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Driss Stitou, Nathalie Mazet, Mauran Sylvain. Experimental performances and optimization of a solid/gas thermochemical process for solar cooling. International Sorption Heat Pump Conference, ISHPC 2014, Mar 2014, Washington DC, United States. paper 1060. <hal-04818275>

HAL Id: hal-04818275

<https://cnrs.hal.science/hal-04818275v1>

Submitted on 4 Dec 2024

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Experimental performances and optimization of a solid/gas thermochemical process for solar cooling

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ABSTRACT

This paper focuses on the analysis of experimental performances and potential optimisations of a solar air-conditioning pilot plant, which is running in PROMES-CNRS laboratory (Perpignan, France) since 2006. This device consists of a solid/gas thermochemical sorption process powered at 60-70°C by 21.6 m² of flat plate solar collectors. The experimental device of a daily cooling capacity of 20 kWh of cold at 4°C, is able to refresh a conference room of 130m² and can provide a cooling power of 5 kW during 4 hours. The thermochemical process is based on the coupling of a liquid/gas phase change of a refrigerant (NH₃) and a reversible chemical reaction between a reactive solid (BaCl₂) and this refrigerant. It operates discontinuously according two phases : a diurnal period during which the reactor is connected to a condenser and heated by the solar collectors loop, and a nocturnal period where the reactor is connected to the evaporator and cooled down by an in-ground geothermal loop. The cold is produced at the evaporator and is stored into a PCM that solidifies at 5°C for a subsequent utilization during the day. In this paper, the analysis of the experimental results collected over two summer seasons is carried out. It leads to an averaged efficiency of 50% for the solar collectors, a process COP ranging from 30 to 40% and a daily cooling productivity of about 0.8 to 1.2 kWh of cold per m² of solar collector. The mean experimental solar COP is about 18% for the summer period (july-august) and decreases to 11% from april to september. A modelling of the whole process has been carried out in order to analyse the unsteady functioning of this solar cooling process under variable operating conditions and optimize its performances. This analysis allows identifying ways of improvements of the design of the different components, and defining new strategies for the control/command of the whole process. As a result, an improvement of the performances of 10% can be achieved by a better adjustment of the trigger thresholds for the different operating phases. The use of more efficient solar collectors and the change of their tilt angle can provide an improvement of 80% of the yearly performances. The simulations showed also that a better design of the thermochemical reactor and the in-ground cooling loop may provide an improvement of 35 % of the yearly produced cold.

1. INTRODUCTION

Nowadays, peaks in electricity demand occur more frequently during the summer period in most developed countries, because of the increasing use of air-conditioning. The reasons lie in higher thermal comfort expectations, in lower initial costs for air-conditioning equipments and in the heat island effect in urban areas, which leads to microclimatic changes. The International Energy Agency (IEA, 2010) has gathered frightening data on energy



International Sorption Heat Pump Conference, March 31-April 3, 2014

consumption trends : during the last four decades (1973–2008) primary energy consumption has grown by 80% and CO₂ emissions by 88%, with an average annual increase of 2.5% (Pérez-Lombard *et al.*, 2008). Moreover, final energy consumption in buildings in the European Union represents about 40% of the total energy consumption and is responsible for about 20% of the total CO₂ emissions (Chwieduk, 2003). Solar assisted cooling appears to be a promising alternative to the conventional electrical driven air-conditioning from an environmental point of view, since it results in lower CO₂ emissions and avoids CFCs and HCFCs uses. Considering the problem of electricity peaks during summer caused by electrically driven air-conditioning systems, and the close coincidence with the maximum solar irradiation, solar assisted refrigeration may be an interesting option to handle successfully the issue of reducing electricity demand peak due to air-conditioning.

