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Research Article

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Assessment of Treated Calcium Chloride Adsorbent for Solar Refrigeration

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ABSTRACT

The characteristics of adsorbent-adsorbate (refrigerant) pairs play an important role in the design of adsorption refrigeration systems. The treatment of adsorbent to increase its adsorption capacity for a refrigerant could increase the refrigeration capacity of adsorbent per unit mass and also the COP of the cycle. Swelling, compacting and disintegration of $CaCl_2$ salt, when used as an adsorbent in a solar powered refrigerator, can be reduced by treating the salt with binding materials.

A rig was designed and constructed to determine the swelling of samples of treated granular $CaCl_2$ upon the first adsorption of NH_3 . The crushing loads and porosities of the samples were determined at the 1st, 3rd, 5th and 7th cycles of adsorption as well as before initial adsorption. The sample, granular 70% $CaCl_2 + 10\%$ Activated Carbon + 20% $CaSO_4$, was the best among the samples from the vantage point of low swelling, high porosity and crushing strength. Its crushing strengths and porosities ranged between 8.3 - 4.8 N/mm² and 42 - 40% respectively for the seven cycles whilst its percentage swell was 10 ± 2 after the 1st adsorption.

Key words: Adsorbent, Adsorbate, Porosity, Swelling, Crushing Strength

1. INTRODUCTION

Srivastava and Eames [1] presented a review of adsorbents and adsorbates in solid-vapor adsorption heat pump systems. Among the adsorbents presented are the commercial hydrophilic solid adsorbents. These include silica gel, activated alumina, zeolites and calcium chloride. Commercial hydrophobic solid adsorbents such as activated carbons, metal oxides, specially developed porous metal hydrides and composite adsorbents were also reviewed.

Nielson et al [2] tested certain proposals for the treatment of halides of alkaline earth metals. The first proposal was the mixing of 95% $SrCl_2$ and 5% $LiNO_3$. This proposal did not restrict swelling. The top layer was light and porous but the bottom layer was closely packed. The degree of adsorption after 16 hours was 43% in $SrCl_2$ and 70% in $CaCl_2$. The second proposal was the mixing of the adsorbent with Portland cement, or $ZnCl_2$ and ZnO, for binding and $NaSiO_3$ for producing porosity upon heating. This mixture was heated with Ammonia. Light granules were produced which crumbled upon handling, swelled and compacted with subsequent adsorption of Ammonia. Hard porous granules were obtained when 85% $CaCl_2$ or $SrCl_2$ and 15% cement were mixed to a thick paste in water, and dried in air in shallow trays at 250-300 °C for several hours. However salt movements were detected in the hard porous granules in the adsorption tube by the 100th cycle. Compaction or disintegration to powder was found upon visual examination after 232 cycles.

Iloeje [3] prepared mixtures of $CaCl_2$ and Portland cement at 0%, 10%, 20% and 30 % compositions by mass of the latter, and of $CaCl_2$ and $CaSO_4$ at 10% and 20% by mass of $CaSO_4$ as hard porous granules of 5-10 mm in size. Ammonia adsorption and generation cycles were carried out for each sample, and the average crushing strength determined at the end of each cycle.

The samples were compared in their strengths, swelling and absorbabilities to ammonia. It was confirmed that the treatment with the binding materials significantly improved the hardness of the adsorbent. The reduction in swelling, by up to a factor of 30, were realized. Portland cement did not impede the adsorption of NH_3 very much, while $CaSO_4$ did. The Portland cement mixture was optimal at the 20% level, while the mixture with 20% $CaSO_4$ was the best of the

samples, when both the strengths and absorption capacities were considered. It is thus evident that the swelling, compaction and disintegration of $CaCl_2$ salt when used as an adsorbent in refrigeration systems can be reduced by treating it with binding materials.

It was reported that if the calcium chloride salt was in powdery form before the adsorption of ammonia, it would expand to about 3- 4 times its original volume on adsorption of the full 8 moles of NH_3 /mole of salt. If allowed, the expansion could make the adsorber/generator bulky. If the containing vessel restricts the expansion, it will impose high pressures on the vessel thus leading to the compaction of the absorbent. It is therefore important to prepare the absorbent in a manner that will make it porous so as to permit the adsorption and desorption of Ammonia. In addition, the adsorbent must be made hard to prevent its being disintegrated into powder after a few cycles of operation. It must also be tightly bound to restrict swelling.

