

LARGE SCALE SYNTHESIS OF NANOSCALE SODIUM-ZEOLITE POWDER FROM RECENT OKINAWA PUMICE STONES, INTENDED FOR INDUSTRIAL WASTE HEAT RECOVERY, STORAGE AND CO₂ CAPTURE

ABSTRACT

Recent pumice stones in Okinawa have become a limiting factor for fishing activities and Ship transport on the surrounding water bodies. This proposal recommends the conversion of these pumice Stones into nanoscale zeolites on a large Scale in order to be used for industrial waste heat utilization, storage and CO₂ capture. Microwave hydrothermal synthesis of zeolite from Pumice and NaOH solution will be engaged in order to ensure uniform-size-composition zeolite particle. Zeolites are crystalline alumino-silicates, characterized by a high specific surface area and wide microporous volumes, which make these materials perfectly suitable for adsorption of fluids such water vapour and CO₂, even at low partial pressures. NanoScale Zeolite powders(50nm) will be synthesized by ball milling and treatment of the subsequent products with both NaOH and Sodium aluminosilicate solutions. Hundreds of tons of Akali-Cation Rich NanoScale Zeolite powder will be packed to form adsorbent beds that will be used as a thermal energy storage facility. A waste incineration plant will use steam from its turbine to heat up the ambient air to 130°C, as the ambient is let into the Zeolite storage (adsorbent beds). This is the Charging process and desorption takes place. The Stored energy will be released during discharging or adsorption and in this case humid exhaust air from the gas fired plant will be passed over the Packed zeolite. The zeolite storage is used as fuel saver to support the gas burner in the drying process. The Zeolite fuel cell can store several Mega Watts of energy and the cost of energy can be reduced to 0.082\$/kWh. In the process thousands of CO₂ per cycle will be saved.

INTRODUCTION

The August-2021 underwater volcanic eruption at Fukutoko-Okano-ba in Ogasawara island chain led to a large number of Pumice stones (100 million cubic meters) washing ashore on the main island of Okinawa Prefecture and other places, as reported by the Watcher's News website. These volcanic materials have negatively affected the fisheries industry and ship operations. Strategies have to be devised dispose of these volcanic waste materials, or possibly make use of them.

Pumice is an amorphous, porous volcanic rock which is composed mainly of SiO₂ and Al₂O₃ (Avishan & Nazari Kudahi,2020; Moradi et al 2016;). Pumice from some localities such as Lipari, Italy contains more than 77% of Silica according to research by Burriesci et al. in 1983. The same research concluded that the Hokkaido Pumice contained 73% Silica. Because of the high proportion of silica, the Pumice surface is negatively charged (Çifçi & Meriç, 2015). Pumice has been used in different sectors for a number of decades such as building material, water and waste water treatment, air treatment and many others (Çifçi & Meriç, 2015) All these applications rely on pumice properties such as dehydration, adsorption and catalysis. Adsorptive abilities of Pumice are the most studied. It is worth noting all these properties of Pumice, including adsorptive ones can be improved with the introduction of appropriate modifications.

Zeolites are the other silica-rich materials with impeccable Adsorption abilities. According to Zeng et al. (2021), Zeolites are a group of crystal-like, nanoporous, inorganic material with regular micropores and exceedingly flexible functionalities. Zeng et al recognizes them as perfect materials for use in catalysis, adsorption, and biomedicine due to their notable key features such as accessible void space, large surface area, and strong acidity. They also have excellent cation exchange ability (Ruíz-Baltazar & Pérez, 2015)

The 'ida-ore' website puts it clearly that Zeolite are rare volcanic minerals with a natural negative charge that can be synthesized by treating Silica-containing substances with sodium aluminate solution at high temperatures. Additionally, Burriesci et al. (1983) discovered that an interaction between Silico-aluminate materials with alkaline salt solutions in appropriate reaction conditions, can yield zeolites.

According to Moradi et al (2016), Zeolite is an effective adsorbent in so many applications but so expensive. In an attempt to reduce the cost of Zeolites by cutting down the cost of its synthesis, it is wise to use freely and abundantly available silica-rich raw materials.