Solar sorption refrigeration technologies such as thermochemical reaction, adsorption, absorption and desiccant cooling processes, are the prevailing option for the utilisation of solar energy in air-conditioning. Solar coolers and refrigerators have been developed for more than 40 years using liquid absorption (Srikhirin *et al.*, 2001; Ziegler, 2009), solid adsorption (Dieng *et al.*, 2001) or thermochemical reaction processes (Spinner, 1993; Stitou *et al.*, 2004; Mauran *et al.*, 2008). Most of solar cooling systems that are currently marketed are of liquid/gas absorption type, while solid/gas sorption processes are still at the development stage. Nevertheless, solid/gas sorption processes have distinctive advantages compared to absorption technology. As the sorbent material is solid, the main difference is that two or more reactors or adsorbers are necessary in order to provide continuous cooling production. Solid/gas sorption systems allow for somewhat lower driving temperatures but have a lower COP and specific cooling power (SCP) compared to absorption systems under the same conditions. Nevertheless, the use of solid/gas sorption cooling technology seems to be preferable for small cooling capacity chillers (Wang *et al.*, 2006).

The present study focuses on experimental investigations carried out on a solar powered solid/gas reaction-based thermochemical pilot plant using flat plate collectors for residential air conditioning. The purpose of this work is to quantify and analyse over two years of operation the energy performances of this thermochemical plant representative for air conditioning in housing in order to identify design and control improvements. In addition, the authors wish to emphasize that the prototype of thermochemical process presented in this paper, is a completely new prototype and in our knowledge, no other similar prototype for solar air-conditioning application has been already experimented.

2. PRINCIPLE OF SOLID-GAS THERMOCHEMICAL SORPTION PROCESS

The principle of thermochemical reaction processes is based on the thermal effect of a reversible reaction between a solid and a reactive gas. By coupling such a solid-gas reaction with a liquid/gas phase change of the same working gas, a sorption cooling production process can be designed:



These two processes are monovariant and their equilibrium conditions follow the Clausius–Clapeyron relation (2). The thermodynamic equilibrium conditions of the reactor are determined by only one parameter (P or T):

$$\ln\left(\frac{p}{p^o}\right) = -\frac{\Delta H_i^o}{R.T} + \frac{\Delta S_i^o}{R} \quad (2)$$

where ΔH_i^o is the standard enthalpy of the transformation process, either solid-gas reaction ΔH_r or liquid-vapour phase change ΔH_v . Similarly ΔS_i^o is the corresponding standard transformation entropy and p^o is a reference pressure

The implementation of a chemical solid/gas sorption unit implies two elements: a fixed-bed reactor that allows the reversible chemical reaction to take place and two-phase heat exchangers in which evaporation or condensation of the reactive gas occurs. The simplest sorption machine consists of a solid/gas reactor coupled with an evaporator, which can also play the role of a condenser. Figure 1 describes such an implementation in its simplest form. Following the right direction of the reaction, the solid S_1 reacts with the gas G produced by the evaporator and forms the solid S_2 (synthesis of salt S_2). This synthesis reaction is exothermic and produces the heat of reaction ΔH_r that is released to the environment at the ambient temperature. In the left direction, the decomposition reaction, or thermal

dissociation, is endothermic and requires a heat input ΔH_r to proceed: salt S_2 is then dissociated into the initial salt S_1 and the gas G. The gas G flows into the condenser which is the coldest part of the system, and condenses into liquid.

A large number of solid-gas working pairs have already been used in refrigeration applications (Wang *et al.*, 2009). Among them, some working pairs are suitable for solar cooling applications such as calcium chloride/ammonia (Iloeje, 1985) or calcium chloride/monomethylamine (Erhard *et al.*, 1997), strontium chloride/ammonia (Erhard *et al.*, 1998). These ammoniated salts have relatively low dissociation temperatures, below 100°C, which make them usable for solar cooling applications using conventional flat plate solar collectors. The reactive salt chosen for the pilot plant described hereafter is the barium chloride, $BaCl_2$, which reacts with 8 moles of ammonia to form $BaCl_2 \cdot 8NH_3$. This salt has been successfully used for ice-making and air-conditioning processes (Le Pierres *et al.*, 2007 ; Rivera *et al.*, 2007). Its main advantage lies in the low decomposition temperature of the salt, which is ranging from 50–70 °C for the high-pressure phase depending on the condensing pressure (Fig. 1) defined by relation (2). For example a condensation temperature of 20°C imposes a pressure of 8.5 bar, which in return requires a minimum decomposition temperature of 48°C. A condensing temperature of 50°C requires that the decomposition reaction occurs at a minimum temperature of 70°C. In addition, this salt presents a high stoichiometry coefficient v that minimizes the size of the reactor.

