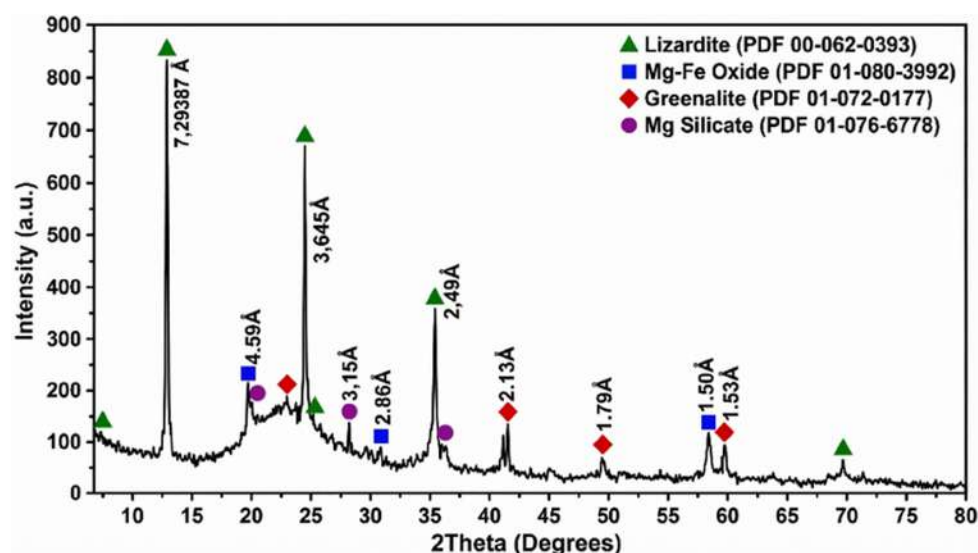
Table 3 Experimental results of magnetic fraction separation

Fraction size (mm)	Quantity (g)	Magnetic fraction				Non-magnetic fraction			
		Yield (%)	MgO	Fe_{total}	SiO_2	Yield (%)	MgO	Fe_{total}	SiO_2
−1 + 0.25	100	17.5	32.1	26.7	23.4	82.5	43.1	3.5	41.0
−1 + 0.25	100	18.0	31.7	28.2	22.6	82.0	42.6	3.9	40.3

The disappearance of the characteristic lizardite reflections and the broad XRD halo at $2\theta = 15\text{--}35^\circ$ indicate substantial loss of crystalline order after acid leaching (Figure 4).

Table 4 Effect of leaching parameters on solid product composition

Parameter	Value	FeO, wt.%	MgO, wt.%	SiO ₂ , wt.%
S:L ratio	1:2	5.9	9.3	60.2
	1:3	5.0	8.5	66.1
	1:4	4.2	8.1	70.7
	1:5	3.4	7.3	75–78
HCl concentration, M	0.35	5.8	9.4	60.7
	0.40	4.0	8.8	67.6
	0.45	3.3	7.1	78.5
	0.50	3.1	6.9	79.1
Leaching time (h)	1	7.1	18.2	55.4
	2	6.6	15.5	65.3
	3	3.4	7.3	78.9
Temperature, °C	65	4.6	10.4	67.3
	75	3.4	7.5	79.5
	85	3.7	7.0	79.9
	95	3.1	6.7	80.8

**Figure 4** Radiograph of residues from asbestos product leaching

The material is predominantly silica-rich, with minor residual crystalline phases (Table 5). FTIR spectra (Figure 5) show a weakening of the bands characteristic of the original serpentine structure and broad O–H and H₂O bands near 3400 and 1620 cm^{−1}, consistent with a hydrated silica-rich residue. Together, these observations support Mg removal and structural transformation during leaching; they do not, by themselves, establish the density or adsorption activity of individual silanol sites (Fritsch et al., 2021; Schroeder et al., 2020).

Because several strong absorption bands approach the upper response range of the recorded spectra, the FTIR interpretation in this study is based primarily on band positions, band broadening, and the appearance or disappearance of characteristic vibrations rather than on a quantitative comparison of absolute band intensities.

3.2.2 Thermal treatment and phase analysis after leaching

Thermal activation of the acid-leached residue promotes dehydration and further transformation of the Mg–Si matrix. To select a treatment temperature, the leached material was examined by simultaneous thermal analysis from 20 to 1000 °C in air at a heating rate of

10 °C min⁻¹ (Figure 6). Its multistage thermal response is consistent with the dehydration, dehydroxylation, and phase transformations reported for chrysotile and related minerals (Bloise et al., 2016).