Wang et al [4] tested adsorption performances of three types of adsorbents: $CaCl_2$ with different expansion space, simple compound adsorbent made by $CaCl_2$ and activated carbon. Ammonia was used as a refrigerant. The solidified compound adsorbent showed the best performance for adsorption icemakers on fishing boats for the larger filling quantity of adsorbent in adsorber. The mass transfer performance was improved by the addition of activated carbon to solidified compound adsorbent at the condition of low evaporating temperature. The volume cooling density of solidified compound adsorbent was about 35% improved at least in comparison with the optimal results of $CaCl_2$ at the evaporating temperature of $-15^{\circ}C$.

The following adsorbents and adsorbates combinations have been used in solid adsorption heat pump systems:

- Zeolite and water [5]
- Zeolite Composites and water [6]
- Activated carbon and ammonia [7]
- Complex Compounds/Salts and ammonia or water [8,9]
- Calcium chloride and methanol [10]
- Metal hydrides and hydrogen [11,12,13]
- Charcoal ammonia [14]

Charters et al [13] produced a comprehensive review of investigation on metal hydride heat pumps. According to Gershion and Alec [15] Lithium chloride and Calcium chloride solid adsorbents have been used in industrial humidifying equipment and in total heat exchangers in air conditioning systems as a means of heat recovery. Sumathy et al [16] stated the factors upon which the choices of adsorbents depend. The factors are:

- high adsorption and desorption capacity, to attain high cooling effect
- good thermal conductivity, in order to shorten the cycle time
- low specific heat capacity
- chemically compatible with the chosen refrigerant
- low cost and widely available

Rekindled interests in Solar Powered adsorption refrigeration have led to recent researches in the field [17-30].

2. MATERIALS AND METHOD

The problem of swelling and early disintegration of Calcium chloride upon adsorption of ammonia was investigated. Calcium chloride was treated with some materials such as calcium sulphate, silica gel, charcoal, activated carbon, cement and bentonite.

2.1. Apparatus

Figure 1 is a sketch of the experimental rig. Ammonia was supplied from a tank (1) which was connected to the permeation cell. The permeation cell, which is essentially a pressure vessel (10), consists of an upper and lower steel pipes with flanges. The two pipes were bolted together by means of eight bolts each of 8 mm diameter screwed into the holes drilled on the flanges, 45° circumferentially spaced. A pressure regulator (2) regulates the pressure of the gas ensuing from the ammonia tank. A pressure gauge (8) measures the pressure of the ammonia entering the pressure vessel.

A steel pipe connects the lower cell to a water trap (15), which was connected by means of another pipe to a water tank (16). The samples in the form of granules were located in the annular space between a cylindrical stainless steel wire mesh of 30mm diameter and the inside surface of the 59 mm internal diameter pressure vessel. A circular stainless steel wire mesh (14) was used to partition the upper and lower cells.

Mains power at 240 V was supplied through a temperature-regulating device to the pressure vessel heater coils during NH_3 generation process. The two steel pipes constituting the pressure vessel were supplied with heat of regeneration by a coil of electrical resistance heated wire._The coil rating was 1 kW at 240 V.

Digital thermometers having Type K thermocouple sensors, having accuracy of $\pm (0.75\% + 2^{\circ}C)$ were used for pressure vessel surface temperature measurements. The thermocouple bead was attached to the vessel surface with araldite. Thermocouples (12, 13) were attached to the vessel below and above the region covered by the heating coil. The containment box was insulated with 5 cm of glass wool.