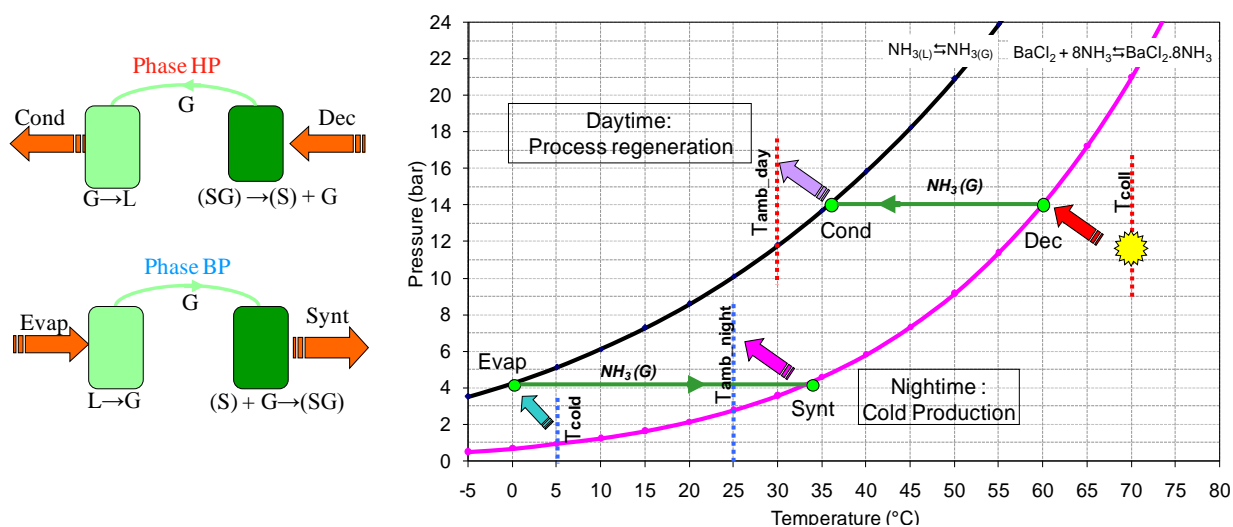


Figure 1 : Basic principle and operating conditions of the solar thermochemical solid/gas sorption process

The implementation of the reactive medium in a porous fixed bed gives rise to general problems of transport phenomena (heat and mass transfers). The heat of reaction from the synthesis phase (or consumed during the decomposition phase) has to be removed (or delivered) by a heat transfer fluid. Equally, the diffusion of the reactive gas, through the reacting porous medium must not limit the progress of the chemical reaction. This kind of limitation can notably happen in synthesis reactions during which an increase of the volume of the reactive medium and a decrease of the bed porosity are observed, thereby diminishing the gas permeability of the reacting medium. Thus, in order to enhance heat and mass transfer in the porous medium, it is necessary to add an inert binder in the reactive bed. For these thermochemical processes, the solid reactant is mixed with expanded natural graphite (ENG), and recompressed together in order to form consolidated reactive blocs. Graphite is an inert porous binder that has a high intrinsic thermal conductivity, an exfoliated structure enabling a high porosity and mechanical elasticity. As a result, the ENG enhances efficiently heat and mass transfers inside the consolidated reactive blocs without taking part to the reaction. It reduces the effect of volumetric variations of the salt occurring with the chemical reaction (Spinner, 1993; Mauran *et al.*, 1993). This innovative implementation was first developed and patented by PROMES laboratory in 1983 to avoid power limitation of thermochemical reactors (Coste *et al.*, 1983). Expanded graphite is now widely used as a porous additive in composite reactive medium due to its high thermal conductivity and gas permeability (Wang *et al.*, 2005).