Table 5 Phase composition after acid leaching and thermal activation

Treatment stage	Phase/component	Chemical formula	Content (wt.%)
After acid leaching	Hydrated silicon oxide	SiO ₂ · nH ₂ O	78–80
	Magnesium–iron oxide	(Mg _{0.7} Fe _{0.3})O	6.5
	Greenalite	Fe ₆ Si ₄ O ₁₀ (OH) ₈	6.3
	Magnesium-containing phase*	Mg(OH) ₂	7.1–7.5
	Magnesium silicate and protopyroxene	MgSiO ₃	4.4
After thermal activation at 650 °C	Amorphous silicon oxide	SiO ₂ · nH ₂ O	85.2
	Forsterite	(Mg,Fe) ₂ SiO ₄	12.5
	Magnesium oxide	MgO	2.3

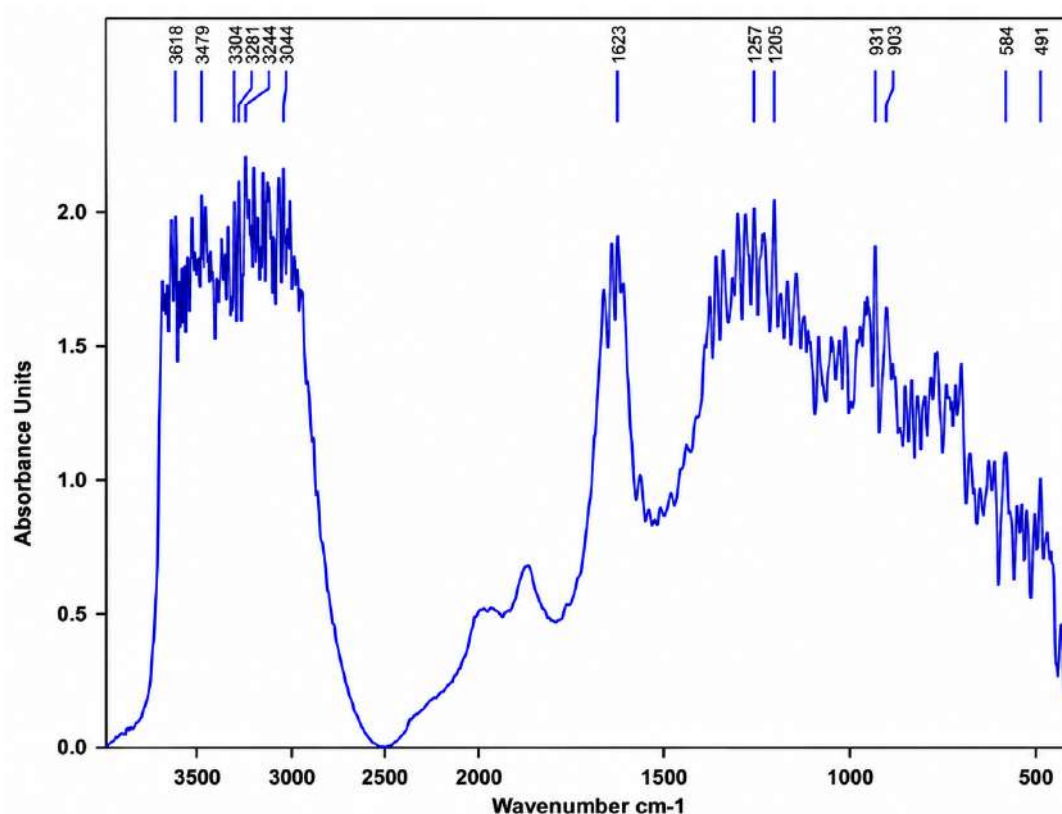


Figure 5 FTIR spectrum of serpentine after leaching

The sample lost 8.45 % of its mass between 40 and 310 °C, with partially overlapping thermal effects near 110, 140, and 170 °C. These events are consistent with the removal of water held with different strengths in the acid-leached, hydrated material. Further thermal changes between approximately 350 and 640 °C are attributable to the loss of residual hydroxyl groups and the transformation of Mg-containing phases. The total mass loss measured between 20 and 1000 °C was 28.6 %. Overall, this sequence agrees with the reported dehydration and dehydroxylation behaviour of serpentine-derived materials (Alizadehhesari et al., 2012). A temperature of 650 °C was selected for activation because it lies above the principal dehydration and dehydroxylation events while allowing the formation of a predominantly silica-rich product. This choice is supported by the phase and surface-area measurements of the product treated at 650 °C; however, the present data do not constitute a comparative optimization of several activation temperatures. Accordingly, 650 °C is identified here as the selected activation temperature,

rather than a demonstrated global optimum.

