

# Reuse of spent molecular sieves as adsorbents: a waste valorization strategy for low-temperature thermal energy storage

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## Research Article

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# Abstract

The increasing demand for sustainable energy systems has motivated the development of circular economy strategies aimed at transforming industrial waste into value-added materials. In this study, used molecular sieves (MS) generated during the purification of natural gas were evaluated as potential materials for thermal energy storage (TES). Their physicochemical, microstructural and thermal properties were compared with a natural zeolite (ZT) and a synthetic hydroxyapatite composite (HApCM) commonly used as remediation materials. The characterization of the materials included particle size analysis, scanning electron microscopy (SEM), X-ray fluorescence (XRF), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). SEM confirmed that the porous aluminosilicate structure had been preserved following industrial use, while thermal analyses demonstrated high thermal stability and reversible behavior up to 343 K. DSC measurements revealed broad reversible endothermic events associated with the progressive desorption of water molecules interacting with adsorption sites of different energetic strength, confirming that the adsorption functionality required for thermal energy storage was retained after industrial use. Overall, the combined physicochemical and thermal characterization demonstrates their potential for valorization as low-temperature adsorption-based thermal energy storage materials, providing a sustainable alternative to common adsorbents while contributing to industrial waste minimization and the circular economy.

## 1. Introduction

Decarbonization of energy systems and the mitigation of environmental impacts associated with industrial processes have become central challenges in the current energy transition. In this situation, extending the service life of industrial materials through reuse and valorization has emerged as an effective circular economy strategy to reduce waste generation, minimize the consumption of virgin resources, and lower the environmental footprint of industrial activities. In this context, improving energy efficiency and promoting circular economy strategies focused on the valorization of industrial waste are key approaches to reducing greenhouse gas emissions and enhancing the sustainability of energy-intensive sectors [1, 2].

In the oil and gas industry, molecular sieves are used in dehydration and purification processes. During operation, contamination and pore blockage progressively reduce their adsorption efficiency, leading to their replacement. The spent molecular sieves are classified as hazardous industrial waste because they contain adsorbed hydrocarbons. Nevertheless, spent molecular sieves may retain significant structural stability and adsorption capacity, suggesting their potential reuse as low-cost thermochemical energy storage materials [1, 3]. Their reutilization could not only reduce disposal requirements but also extend the functional lifetime of these materials, creating an opportunity to integrate waste management and energy storage within a circular economy framework.

Although the recovery and reuse of industrial waste in high-value applications have attracted increasing attention, the potential of spent molecular sieves for TES remains largely unexplored. Most previous

studies have focused on virgin zeolites or commercially available molecular sieves, while the physicochemical, thermal, and adsorption properties of spent industrial materials after service have received limited investigation [4]. Despite the growing interest in waste valorization, the reuse of spent molecular sieves as functional adsorbents for thermochemical energy storage has received little attention, particularly considering their potential environmental and economic benefits.

Thermal energy storage (TES) technologies perform a crucial role in improving energy efficiency and enabling the integration of intermittent renewable energy sources into industrial systems. Among the available TES approaches, thermochemical energy storage stands out due to its high energy storage density and its ability to store energy over long periods with minimal losses, through reversible adsorption–desorption processes or chemical reactions [5–9].

Zeolites have been widely investigated as thermochemical materials for TES, particularly in solar thermal energy storage and low- to medium-temperature heat recovery systems. Natural zeolites, such as chabazite and clinoptilolite, exhibit high thermal and hydrothermal stability and significant energy storage capacity through reversible water vapor adsorption [10]. Zeolite-based molecular sieves have also been extensively studied due to their well-defined microporous structure and favorable water vapor adsorption kinetics. Although they generally present moderate energy storage density and relatively high cost, these characteristics have motivated the development of more cost-effective alternatives, including spent molecular sieves, for TES applications [11–13]. Experimental studies have shown that the performance of zeolite–water vapor systems depend mainly on operating conditions, such as temperature and vapor flow, while the zeolitic structure remains stable. These findings suggest the suitability of zeolites for low- to medium-temperature TES applications [14–16]. However, the extensive use of synthetic zeolites in TES is still limited by material cost and the environmental impacts associated with the production of virgin adsorbents, highlighting the need for more sustainable alternatives.

The present study aims to evaluate the feasibility of reusing spent molecular sieves as adsorbent materials for low-temperature thermal energy storage through comprehensive physicochemical and thermal characterization. In order to provide a more comprehensive assessment of their viability for thermal energy storage, the molecular sieves used were compared with two reference porous materials that exhibit different adsorption mechanisms: a natural zeolite, which represents the conventional class of aluminosilicate adsorbents that have been extensively studied for TES, and a hydroxyapatite-based compound, which represents a non-zeolitic porous adsorbent with high affinity for water and thermal stability.

