

# APPLICATION OF SYNTHESISED ZEOLITE A FROM KANKARA KAOLIN FOR SOLAR ADSORPTION REFRIGERATION

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## ABSTRACT

*This paper presents the synthesis, characterization and application of a synthesised Zeolite A from Nigerian clay (kankara) for application in solar adsorption refrigeration. On the basis of X-ray diffraction, TGA and DTA experiments Zeolite A was confirmed with an adsorption capacity of 0.3 kg adsorbate/0.85 kg adsorbent, regenerative temperature of below 200°C and structural stability below 800°C. The refrigeration system used in the test consists of a 0.6 by 0.45 m<sup>2</sup> parabolic trough concentrator, 0.6 m long and 0.25 m diameter black coated absorber, an air cooled condenser and cooling box of volume (evaporator) 0.048 m<sup>3</sup>. The refrigerator was constructed and tested at the Mechanical Engineering Department Zaria, Nigeria at location 11.11'NE in the month of April, a month with one of the highest of average solar irradiation of 900W/ m<sup>2</sup>. The lowest evaporator temperature attained was 9.8°C with a C.O.P of 28.5%.*

**KEYWORDS:** Zeolite A, Adsorption, Desorption, Refrigeration, Solar, Kankara DTA/TGA

## 1.0 INTRODUCTION

Widespread Research and development to provide solar-thermal driven adsorption cooling system using adsorbent/refrigerant pair to help to reduce many of the challenges related to cooling demand especially in regions enjoying large solar resources because the incident radiation and the need for cold production both reach maximum levels in the same period (Solmus, et.al, 2010, Hassan et.al, 2011).

These systems make use of the unique features of certain adsorbent-refrigerant pairs to complete refrigeration cycles for cooling or heat pump

purposes which are well adapted to simple technology applications which operate without moving parts and with low grade heat from different sources such as residual heat or solar energy. The use of sorption processes to produce refrigeration has been extensively studied as a technological alternative to vapour compression systems using Various adsorbents and have successfully being employed which include Adsorbents like Zeolite, silica gel, activated carbon and alumina are physical adsorbents that have highly porous structures with surface–volume ratios in the order of several hundred that can selectively catch and hold refrigerants Wang, et.al 2010).

The adsorption cooling cycle is identical to the conventional vapor compression refrigeration cycle except that the compressor unit is replaced by thermal compressor made up of porous adsorbent and adsorbate (Hassan et.al, 2011). The adsorption-desorption cycle can be summarized in four stages and presented by clapeyron diagram showing the pressure-temperature concentration (p-T-x) by thick lines ABCD in Figure 1.

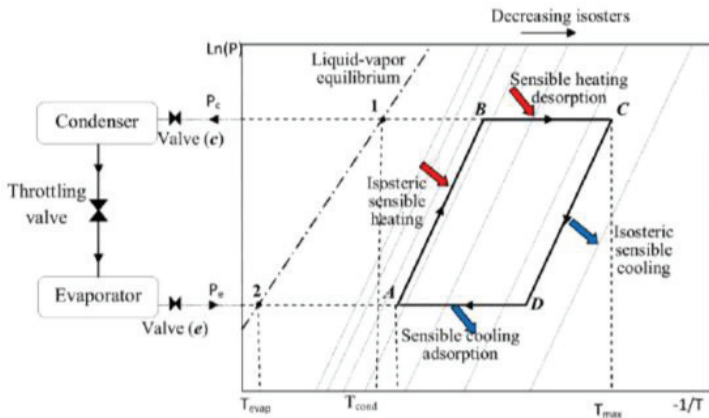


FIGURE 1

Clapeyron diagram for a conventional adsorption cycle. Source ; Hassan et.al, 2011

- Step (A→B): Isoteric heating
- Step (B→D): Desorption and condensation
- Step (D→F): Isoteric cooling
- Step (F→A): Adsorption and evaporation

Adsorption technology based on the working pair of Zeolite/water is well suited for cooling and as an alternative to the negative environmental consequences related to conventional vapour compression refrigeration machines has the benefits of utilisation of refrigerants are regarded as absolutely benign for the environment, i.e. refrigerants that satisfy the Montreal protocol on ozone layer depletion and the Kyoto protocol on global warming (El Fadar et.al, 2009).