3. PILOT PLANT DESCRIPTION

3.1 Operating mode

This solar sorption system operates discontinuously according to two different phases: the diurnal period during which the system is regenerated, and the nocturnal period where the cooling occurs. Figure 1 presents the pressure vs. temperature operating conditions of the two main steps of this basic sorption cycle at high and low pressures. During the day time, the reactor is heated by solar energy and desorbs the gas that flows to the condenser and condenses at the diurnal outdoor temperature T_{amb_day} , which is greater than the nocturnal outdoor temperature T_{amb_night} . The high operating pressure of this step is imposed by the condensation temperature of the reactive gas. During the night time, as the reactor is cooled down, it reabsorbs the ammonia gas and induces a pressure decrease in the reactor linked to the evaporator. This enables the boiling of the liquid ammonia in the evaporator and produces the cooling effect. The ammonia gas produced in the evaporator is then absorbed by the reactor, which releases the heat of absorption at the nocturnal ambient temperature. As the cooling effect is produced during the night, a cold storage is required for its subsequent utilization the next day.

3.2 Components of the pilot plant

The pilot plant was designed to provide a cooling capacity of 20 kWh of cold per day. By considering a specific refreshing demand of 50 W per m² of floor, the cooling energy produced by the thermochemical unit corresponds to air-conditioning needs of a conference room of 100m² during approximately 4 hours.

Figure 2 displays some views of the pilot plant and a schematic diagram of the installation. The pilot plant consists of four subsystems (Fig.2) : a solar heating loop, a thermochemical sorption unit, a ground cooling loop and a chilled water production/distribution loop.

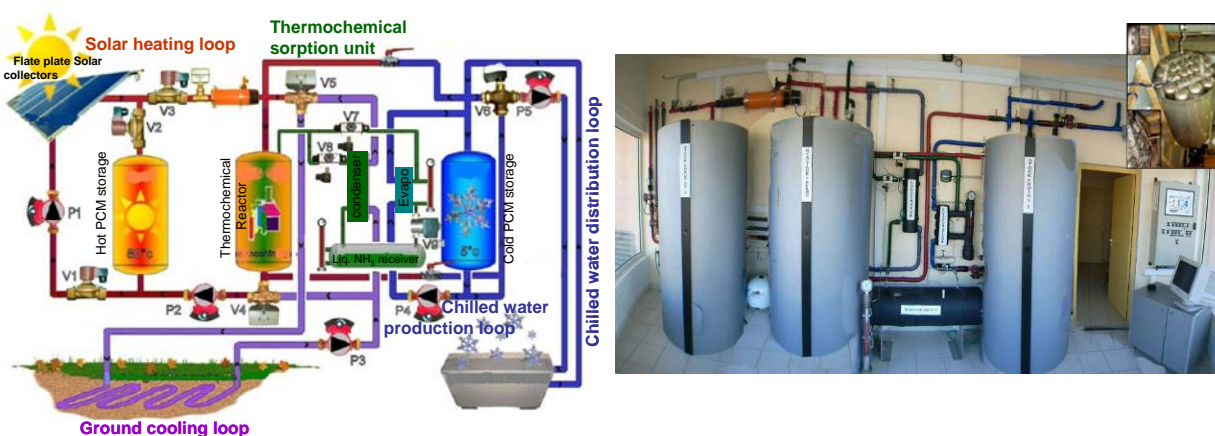


Figure 2 : Schematic description and view of the solar thermochemical sorption pilot for air-conditioning

The solar heating loop is composed of 21.6 m² of flat plate collectors manufactured by HelioAkmi (ST2000 model). These collectors are tilted at 30° and south oriented, and are characterized according to the European standard certification EN-12975 by an optical efficiency $\eta_o = 0.72$, and heat loss coefficients of first order $a_1 = 4.804 \text{ W/m}^2\cdot\text{K}$ and second order $a_2 = 0.04 \text{ W/m}^2\cdot\text{K}^2$. The solar collector loop is connected during the day to the thermochemical reactor and a hot thermal storage, which is filled with 360 kg of a phase change material (wax RT80 from Rubitherm GmbH) that melts at 75-80°C. This hot PCM storage enables storing the excess solar heat if the decomposition reaction is completed before the end of the afternoon, and reversely the heating of the reactor at the beginning of the day or when the solar heat is not sufficient.