The results provide insight into the feasibility of incorporating spent molecular sieves into a circular economy approach by transforming an industrial waste into a value-added thermochemical energy storage material, thereby contributing to both resource efficiency and the development of sustainable, low-cost TES technologies.

## 2. Materials and methods

Spent molecular sieves (MS) were obtained from adsorption towers used in a gas purification process in the oil and gas industry (Fig. 1). The industry generates approximately 50 tons of MS per year. In similar gas processing facilities, the generation of spent molecular sieves is also significant. Some authors have reported the disposal of approximately 106 t of MS as solid waste over the same period for a single industrial plant [17]. According to supplier specifications, the material corresponds to a type A synthetic zeolite with nominal composition  $\text{Na}_2\text{Al}_2\text{SiO}_7 \cdot \text{H}_2\text{O}$ . During operation, these materials adsorb water vapor and other impurities until saturation, after which they are discarded as industrial waste. The sample was obtained via the quartering technique, in accordance with ASTM D75/D75M-23 [18].

For comparative purposes, MS was evaluated with two reference materials: a natural zeolite (ZT) obtained from a mineral natural deposit and a synthetic hybrid hydroxyapatite composite (HApCM) produced under laboratory conditions [19]. ZT was selected as a conventional adsorbent extensively investigated for adsorption-based thermal energy storage, whereas HApCM was included as a representative non-zeolitic porous adsorbent previously developed for environmental remediation applications and characterized by its high adsorption capacity and thermal stability. The physicochemical and microstructural properties of MS, ZT and HApCM were determined using the following techniques under identical experimental conditions to ensure comparability. Original particle size distribution of the MS, ZT was determined in accordance with ASTM C136 [20]. Due to the limited amount of HApCM available, sieve analysis could not be performed. Therefore, particle size was qualitatively assessed by scanning electron microscopy (SEM) images. Morphological and microstructural analysis was conducted via SEM with a Zeiss EVO MA10 microscope. MS were milled to produce MSm with a ball mill. The particle size of the MSm was also determined with a sedigraph (Micromeritics Sedi-Graph 5000). The milling was carried out exclusively for the purpose of obtaining a uniform particle size suitable for physicochemical and thermal characterization. Since during this process no chemical or thermal treatment was applied, the results obtained for the MSm were considered representative of the intrinsic properties of MS used.

Then, Msm, ZT and HApCM samples were oven-dried at 343 K for 72 h to constant mass to eliminate moisture. Chemical analysis of zeolites was performed by X-ray fluorescence (XRF) with the Malvern Panalytical Axios Fast instrument.

Samples stability was studied by monitoring mass loss using thermogravimetric analysis (TGA). Approximately  $10 \pm 1$  mg of sample was analyzed from ambient temperature to 973 K, using a heating rate of 10K/minute. A TA Instruments 5500 was used for testing. Analyses were performed under  $\text{N}_2$  atmosphere.

Differential Scanning Calorimetry (DSC) measurements were carried out using a TA Instruments® Q2000 instrument equipped with an  $\text{N}_2$  flow-based cooling system for the process cooling stage. Approximately  $7 \pm 1$  mg of sample were placed in TZero-type hermetic aluminum capsules and heated from 298 to 573 K at a constant heating at a rate of 5K/minute. Both TGA and DSC measurements were performed in triplicate under the same experimental conditions.

The DSC experiments were conducted to evaluate the calorimetric response of the materials during heating and to identify the thermal events associated with water desorption from the porous structure of materials. As the adsorbents analyzed within this work are hygroscopic materials, the measured heat flow includes contributions from both sensible heating of the solid matrix and the endothermic heat associated with progressive dehydration. In consequence, the conventional determination of the specific heat capacity ( $C_p$ ) from DSC heat flow data was not considered appropriate under the present experimental conditions, since no specific heat capacity calibration procedure under controlled hydration conditions was performed. So, the DSC results were analyzed as the overall calorimetric response associated with dehydration and thermal stability. This approach was conducted considering that the properties mentioned are most directly related to the performance of adsorption-based thermal energy storage materials.

Based on the physicochemical and thermal characterization described above, the potential use of the MS as low-temperature thermal energy storage material was evaluated. In low-temperature thermal energy storage systems employing porous adsorbents, thermal performance is strongly influenced by the structural stability of the material, its affinity for water, and its ability to undergo repeated heating and cooling cycles without significant degradation [21]. Therefore, the suitability of the investigated materials was assessed through their microstructural characteristics together with their thermogravimetric and calorimetric behavior.