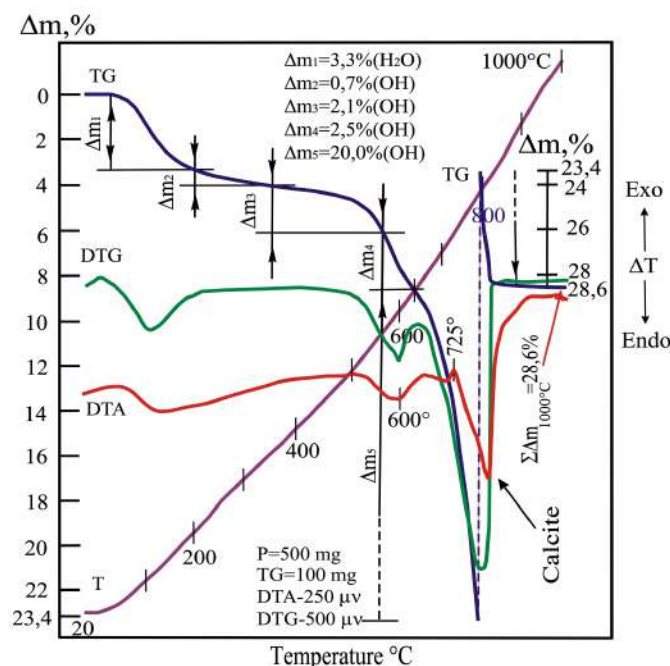


Figure 6 Thermogravimetric diagram of the non-magnetic fraction of asbestos waste

SEM provides complementary evidence of morphological transformation (Figure 2c). In contrast to the needle-like features visible in the untreated material (Figures 2a,b), the examined region of the activated sample consists mainly of irregular, compact aggregates. This change is consistent with thermal alteration of the original serpentine structure, as described for heat-treated asbestos-containing minerals (Hashizume, 2022; Kusiorowski et al., 2012). Although the micrograph supports a reduction in the visible fibrous morphology, confirmation of complete fiber elimination and toxicological safety would require dedicated fiber-counting and biological assessments.

Following activation at 650 °C, the material contains a predominantly amorphous silica-rich component (85.2 wt.%), together with forsterite (12.5 wt.%) and MgO (2.3 wt.%) (Table 5). The broad XRD scattering feature supports the presence of substantial amorphous material, while the identified crystalline phases demonstrate that part of the Mg–Si matrix underwent further transformation. Formation of forsterite from Mg- and Si-containing precursors during heating is consistent with studies of related silicate systems (Amiour et al., 2025; Laziri et al., 2024). The coexistence of amorphous silica-rich material and crystalline magnesium-containing phases offers a plausible basis for combining accessible surface with thermal robustness. Direct measurements after prolonged operation would nevertheless be needed to establish the extent to which forsterite preserves the pore structure under guard-bed conditions.

3.2.3 Electron-defect structure of the active component: role of paramagnetic centers in the sorption activity

The formation of a functional surface of the adsorbent from chrysotile-asbestos waste is accompanied by the emergence of a significant number of structural defects, vacancies, and broken chemical bonds. The most sensitive and informative method for identifying such defects, particularly those carrying unpaired electrons, is electron paramagnetic resonance (EPR). This method not only detects paramagnetic centers (PMCs) but also characterizes their nature, local environment, energetic stability, and reactivity, which directly determine the catalytic and sorption activity of the material.

