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Natural Zeolite Minerals as Storage of Solar Energy

Oyku Bilgin,
Sirnak University, Faculty of Engineering, Mining Engineering Department, Sirnak, Turkey,

***Abstract*—Zeolites is a mineral group as a result of variation of volcanic ashes in the aquatic environment millions of years ago consisting of alkaline and soil alkaline's hydrated natural silicates. The most important zeolite minerals are heulandite, chabazite, analcime, erionite, natrolite, philippsite, mordenite. Zeolite's have wide application areas. Zeolite's important but uncommon usage is solar storage. Solar energy is a kind of energy source used for heating house, heating ground and cooling, providing to process heat in industry, watering in agriculture, drying and cooking. Solar energy technologies are wall systems and roof systems which collecting heat, energy recovery, active solar collection, solar repositories, solar collectors, satellite power systems. Studies have put forth materials solar storage features which have adsorbent properties. Natural zeolite mineral is used in solar storage depending on adsorption and ion change properties. Depending on temperature, clinoptilolite and chabazite, heating and conditioning the small structures, in other words, it is possible to use zeolites as heat changer. Also natural zeolite can keep the stored energy long time and the stored energy have transferable feature.**

Index Terms*— Energy storage, Solar energy, Usage area, Zeolite.

I. INTRODUCTION

Energy is an compusory necessity for human. Nonetheless, the conventional sources of energy fossil fuels are just not enough to meet the constantly growing energy demand. Mankind has received a gift which is solar energy from nature and from times immemorial man has tried to explore the use of this large and plentiful energy source. Thus, solar energy seems to be the most promising renewable energy source [1-3] and the usage of solar energy is very fascinating aspect of science.

Zeolite's general chemical formula is Mx Dy $[Al_x+2y\ Si_n-(x+2y)O_2n].mH_2O$. In this formula, M formulates Na, K or the other (+1) valency cations, D formulate Mg, Ca, Si, Ba and the other (+2) valency cations [4]. Zeolite, belonging to the alumina silicate group, literally means "fusing rock". When heated, it explodes and disperses. Zeolites is a mineral group as a result of variation of volcanic ashes in the aquatic environment millions of years ago which consisting of alkaline and soil alkaline's hydrated natural silicates. Feldspar and the other alumino-silicates transformation is called zeolitization. Natural zeolite that is more than 40 minerals are known.

The most importants are clinoptilolite, heulandite, chabazite, analcime, erionite, natrolite, fillipsit, mordenite. In addition, more than 150 synthetic minerals are also available.

Zeolite minerals have alumino-silicate structure which connected to each other by sharing oxygen atoms and consisting of tetrahedral AlO_4 and SiO_4's extended unlimited three-dimensional system. Its structure is contained similarly honey comb or cage and changeable cations and water.

Micro-pores which are between its units combine with micro windows and create one, two or three dimensional pore systems and canals. Displays of scanning electron microscopy is shown in Fig. 1. The amount of space is between 20-50% of total volume. Natural zeolite's physical properties are shown in Table I. Zeolite mineral's the most important feature is that molecular sieve that can easily enter this spaces and change place which arising from liquid and gas molecules with soil alcaline ions. Zeolites have wide range usage areas. For example, used in agriculture due to the properties such as ion change, water and gas storage, fisheries, water, gas and radioactive wastes' clening, drying, solar energy and gas storage, odor control, structural component, good quality paper production and many fields [5].

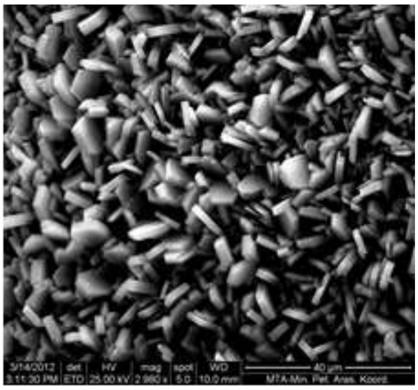

Fig. 1. Displays of scanning electron microscopy for zeolite mineral (clinoptilolite)