This study proposes the use of the huge volume of recently ejected Pumice stones in Okinawa as a silica-rich raw material for the Synthesis of Zeolite that can be modified for adsorption Thermal Energy Storage and CO₂ Capture. The zeolite storage will be used as a fuel saver and a support for the gas burner in the drying process

LITERATURE REVIEW

Zeolites

Zeolites are materials crystalline and hydrated in nature and can exist naturally or can be synthesized. They have an aluminosilicate composition and are characterized by a microporous structure, tunable functionalities, great thermal stabilities and high adsorption properties ((Noviello et al., 2021; Ma et al., 2020). Król (2020) reported that the origin of natural zeolites is attributed to both hydrothermal and volcanic processes. They assume both a crystalline form localized in igneous and metamorphic rocks, and granular form amassed in sedimentary rocks. Krol adds that zeolites are abundantly found in ocean bottom sediments which are yet to be accessible to humans. Core components of clay or tuff are arguably found in zeolite minerals. According to sas.upenn website, zeolites have a general formula $[(\text{SiO}_2)(\text{AlO}_2)_x]\text{M}_{x/n}^{n+} \cdot w \text{H}_2\text{O}$. M is a usually a group I or II metal ion with n positive charge. The interconnected tetrahedral structural framework is provided for by the Silica and Aluminum oxide part. The inner open area (usually connected and serve as channels) of the compound are occupied by the metal ions. The pores in zeolite exhibit a nanoscale size with diameters less than 0.8nm. Natural zeolites are of so many kinds and some are synthesized in the laboratory for commercial or research purposes. Zeolites bear a honeycomb framework of micropores that is negatively charged. Adsorbate molecules can be adsorbed into this framework (Rhodes, 2010).

Current Synthesis of Zeolite

Naturally, zeolites were formed when volcanic ash reacted with the waters of basic lakes and this process lasted thousands of years (Król, 2020).

Pumice samples have to be very finely powdered before being subjected to the zeolitization process in the presence of an alkaline media (Falyouna et al., 2020).

According to Wu et al. (2018), Zeolites rich silica, aluminosilicate and aluminophosphate can be effectively prepared by mixing, grinding and heating starting solid materials in the absence of a solvent. The starting raw materials for hydrothermal zeolite synthesis according to Deneyer et al., (2020), can be a silicon or aluminium source, water, a mineralizing agent and structure directing agent. The same author provides examples of Silicon sources such as silica, alkali silicates, silicon alkoxides and many others. Aluminium sources include aluminium hydroxides and oxides, aluminium nitrates and others. The mineralizing or mobilizing agent can be hydroxyl or fluoride ions. Pumice has already been stated in the introduction part as having a high concentration of silica and aluminum oxide. Hydrothermal Synthesis can be costly, because of the cost of resources and processing time. Deneyer et al. 2020 recommends the use of microwaves (300 MHz–300 GHz) and ultrasonic irradiation (20kHz-10 MHz) during the synthesis in order to reduce the synthesis time or make the process run faster. Microwave assisted hydrothermal synthesis can lead to a uniform composition and even dimensions of the product.

The look.chem website mentions that Silica containing compounds being treated with Sodium aluminate solution at high temperature can be yield zeolite. The same website puts it clearly that zeolite types A, X and Y are manufactured first by mixing sodium aluminate and sodium silicate solutions to form a sodium aluminosilicate gel is formed, and then SiO₂- and Al₂O₃-containing compounds pass into the liquid phase, from which the zeolites are formed by crystallization. Pumice is rich in both SiO₂ and Al₂O₃.

Prajaputra et al. (2019) puts it clearly that reacting pumice with NaOH in the presence of heat (100°C) for 24 hours, followed by washing with distilled water and then drying again for 12 hours at 100°C, can yield zeolite. An alkali-Cation rich Zeolite is a target of synthesis in this proposal.

Principles of Adsorption Heat Storage

The literature is mainly provided by Vasta et al. (2018). Adsorption heat storage technology is based on the interaction between a liquid sorbate, usually water, and a solid sorbent (e.g., zeolites, silica gels, activated carbons). This interaction occurs between the sorbate molecules and the available surface of the solid. In order to explain the working principle of an adsorption heat storage, it is necessary to distinguish between direct and indirect heat storage methodologies (Hauer, 2007). The direct heat storage is the distinctive technology engaged with heat storage both in sensible and latent form. However, this proposal is focusing on indirect heat Storage to which adsorption heat storage is a subset.