The suitability of spent molecular sieves for thermal energy storage was assessed from their combined physicochemical, structural and thermal characteristics. Attention was given to the reversible heat absorption associated with water desorption, since this process constitutes the fundamental mechanism governing adsorption-based thermal energy storage. Accordingly, the DSC analysis was used to evaluate the thermal response of the materials during heating rather than determine the intrinsic heat capacity of the solid framework.

## **3. Results and discussion**

### **3.1 Characterization**

MS particles' nominal size ranged from 1.2 to 4.8 mm, according to the granulometry of a representative sample of the sieves (Table 1). MS shows a particle size distribution like ZT.

Table 1  
Granulometry of MS  
and ZT [%]

| Sieve | MS  | ZT  |
|-------|-----|-----|
| N°3/8 | --  | --  |
| N° 4  | --  | 7   |
| N° 8  | 91  | 55  |
| N° 16 | 99  | 98  |
| N° 30 | 100 | 100 |

SEM images (Fig. 2) verify that the MS maintain their porous microstructure following industrial use. The exterior surface shows a rough and granular texture typical of aluminosilicate materials [22, 23]. Internal micrographs reveal a clearly defined porous structure with interconnected pores, demonstrating that the zeolitic structure retains structural stability. These data validate that the industrial operating conditions did not result in significant microstructural degradation, consequently affirming the viability of recycling MS as thermal energy storage materials. SEM micrographs qualitatively show that HApCM has significantly smaller particles than MS and ZT ( $< 10 \mu\text{m}$ ).

After MS had been milled, the particle size distribution was measured by a sedigraph. Three characteristic particle diameters of MSm, determined from particle size distributions, are given in Table 2. D values represent the particle diameter. D90 means that 90% of the particles in the sample have a specified diameter value or smaller, D50 value represents the mean particle diameter, and D10 is the size that 10% of particles with a diameter less than this value. Based on the particle size analysis of a representative MSm sample it was ascertained that the predominant proportion of particles exhibits a nominal size within the range of 30 to 300  $\mu\text{m}$ . Particle size reduction increases the external surface area and improves pore accessibility while preserving the MS intrinsic structure, due to the type of milling process used [16]. This modification is advantageous for thermal storage systems, as smaller particles can increase the efficiency of heat transfer and adsorption-desorption kinetics without compromising the fundamental physicochemical properties of the material [24].

Table 2  
Characteristic  
particle size  
diameters of MSm  
[ $\mu\text{m}$ ]

| D <sub>10</sub> | D <sub>50</sub> | D <sub>90</sub> |
|-----------------|-----------------|-----------------|
| 35              | 65              | 212             |

The XRF analysis (Table 3) indicates that MSm exhibits a Si/Al ratio of 1,52, reflecting a relatively high aluminum content within its aluminosilicate framework. Compared with ZT, which shows a higher Si/Al

ratio, MSm is characterized by a greater proportion of framework aluminum relative to silica. In aluminosilicate materials, a decrease in the Si/Al ratio leads to an increase in the net negative charge of the framework due to the isomorphic substitution of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$ . This structural charge imbalance is compensated by exchangeable cations, thereby enhancing the polarity and hydrophilicity of the material surface. Consequently, MS is expected to exhibit a higher affinity for polar adsorbates, particularly water vapor, which is a key requirement for adsorption-based thermal energy storage applications, where water uptake governs the storage capacity and overall system performance.

In contrast, ZT, with its higher Si/Al ratio, possesses a comparatively more siliceous framework, resulting in a lower density of framework negative charge and consequently reduced surface polarity. ZT shows weaker interactions with water molecules and potentially lower adsorption capacity under identical operating conditions [2, 11, 25]. Regarding HApCM, its chemical composition differs fundamentally from that of aluminosilicate-based materials, as it does not contain a Si–Al framework. Therefore, the Si/Al ratio is not applicable. Instead, its structure is dominated by calcium phosphate phases, where water interaction is primarily governed by surface hydroxyl groups and calcium–phosphate ionic sites. This implies that water uptake in HApCM is expected to occur predominantly through surface hydration mechanisms rather than framework-driven physisorption, as observed in MSm and ZT. Consequently, while MSm and ZT operate within an aluminosilicate adsorption mechanism governed by framework charge and porosity, HApCM may contribute to thermal system performance through distinct hydration-driven processes, potentially influencing adsorption kinetics and reversibility within hybrid storage systems.