Over 40 naturally occurring Zeolites and over 140 synthetic Zeolites (Baerlocher, 2007, Srivastava and Eames, 1998 There, 1978), most Zeolites are

simply molecular sieves which capable of losing water fairly continuously over a temperature range of 150 to 400°C without collapse of the framework structure and reabsorb it from the atmosphere at room temperature a characteristic which makes attractive as an adsorbent in refrigeration systems, (Baerlocher, et.al, 2007). . Their ability to interact with water in the presence of other molecules decreases with decreasing concentration of aluminium per unit cell altering their pore to volume ratios (Aderemi, 2004, Baerlocher, et.al 2007), an additional advantage of zeolites is that even after several thousand adsorptions desorption cycles the structural changes of the crystals are insignificant in the process parameters such as pressure adsorption and temperature

The objective of this paper is to synthesise Zeolite A from kankara kaolin, and on confirmation of the sample, apply it to a simple designed solar adsorption refrigerator for food and vaccine storage.

Several theoretical and experimental studies have successfully demonstrated the application of different zeolites in solar adsorption refrigeration systems; natural (Tchernev 1978, 1984, Ismail, 2010) and synthetic Zeolites13X (Wei-Dong et.al, 2009), and Zeolite A (Miguel, 2003, Segfried and Detlef ,1998). Their performance reported in most works are linked to their selectively to adsorb molecules is on the basis of their size, shape or electrical charge

However adsorption refrigeration systems suffer drawbacks, such as high costs, low specific cooling power, relatively long adsorption-desorption time, system intermittency and low coefficient of performance, due to the weak heat transfer within the absorbers (Critoph, 1988). Thus, in order to overcome these limitations and attain higher performance, several approaches have been undertaken such as enhancement of heat transfer properties in the adsorbent beds (Critoph, and Zhong, 2004), design and investigation of advanced cycles, and improvement of regenerative heat and mass transfer between beds (El-Fadar. Mimet Perez-Garcia, 2009).

This paper presents the synthesis and characterisation of a hydrothermally synthesized Zeolite A from kankara kaolin and its application in the solar adsorption refrigeration system.

## **2.0 METHODOLOGY**

### **2.1 Zeolite Synthesis**

Zeolite A was produced from Kankara kaolin obtained from Katsina State, Nigeria. 2 kg of the kaolin was mixed with 2500 cm<sup>3</sup> of distilled water and where the resulting mixture was allowed to soak for four days with intermittent stirring at pre determined intervals. On the fourth day the mixture was thoroughly stirred and sieved using a 75µ mesh. The filtrate was then allowed to settle, and the column water decanted. The clay part was centrifuged to

remove excessive water from it. On completion of the centrifuge stage, the kaolin clay was dried in an oven at a temperature of 50°C for 24 hours after which it was pulverized in a mortar and sieved further with a 53 $\mu$  mesh sieve to give an extra fine texture in readiness for calcinations. The crystalline clay was converted to amorphous metakaolin by thermal treatment in a furnace under controlled conditions at a temperature of 600°C for 8 hours.

Procedures outlined in Howell (2006) were used in the Zeolite A synthesis. 600g of metakaolin was mixed thoroughly with 518g of sodium hydroxide pellets dissolved in 4665.6 g of distilled water. The mixture was allowed to age for three days at room temperature in a polypropylene bottle and then placed in an autoclave (WS2-84-64, model-7101) set at 100°C for 8 hours. After the synthesis the samples were then allowed to cool; washed with distilled water to remove excess sodium hydroxide, dried at 150°C for 3 hours and subsequently calcined at 300°C. The samples were characterized X-ray diffraction (XRD), differential thermal analysis (DTA) and thermo gravimetric analysis (TGA).

