CLOSED CYCLE SOLAR REFRIGERATION WITH
THE CALCIUM CHLORIDE SYSTEM

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ABSTRACT

A closed cycle solid absorption intermittent refrigerator, using CaCl₂ absorbent and NH₃ refrigerant, was constructed and tested to obtain the instantaneous and cumulative available overall COP. The combined collector/absorber/generator unit had double glazing of 1.14 m² exposed areas. The system was fitted with a stagnant passive evaporative condenser with porous sandcrete wall, which produced condenser water temperatures varying from 3 – 10 deg C below ambient, during NH₃ generation and condensation.

The instantaneous available overall COP rose to a peak which depended on the solar fluxes and starting pressure, as well as on the condenser and ambient temperatures. The peak varied from 0.07 to 0.08. It fell as solar flux decreased towards late afternoon, but rose again slightly due to the combined effect of decreasing collector plate temperature and solar flux. The cumulative overall COP rose steadily to peak values in the range of 0.07 to 0.08, by the end of the generation period. The COP was a strong function of starting generator pressure or evaporating temperature, and fell as the pressure decreased. The cumulative overall COP is much lower than the peak instantaneous COP as a result of system inertia, caused by high collector plate and tube mass, and large system free volume.

The refrigerator is capable of maintaining evaporator temperature of -10 °C during the cooling phase, and is well suited for vaccine and food storage applications.

1. INTRODUCTION

There are many possible techniques for the utilization of solar energy in refrigeration and air-conditioning machines. These include the vapour compression, the vapour absorption and the thermoelectric methods. Figure 1 gives an option tree of the alternative schemes. When the energy of the vapour compression machine is solar, the electrical power for driving the compressor can be provided by photovoltaic panels. Alternatively, a concentrating or flat plate solar collector may be used to replace the boiler in a rankine cycle engine which produces the mechanical power for the compressor. In the absorption refrigerator, (fig. 2), the motor-compressor combination of the vapour compression system is essentially replaced with an absorber compound and solar collector. The absorbent, which may be liquid or solid, absorbs the refrigerant exothermically at low pressure and releases it endothermically at high pressure while absorbing solar energy. In the solar powered thermoelectric refrigerator working on the peltier principle, either a solar powered thermoelectric generator working on the seebeck effect, or a photovoltaic cell, may be used to provide the electric current required by the refrigerator.

Photovoltaic generators are quite expensive, and have low efficiencies of 8% - 10%. The more efficient thermoelectric and Rankine power units require high solar collection temperatures, and hence need concentrating collectors. The collector/generators of absorption plants can operate at temperatures around...
100°C which are possible with simple flat plate solar collectors. The absorption system therefore lends itself more easily to use with solar power.

2. OPEN AND CLOSED CYCLE ABSORPTION REFRIGERATION

Any of the viable absorbent-refrigerant combinations, such as H$_2$O-NH$_3$, LiBr - H$_2$O, CaCl$_2$ - NH$_3$, SrCl$_2$-NH$_3$, activated carbon ethanol, silica gel-water, zeolite-water, may be used in open or closed systems. With open systems, the refrigerant performs only one flow pass through the system, after which it is discharged to waste. For closed systems, the refrigerant is re-circulated through the system. Expensive and polluting refrigerants such as NH$_3$, ethanol and methanol may therefore not be used with open systems, while water may be used. Figure 2 illustrates both the open and closed cycles. The major advantage of the open system is that it dispenses with the condenser unit and associated equipment. However, since water is most often the refrigerant, it requires high vacuum for refrigeration. Provision must also be made for pumping and replenishment of the consumed refrigerant. A LiCl-H$_2$O open system was designed, built and tested as reported in [1]. Two tons (7kw) of cooling with chilled water temperatures of 10-12 °C and a COP of 0.7 were demonstrated. Jung and others [2] reported an intermittent open system utilizing silica gel or zeolite, with direct evaporative cooling of the air, to produce a conditioned air temperature of 10°C.

Closed cycle solar powered absorption refrigeration has been well reported in the literature, in the recent past. Nielson and others [3] gave a survey of intermittent systems including those using CaCl$_2$ as absorbent. Two stage, closed cycle absorption refrigeration systems using LiBr-H$_2$O, H$_2$O -NH$_3$ and LiNO$_3$ -NH$_3$ have been studied by Kaushik and Kumai [4]. Two stage thermodynamic COP's of 0.19 - 0.45 were shown to be possible.

A CALCIUM-CHLORIDE - AMMONIA CLOSED CYCLE REFRIGERATOR

A sketch of the cycle is shown in Fig. 2b. Since the solid absorbent does not circulate through the system the cycle is necessarily intermittent, with the same unit serving as both collector, absorber and generator. The design and testing of the absorption refrigerator, with its water cooled passive evaporative condenser, were reported in [5]. As observed in [6], CaCl$_2$ upon absorption of NH$_3$, experiences tremendous swelling. About 300 - 400% are possible. This led, in [6], to distortions and bursting of containment chamber, blocking of ammonia passages and inhibition of further absorption. During generation, the ammoniate mass experienced cracking, disintegration and migration. Ultimately the refrigerator to operate after a few cycles.

