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*Review Article*

# Exploring the potential of natural zeolites to enhance solar energy systems: A concise review

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**Abstract**

When examining the initial applications of natural zeolites for solar energy in recent history, it becomes apparent that homes in hot climates are often constructed with very thick walls with a high thermal mass. These walls absorb heat during the day and release it at night, maintaining a cooler indoor environment throughout the day. In countries like Turkey and Italy, where zeolitic tuff deposits are abundant, it is common to find structures with thick walls made from this natural stone. This study aims to explore the potential of natural zeolites for enhancing solar energy systems. The general properties of natural zeolites are examined, and topics such as the history of natural zeolites, reserves and consumption, application areas, and the thermo-physical properties of these materials are discussed. Existing solar energy systems utilizing natural zeolites have been reviewed, while innovative solar applications for both residential and industrial settings are proposed. It is hoped that this study will offer a multidisciplinary perspective for researchers and practitioners alike contribute the design solutions for such systems.



## 1. Introduction

Solar energy has an intermittent and irregular nature throughout the day, with its availability fluctuating based on time of day, season, and weather. Consequently, it is essential to develop effective storage methods to harness solar energy obtained during sunlight hours for use at other times, thereby ensuring a longer-lasting and stable thermal output from solar energy systems. Natural zeolites, of which over 40 naturally occurring frameworks are known, are industrially produced and widely used for many products across various sectors [1].

Although natural zeolites are already utilized in many areas, further research into their various types and properties could transform them into high-value products with additional applications in existing systems. This study presents an overview of the general and thermophysical properties of natural zeolites and their potential applications in design of solar energy systems, as well as recent research conducted in this area. For the first time in the literature, innovative solar energy systems utilizing the sensible heat storage capacity of natural zeolites are introduced.

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## 2. General Properties of Natural Zeolites

### 2.1. History of Natural Zeolites

The term 'zeolite' was first introduced in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who named it 'boiling stone' due to its ability to produce steam when it acts as an adsorbent [2]. The utility of zeolites began to be recognized in research by chemists Weigel and Steinhoff nearly two centuries after the discovery of the first zeolite mineral. They found that evaporated zeolites could adsorb small organic molecules but did not accommodate larger ones. In 1932, McBain coined the term 'molecular sieve' for zeolites due to their capacity to separate molecules based on size. Research between 1940 and 1945 further highlighted their industrial and commercial importance, particularly due to their adsorption and gas separation capabilities. In 1948, Milton and colleagues synthesized the first synthetic zeolite crystal, known as Linda A, and today over 400 synthetic zeolites exist. Zeolites, a group of over 40 naturally occurring microporous aluminosilicate minerals, are widely utilized as adsorbents, catalysts, and in various industrial applications. Of these, 14 types hold particular industrial significance and are commonly used. The most prevalent natural zeolite minerals include phillipsite, chabazite, heulandite, laumontite, natrolite, stilbite, erionite, and clinoptilolite. Since 1977, the International Zeolite Association (IZA) has been compiling and preparing zeolite structural data for scientific use [3].

Looking at historical solar energy applications, we observe that homes in hot climates are often constructed with thick walls with high thermal mass, which store heat during the day, releasing it at night to maintain cool temperatures indoors. In countries like Turkey and Italy, where zeolitic tuffs are abundant, it is common to encounter structures with thick walls made from this natural stone.

### 2.2 Natural Zeolite Reserve and Consumption

There are no reliable data on the estimation of natural zeolite reserves for the whole world. Although zeolite is mined in many countries, most of these reserves are of low or medium concentration volcanic tuffs. According to the U.S. Geological Survey, Mineral Commodity Summaries report published in January 2020, reserve estimates should be adjusted according to these concentration ratios. Although it varies according to the zeolite percentage, chemical and physical properties, particle size, surface modification and/or activation, the average zeolite sales price is stated in this report as $125 per ton [4].