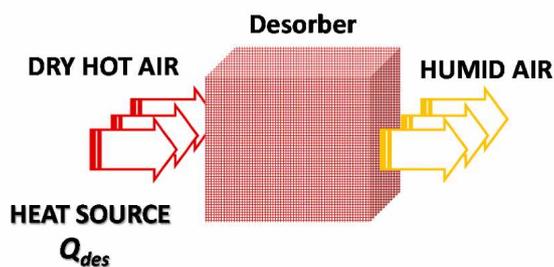
Vaster et al that under indirect TES, heat is converted into a different form of energy (such as mechanical, chemical), which is stored short of any limitation. This means there are no heat losses to the ambient. As this technology is based on an energy conversion process, the converter needs to be connected to an external sink (such as the ambient) through which the produced waste heat

and entropy, due to irreversibility, must be dissipated. The reverse phenomena, which exploits a flux of heat and entropy from the ambient is exploited in a reverse format where the stored energy is converted into useful heat again. This is the discharging phase. A need to connect to different sources/sinks makes TES technology an indirect process.

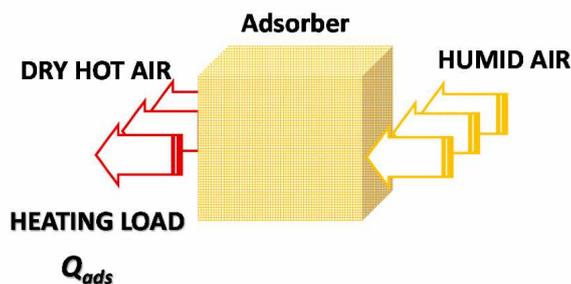
Under Adsorption heat storages, heat is employed to drive a desorption process, which means that energy is stored in the form of adsorption potential energy. In this way, heat is stored and conserved until the adsorbate is kept separate from the adsorbent.

Closed- and Open-cycle are the two system configurations in general. Our focus will be on the Open system. Under the open adsorption TES system, represented in *Figure 1*, continuously exchanges mass (adsorbate) with the ambient. The two charging/discharging phases are, in fact, similar to those already described for the closed cycle. In this case, heat is provided and extracted by fluxing air through the adsorbent bed. Specifically, during the charging/desorption phase, a hot and dry air flux enters the storage, causing the desorption of adsorbed water, and exits at a lower temperature and higher humidity content.

a) CHARGING PHASE (Desorption)



b) DISCHARGING PHASE (Adsorption)



An open adsorption heat storage cycle: (a) charging phase; (b) discharging phase (*Vasta et al., 2018*)

During the discharging/adsorption phase, a humid and cooled air flux is provided to the dry adsorbent, which triggers the adsorption and consequent release of the stored heat. The stored heat is released as hot and dry air flux exiting the system. Some clear differences must be highlighted between closed and open adsorption TES.

Adsorbent Materials for TES

According to Vasta et al. (2018), development of adsorbent materials for adsorption Thermal Energy Storage (TES) is strongly related to the adsorbate to be employed. Zeolites are crystalline alumino-silicates, characterized by a high specific surface area (about 800 m²/g) and wide microporous volumes, which make these materials perfectly suitable for water vapor adsorption. Owing to their porous structure, zeolites are usually highly hydrophilic, which allows them to obtain high adsorption capacities even at low partial pressures. This high affinity with water, of course, points to strong bonding that requires higher temperatures (greater than 150°C) to be broken compared to silica. Zeolites type A, 13X and Y are the most common classical synthetic zeolites employed for open adsorption heat storage. These materials have high regeneration temperatures and this qualifies them for Industrial waste heat recovery and storage. Therefore, air is the most effective heat transfer medium.

Due to their crystallinity, (contrary to the amorphous structure of silica gels), a greater lasting hydrothermal stability is an assurance, thus offering a more reliable option for applications where several adsorption and desorption cycles are expected (Vasta et al., 2018).

Adsorption Material Heat Storage Calculations

Bales et al. (2005) reported these calculations. The authors reported that these calculations are only performed for closed systems with water as the adsorbate, as these are still the most widely employed adsorption TES under investigation. By and large, in order to estimate the most effective adsorbent material for TES, the most vital parameter to be investigated is indicated by the integral enthalpy of adsorption, and can be calculated with no trouble according to the following equation

$$H_{ads} = \Delta H_{ads} (w_{max} - w_{min}) \text{ [J/g}_{ads}\text{]}$$

where:

H_{ads} [J/g_{ads}] is the enthalpy of adsorption, which can be considered as the achievable heat storage density at a material level;

ΔH_{ads} [J/g_{water}] is the differential enthalpy of adsorption referred to the adsorbed amount of water; w_{max} and w_{min} [g_{water}/g_{ads}] are the maximum and minimum adsorption amount of water over the adsorbent material, at the given working boundary conditions.