Table 3  
Composition of MSm, ZT and HApCM [%]

| Element           | MSm     | ZT    | HApCM |
|-------------------|---------|-------|-------|
| Silicon           | 11,82   | 33,72 | n/d   |
| Aluminum          | 14,19   | 9,50  | n/d   |
| Sodium            | 12,09   | 1,70  | 2,08  |
| Sulphur           | 1,16    | 0,088 | n/d   |
| Magnesium         | 0,854   | 0,598 | n/d   |
| Iron              | 0,287   | 2,48  | 20,08 |
| Potassium         | 0,226   | 0,777 | n/d   |
| Phosphorus        | 0,040   | 0,015 | 7,82  |
| Titanium          | 0,029   | 0,190 | n/d   |
| Vanadium          | < 0,010 | n/d   | n/d   |
| Chlorine          | < 0,010 | 0,032 | n/d   |
| Barium            | n/d     | 0,161 | n/d   |
| Calcium           | n/d     | n/d   | 18,67 |
| Oxygen            | n/d     | n/d   | 50,10 |
| n/d: not detected |         |       |       |

## 3.2 Thermal analysis

### *Thermogravimetric assays*

Thermogravimetric assays (TG) were conducted in all materials to evaluate the thermal stability, dehydration behavior, and structural resistance under continuous heating. Besides providing information on mass loss, thermograms are particularly useful for identifying the nature of volatile species released during heating and for assessing the suitability of porous adsorbent materials for thermal energy storage applications. In adsorption-based thermal energy storage systems, the thermal stability of the proposed storage material directly influences its operational lifetime, cycling durability, and regeneration requirements. The curves obtained from mass loss as a function of temperature are displayed in Fig. 3. From the thermograms it could be observed that all materials exhibited progressive mass loss with increasing temperature, although significant differences were observed in both the magnitude and temperature range of the decomposition processes. This behavior reflects differences in chemical composition, pore structure, and water–solid interactions.

All materials exhibited an initial mass loss below 423 K, which is commonly attributed to the removal of physically adsorbed water or moisture weakly retained on the surface and in the porous structure of the materials. This behavior is expected for porous adsorbent materials and confirms their affinity for water molecules [14, 26, 27]. For zeolite material the broad temperature interval over which dehydration occurred suggests that the water molecules were adsorbed in several sites with different binding energies rather than homogeneous equivalent adsorption sites. Water molecules located on the external surface of a material require relatively little energy to desorb, meanwhile water molecules confined inside the porous or cavities could coordinate to exchangeable cations, and they are gradually removed at higher temperatures [28].

Between 423 and 523 K, distinct differences emerged among the materials. MSm exhibited a more pronounced mass reduction than ZT, suggesting the release of more strongly bound water molecules located within the aluminosilicate's microporous framework. This behavior is consistent with the lower Si/Al ratio previously determined by XRF analysis, which indicates a higher framework charge density and consequently stronger interactions with polar molecules such as water [26].

ZT showed the smallest mass loss throughout the temperature range analyzed, indicating superior thermal stability and lower volatile content which is consistent considering the inorganic composition of the material. The relatively high residual mass and gradual mass-loss profile of ZT suggest that the natural zeolite possesses a stable aluminosilicate framework capable of maintaining structural integrity under thermal treatment [29].

The most significant difference was observed for HApCM. While its behavior was initially like that of ZT and MSm materials, a marked mass-loss event occurred between approximately 573 and 673 K. This phenomenon is attributed to the thermal degradation of the organic phase incorporated into the composite. Such decomposition is absent in both MS and ZT, confirming the hybrid organic–inorganic nature of HApCM.

Above 673 K, MSm and HApCM continued to exhibit gradual mass loss, whereas ZT remained comparatively stable. The continuous decrease observed for MSm may be associated with the removal of residual adsorbed species accumulated during its industrial service life. It may be associated with continued release of strongly bound water together with residual adsorbed species accumulated during industrial service. In contrast, the mass loss in HApCM likely reflects the continued degradation of carbonaceous residues originating from the organic component (carbonaceous origin). At 973 K, the residual mass followed the order: ZT > MSm > HApCM indicating that ZT possesses the highest thermal stability among the materials investigated. Nevertheless, MSm retained a substantial fraction of its original mass, demonstrating that despite its previous industrial use, the spent molecular sieve maintains significant structural stability under thermal treatment.