The EPR spectra were recorded at room temperature using a JEOL JES-FA200 spectrometer (X-band, operating frequency 9.445 GHz, central magnetic field 340 mT, modulation ampli-

tude 0.6 mT). A reference sample of Mn^{2+} in MgO was used to calibrate the g-factor, ensuring high reproducibility and accuracy in determining signal parameters. The studies were conducted on both the original active component and a sample that underwent additional hydrogen plasma treatment for 30 min at 400 °C. The EPR spectrum of the active component (Figure 7) exhibits high signal intensity and low anisotropy, indicating a significant concentration of PMC with low spin-orbit coupling. Such centers are usually associated with incomplete coordination sites on the surface of amorphous SiO_2 , particularly with three-coordinated silicon atoms ($\equiv\text{Si}\cdot$), oxygen vacancies (E' -centers), and radical groups ($\equiv\text{Si}-\text{O}\cdot$), formed during thermal dehydroxylation of silanol groups. Furthermore, the spectrum exhibits a weak but distinct component in the region of $g \approx 4.3$, characteristic of isolated Fe^{3+} ions in a highly distorted octahedral environment. These ions are likely residual impurities that resist acid leaching and are incorporated into the crystalline phases (forsterite, greenalite) identified in the X-ray diffraction pattern. The assignment of the $g \approx 4.3$ signal to isolated Fe^{3+} in distorted octahedral sites is consistent with the canonical EPR signature of high-spin Fe^{3+} ($S = 5/2$) under strong zero-field splitting, as documented in silicate glasses and thermally treated serpentinites (Adami et al., 2025; Iarlori et al., 2001). Similarly, the broad isotropic signal centered near $g \approx 2.0$ is characteristic of E' -type centers ($\equiv\text{Si}\cdot$) and peroxy radicals ($\equiv\text{Si}-\text{O}\cdot$), which form during the dehydroxylation of silanol nests in amorphous silica above 500 °C (Iarlori et al., 2001). These defects are not merely structural imperfections but also serve as electron-donor/acceptor sites that facilitate charge transfer interactions with metalloporphyrins, particularly $\text{V}^{4+}=\text{O}$ and Ni^{2+} complexes, whose redox activity enhances the binding affinity to paramagnetic surfaces (Xie et al., 2020). Despite their low concentration, such ions contribute to the electronic activity of the surface and can act as Lewis acid centers that coordinate electron-donating atoms (N, S, O) in the molecules of vanadium and nickel organometallic compounds.

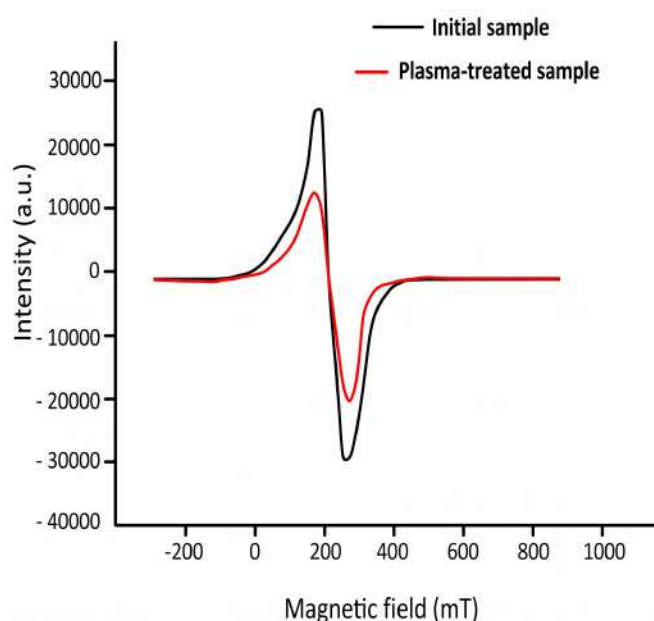


Figure 7 Electron paramagnetic resonance spectra of the samples

Selective passivation of PMCs was observed during hydrogen plasma treatment. After such treatment, a $\sim 40\%$ decrease in EPR signal intensity is observed, whereas the overall spectral shape remains unchanged. This indicates that hydrogen plasma preferentially interacts with highly reactive surfaces and weakly bound defects. The atomic hydrogen and proton particles generated in the plasma effectively compensate for the unpaired electrons, forming diamagnetic $\equiv\text{Si}-\text{H}$ or $\equiv\text{Si}-\text{OH}$ groups. Simultaneously, deep and thermally stable PMCs, such as Fe^{3+} -containing complexes or E' -centers embedded in the silica matrix, retain their activity. Such

differential reactivity among defects has important technological implications. First, it indicates the possibility of fine-tuning the adsorbent surface to optimize the balance between the overall reactivity and the selective stability of the active centers. Second, the preservation of stable PMCs during plasma treatment explains the high thermal stability of the adsorption activity under thermocontact processing conditions at 360 °C. These centers, which have a high electron density and are capable of forming covalent-like bonds, provide the chemisorption nature of interactions between the adsorbent surface and organometallic complexes, which is confirmed by a high degree of demetallization (up to 58 %) even at a moderate contact time (60 min). Thus, EPR spectroscopy data confirm the high defectiveness and electronic activity of the synthesized material and establish a direct correlation between the concentration of stable paramagnetic centers and the demetallization efficiency. Therefore, EPR is not only a diagnostic tool but also a prognostic tool in the development of functional adsorbents based on processed mineral waste.