According to this report, two leading mining companies in America stated that their total zeolite reserves were 80 million tons. However, although it is known that the reserves are very abundant throughout the world, exact figures are not available. In the Fig.1, zeolite mineral production values by countries were presented. When we look at the zeolite deposits in Turkey, zeolite deposits are rich in regions such as Balıkesir - Bigadiç, Manisa - Gördes, İzmir - Urla, Kütahya - Şaphane and Cappadocia. Clinoptilolite, chabazite, mordenite, erionite and analcime minerals are mostly concentrated in these deposits. Clinoptilolite is the most sought-after zeolite mineral in the world, and today it accounts for 80% of mining in Gördes (Manisa) and Bigadiç (Balıkesir) regions [5]. In 2001, upon a question directive given to the Turkish Grand National Assembly regarding zeolite reserves, it was stated that the existence of zeolite reserves in Turkey was understood in 1971, only Bigadiç among the zeolite deposits was investigated, and there were 500 million tons of zeolite reserves that could be processed here. In addition, together with these reserves, the answer was presented that Turkey's possible total zeolite reserves are estimated to exceed 50 billion tons. [6]. Although the exact values are not known, it is stated that 62% of the natural zeolite reserves in the world are in Turkey [7]. Despite the large reserves, the necessity of producing high value-added products that can be imported has been expressed for many years.

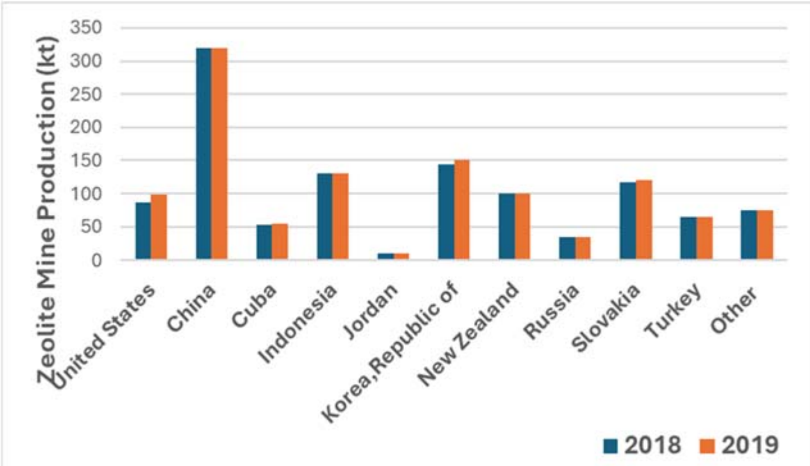


Fig. 1. Zeolite mineral production for the years 2018 and 2019 by countries [Data were adopted the U.S. Geological Survey, Mineral Commodity Summaries report, 2020]

### 2.3 Usage Areas of Natural Zeolites

The main physical and chemical properties of eoliths are; The ability to exchange ions, adsorption and the resulting molecular sieve structure, silica content, as well as the light color, lightness and pore structure of small crystals in sedimentary zeolites have led to the use of zeolites in a wide variety of industrial areas. The areas of use where one or more of these properties of natural zeolites, which have become an important industrial raw material in recent years, are required can be grouped into 5 main sections: pollution control, energy, agriculture-livestock, mining-metallurgy and other fields. In Table 1, usage areas and natural zeolites types are reported [8].

Table 1. Usage areas and zeolite types

| Area | Materials for which zeolite can be used as a substitute |
|---|---|
| Animal husbandry | Bentonite, sepiolite, dolomite, gypsum, iodine, iron oxide, limestone, magnesite, manganese, perlite, phosphates, salt, sulfur, talc, vermiculite |
| Ion carrier | Attapulgite / sepiolite, bentonite, diatomite, kaolin, pumice, pyrophyllite, talc, vermiculite |
| Detergent production | Sodium tripolyphosphate, sodium silicate, citrate |
| Lightweight aggregate | Clays, perlite, pumice, shale, vermiculite |
| Molecular Sieve | Activated carbon, activated clays, powdered alumina, attapulgite / sepiolite, bentonite, silica gel |
| Animal Litter | Diatomite, attapulgite / sepiolite, bentonite, kaolin |
| Radioactive Waste, Cleaning of Waste Water, Cleaning of Flue Gases, Cleaning of Oil Spills | Clinoptilolite and mordenite |