The value of the differential enthalpy of adsorption is generally calculated through the measurement of the equilibrium adsorption curves according to the well-known Clausius-Clapeyron equation (Talu and Kabel, 1987). Nevertheless, classical zeolites whose integral heat of adsorption is very limited at 90 °C of regeneration temperature, become very attractive when higher temperatures (about 160 °C) are available instead.

It must be emphasized that these calculations have been performed for unit mass. Usually, TES density is calculated on a volumetric basis, since the occupied volume can be an issue, for instance, in the domestic sector. Nevertheless, to calculate the volumetric adsorption storage is quite complicated, since the bulk adsorbent material density strongly depends on grain size and composition. For this reason, in order to compare different adsorbent materials, the gravimetric TES density is taken as a reference parameter.

Zeolites as heat Stores

Zeolites have been successfully used in heat storage. One successful example is that provided by Krönauer et al. (2015). These authors report about a mobile heat storage facility that utilized 14 tons of packed zeolite powder on a track with a waste incineration plant as the heat source and the Industrial drying process as the heat recipient. Steam from the incineration plant heated up the ambient air during the charging process where the storage capacity of 2.3 MW was reached. Exhaust air from the drying plant at 60°C with humidity of 0.09kg/kg was used in the discharging process. For each cycle 1MW of electric power was saved, and more than 600 of CO₂ saved. The energy cost was lowered to 0.082 \$/kWh

Nanosized Zeolites

Creating nanosized zeolite particles would increase the surface area of the adsorbent and thus enhance its interactions with fluid adsorbates. This would be translated into a high adsorption capacity and selectivity. Zeolites during adsorptive separation face a challenge of intrapore diffusion. The feasible solution to this challenge is shortening of diffusion path and this can be achieved by reducing zeolite crystal sizes to less than 50nm (Bakhtyari et al., 2020).

Planetary ball milling can be used in the process of the formation of nanosize zeolites followed by treatment with NaOH solution to dissolve amorphous form particles with size 70-300nm as the first step. Secondary growth by washing the subsequent highly crystalline product with Sodium aluminosilicate solution resulted in crystalline Zeolites with a particle size of 50nm with near full recovery of the crystalline zeolite particles. (Valtchev & Tosheva, 2013; Wakihara et al. 2011;2012).

CO₂ adsorption by Zeolites

Zeolites with alkali-cations such as Li⁺ and Na⁺ have a high adsorption efficiency for acidic fluids such as Carbondioxide. The presence of cations in the zeolite structure promotes their electrostatic interactions with the carbondioxide thus enhancing adsorption. (Bakhtyari et al., 2020). This proposal suggests alkali-cations-rich zeolites that will exhibit a great adsorption ability for Carbondioxide released from exhaust air of the Industrial drying plant

MATERIALS AND METHODS

Materials:

Synthesis of Zeolite from Pumice samples: Pumice Samples, Sodium hydroxide Solution, heat source/microwave and Ultrasonic irradiation source

Synthesis of Nanoscale Zeolite: Planetary Ball milling apparatus, Zeolite Powder, Sodium hydroxide Solution, Sodium Aluminosilicate Solution.

Methods

Synthesis of Na-Zeolite Material

Sodium rich Zeolite was synthesized using the procedure described by **Prajaputra et al. (2019)**. Pumice Powder was mixed with 2.5M NaOH solution in the ratio of 1 kg Pumice per 8 litres of NaOH and dried in an oven at 100°C for 16 hours in the presence of microwaves (300 MHz–300 GHz) and ultrasonic irradiation (20kHz-10 MHz). The product obtained was filtered, rinsed with distilled water and in order to attain a pH of about 9, and then dried for 8 hours at 100°C in the presence of microwaves (300 MHz–300 GHz) and ultrasonic irradiation (20kHz-10 MHz). The final product obtained was further crushed and passed through a 100 mesh.

Top Down Approach for the Preparation of nano-scale zeolite Powder

Planetary ball milling will be used in the treatment of synthetic zeolites (in the range of mm to μm). The product subjected to ball milling will be treated with sodium hydroxide solution. The alkaline solution dissolve and wash out the amorphous part of the sample thus high crystalline product containing particles in the range 70– 300 nm. The secondary growth will be performed after the milling procedure using sodium aluminosilicate solutions and this can result in almost 98% recovery of zeolite. Additionally, zeolite crystal size will decrease from several micrometers to 50 nm without substantial loss of crystalline material.