### **3.0 REFRIGERATION SYSTEM**

The system was fabricated and tested in Department of Mechanical Engineering Ahmadu Bello University, Zaria, Nigeria at a geographical location 11°11''NE. The prototype system produced (Figure 1) consists of a parabolic trough concentrator, absorber (generator), condenser accumulator, insulated cooler box, evaporator, control valves and transport pipes.

0.3kg of the synthesized Zeolite A; 53 $\mu$ m particle size was loaded in the annular space of the absorber pipe with dimensions 600mm length and 25.4 mm O.D coated with black paint of absorptance of 0.95 which and is sealed to be air tight.

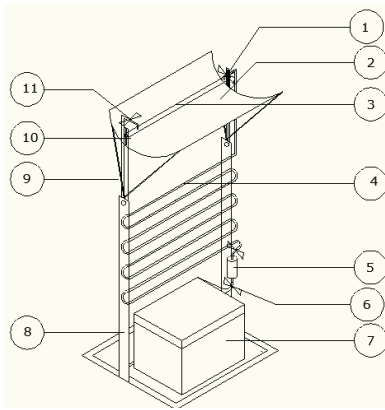
On the basis of the maximal adsorption capacity of Zeolite-water pair at ambient temperature (Miguel et.al, 2003), 0.02m<sup>3</sup> of distilled water is poured into the evaporator via the accumulator.

The system operates in two loops; loop 1 desorption process and loop 2 adsorption process and Due to the cycle intermittency, it was necessary to use valves to direct the adsorbate in both processes and the. One valve ( $V_1$ ) positioned at the top of the absorber and connects the evaporator directly to the absorber is opened, while a second valve ( $V_2$ ) situated between the absorber and condenser and a third valve ( $V_3$ ); between the condenser and the evaporator.

To initiate the process a vacuum pump was used to set the system pressure to the saturation pressure at ambient temperature and Figure 3 presents the timeline which was used to operate the system.

As the absorber receives solar irradiation from the parabolic trough concentrator of aperture area (600 x 450) mm<sup>2</sup> absorber temperature increases (process AB figure 1) with valves V<sub>1</sub> and V<sub>3</sub> closed, valve V<sub>2</sub> opened desorption occurs and the concentration of the adsorbate decreases until a minimum value which flows through connecting pipes to the condenser and condenses at ambient temperature into the accumulator and then to the evaporator. Loop 1.

For the adsorption stage, loop 2, (the night cycle), the working fluid is forced to flow towards the absorber, with V<sub>1</sub> opened, V<sub>2</sub> and V<sub>3</sub> closed getting the water to change from the liquid phase to vapour at the saturation pressure of the evaporator temperature. The respective timelines associated with each stage is presented in the chart in Figure 3 below. In order to evaluate the system performance, temperatures were measured in different points of each component of the prototype using thermocouple (Pt-100) at an hourly interval over the time of 8 the day.



No	COMPONENT
1	Outlet valve -V2
2	Parabolic trough
3	Absorber
4	Condenser
5	Accumulator
6	Valve -V3
7	Cooling box/Evaporator
8	Refrigerator frame
9	Trough Supporting arm
10	Return pipe
11	Valve -V1