From the perspective of thermal energy storage applications, the TGA analysis provides valuable information regarding the operational temperature limits of the materials proposed for the intended application. ZT exhibited the lowest overall mass loss and the highest residual mass, indicating excellent

thermal stability and suggesting suitability for repeated thermal cycling. However, its relatively low mass loss also suggests a lower quantity of adsorbed water available for adsorption-based heat storage processes [14, 30–33]. Furthermore, MSm displayed an intermediate behavior characterized by greater water release at low and moderate temperatures while maintaining acceptable structural stability up to 973 K. This behavior is particularly relevant because adsorption-based TES systems depend on reversible water sorption phenomena. Therefore, the larger amount of thermally removable water observed in MSm indicates a higher potential storage capacity compared with ZT. On the other hand, HApCM showed the largest total mass loss due to decomposition of its organic fraction. Although this material could possess interesting adsorption properties, the thermal degradation observed between 523 and 648 K should limit its application in systems requiring long-term thermal stability or repeated high-temperature cycling. In consequence, among the materials evaluated, MSm offers the most attractive compromise between adsorption capacity and thermal stability, supporting its potential valorization as a low-cost thermal energy storage material derived from industrial waste. The retained thermal stability supports the reuse of MS, extending their service life while reducing waste generation and promoting resource efficiency.

#### *Differential Scanning analysis*

The DSC curves of MSm, ZT, HApCM materials are shown in Fig. 4. It is important to highlight that DSC curves were carried out duplicate for each material to assess the reproducibility of thermal behavior. Since all samples exhibited similar thermal profiles, only representative thermograms are shown in the figure. All materials exhibited a continuous heat flow profile without a sharp endothermic or exothermic transition along the temperature range analyzed (298 to 573 K). This behavior is indicative of the absence of phase transformations, crystallographic rearrangements or thermal degradation process under the operation conditions. Therefore, materials that display this behavior are potential adsorbent for thermal energy storage systems, because this ensures that the heat could be stored and then released through reversible temperature changes rather than irreversible structural transformations [14]. Although the three materials exhibited similar thermal profiles, differences in the intensity and temperature range of the endothermic dehydration region were observed. Among the studied materials, ZT showed the highest endothermic heat flow, followed by MSm, whereas HApCM exhibited the lowest thermal response. These differences suggest distinct amounts and binding strengths of adsorbed water, reflecting the specific pore structure and surface chemistry of each material.

As can be observed from the figure all materials display a relatively broad endothermic peak, this phenomenon provides information regarding the energetic heterogeneity of the adsorption sites, specifically water and other species. The porous structure and abundance of active adsorption sites of MSm, ZT and HApCM favor water retention in different adsorption states [34]. The water interactions could be weakly physisorbed or external (around 298 to 353 K), confined within the pores, and more strongly bound associated with internal cations like in the aluminosilicates framework or surface hydroxyl groups like in the hydroxyapatite in HApCM, associated at temperatures over 373–423 K. In

consequence, the dehydration process could occur in a wide range of temperatures producing a broad endothermic peak in DSC thermograms as it can be observed from Fig. 4.

The DSC thermograms of HApCM exhibited a broad endothermic event centered between 333 and 343 K and it extended up to 373 K, which can be attributed to the release of physically absorbed water and evaporation of water, together with dehydration of hydroxyl surface moieties [35]. This event is in accordance with the first mass loss identified in thermogravimetric analysis. From the results, no significant thermal events were detected at higher temperatures, indicating the high thermal stability of hydroxyapatite composite material within the temperature range investigated (298–573 K). This behavior suggests that no major structural transformations of the inorganic component occur during heating, which is advantageous for thermal energy storage applications. The thermal response of HApCM material could be dominated by adsorption/desorption phenomena and sensitive storage.

The ZT thermogram displayed the most intense endothermic dehydration region among all materials, extending approximately from 313 to 383 K. This behavior is attributed to the removal of physically adsorbed and weakly bound water molecules located within the porous channels of the zeolitic framework. The relatively high intensity of this thermal event suggests that a considerable amount of thermal energy is consumed during dehydration, so strong affinity of the aluminosilicate framework toward polar water molecules is present [27]. Other authors observed similar calorimetric behavior when studying the thermal properties of natural clinoptilolite which has comparable aluminosilicate structure [31]. The authors evaluated thermal properties of natural clinoptilolite and found that around 55°C (328 K) is an endothermic event associated to physically adsorbed water. They also studied the thermal decomposition of minerals above 800°C (1073 K) but no change in the thermograms were observed in the temperature range 100–300°C (373–573 K), studied in the present research. Furthermore, De Gennaro et al., [14] investigated the thermal properties of natural and synthetic zeolites to consider them for thermal energy capture and storage. This study was carried out by determining the loss of water after different activation thermal treatments and they confirmed that the thermal storage mechanism is consistent with a storage mechanism dominated by reversible water adsorption/desorption. No additional thermal transitions were observed up to 573 K, indicating that the zeolites structures remain thermally stable within the studied temperature range. Csáki et al. [35] observed similar results in composites of HApCM-ZT, considering that in their study the HApCM used was natural obtained by bovine bones.