TABLE I: THE ARRANGEMENT OF CHANNELS

Zeolite	Pore volume(%)	Heat balance	Ion change capacity (meq/g)	Specific gravity (g/cm3)
Analcime	18	High	4.54	2.24-2.29
Chabazite	47	High	3.84	2.05-2.10
Clinoptilolite	34	High	2.16	2.15-2.25
Erionite	35	High	3.12	2.02-2.08
Heulandite	39	Low	2.91	2.18-2.20
Mordenite	28	High	4.29	2.12-2.15
Philippsite	31	Middle	3.31	2.15-2.20

II. Structural Characteristic of Zeolites

A. Adsorption Desorption Property

Adsorption is the adhesion of atoms, ions, biomolecules or molecules of gas, liquid, or dissolved solids to a surface [6]. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It differs from absorption, in which a fluid permeates or is dissolved by a liquid or solid (the *absorbent*) [7]. The term sorption encompasses both processes, while desorption is the reverse of adsorption. It is a surface phenomenon.

Similar to surface tension, adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. Ion change capacities of zeolite are shown in Table. II. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction [7].

TABLE II: Ion Change Capacities of Zeolite

Ion type	Ion change capacity (meq/g)										
	1.50	1.75	2.00	2.25	2.50	2.75	3.00	3.25	3.50	3.75	4.00
	Ion amount (g iyon/g zeolite)										
Na^{+}	0.034	0.040	0.046	0.052	0.057	0.063	0.069	0.075	0.080	0.086	0.092
K^{+}	0.057	0.068	0.078	0.088	0.098	0.108	0.117	0.127	0.136	0.147	0.156
Mg^{+2}	0.018	0.021	0.024	0.027	0.030	0.033	0.036	0.040	0.043	0.046	0.049
Ca^{+2}	0.030	0.035	0.040	0.045	0.050	0.055	0.060	0.065	0.070	0.075	0.080
NH_4^{+}	0.028	0.033	0.037	0.042	0.047	0.051	0.056	0.061	0.065	0.070	0.075
Cs^{+4}	0.049	0.058	0.066	0.074	0.082	0.091	0.099	0.107	0.115	0.123	0.132
Cu^{+2}	0.048	0.056	0.064	0.071	0.079	0.087	0.095	0.103	0.111	0.119	0.127
Pb^{+2}	0.155	0.181	0.207	0.233	0.259	0.285	0.311	0.337	0.363	0.389	0.414

Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins, increase storage capacity of carbide-derived carbons for tunable nanoporous carbon, and water purification. Adsorption, ion change, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Lesser known, are the pharmaceutical industry applications as a means to prolong neurological exposure to specific drugs or parts thereof.

Zeolites are natural or synthetic crystalline aluminosilicates which have a repeating pore network and release water at high temperature. Zeolites are polar in nature. They are manufactured by hydrothermal synthesis of sodium aluminosilicate or another silica source in an autoclave followed by ion change with certain cations (Na+, Li+, Ca_2+, K+, NH_4+). The channel diameter of zeolite cages usually ranges from 2 to 9 Å (200 to 900 pm). The ion change process is followed by drying of the crystals, which can be pelletized with a binder to form macroporous pellets. Zeolite is a tecto-silicate, its structure is open which diferent the other tecto-silicates (felspar, quartz) and has a 3 dimensional tunnel and cage system. This system provide to the molecules which small than its spaces and so zeolite's has a name that molecular sieve [5].

Zeolites are applied in drying of process air, CO_2 removal from natural gas, CO removal from reforming gas, air separation, catalytic cracking, and catalytic synthesis and reforming. Non-polar (siliceous) zeolites are synthesized from aluminum-free silica sources or by dealumination of aluminum-containing zeolites. The dealumination process is done by treating the zeolite with steam at elevated temperatures, typically greater than 500 °C (930 °F). This high temperature heat treatment breaks the aluminum-oxygen bonds and the aluminum atom is expelled from the zeolite framework.

B. Ion Change Feature

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$$\underset{\text{Solid}}{C{+}A^-} + \underset{\text{Solution}}{B^-} \rightleftharpoons \underset{\text{Solid}}{C{+}B^-} + \underset{\text{Solution}}{A^-} \qquad (1)$$

Ion change that occur reversible between solution phase and insoluble solid phase (ion changer). For example, in C^-A^+ ion changer M^- is constant insoluble anion in the crystal structure and A^+ is replaceable cation. If the C^-A^+ ion changer put in a water solution which including B^+ cations, this ion change reaction (cation change reaction) occur. Refer to

"(1)," ion chance.