FIGURE 2  
Assembly View of solar Adsorption Refrigerator

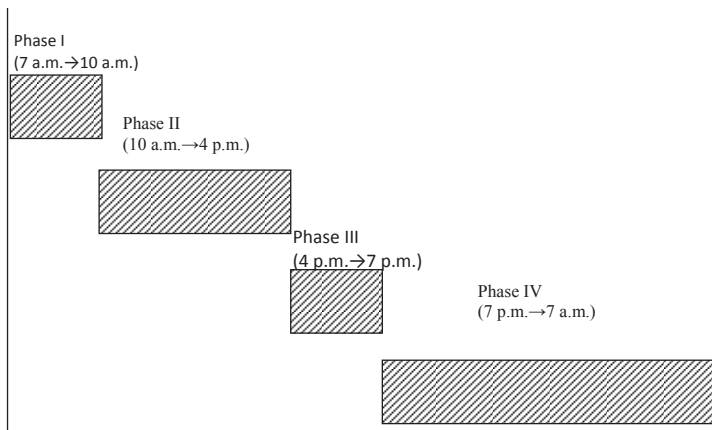


FIGURE 3  
Timeline for operation of the solar adsorption refrigerator

## 4.0 RESULTS AND DISCUSSION

### 4.1 Zeolite A Synthesis and characterisation

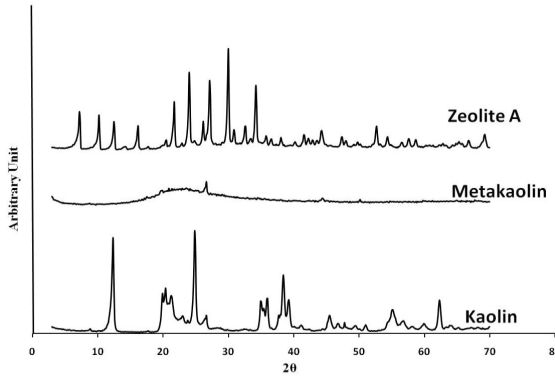


FIGURE 4  
XRD Patterns of Zeolite A ,Metakaolin and Kaolin

The XRD patterns of kaolin, metakaolin and synthesised Zeolite A sample are presented in Figure 4. Peculiar peaks of the kaolin  $2\theta$  were observed similar to that reported by Feng et.al (2009). The crystalline kaolin was converted to an amorphous phase metakaolin by thermal treatment at 600oC and which was confirmed by the broad XRD patterns (Feng, et.al 2009). Conversion of the reactive metakaolin was done in an alkaline medium for 8 hours at 100°C. The peaks in the ranges of  $2\theta=7-18^\circ$  and  $21-35^\circ$  are characteristic of Zeolite A type (Baerlocher et.al, 2007). No other peaks were observed in the XRD pattern of the synthesised zeolite. This indicates the formation of pure phase zeolite A.

The DTA and TGA results are presented in Figures 5, 6 and 7 for kaolin, metakaolin and Zeolite A respectively which are treated up to elevated temperatures of 1000°C. The TGA results of the kaolin (Figure 5) and metakaolin (Figure 6) reveal a weight loss of 15(%)for the kaolin and about 3% for metakaolin . The reason for the disparity in weight (%) loss of the kaolin and the metakaolin is that metakaolin was formed by the subjection of kaolin to heat treatment at 600°C for 8 hours with most of the free and structural water lost. The DTA of the kaolin (Figure 5) supports this argument of the loss of structural water as depicted by the endothermic peak observed at 560°C. However the DTA of metakaolin (Figure 6) shows no significant thermal transformation at similar temperature (560°C) but for the loss of free water that might have been reabsorbed at about 100°C