## 3. Thermo-Physical Properties of Natural Zeolites

When we consider them as sensible heat storage materials, the most basic thermo-physical properties of natural zeolites are density, thermal conductivity and specific heat. In Table2, Table3 and Table 4, thermal conductivity, density, specific heat and some descriptive structural features of natural zeolites are presented [9,10]. From Table 2, as particle size increases from Z1 to Z3, both thermal conductivity and density decrease. Plate forms show higher thermal conductivity and lower density compared to particle forms, indicating potential for applications requiring enhanced thermal conductivity and reduced weight. Plate forms display significantly higher thermal conductivity compared to particle forms, with values between 0.514 W/m·K and 0.550 W/m·K, increasing slightly from Z1 to Z3. Table 3 provides data on the thermal conductivity and specific heat of three different zeolite samples (Z1, Z2, Z3) across a temperature range from 30°C to 100°C. Thermal conductivity decreases with increasing temperature for all samples. Z1 has the highest thermal conductivity values, ranging from 0.187 W/m·K at 30°C to 0.151 W/m·K at 100°C. Z2 has intermediate values, starting at 0.142 W/m·K at 30°C and dropping to 0.096 W/m·K at 100°C. Z3 has the lowest thermal conductivity, decreasing from 0.124 W/m·K at 30°C to 0.083 W/m·K at 100°C. On the other hand, specific heat generally increases with temperature across all samples, though there are minor fluctuations. Z1 starts with a specific heat of 410 J/kg·K at 30°C and reaches a peak of 1810 J/kg·K at 80°C, then declines slightly at higher temperatures. Z2 shows a consistent increase in specific heat, from 1140 J/kg·K at 30°C to a peak of 2980 J/kg·K at 80°C, then decreases at higher temperatures. Z3 follows a similar trend, with specific heat increasing from 1100 J/kg·K at 30°C to 3030 J/kg·K at 80°C, before slightly reducing at higher temperatures. Some detailed structural properties are given in Table 4 for Gördes clinoptilolite [11].

Table 2. Thermal conductivity and density with particle size and plate form

| Particle size (mm) | Thermal conductivity (W/mK) | Density (kg/m3) |
|---|---|---|
| 0.1-1 (Z1) | 0.150 | 1905 |
| 1.0-3.0 (Z2) | 0.134 | 1780 |
| 4.0-5.0 (Z3) | 0.099 | 1667 |
| Plate form Z1 | 0.514 | 1503 |
| Plate form Z2 | 0.549 | 1470 |
| Plate form Z3 | 0.550 | 1428 |

## 4. Proposed Designs of Novel Solar Energy Systems with Natural Zeolites

In many studies in the past, both natural and synthetic zeolites have been used as a type of heat exchanger in heat pumps thanks to their adsorption properties [12]. However, this study focuses on systems developed by taking advantage of the sensible heat storage properties of natural zeolites. Considering the use of natural zeolites with solar energy, they have the potential to be an important component in establishing a structure that will provide more stable and stable storage of solar energy and retain heat, thanks to their heat storage properties.

Table 3. Thermal conductivity and specific heat with temperature

| Temperature (˚C) | Thermal conductivity (W/mK) | | | Specific heat (J/kgK) | | |
|---|---|---|---|---|---|---|
| | Z1 | Z2 | Z3 | Z1 | Z2 | Z3 |
| 30 | 0.187 | 0.142 | 0.124 | 410 | 1140 | 1100 |
| 40 | 0.172 | 0.131 | 0.119 | 520 | 1390 | 1520 |
| 50 | 0.164 | 0.124 | 0.114 | 1260 | 1930 | 2010 |
| 60 | 0.161 | 0.119 | 0.102 | 1540 | 2650 | 2450 |
| 70 | 0.158 | 0.11 | 0.106 | 1660 | 2950 | 2800 |
| 80 | 0.154 | 0.102 | 0.098 | 1810 | 2980 | 3030 |
| 90 | 0.151 | 0.108 | 0.092 | 1670 | 2870 | 3010 |
| 100 | 0.151 | 0.096 | 0.083 | 1490 | 2670 | 2830 |