Spent molecular sieves showed intermediate thermal stability during TG analysis, but exhibited a broad heat absorption region extending from room temperature to approximately 423 K. This behavior is attributed to the gradual desorption of physically and strongly adsorbed water molecules retained within the microporous aluminosilicate framework. The low Si/Al ratio determined by XRF suggests a highly polar surface, which is favorable for water adsorption and may enhance thermal storage performance. Such structural characteristics increase the polarity of the adsorption sites and strength electrostatic interactions with polar water molecules. This is in accordance with TG results of between 423 and 523 K and supports the hypothesis that MSm retains significant adsorption functionality despite its previous

industrial use. In this material, a broader endothermic peak was also observed, which suggests the coexistence of different sites of adsorption and therefore different energies interaction. This could reinforce the heterogeneous chemical composition of the molecular sieve which was probably generated after its uses in prolonged industrial operation. From the analysis of the chemical composition of the molecular sieves and the estimated Si/Al ratio, these materials are comparable in composition to zeolites, due to their porosity and silicon and aluminum content; for this reason, the analyzed thermal properties could be compared with analogous materials that have been more extensively studied [14]. Synthetic zeolites are widely used as molecular sieves, because of their high hydrophilicity, microporous aluminosilicate structure, and their capacity of reversible water adsorption. These materials are characterized by having a low Si/Al ratio, so it directly impacts on the increase of negative charge in the structure and therefore, presence of cations in the domain structure. This originates highly polar adsorption sites which interact strongly with water molecules. As consequence, the dehydration procedure occurs gradually over a broad interval of temperature [33]. This behavior was observed by the analysis of the spent molecular sieves studied within this work.

Although the DSC signals offer the possibility to be used to estimate the specific heating capacity of a material, the direct determination of an absolute ( $C_p$ ) was not considered appropriate for the adsorbent materials studied within this work. During heating, the measured heat flow is not solely attributable to sensible heat but also includes the endothermic contribution from the progressive desorption of physically adsorbed and more strongly bound water molecules. Consequently, the recorded calorimetric response reflects the combined effects of heat capacity and dehydration, preventing the direct measurement of absolute  $C_p$ . A recent methodology proposed for zeolite 4A and zeolite 13X Sculler et al. [36] demonstrated that reliable determination of the intrinsic specific heat capacity of hygroscopic adsorbents requires correction of the DSC signal by subtracting the heat associated with the desorption process under controlled humidity conditions. Therefore, under the experimental conditions employed in the present work, the broad endothermic events observed below approximately 423 K should be interpreted as the overall calorimetric response associated with progressive water removal rather than as the intrinsic heat capacity of the solid structure. This behavior is characteristic of porous aluminosilicate adsorbents employed in adsorption-based thermal energy storage, where water desorption constitutes the dominant energy storage mechanism and largely governs the measured heat flow [14, 30].

It is important to highlight that due to the impossibility of carrying out the thermal assays in a wider temperature range due to the restriction of the equipment used, the results obtained are limited to the use of these materials for energy storage at low temperatures. From the viewpoint of thermal energy storage applications, the total calorimetric response recorded during dehydration may be even more relevant than the intrinsic heat capacity itself, because it reflects the actual amount of thermal energy absorbed by the materials during the application. Therefore, the broad endothermic events observed in the calorimetric assays constitute a direct indication of the energy required for water desorption from adsorption sites exhibiting different interaction strengths, which is one of the fundamental characteristics governing the performance of adsorption-based thermal energy storage materials.

The combined interpretation of DSC and TG analyses provided valuable insight into the thermal response mechanisms governing the reutilization of materials porous adsorbents used in environmental application or industry process. Whereas TG quantifies the quantity of volatile species released during heating and/or matter degradation, DSC measures the associated heat flow and thermal events [37]. Their potential applicability in thermal energy storage systems represents added value to these materials. From the results obtained by thermal analysis it could be suggested that the main events detected in the materials are predominantly governed by dehydration, desorption and thermally induced structural changes rather than phase transition mechanisms [38].

Overall, the combined physicochemical, microstructural, and thermal characterization demonstrates that the industrial service life of molecular sieves does not necessarily eliminate the functional properties required for adsorption-based thermal energy storage. Despite being discarded as hazardous industrial waste after gas purification processes, MSm retained their porous structure, hydrophilic character, thermal stability, and reversible dehydration behavior. These findings indicate that materials traditionally regarded as waste may still possess significant functional value, supporting their incorporation into circular economy strategies through their reutilization as low-temperature thermal energy storage adsorbents.