Absorbent stabilization treatments were studied experimentally in [7] so as to increase the strength and decrease the swell while maintaining good NH$_3$ absorption capacity. Of the treatments studied, the mixture with 20% CaSO$_4$ proved to be the best, and this was use in the system of reference [5]. The absorbent granules, of sizes 5-10 m., were packed in the annulus of each of six steel tubes at a density of 0.61 kg/l. Each tube had a central perforated NH$_3$ distribution pipe, and was bonded to the black painted collector plate. Total granule mass was 7.5 kg, and collector exposed area was 1.41 m$^2$. During NH$_3$ generation and consideration, value B (fig. 2b) was open while valves A and C were shut. During cooling both value C and B were shut, permitting the collector pressure to fall as it cooled. Consequently, when valves A and C were opened to start evaporation and re-absorption at night, the liquid evaporated at low pressure and saturation temperature, and produced
refrigeration at the evaporator. Cold element temperatures of -10°C or less and ice production of 0.41 kgm⁻² per day, were obtained. It may be observed that Hartoulari and Dufour [8], showed that cold element temperature of 30°C, a cold element temperature of -33°C was theoretically possible.

**INSTANTANEOUS AND CUMULATIVE EFFICIENCIES**

The closed cycle solid absorption refrigerator of reference [5] was rigorously tested, after further improvement to the throttle valve and piping seals, to determine the instantaneous and cumulative performances, defined by the available overall COP, where:

Instantaneous

Available Overall COP = \( h_{r}m/1 \ A_c \)  \hspace{1cm} (1)

Cumulative Available Overall COP = \( \int_{t_0}^{t_f} h_{r}m \ d t \)

\( \int_{t_0}^{t_f} \ A_c \ d t \)  \hspace{1cm} (2)

Where \( t \) and \( t_r \) are starting and ending times of the generation period. During generation stage, the surface temperature of a central collector tube was measured with a copper constant thermocouple. The generation pressures, condenser water and ambient temperatures, and condensate volumes were recorded. An Epply pyranometer gave the cumulative solar radiation. Data were taken at 30 minute intervals. Consequently, the instantaneous NH condensation rate and solar fluxes were obtained by numerical differentiation of the recorded tabular data, using the Lagrangian interpolation polynomial of degree 2, for three successive data points, [9].

Figures 3 - 7 show the plots of some of the results with time. The generation phase lasted over a period of 7 - 8 hours. Condensation did not start until around 12.00 noon to 1.00 pm. Thus, about the first 50 - 60% of the total generation time was used in heating up the collector plate and granules to the generation temperatures corresponding to the condensing pressure, and in pressurizing the system. Cumulative solar radiation during this heat up period amounted to 40 - 50% of the day's total. It may be seen that the system, as designed, had considerable inertia. This arose partly from the considerable mass of the collector plate, tubes and granules, (53kg), and from the large combined free volume of the condenser, liquid receiver, piping, collector distribution tube, and the allowance for absorbent expansion within the collector tubes, (18 liters). The allowance amounted to 12% of the total volume of the annular space provided for the granules. The system inertia delayed the onset of condensation.

Figure 3 is for a sunny dry season day with a peak solar flux of about 0.8 KW/m² and a total radiant intensity of 15127 KJ/m² during the generation period. The instantaneous available overall COP rose to a peak of 0.18 around 2.00 pm and fell thereafter. The slight increase in the late afternoon (after 3.00 pm) may be attributed to the combined effect of decreasing collector plate temperature and decreasing solar flux. Part of the sensible energy lost by the collector plate and tubes as their temperatures fell, would be transferred to the absorbent and used for NH₃ generation, - during a period when the instantaneous solar flux was falling. An increase in the instantaneous COP may therefore be expected. Beyond 4.30 pm, for this particular run, no additional generation of NH₃ was observed. The instantaneous COP would therefore drop to zero.

Calcium Chloride can absorb 8 moles of NH₃ per mole of the salt at saturation. The absorption reactions occur in three distinct steps involving 2, 2, 4 moles of NH₃. Figure 8 shows the equilibrium lines for pure NH₃ and for the last two reactions. The average condensing pressure for the run of fig. 3 was 1125 kPa. From fig. 8 absorbent temperature had to reach 84°C for the first 4 moles to be
released, and 96°C for the release of the next two moles. The collector tube temperatures plotted in fig. 3 would necessarily be higher than the absorbent temperatures. Since the collector tube temperatures rose only slightly above 96°C, and for a short part of the generation period, it may be assumed that the second generation reaction aid not have much opportunity to occur. The total NH$_3$ condensed at the end of the generation period was only about 50% of the total generation capacity of the absorbent, if all the four moles per mole of CaCl$_2$ were released. It follows that even the first generation reaction was not complete.