3.2.4 Textural and functional characteristics of the active component and their functional significance

The key factor determining the efficiency of an adsorption material in the processing of heavy petroleum products is not only the chemical nature of its surface, but also the textural organization of the pore space, which controls the accessibility of active centers for large-sized organometallic compounds. To quantitatively evaluate these parameters, a low-temperature nitrogen adsorption-desorption analysis was performed at 77 K, followed by calculation of the specific surface area using the BET model, the specific pore volume using the t-plot method, and the pore size distribution using the BJH model. The resulting pore size falls within the lower mesopore regime (2–10 nm), consistent with the H1-type hysteresis loop and the molecular dimensions of metalloporphyrins (1.5–2.5 nm), ensuring minimal diffusion resistance. The use of the BJH model for pore size distribution is justified for silica-based mesoporous materials with cylindrical pore geometry, as confirmed by the sharp capillary condensation step in the adsorption isotherm (Karolczak et al., 2004). After chemical-thermal activation, a radical transformation of the pore structure is observed: the specific surface area increases more than eleven-fold, up to 318.4 m²/g, the specific pore volume up to 0.137 cm³/g, while the average pore size remains practically unchanged (1.714 nm). At first glance, the constancy of the average diameter may seem paradoxical, but this is explained by the homogeneity of the pore formation mechanism. Acid leaching selectively removes Mg²⁺ and Fe³⁺ from the layered structure of serpentine, accompanied by local collapse of octahedral layers and the formation of mesopores (2–50 nm) along the boundaries of amorphous SiO₂ aggregates (Table 6). Since these pores are formed by a single mechanism (destruction of the same mineral fragment), their size spectrum is narrow and exhibits a stable average value.

Table 6 Specific surface area, pore volume, and average pore size of the samples

Sample	Specific surface area (m ² /g)	Specific pore volume (cm ³ /g)	Average pore size (nm)
Chrysotile-asbestos waste	27.3	0.012	1.713
Active component	318.4	0.137	1.714

Analysis of the adsorption isotherm, identified as type IV according to the IUPAC classification and exhibiting a characteristic H1 hysteresis loop, confirms the presence of an ordered mesoporous structure with predominantly cylindrical pore geometry, which is fully consistent with the SEM-enhanced aggregate morphology. Such a pore architecture is particularly advantageous for the transport and selective adsorption of metal-containing petroleum species because pore dimensions comparable to those of petroporphyrin molecules can promote their accessibility while restricting the transport of larger asphaltene aggregates (Mironov et al., 2024). Moreover, the narrow pore-size distribution enhances the adsorption process selectivity by reducing the likelihood of undesirable uptake of lighter hydrocarbon fractions. The obtained textural charac-

teristics are comparable to those of leading commercial mesoporous adsorbents, such as SBA-15 with specific surface areas of 600–800 m²/g and MCM-41 with 900–1000 m²/g, yet the synthesized material offers two significant advantages. First, it is substantially more cost-effective owing to the use of low-value waste as the precursor. Second, it demonstrates thermal stability up to 650 °C due to the presence of a forsterite crystalline phase, which ensures structural integrity under conditions typical of thermal contact processing at approximately 360 °C, whereas many synthetic mesoporous materials tend to undergo sintering and pore collapse under similar thermal loads.

As shown, chemical-thermal activation not only increases the surface area but also creates a functional pore architecture optimized for heavy petroleum product demetallization. Beyond the pore architecture, the final adsorbent's particle size distribution is a critical parameter for fixed-bed applications. The synthesized material exhibited a median particle size (D_{50}) of 45–60 μm , with a narrow distribution (85 % of particles in the 20–100 μm range). This granulometric profile minimizes pressure drop across the guard bed while ensuring adequate contact between the adsorbent surface and the viscous heavy oil feedstock. The high specific surface area, combined with mesoporosity, thermal stability, and surface reactivity, accounts for the observed vanadium and nickel removal efficiencies (56–58 %) and supports the chosen synthesis strategy.