Table 4. Structural features of Gördes clinoptilolite [11]

| Parameter | Value |
|---|---|
| Chemical formula | (Na0.5K2.5)(Ca1.0Mg0.5)(Al6Si30)O72.24H2O |
| Mineralogical composition of the raw material | Clinoptilolite (%85-90) + Smectite(%5-6), Opal-CT(5-6)+Quartz(<3) |
| Clinoptilolite identification | Rich in potassium, potassium, calcium, clinoptilolite |
| Color | Natural rock; white, beige, light beige, almond green |
| Toughness (Mohs) | 3 |
| Bulk density | 500-1200 kg/cm$^3$ (depending on grain sizes ranging from powder to < 15 mm) |
| Volumetric weight (dry) | 1.4-1.7 g/cm$^3$ |
| Volumetric weight (saturated) | 1.8-2.0 g/cm$^3$ |
| Specific weight | 2.1 g/cm$^3$ |
| Visible porosity | 35% |
| Water adsorption capacity | 135% |
| Resistance to acid, base environment (pH): | 2.0-12.0 |
| Surface area | 40.79 m$^2$/g |
| Thermal resistance | up to 750 °C |
| Pressure Strength | 10.10 MPa |
| Clinoptilolite crystal size | 5-15 µm |
| Average pore radius | 0.041 µm |
| Water absorption by weight | 23% |
| Ammonium (NH4) ion exchange capacity | 1.6-2.0 meq/g |
| CO2 adsorption | 94 mg $CO_2$/g |

According to IS0 and CEN standards, materials with a thermal conductivity coefficient of less than 0.065 W/mK are defined as thermal insulation materials and are the most decisive feature in the selection of thermal insulation materials. Ozcelik (2010) investigated physical and mechanical properties of foam materials which are obtained by using natural clinoptilolite samples and foaming materials. It was observed that the clinoptilolite samples also formed a porous structure at 1300 °C. It has been revealed that the thermal conductivity coefficients of the majority of SiC-containing foam materials are much lower than 0.065 W/mK (up to 0.029 W/mK) [13]. In this section, in the light of these thermophysical properties, the application and potential improvements of natural zeolites to known solar energy systems will be discussed.

### 4.1 Solar Thermal Collectors Enhanced with Natural Zeolites (STC-NZ)

Structure of solar thermal collector improved by natural zeolite plates is given by Fig.2. In the framework of an ongoing project [14], a conventional solar thermal collector has been improved by natural zeolite plates and some experiments have been conducted. As known, output temperature of a STC changes by incoming solar radiation. It is possible to obtain the thermal energy from this system at a more constant temperature, to balance temperature changes during the day and to continue obtaining thermal energy after sunset, thanks to the heat storage feature of natural zeolites. The qualitative results of this project will be the subject of another study.

Fig. 2. Structure of STC-NZ [14]

### 4.2 Photovoltaic thermal (PVT) system enhanced with natural zeolites (PVT-NZ)

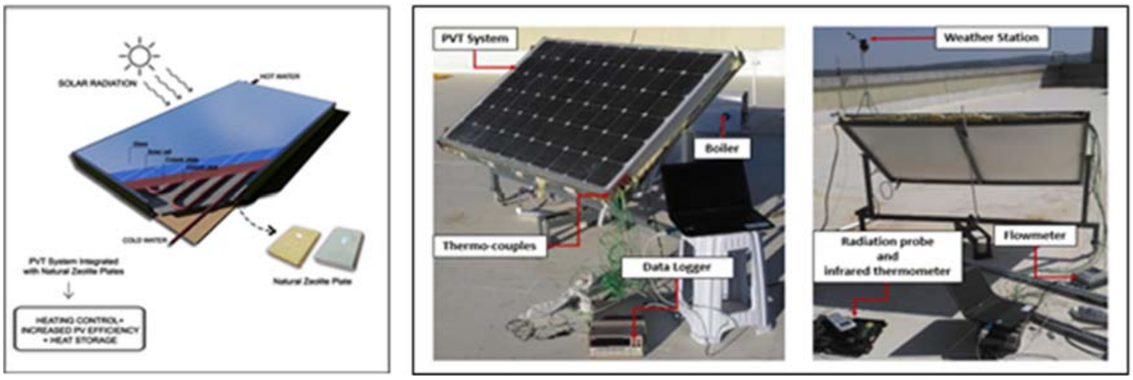


Fig. 3. Structure and test system of PVT-NZ [15]