The thermochemical sorption unit consists of one reactor made of a set of 19 tubes filled with a composite reactive porous medium (Fig. 5). The reactive composite consists of a compressed mixture of 140 kg of anhydrous BaCl₂ and 35 kg of expanded natural graphite, which is an inert binder that enhances heat and mass transfer. The reactor is either connected to a condenser during the day or to the evaporator during the night through the valves V8 and V7,

respectively. The condensed ammonia is stored in a 100 litres tank in order to be used during the night. A level gauge is located in this tank to measure the amount of ammonia released or absorbed by the reactor.

The ground cooling loop enables alternatively the cooling of the condenser during the day and the cooling of the reactor during the night thanks to a set of two 3-way valves (V4 and V5). This cooling loop is made of a horizontal in-ground plate heat exchanger of 16m², which is buried at two meters depth.

The chilled water loop is connected to the evaporator. The chilled water is produced at about 0-5°C during the night phase. This cooling capacity is then stored into a second PCM storage, which is filled with 340kg of a wax that solidify at 5°C (wax RT5 from Rubitherm GmbH). During the day, fresh water at 13°C is distributed from the PCM storage via a mixing valve V6 to the fan-coil units located in a conference room.

3.3 Control of the solar process

The entire pilot plant is instrumented and its operation is controlled under Labview software. The solar heating loop is controlled by the pyranometer and temperature measurements of the heat transfer fluid of solar collectors, inside the reactor and hot PCM storage. By comparing these temperatures, different control strategies are possible: the reactor can be heated either by the collectors or by the hot PCM storage in the morning, the collector field can supply heat to the hot storage only or both the reactor and the hot storage, the reactor can also heat up the hot storage tank,...All these strategies are implemented into a supervisory control and data acquisition Labview software (SCADA). This SCADA system monitors and controls the whole solar process by managing the operating phases.

The connection of the reactor with either the condenser or the evaporator is controlled by pressure sensors (reactor, evaporator and condenser) and a level gauge located in the reservoir of the condensed ammonia. When the high level is reached then the decomposition phase stops, and the reactor is cooled down by the cooling loop. The synthesis phase is stopped when a low level in the liquid reservoir is reached due to the absorption of ammonia by the reactor. The cooling of the condenser is started when the reactor is connected to the condenser during the decomposition reaction, while the cooling of the reactor is started when the pyranometer indicates a low irradiation value at the end of the afternoon or when a high level of liquid ammonia in the reservoir is obtained. The ground cooling loop feeds separately either the reactor or the condenser. The chilled water loop is started when the reactor is connected the evaporator and if the evaporating temperature is lower than the cold PCM storage temperature. The distribution of the fresh water from the cold PCM storage to the fan-coil units is activated on user's demand during the day. Some security procedures are foreseen to prevent an overpressure that may occur during hot summer days in the reactor. In this case, the solar heating loop is stopped and/or the connection between the reactor and the condenser is strained.

4. EXPERIMENTAL RESULTS

4.1 Cycling analysis

A typical cycling of the pilot plant over several days in June is shown in figure 3. Figure 3a shows the evolutions of the outlet temperature of solar collectors, inlet and outlet temperatures of the reactor, hot storage, and ground cooling loop, and the ammonia temperature at the inlet and outlet of the condenser. Temperatures of the chilled water (cold storage/evaporator loop) and distributed chilled water are also shown. During these days, the distribution loop was in operation from 10A.M. to 5P.M.