Ion's total valencies are equal to each other in ion change process from solid phase to solution, from solution to solid phase and always system is neutral as electrically. Cations which inside crystal structure of zeolites, are connected to tetrahedral structures with weak bonds and are replaced with solutions ions. Ion change's amount is described with ion change capacity (ICC). ICC's measure is gram or changeable mole concept per 100 g zeolite. Periodic working cooling system is illustrated in Fig. 2. Sometimes can be used equivalent weight term instead of mole concept [5].

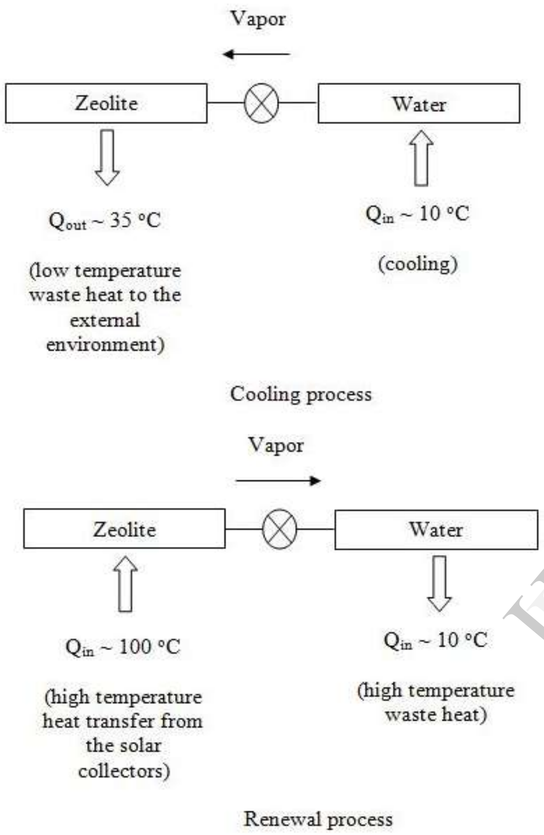

Fig. 2. Periodic working cooling system [6]

Catalyst Feature

Natural zeolites are used as catalyst in some chemical reactions either as they are or as change some properties. Zeolites have different characteristics than other catalyst materials. One of these characteristic is Si and Al tetrahedral's specific and repetable sequences which in zeolite's crystal structure. In most cases, showing catalytic activity center points are cation's locations in their structures. The reason of zeolite's usage as catalysts are to protect activeness, selectivity, chemical stability and etc. properties long time, easy and repeatable regeneration and durable for external influences such as heat and pressure [5].

C. Molecular Aieve Feature

Molecular sieving is defined as cation's selective adsorbtion which depend on its physical properties and electrical charge distribution. Porous structure which has uniform distribution allows specific molecules adsorption which pass only from the pores in a solution. Molecules which is bigger than the pore space stay out of zeolite. When zeolites are compared with the other minerals (active carbon, silica gel etc.) which have molecular sieve feature, they are more advantageous for molecular sieving [8].

Molecular sieving affected for heating of zeolite and its dehydratation. Increasing of temperature cause deterioration of the crystal structure and proportionally with residual temperature with amount of structural oxygen cause broadening the window. On the other hand dehydratation cause change of cation settlement and electric load distribution. Dehydrated zeolites adsorb polar molecules selectively such as H_2O, CO_2, and H_2S [5].