Characterization of Pumice and Nano Zeolite

Chemical analyses of pumice samples will be carried out by means of X-ray fluorescence (XRF) and identification of the synthetic products by conventional X-ray powder diffraction analysis using cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The degree of zeolitization will be estimated by the determination of the weight yield R% (weight ratio of zeolitic products and starting material) and by means of X-ray diffraction.

Design of Zeolite Heat Storage (Charging and Discharging)

Schematic designs for the charging and discharging processes for the energy storage system are summarized in figure 1 and 2 respectively. For the charging process, the storage system should be fitted with both a steam-air, and cross flow air/air heat exchangers. The air flow through the storage should be reversed for the discharging system. The beds are packed to provide insulation properties thus minimizing heat losses.

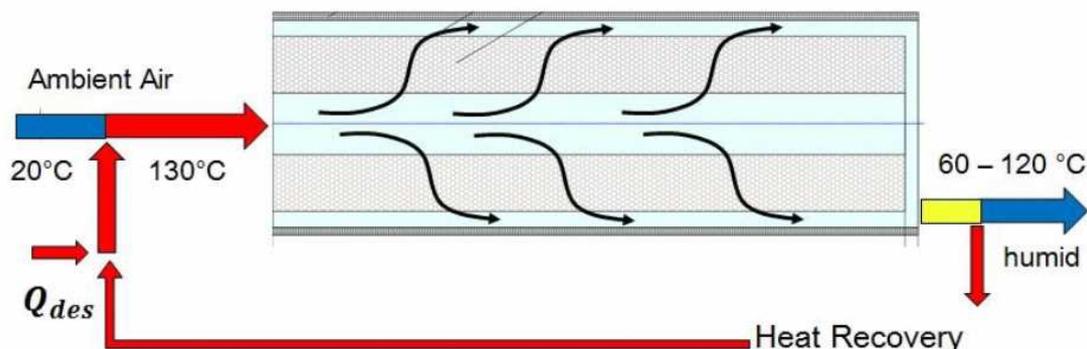


Fig.2 A schematic for the Charging (Desorption) Process. (*Krönauer et al., 2015*)

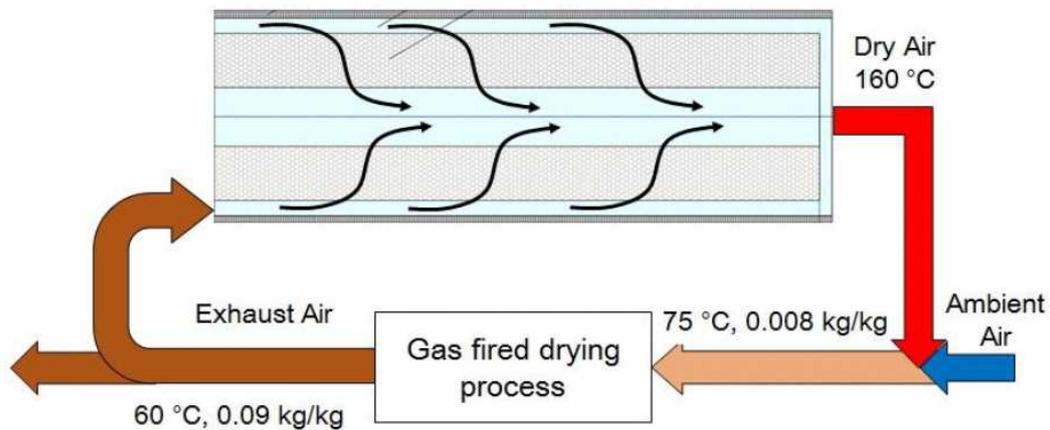


Fig.3. Schematics of the discharging (Adsorption) process. (Krönauer et al., 2015)

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Massive amounts of pumice stones washing ashore in Okinawa, may affect nuclear power plants, Japan. <https://watchers.news/2021/10/28/pumice-okinawa-japan-october-2021/#:~:text=A%20large%20number%20of%20pumice%20stones%20produced%20by,reported%20in%20the%20Amami%20region%20of%20Kagoshima%20Prefecture.> Retrieved on 23rd Nov 2021 15:43 EAT

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