Figure 3 illustrates also the typical pressure swings of the reactor, condenser and evaporator over several days. The evolution of the amount of condensed or evaporated ammonia is also shown. The solar collectors deliver hot water at a maximum temperature of 75-80°C and enable the heating of the reactor, which reaches a maximum temperature of 68°C. At the beginning of the day, the reactor at low temperature is quickly heated up by the hot PCM storage: its temperature increases from 25°C to 45°C, then it is heated up by the solar collectors. As the reactor is closed, its pressure increases. The reactor is then connected to the condenser when its pressure becomes greater than the condenser pressure. The gaseous ammonia is desorbed from the reactor, then condensed and stored in the tank: the level of liquid ammonia increases. At the end of the day, when solar irradiance becomes insufficient, the reactor is disconnected from the condenser and cooled down by the ground loop. The reactor pressure decreases as the salt reabsorbs ammonia. When the reactor pressure becomes lower than the evaporator pressure then a connection reactor-evaporator is established.



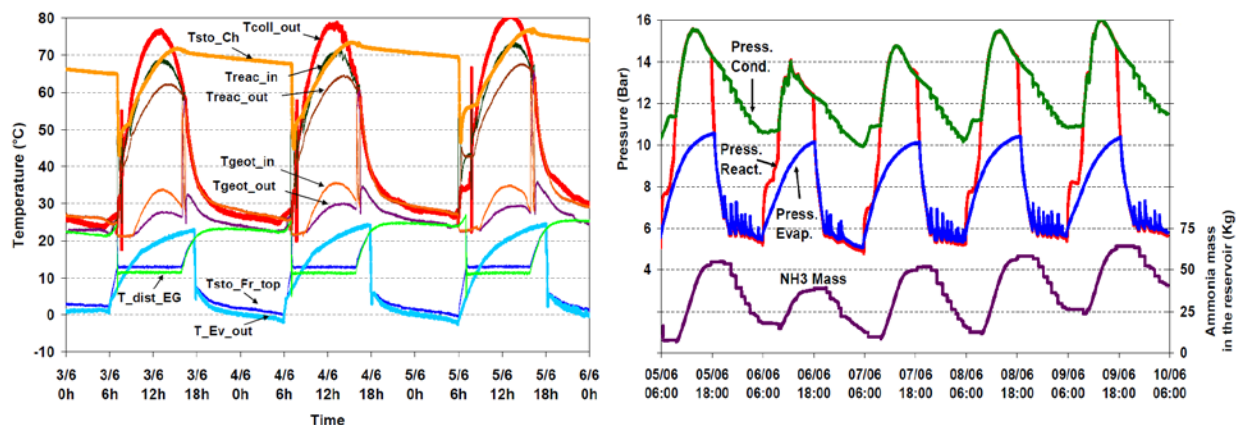


Figure 3: Typical temperature evolutions of the components of the solar loop (collectors, hot storage and reactor), geothermal sink and chilled water loop (evaporator, cold storage and distribution). Evolution of pressures of the reactor, condenser and evaporator and condensed ammonia mass

During the night, the reactor is cooled down below 40°C , it absorbs the ammonia gas produced by the evaporator and enables a cooling production at a temperature of about 0°C . The liquid ammonia level in the evaporator is controlled and maintained more or less constant by a second level gauge that acts on the valve V9 located between the evaporator and the liquid ammonia tank. The valve V9 is opened when a low level set point is reached and liquid ammonia flows from the ammonia tank to the evaporator due to the pressure difference. When the high level is reached, the valve V9 is closed. This level control induces pressure peaks in the evaporator and a discontinuous decrease of the ammonia level in the reservoir. Chilled water is then produced at a temperature below 3°C , which is enough to solidify the PCM in the cold storage. During the day after, the evaporator is closed and the cold PCM storage is discharged. The temperature of the evaporator increases during all the day as it is disconnected from the rest. Chilled water at 5°C is mixed with returned fresh water by a mixing valve in order to provide water at $12\text{--}13^{\circ}\text{C}$ to fan-coil units of the conference room.