Structure and test system of PVT-NZ present by Fig. 3. In photovoltaic panels, solar radiation that cannot be converted into electricity causes overheating. This excess heat can be removed from the PV back surface with different fluids in PVT systems. This heat can be used as thermal energy. In PVT systems, both phase change materials containing latent heat and sensible heat storage materials can be used. Thus, the waste heat generated during electrical conversion is removed, ensuring that the electrical efficiency of the PV panel does not decrease, and this heat can also be used as a thermal energy source. Natural zeolite plates enable waste heat to be absorbed and used as thermal energy in PVT systems. The performance of PVT systems integrated with natural zeolite plates increases with their porous structure and high heat storage properties [15,16]. In the experiments, thermal efficiency of up to 69% and leaving water temperatures of 53.4 °C were achieved. For the proposed system, the payback period is calculated as 1.99 years for industrial applications and 3.76 years for residence tariff. Detailed qualitative results of the experiments will be presented as a result of another study.

**4.3 Natural Zeolites for Nearly Zero Energy Building (nZEB) Applications**

In general, near-zero energy buildings (nSEB) are considered highly energy efficient buildings powered by renewable energy to compensate for the energy demand. The concept is taken from the European Parliament Energy Performance of Buildings Directive (EPBD) [Directive (EU) 2010/31/EU]. The directive stipulates that buildings constructed after 31 December 2020 and that need to be heated or cooled according to their purpose must be built as nSEB. Trombe wall systems, one of the passive solar energy techniques, are low-cost, high-efficiency systems that have been known for many years and can be applied to existing buildings. The energy heated and stored by solar radiation throughout the day heats the indoor air and the interior is naturally heated thanks to the natural circulation that occurs. Thanks to the high heat storage capacity of natural zeolites, the stored energy will continue to provide thermal energy to the environment at the end of the day. The effectiveness of Trombe walls has the potential to be increased by using natural zeolite composite plates as thermal mass. In Fig. 4, prototype test room of Composite Trombe Wall (CTW) studied in ongoing project is given. In this study, Perlite was added to natural zeolite to reduce thermal conductivity. Natural zeolite-perlite composite plates low thermal conductivity (about 0.10 W/mK) and high heat capacity (about 5.29x106 J/m3K) can be used in the construction sector as a building material with their low-cost superiority. It can be used as a heat storage material within the scope of zero energy buildings. It will ensure that passive solar energy systems become widespread in the Renewable Energy systems sector. CTW offers the Trombe wall system as a strong option within the scope of nSEB, with its applicability to existing buildings, offering a wide range of architectural options, being usable in every climate zone, low cost and high efficiency potential, especially in heating.

Fig. 4. Test system of Composite Trombe Wall [17]

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## 5. Conclusions

It is important to transform natural resources into high value-added and economical products in different areas. Disadvantages of solar energy systems, which are the leading renewable energy source, such as storage and intermittency, can be minimized with sensible heat storage materials. In this study, general and thermophysical properties of natural zeolites and effective system suggestions for improving solar energy systems are put forward. Due to reasons such as the difficulty of application of phase change materials, their cost and limited lifespan due to the charge-discharge cycle, the potential of using natural zeolites, one of the sensible heat storage materials, in solar energy systems attracts attention. Some significant indications made in this study are given below:

- The usage areas of natural zeolites can be expanded as sensible heat storage materials.
- By making different additives to natural zeolites, their thermophysical properties can be made suitable for use in solar energy systems.
- Natural zeolite composite plates have a significant potential in obtaining regular and stable thermal energy in solar energy systems.
- Low-cost composite natural zeolite plates can be used to improve performance in STC, PVT and Trombe wall systems.
- It may be possible to use composite natural zeolite plates as a sensible heat storage material in every climate and geography, as an alternative to phase change materials.

Natural zeolites will certainly have potential and new applications that are expected to be discovered, which cannot be listed here. Transforming low-cost and abundant raw materials into high added value products and increasing the efficiency of solar energy systems will make significant contributions to the spread of renewable systems and sustainability.

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