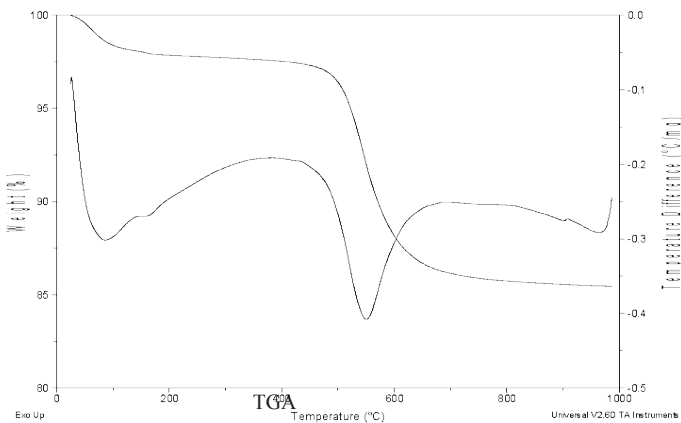


FIGURE 5  
TGA and DTA Patterns for Kaolin

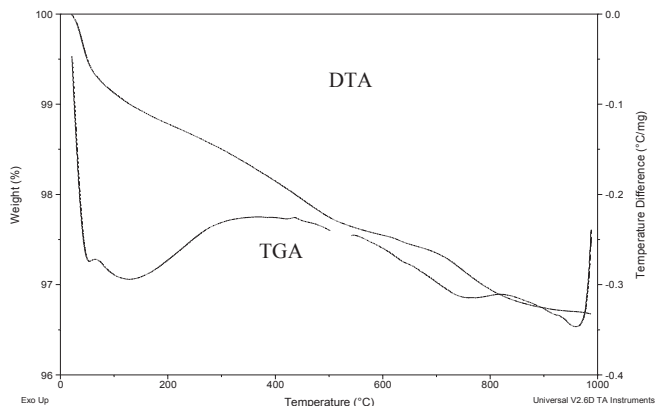


FIGURE 6  
TGA and DTA Patterns for Metakaolin

The TGA/DTA of the synthesised zeolite A is presented in Figure 7. The TGA graph shows weight loss of about 20% for Zeolite A is depicted by an endothermic peak observed at 100°C in the DTA of Figure 7. The DTA of the Zeolite A reveals thermal stability up to about 800°C, above which a collapse in the Zeolite structure is seen at above this point.

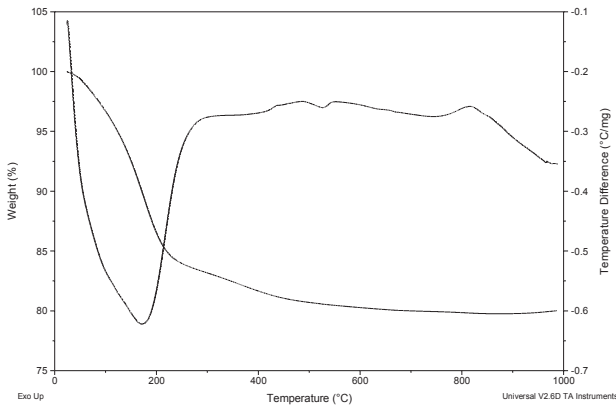


FIGURE 7  
TGA and DTA Patterns for Zeolite A

#### 4.1 Solar Adsorption Refrigeration System tests

Figure 2 shows the refrigerator diagram in which the synthesized zeolite A is tested. Testing was done at the Department of Mechanical Engineering, Ahmadu Bello University test field (11°11'NE) in the month of April with an average solar incident insolation of 700W/m<sup>2</sup>.

The synthesized zeolite A, on its confirmation was found to have a maximum adsorption capacity of about 0.3 kg of adsorbate/ 0.85 kg of adsorbent.

To initiate the refrigeration, 0.3kg of the powdered was loaded into the absorber of the refrigerator system which is connected to the evaporator system containing 0.02 m<sup>3</sup> of water via transport pipes which are air tight. The refrigerator is evacuated to a pressure of 5 hpa using an evacuation pump and placed under the sun facing the East West direction during the day. Regeneration of Zeolite at low temperatures is forced to occur within a (air tight) closed absorber pipe using control valves V<sub>1</sub> and V<sub>2</sub> (Figure 2) by pre-setting the start-up pressure and using an air cooled condenser. The operation of the refrigeration followed strictly the operational timeline of Figure 3. For condensation and evaporation pressures of 1 and 0.1 psia, respectively, for most zeolites the differential water loading is about 10%by weight between ambient temperature and 120°C which was taken here as the reference point.