3.3 Temperature-Dependent Adsorption

The efficiency of using adsorption materials in the processing of heavy oil products is determined not only by their static capacity but also by the kinetics of mass transfer, the temperature dependence of adsorption, and molecular selectivity in relation to various classes of impurities. In this study, a comprehensive investigation of the thermocontact demetallization of a model tar was conducted using a synthesized chemical adsorbent based on chrysotile asbestos waste. The tests were conducted in a laboratory reactor at 8–10 atm, a contact time of 60 min, and a temperature of 300–360 °C, corresponding to typical conditions for the preliminary stage of catalytic cracking or hydrotreating. Tar from the delayed coking unit of Pavlodar Petrochemical Plant LLP was used as the feedstock with the following composition: V, 180–220 mg/kg; Ni, 50–70 mg/kg; Fe, 50–70 mg/kg; and sulfur, 1.7–2.5 wt.%.

The experimental program was designed with three principal objectives: first, to identify the temperature thresholds at which the adsorption process becomes activated; second, to quantify the extent to which intrapore diffusion governs the efficiency of metal extraction; and third, to assess the selectivity of the synthesized adsorbent toward metal-containing species relative to sulfur-bearing compounds. By systematically addressing these interconnected goals, this study seeks to establish a mechanistic understanding of the demetallization process and provide a rational basis for optimizing the performance of adsorbents under industrially relevant conditions. Table 7 presents the results of the demetallization experiments. A clear monotonic dependence of the degree of metal removal on the temperature of the process is observed. At 300 °C, the adsorption efficiency is minimal: the vanadium removal is only 0.9–2.2 %, nickel is 0–6.2 %, and iron is 3.7–13.0 %. This behavior indicates that at low temperatures, the molecular mobility of asphaltene-resin aggregates containing organometallic complexes is insufficient to overcome diffusion barriers, and the surface centers of the adsorbent ($\equiv\text{Si-OH}$, MgO , paramagnetic defects) are in a thermodynamically inactivated state.

At 320 °C, a sharp increase in efficiency is observed: V removal increases to 20–27 %, Ni removal to 29–36 %, and Fe to 26–30 %. This temperature can be interpreted as the activation threshold for the thermal destabilization of metalloporphyrin complexes, which are the main forms of vanadium and nickel localization in heavy fractions. According to the literature (Aitkaliyeva et al., 2025), the thermal decomposition of V- and Ni-porphyrins begins at 300–330 °C and is accompanied by the weakening of M–N coordination bonds, thereby facilitating their interaction with surface-active sites. At 340 °C, an industrially significant level of demetallization is achieved: V, 49–52.5 %; Ni, 43–48 %; and Fe, 40–43 %. In this case, vanadium

is extracted more efficiently than nickel, which is consistent with the higher thermal lability of V–N bonds compared to Ni–N, as well as with the increased polarity of vanadium-containing compounds. Iron shows a somewhat lower degree of removal, which may be due to its presence not only in the form of metalloporphyrins, but also in the form of colloidal oxides (Fe_3O_4 , Fe_2O_3) and inclusions of mineral dust, which are capable of physical, but not chemisorptional, capture. Maximum efficiency is achieved at 360 °C: vanadium and nickel removal rates are 56–58 %, and iron removal rates are 50–52 % (Figure 8). Further increases in temperature (from 400 °C to 450 °C) are impractical due to the risk of asphaltenic thermal cracking, coke formation, and pore closure.

Table 7 Metal extraction as a function of temperature

Volumetric feed rate of raw materials, h ⁻¹	Metal content (mg/kg)			Sulfur content, %	Metal removal rate (%)		
	V	Ni	Fe		V	Ni	Fe
<i>T = 300 °C</i>							
initial	200	65	54	1.97	–	–	–
1	196.5	63	52	1.97	1.75	3.08	3.70
2	198.2	65	47	1.95	0.90	0.00	12.96
3	195.7	61	51	1.96	2.15	6.15	5.56
<i>T = 320 °C</i>							
initial	200	65	54	1.97	–	–	–
1	157	46	40	1.60	21.50	29.23	25.93
2	146	42	38	1.48	27.00	35.38	29.63
3	160	45	36	1.80	20.00	30.77	33.33
<i>T = 340 °C</i>							
initial	200	65	54	1.97	–	–	–
1	98	35	32	1.72	51.00	46.15	40.74
2	102	37	31	1.67	49.00	43.08	42.59
3	95	34	32	1.70	52.50	47.69	40.74
<i>T = 360 °C</i>							
initial	200	65	54	1.97	–	–	–
1	87	28	27	1.36	56.50	56.92	50.00
2	85	28	29	1.56	57.50	56.92	46.30
3	88	30	26	1.40	56.00	53.85	51.85