Figure 4 gives the results for another sunny day. Compared with fig. 3, the general trends of the COP and $T_s$ profiles are similar. For both tests, the ambient temperatures were identical, and the total solar fluxes during the generation period were approximately the same. Collector plate temperatures also had identical values. However, the peak solar flux and starting pressure for fig. 3, were higher, and so also was the condenser water temperature. The results show higher instantaneous COP for the test of fig. 3. The higher peak solar fluxes for this test, occurring at a time when the absorbent temperature was high enough to permit the release of NH$_3$, favoured the higher performances. Equally important is the fact that the starting pressure was higher for the test. For the run of figure 4, a lot more NH$_3$ needed to be generated in order to pressurize the system from its low starting pressure of 195 kpa to the average condensing pressure of 1176 kpa. This not only delayed the onset of condensation, but led to the depletion of the NH$_3$ content of the outer hotter granules, within the tubes, by the time condensation started. It was therefore possible for the incident solar flux, though lower for this test, to raise the collector plate temperature to the same levels as for the run of fig. 3, thereby making the heat losses to the environment similar. Since the incident solar fluxes were lower for fig. 4 during the condensing period, the energy available for NH$_3$ generation was therefore lower, hence the lower performances. The lower condenser liquid temperature for fig. 4 should lead to higher performances. However, this was apparently not enough to offset the effects of solar flux and starting pressure described above.

Figure 5 gives results for the dusty harmattan period. The effect of seasonal variations on the overall performances of the refrigerator were dealt with in [10]. However, lower performances are indicated for the harmattan than for the sunny dry season. Figures 6 and 7 show the variations of the cumulative performances with time. Figure 6 indicates a maximum cumulative Available overall COP of 0.073. The conditions for the two tests of figure 7 were nearly similar except for the starting pressure. The differences in the cumulative performances are clearly marked. A starting pressure of 495 kPa represents an evaporation temperature of approximately 4°C, which is appropriate for some air-conditioning applications. A starting pressure of 195 kPa corresponds to an evaporation temperature of 16°C. It is clear therefore that lower evaporating temperatures reduce the performances, and that the system should perform better when, used for air-conditioning than for refrigeration applications. When used in the refrigeration mode, it is however possible to charge the system with NH$_3$ such that the starting pressure is higher than the design evaporating pressure. When this is done, most of the evaporation and absorption stage will take place at the lower evaporating pressure, and hence temperature. The pressure will however rise to the higher starting value towards the end of the evaporating period.
CONCLUSION

Despite the deficiencies of the present system, the performances are very, encouraging. An improved design which will reduce the heat up time should yield very significant increases in performance. The unit is capable of sustaining very low temperatures (-10°C) during evaporation and of producing ice, as demonstrated in [10]. Application possibilities exist in the storage of vaccine for rural health care schemes. Vaccine storage temperatures of 4°C can easily be attained. Chilling and storage of meat, and storage of vegetables, requiring temperatures of around 0°C, are within the scope of the unit. The intermittent nature of the passive solid absorption system does not make it easily applicable to comfort air-conditioning since cooling is required during the, daytime generation period. This difficulty can, however, be overcome by latent or sensible storage of the cold, or by use indirect solar heating with multiple absorption/generation systems, and phased cycling.

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NOMENCLATURE

\( A_c \) - Collector area \( \text{m}^2 \)

COP - Coefficient of Performance

\( I \) - Solar Flux \( \text{KWh/m}^2 \)

\( m \) - \( \text{NH}_3 \) condensation rate \( \text{kg/s} \)

\( T_c \) - Collector tube temperature \( \text{°C} \)

\( T \) - Time \( \text{sec} \)

\( h_{ev} \) - Heat of evaporation \( \text{KJ/kg} \)

REFERENCES


Fig. 1 Types of Solar Refrigerator Systems.
Fig. 2: Open and Closed Cycle Intermittent Solid Absorption Coolers
Fig. 3: COP, Solar Flux Plate Temp. vs Time

- **Run 31**
- **Tc = 27°C**
- **Ta = 34°C**
- **Start time 08:35**
- **P-start = 495 kPa**
- **Total solar = 15127 kJ/m²**
Fig. 4: COP, Solar Flux Plate Temp. vs Time

- $T_c = 24.5 \, ^\circ C$
- $T_a = 34 \, ^\circ C$
- Start time 08:30
- Run 36, $P_{start} = 195 \, kPa$
- Total solar flux = 15210 \, kJ/m^2
Fig. 5 COP, Solar Flux, Plate Temp. vs Time
Run 31
P start = 49.5 kPa
T start = 08:35 am
Total solar = 21329 kJ

Fig. 6 Cumulative COP vs Time From Start
Fig. 7: Cumulative COP vs Time From Start
\[ CaCl_2 \cdot 8NH_3 \rightleftharpoons CaCl_2 \cdot 4NH_3 + 4NH_3 \]  \hspace{1cm} \text{(3)}

\[ CaCl_2 \cdot 4NH_3 \rightleftharpoons CaCl_2 \cdot 2NH_3 + 2NH_3 \]  \hspace{1cm} \text{(4)}

**Figure 5**  
Equilibrium Diagram for the Reactions of Calcium-Chloride and Ammonia (2)