The combined physicochemical, microstructural, and thermal characterization allows a comparative assessment of the investigated materials regarding their suitability for low-temperature adsorption-based thermal energy storage. Table 4 summarizes the main strengths and limitations identified for each material based on the results obtained in this study.

Table 4  
Comparative assessment of the materials studied for low-temperature adsorption-based thermal energy storage applications.

| Structural integrity after use            | MS       | ZT              | HApCM    |
|-------------------------------------------|----------|-----------------|----------|
|                                           | ✓✓✓      | ✓✓✓             | ✓✓✓      |
| Thermal stability                         | ✓✓       | ✓✓✓             | ✓        |
| Water affinity                            | ✓✓✓      | ✓✓              | ✓        |
| Reversible dehydration                    | ✓✓✓      | ✓✓✓             | ✓✓       |
| Circular economy impact                   | ✓✓✓      | ✓               | ✓        |
| Expected cost                             | Very low | Low             | High     |
| Overall potential for low-temperature TES | High     | Moderate - High | Moderate |

## 4. Conclusions

This study demonstrates that MS generated during natural gas purification, although currently classified as hazardous industrial waste, retain the physicochemical and thermal characteristics required to be

considered promising candidates for low-temperature adsorption-based thermal energy storage. By combining waste valorization with energy storage applications, the proposed approach extends the functional lifetime of an industrial adsorbent while contributing to circular economy strategies and more sustainable management of industrial residues.

Thermal analyses further supported the viability of MS for thermal energy storage applications. TGA results revealed good thermal stability up to 973 K, with dehydration occurring primarily through the release of physically and structurally adsorbed water. DSC measurements revealed reversible thermal behavior within the studied temperature range and the absence of irreversible phase transitions, indicating that the material can undergo repeated heating and cooling cycles under low-temperature operating conditions.

The reversible calorimetric response associated with the progressive desorption of water demonstrates the material's ability to absorb thermal energy during heating, suggesting its suitability for adsorption-based low-temperature thermal energy storage.

From an environmental perspective, the proposed approach offers an alternative use for approximately 50 metric tons of dry matter generated annually by the studied gas processing facility, thereby reducing the amount of waste sent to landfills while simultaneously replacing virgin storage materials. This strategy contributes to the principles of the circular economy by extending the useful life of industrial materials and improving resource efficiency.

This study demonstrates that molecular sieves that have reached the end of their primary service life can retain considerable structural and thermal functionality that can be harnessed in secondary energy applications. This represents an effective strategy for reducing waste generation while extending the service life of the materials. Beyond the specific case of molecular sieves, this work demonstrates the feasibility of extending the functional lifespan of industrial adsorbents by integrating them into thermal energy storage systems. This approach contributes to waste recovery, resource efficiency, and the transition toward circular industrial processes, in line with current strategies for sustainable materials management. Future work should focus on evaluating their stability under long-term thermal cycling, their heat transfer performance under real-world operating conditions, and conducting technical-economic and life-cycle assessments to quantify the environmental and economic benefits of their large-scale implementation.

## **Declarations**

## **Competing interests**

All authors certify that they have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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# Author Contribution

Conceptualization: [RPR, FH and ND]; Methodology: [RPR, NS and FH]; Investigation: [RPR]; Data curation: [RPR, FH and ND]; Writing—original draft preparation: [RPR]; Writing—review and editing: [RPR, FH and ND]; Visualization: [RPR]; Supervision: [FH]. All authors have read and agreed to the published version of the manuscript.