Temperatures of the key parts of the refrigerator; absorber, condenser and evaporator were continuously measured simultaneously using a digital thermocouple (pt-100) from 7:00am to 17pm daily. Figure 8 shows the results obtained for 3 of the days with the most promising results. The refrigeration temperatures was 9.8°C then 11°C respectively on day two and day three and an overall system efficiency of 28.5% was obtained. The low regeneration temperatures of the absorber and long desorption times of the zeolite A as well as high convective heat losses for the absorber are attributed to the poor performance of the system.



The exothermic peak seen in the DTA/TGA suggests that in order to regenerate this zeolite temperature of less than 200°C will be suitable.

The temperatures at which zeolites are regenerated determine the amount of time required to refrigeration to occurs, at much higher temperature. Long desorption time associated low regenerative temperatures of water from Zeolites are suggested to be responsible for the low refrigeration obtained from the refrigerator system. The desorption curves for Zeolite A obtained at atmospheric pressures with samples of Zeolite put at different temperatures given in Miguel et.al, (2003), suggests that that at 250°C, 2.5 hours is required to obtain 5% humidity (with 84% of the water extracted) and at 200°C 6 hours is needed to reduce humidity to 10%( extracting 66% of the water). The maximum theoretical efficiency for cooling with a zeolite is roughly equal to the heat of vaporization of water - about 2.326 kJ/kg divided by the heat of adsorption of water on the zeolite. Since synthetic zeolites used for drying gases have heats of adsorption of about 4.187 kJ/kg of water, their maximum theoretical efficiency is only about 55% (Tchernev, 1983). On this basis it is not recommendable to reduce the humidity from its initial 30-35% (dry bases) at saturation to below 5% as further drying would result only in a small improvement of the capacity of the Zeolite to adsorb water, but at the expense of a big amount of additional energy and time require

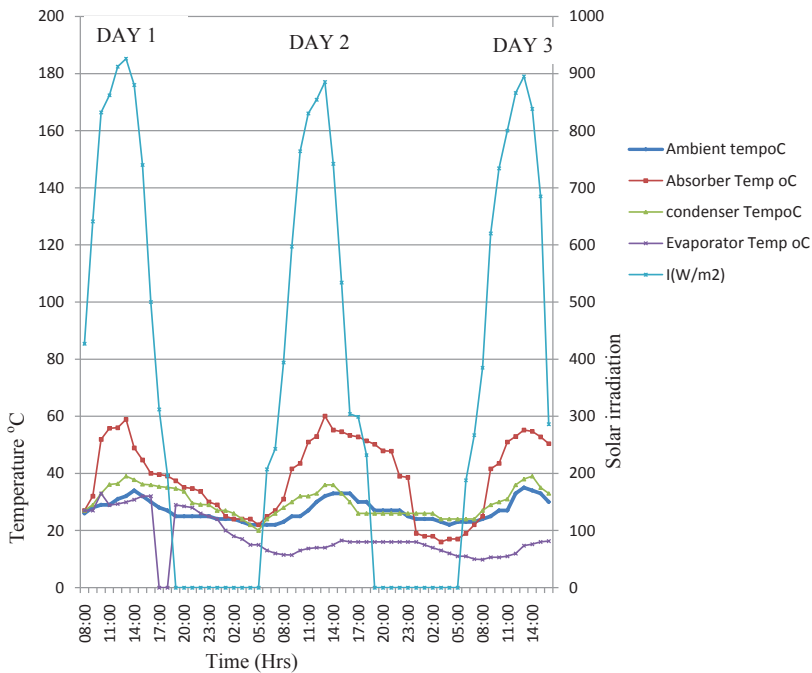


FIGURE 8  
Solar Irradiation, ambient and component temperatures

## 5.0 CONCLUSION

Zeolite A was successfully produced from kankara clay and tested in a solar adsorption refrigerator. Different tests have been used to characterize it showing the Zeolite to be thermally stable at 800°C and have a regenerative temperature of 200°C. The system attained a very low COP and the long desorption times as well as the other shortcomings of this group of refrigerator was also experienced. Strong potentials for improvement for this refrigerator are shown from the test. Work is continuing to improve the system which is aimed at improving the systems efficiency.

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