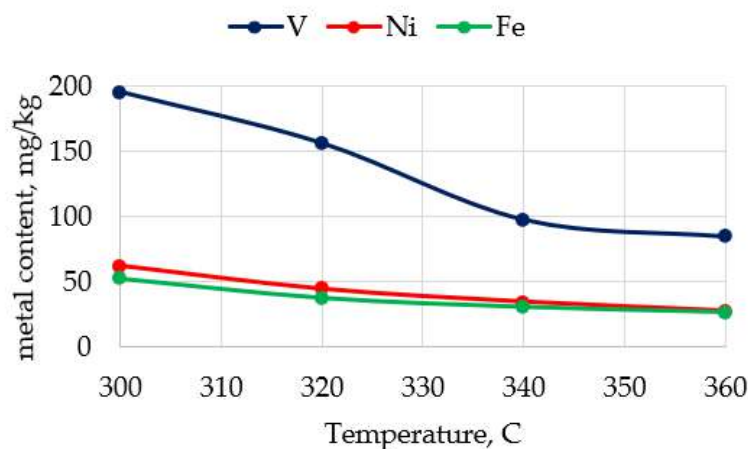


Figure 8 Adsorption of heavy metals by the active component (initial concentration, mg/kg: V, 200; Ni, 65; Fe, 54)

The adsorbent's selectivity for sulfur is particularly significant. As shown in Table 7, the degree of desulfurization remains limited even at 360 °C, with the sulfur content decreasing from 1.97 wt.% to 1.36–1.56 wt.%. This indicates that the adsorbent surface interacts primarily with the coordinatively unsaturated centers of transition metals, rather than with the covalently bonded thiophene and mercaptan groups characteristic of organic sulfur. This selectivity can be rationalized by considering the nature of the active sites on the adsorbent surface. The paramagnetic defects ($\equiv\text{Si}\cdot$, $\equiv\text{Si}-\text{O}\cdot$) and Lewis basic MgO sites generated during thermal activation are particularly well-suited for coordination with the electron-deficient metal centers in metalloporphyrins ($\text{V}^{4+}=\text{O}$, Ni^{2+}), where d-orbital participation enables strong chemisorptive bonding. In contrast, thiophenic sulfur and mercaptans, which feature delocalized π -electron systems and weaker Lewis basicity, only weakly interact with such sites under the non-reductive conditions of thermal contact processing. Consequently, no significant competitive inhibition between sulfur- and metal-bearing species occurs, preserving the adsorbent's capacity for targeted demetallization. As discussed by Zhao et al. (2015), the Lewis basicity of the porphyrin macrocycle and the redox activity of coordinated vanadium and nickel centers render metalloporphyrins significantly more susceptible to chemisorption on oxide surfaces than thiophenic compounds. Such selectivity is highly desirable in industrial conditions: it enables the targeted removal of catalytic poisons (V, Ni) without significant consumption of adsorption capacity for sulfur-containing molecules, which are more rationally removed at the hydrotreating stage in the presence of hydrogen and specialized catalysts (Yusubov, 2021).

Analysis of the temperature-dependent performance, combined with the textural (BET) and electron-defect (EPR) characteristics, allows us to propose a mechanistic model for the process. The observed threshold behavior at 320 °C suggests the combined resistance of:

1. The intrapore diffusion of large-sized asphaltene aggregates (size 1.5–5 nm) into narrow mesopores (1.714 nm);
2. Thermal activation of surface centers ($\equiv\text{Si}-\text{OH}$, MgO), the energy barrier for which is overcome only at $T \geq 320$ °C.

While a rigorous kinetic modeling would require time-resolved concentration profiles to distinguish between diffusion and surface reaction contributions (beyond the scope of this study), the strong temperature dependence and selectivity patterns support a mechanism dominated by activated chemisorption rather than simple physisorption.