D. Usage Areas of Zeolites

Areas of usage for zeolites can be described under four main heads which are pollution control, energy sector, agriculture and stockbreeding. Applications for pollution control are marginalizing heavy metals like Pb, Cu, Zn, Cd and Hg from industrial waste waters, marginalizing ammonium (NH_4^+) which has a toxic effect from city waste waters and drinking water, lowering water hardness, regulating pH-conductivity and raising the quality of drinking water, purifying chimney gases, cleaning up oil leaks, binding air pollutant gases such as SO_2, CO, CO_2, H_2S, NH_3, NO_x, garbage disposal areas, metallurgy applications and marginalizing radioactive materials such as Cs, Sr, Rb from nuclear wastes. Zeolites' ion exchange, adsorption and molecular sieving properties are used for these applications. Applications regarding naturalizing and drying of natural gases, heat storage, oxygen generating, processing coal gases, separating industrial gas compounds such as CH_4/N_2 and N_2/H_2, oil raffination and sun energy storage systems can be performed with the help of zeolites' ion exchange, adsorption, molecular sieving and catalyst properties. In agriculture and stockbreeding zeolite with its ion exchange, adsorption and molecular sieving properties can be used as fertilizer additive, in reclaiming soil by extracting excess water, conditioning soil for agriculture, preventing washing off of plant nutrients, stabilizing pH on agricultural soil and regulating soil as carrier material for pesticides, moisture and insect control in grain stores, preventing ripening and hardening in fertilizers during storage, transferring nutrient ions on agricultural grounds, binding cations of unwanted heavy metals such as Pb, Cd, Zn and Cu as additive for animal feed in cleaning ponds in fish farms in order to provide enough oxygen, preventing effluvia in barns as cat soil, strengthening bones, enhancing egg and bone development and bone meal applications [5]. Also zeolite with its ion exchange, adsorption and catalyst properties are known to be used as filling material in paper production for seeking uranium beds in mining as light component element and cement additive in construction in water culture applications, powder detergent applications as defroster in highways and many other industries such as medicine [9, 10].

III. Storage Methods of Solar Energy

Solar energy which not storaged as direct radiation energy, to use this energy it must be transformed into other types of energies. Solar energy can be transformed into other forms with absorption, pyrolysis and photovoltaic systems. This transforme energy is thermal or electricity energy forms. It can be used or storaged with special methods to use later. Generally, energy storage is chemical storage (thermochemical, electrochemical), mechanic storage (hydroelectricity), thermal storage (sensible heat, latent heat).

A. Usage of Zeolites in Solar Energy Storage Systems

Solar energy is an energy clean, renewable, safe, available all over the world, transposable to mechanic and electricity energy, for domestic usage, heating and cooling, industrial usage, agricultural watering, drying and coking. Passive thermal systems, active solar collection systems, solar ponds, collectors, satellite power systems are solar utilization areas [5].

According to zeolite's water exchange feature, in clinoptilolite and chabazite applications it seems possible to use zeolites as heating and air-condition of small structures in other words heat changers to transfer solar energy [11]. Energy is stocked similar as condensation-evaporation process. When gas is adsorbed on the solid side, generally a heat discharge occur. The reverse process requires heat charging. Zeolite material is dried with solar collector's hot air in water-zeolite system. When the zeolite is heated, adsorbed water gave off. As a result of this process, air becomes filled with water. Vapor is condensed with using a suitable heat changer and condensation heat is gave off. When zeolite dehydrated it became potential for heat production. Water vapor is adsorbed by zeolite and adsorption heat is give off. Dry-warm air is obtained [12].

B. Storing Solar Energy Principle of Zeolites

Some examples about citation of journal articles, books and websites are shown below. Zeolites have extremely nonlinear adsorption isotherms to water. The feature of adsorbing and desorbing water makes zeolites a new type of material for storing solar energy and to be showed off. When zeolites are heated, water molecules in it escape, and heat energy is stored in it in the meantime; when water molecules are adsorbed again, the heat energy in zeolites is released. These two processes can be shown by chemical equation as follow:

$$AmXpO2p \bullet nH2O = AmXpO2p{+}nH2O\neg \quad \text{(endothermic)} \qquad (2)$$

$$AmXpO2p \bullet nH2O = AmXpO2p{+}nH2O \quad \text{(endothermic)} \qquad (3)$$

When zeolites absorb heat and desorb crystal water molecules, the temperature of it does not vary, therefore, this process belongs to the one of latent heat storage. So long as zeolites, of which water molecules are desorbed, keep apart water, the heat energy of it can be stored as long as you like. The energy storing density of zeolites is higher than the aforementioned three types of ways of storing energy. When the heat energy in zeolites is desorbed, we can control the speed of desorption by controlling the speed of water absorption. Therefore, zeolites have better merits than the aforementioned ways of storing energy.

IV. Conclusion

Thermal energy is used which stored in natural zeolites are used in heating, drying and cooling systems for storage the thermal energy long and short times which obtained from sun. Thermochemical storage is used this process due to natural zeolites structure. Materials must have some features to use in thermochemical storage process such as storage material's weight, effective energy density, price of storage material, renewability feature, antitoxin effect, simply design. Considering these properties, zeolites importance is understood than the other conventional storage materials.

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