(1) Ammonia tank, (2) Pressure regulator, (3,4) Valves, (5,6,7) Coupling, (8) Pressure gauge, (9)Pressure vessel, (10) Upper cell, (11) Lower cell, (12,13) Thermocouple, (14)Gasket/ Perforated circular partition covered with wire gauze, (15) Water trap, (16) Water tank, (17) Pipe.
Fig. 1 Schematic diagram of the experimental rig

2.2. Adsorption and Generation

The test rig was connected up as previously described (Fig 1). The valve (3) was partially opened, while the valve (4) was controlled until bubbles were issuing into the water bucket at a slow but steady rate. Water at room temperature (about 28° C), was poured into the containment vessel. The adsorption time (5-7 hours) was noted. After adsorption, the vessel was weighed, opened, visually inspected, and the depth of the top of the granules determined using a dipstick. The vessel was then re-connected to the test loop for the generation test. The water in the containment vessel was drained off, and the test vessel and heater were allowed to dry. With the valve (3) shut, the valve (4) was opened, and power was turned on. The vessel surface temperatures were measured at intervals. Ammonia generation was indicated by bubbles issuing through the pipe, which dipped into the water bucket. The generation time was noted.

2.2.1. Preparation of Adsorbent Granules

The required masses of the constituents of the samples were weighed out. The $CaCl_2/Activated$ carbon and $CaCl_2/Silica$ gel composites were mixed with traces of the binding material (Bentonite clay, $CaSO_4$ or Cement) and water, to a thick paste. The sample compositions are as shown in Table 1.

Table -1 Sample compositions			
Sample	Composition %		
	CaCl ₂ Activated Carbon		
А	80	20 + Cement (trace)	
В	80	20 + Bentonite (trace)	
С	70	30 + Cement (trace)	
D	70	30 + Bentonite (trace)	
	CaCl ₂	CaSO ₄	
Е	80	20	
F	70	30	
	CaCl ₂	Silica gel	
G	20	80 + Cement (trace))
Н	20	80 + Bentonite (trace)	
	CaCl ₂	Activated Carbon	CaSO ₄
Ι	70	20	10
J	70	10	20
Κ	80	10	10

The paste was transferred to a drying bowl whose cover was perforated with a few 2 mm holes to give a restricted release of vapor to the atmosphere during the drying process. The paste was heated at an average temperature of 100 °C for about 1 day, in an oven gradually increased in steps, over the next 24 hours, by which time the temperature of the mixture had reached about 150 °C. It was left at this setting until it was fully dried and hard. A few bubbling sites could be seen on top of the mass as the drying progressed. The power was again increased for a final drying at about 200 - 250 °C. The total drying time was 60 hours. The dried mass was removed, broken to granules and sieved to size of 10mm. Some granules were randomly selected and shaped with a sharp knife into flat rectangular prisms of dimensions 12 mm x 16 mm x5 mm thick. These samples were to be used for the crushing test, before exposure to NH₃. Porosity tests were also carried out on some samples before the adsorption and after the adsorption/generation cycle(s).

Final oven drying to drive out the moisture absorbed during handling was done at 400 °C for 2 hours for all the samples. The granules were stored in a desiccator ready for use.

2.3. Porosity Measurement

Each sample was permanently set on a rectangular stainless wire net with a frame by means of epoxy resin. The wire net with the sample was immersed in a glycerol-filled container. The filled container was then placed in a desiccator which was evacuated by a vacuum pump for about forty five minutes until no more air bubbles were observed coming out of the glycerol-covered wire net having the sample set on it. The vacuum on the desiccator was released and the wire net with the sample placed on it was then removed from the glycerol. The wire net/sample combination was allowed to stand freely in an upright position for thirty minutes ensuring that no contact was made with its sides. After the standing time, the excess drops of the glycerol hanging from the bottom of the plate were carefully removed. The wire net/sample combination was re-weighed and its mass recorded. It was then suspended from a wire and crocodile clip and carefully immersed into the container filled with the glycerol whilst ensuring that it hanged freely, completely immersed without touching the sides of the container. Precaution was also taken against the supporting crocodile clip getting immersed in the glycerol. The apparent mass of the wire net/sample combination was then recorded.

A summary of the data and the relevant parameters used in determining the porosity of the samples is given in Table 2.