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# Data Availability

All data supporting the findings of this study are available within the paper

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## Figures

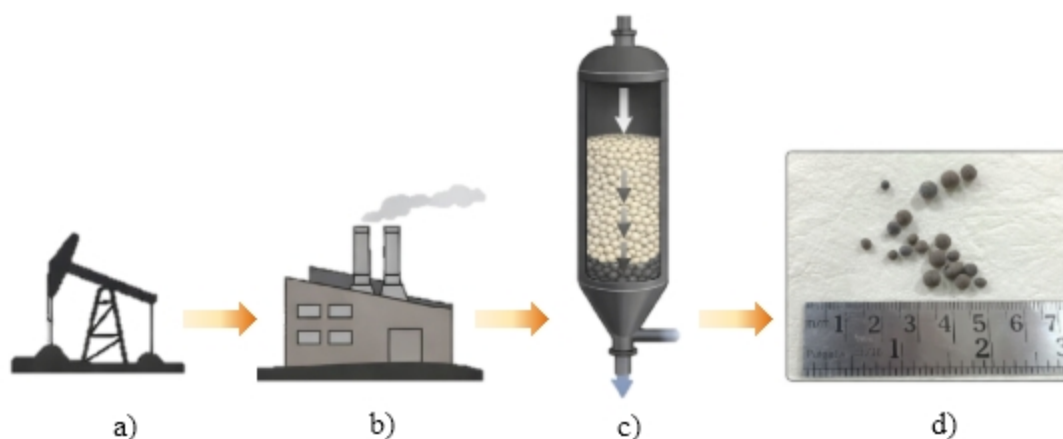


**Figure 1**

Gas processing: a) Extraction. b) Purification unit. c) Adsorption tower. d) Spent MS.

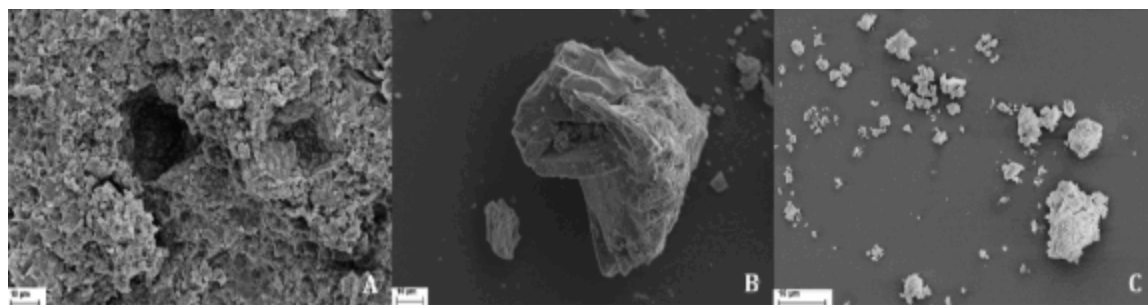


**Figure 2**

SEM microscopy. A) MSm B) ZT C) HApCM

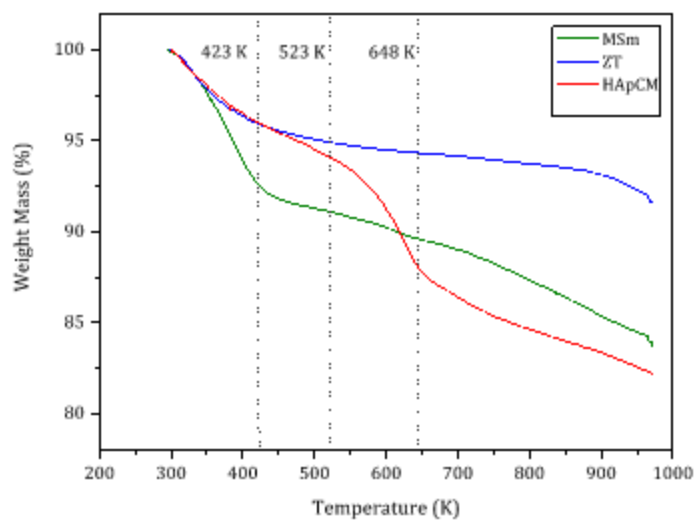


**Figure 3**

TG of MSm, ZT and HApCM

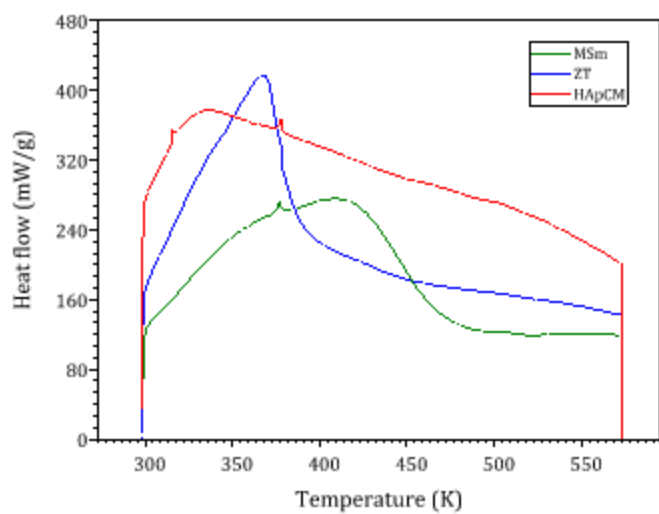


**Figure 4**

DSC curves of MSm, ZT and HApCM