To contextualize the performance of the synthesized adsorbent, the demetallization efficiency achieved in this work is compared with representative data from recent literature on both adsorption-based and catalytic hydroprocessing methods. The CAW-derived adsorbent demonstrates competitive metal removal efficiency (56–58 % for both V and Ni at 360 °C) compared to conventional systems, including activated carbon (40–45 % V removal) (Ali & Abbas, 2006), Al_2O_3 – SiO_2 composites (48–53 % V removal) (Kirgizov et al., 2022), and chitosan/zeolite-X composites (50–55 % V removal) (Marhoon et al., 2024). While hierarchical $\text{NiMo}/\text{Al}_2\text{O}_3@/\text{SiO}_2$ catalysts achieve slightly higher efficiencies (58–62 % V removal) (Li et al., 2025), they require significantly more complex synthesis involving organic templates and noble metal impregnation, resulting in substantially higher production costs.

Notably, despite having a moderate specific surface area (318 m^2/g) compared with that of templated mesoporous silicas (typically 600–1000 m^2/g), the CAW-derived adsorbent achieves comparable or superior performance to many commercial systems. This is attributed to the high density of specific chemisorption sites (paramagnetic E' -centers, $\equiv\text{Si}-\text{OH}$ silanol nests, and Lewis basic MgO sites) rather than purely textural properties. Furthermore, the forsterite-reinforced structure provides exceptional thermal stability under guard-bed conditions (360 °C, 8–10 atm), whereas many synthetic adsorbents undergo progressive sintering and pore collapse under similar operational stresses.

Table 8 Performance of adsorbents and catalysts for heavy oil demetallization under thermal or hydroprocessing conditions

Material type	Surface area (m ² /g)	Temp. (°C)	Metal removal (%)	Method	Ref.
Activated carbon	800–900	340–360	40–45 (V)	Adsorption	(Ali & Abbas, 2006)
Al ₂ O ₃ –SiO ₂	250–300	350–370	48–53 (V)	Hydroprocessing	(Kirgizov et al., 2022)
Chitosan/Zeolite-X	400–450	330–350	50–55 (V/Ni)	Adsorption	(Marhoon et al., 2024)
NiMo/Al ₂ O ₃ @SiO ₂	350–400	360–380	58–62 (V)	Hydroprocessing	(Li et al., 2025)
This work (CAW-derived)	318	360	56–58 (V/Ni)	Adsorption	This work

4. Conclusion

This study demonstrates an effective route for converting hazardous chrysotile asbestos waste into a functional adsorbent for heavy-oil demetallization through magnetic separation, mild acid leaching, and thermal activation at 650 °C. The resulting material comprises an amorphous silica-rich matrix containing forsterite nanocrystals and combines a mesoporous structure with chemically active surface sites. Comprehensive characterization, including electron paramagnetic resonance spectroscopy, indicates that the adsorption performance is governed not only by the porous architecture but also by stable paramagnetic defect sites and hydrogen-bonded silanol groups that promote coordination-driven interactions with metal-containing species. Under thermal contact conditions, the adsorbent achieved removal of vanadium and nickel porphyrins at 360 °C, while sulfur-containing compounds remained largely unaffected, demonstrating preferential removal of metal-containing components from the heavy-oil matrix. The temperature-dependent adsorption behavior further indicates a combined mechanism involving the intrapore transport of bulky asphaltene-associated species and thermally activated chemisorption at surface defect centers. These findings establish a direct relationship between the structural transformation of chrysotile asbestos waste, active adsorption site formation, and selective removal of Ni- and V-containing species. Overall, the proposed approach integrates the detoxification and valorization of asbestos-containing waste with the development of a thermally stable adsorbent for heavy-oil demetallization, providing a basis for further evaluation in guard-bed applications and more sustainable refinery processing.

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Author Contributions

Galymzhan Maldybayev: Conceptualization, methodology, supervision, funding acquisition. **Rustam Sharipov:** Investigation, data collection, formal analysis, writing – original draft. **Adam Mohd Ridhwan:** Methodology, investigation, data analysis, writing – review and editing. **Raushan Urlibay:** Investigation, data collection, visualization, writing – review and editing. **Omirserik Baigenzhenov:** Conceptualization, supervision, writing – review and editing. **Zaher Mundher Yaseen:** Formal analysis, validation, writing – review and editing. **Medet Mendeke:** Investigation, data analysis, visualization, writing – review and editing. **Ahmad Hosseini-Bandegharai:** Validation, writing – review and editing. All authors reviewed and approved the final manuscript.

Conflict of Interest

No potential conflict of interest was reported by the authors.

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