Table -2 Calculations for determining the porosity of samples by means of the glycerol displacement methodMass of wire mesh = m1Mass of wire mesh = m2Mass of glycerol soaked wire mesh + sample = m3Mass of glycerol soaked wire mesh + sample = m3Mass of wire mesh + sample completely immersed in glycerol = m4Wire mesh density = ρ_w Sample mass = m5 = m2-m1Sample absolute density, $\rho_s = m_5 / [(m_2 - m_4/1.264) - (m_1/\rho w)]$ Bulk density, $\rho_B = 1/(1/\rho_s - v_p)$ Specific pore volume, $v_p = [(m_3 - m_2)/1.264m_5]$ % porosity = $\rho_B v_p x 100 = 100 \rho_B v_p$

Source: Ferg et al [31]

Density of glycerol at 20 °C = 1.264 g/cm³, ρ_w , density of wire mesh = 7.700 g/cm³

2.4. Crushing Test

Besides the samples prepared for the porosity test, some other similar samples were prepared for the crushing test. A Universal Material Testing Machine model TQ SM 100 with a capacity of 100 kN was used for measuring the crushing loads for the samples/specimens.

After generation, the vessel was disconnected, opened and inspected. Some granules from the top layer were brought out, shaped and dried in the oven at 100 °C for 45 minutes, to drive out the moisture absorbed during shaping. Their crushing loads were then determined. This was done at the end of the 1st, 3rd, 5th and 7th cycles; as well as before initial adsorption.

2.5. Swelling Measurement

The samples were ground with a mortar-and-pestle before mixing it with water to a thick paste.

The pasty mixture was dried with the combined use of an electrically heated oven and a hot plate. The depth of the bottom of the annular column was noted.

Finally, the depths of the test specimen packing in the permeating cell (the pressure vessel) annulus were measured at the four locations, 90° circumferentially spaced, and averaged using a dipstick and meter rule before the adsorption and after the initial adsorption. The percentage swell upon adsorption of ammonia was determined from these measurements.

3. RESULTS AND DISCUSSION

Fig. 2 shows the plot of Crushing Load against the Number of Cycles for the samples. The crushing load decreased rapidly at the first cycle, with the rate of decrease falling with the number of cycles. For the sample, H (25% $CaCl_2 + 75\%$ silica gel + trace of bentonite), the rate fell almost to zero by the seventh cycle although the sample in its untreated powdery state exhibited the highest adsorption capacity in an experiment earlier carried out. Its poor crushing strength made it not suitable as an adsorbent of Ammonia. The samples, J (70% $CaCl_2 + 10\%$ Activated Carbon + 20% $CaSO_4$) and E (80% $CaCl_2 + 20\%$ $CaSO_4$) possessed the highest crushing strengths than all the other samples. The crushing strengths for the sample, J ranged between 8.3 N/mm² and 4.8 N/mm² for the seven cycles whilst the crushing strengths for the samples F and E ranged between 7.4 N/mm² and 5.1 N/mm² and 8.1 and 3.9N/mm² respectively.

Table 3 shows the percentage swell of the samples after first absorption. From the vantage point of % swell, the samples I and J were the best with both having a percentage swell of 10 after the first adsorption. The sample, G (20%

 $CaCl_2 + 80\%$ Activated carbon + trace of Cement) swelled most among all the samples. Low swelling is important in bringing significant reductions in collector / absorber bulk.

Fig. 3 shows the plot of porosity against the number of cycle for the samples. The sample, J exhibited the best porosity among all the samples. Its porosity ranged between 40 - 42 % over the seven cycles. From the foregoing, the sample, J was adjudged the best among all the samples from the vantage point of porosity crushing strength and percentage swell. **Table -3 Percentage swell of the samples after 1**st Adsorption

Sample	% Swell after 1 st Adsorption
А	20+1
В	25+2
С	18+1
D	22+1
E	12+2
F	26+1
G	29+3
Н	27+2
Ι	10+2
J	10+2
Κ	14+2

4. CONCLUSION

Among all the samples investigated treated granular $CaCl_2$ (70% $CaCl_2 + 10\%$ activated carbon + 20% $CaSO_4$) was the best adsorbent of ammonia from the vantage point of porosity, swelling and crushing strength. In the light of this it is evident that the utilization of treated granular $CaCl_2$ (70% $CaCl_2 + 10\%$ activated carbon + 20% $CaSO_4$), in a solar refrigerator having ammonia as adsorbate, would enhance better Coefficient of Performance (COP).

The solar refrigerator may provide an alternative way for cold storage of food and vaccine in countries where most towns/villages/cities receive an abundant solar radiation annually. The solar refrigerator is advantageous in that it has no moving parts and there is no need for electricity to power it.

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