4.2 Performances analysis

Figure 4 shows the evolution of the thermal powers for different components of the process over three consecutive days. The solar collectors supply a maximum power P_{coll} of 10 kW under a global solar irradiation P_{sol} of 18 kW. The decomposition reaction ($P_{\text{reac-dec}}$) in the reactor absorbs approximately 70% of this input power and the remaining part is stored in the hot PCM (P_{stor}). The efficiency of the solar collector is about 55% for these sunny days. During the night, the evaporator enables a cooling power of about 2 kW during 10 hours. The heat of synthesis reaction is released into the ground with a power about 3 kW.

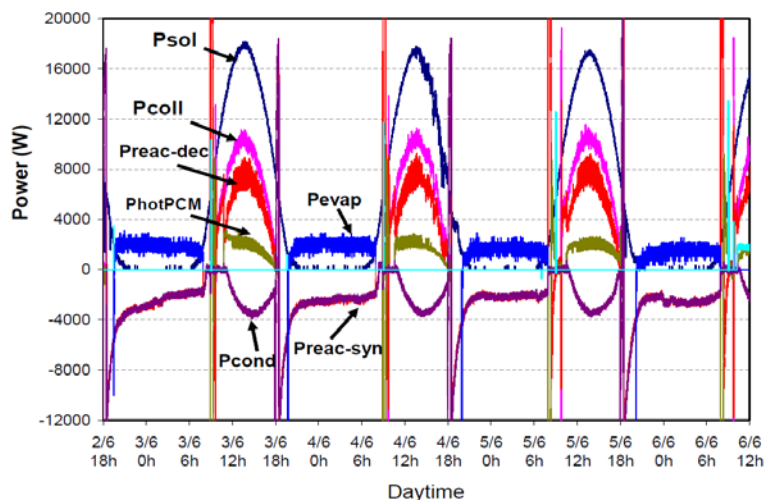


Figure 4 : Evolutions of powers involved in the main components of the process

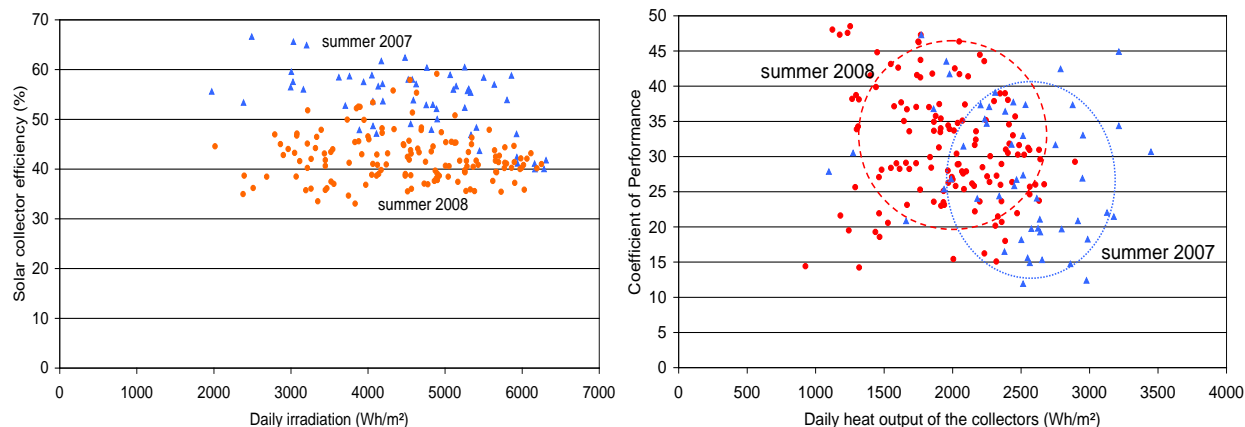


Figure 5 : Evolutions of solar collector efficiency and the daily process COP over two summer periods

According to the operating configurations, a part of the daily collected solar energy E_{coll} is stored into the hot storage ($E_{coll \rightarrow stor}$) and the other part is used to heat up the reactor ($E_{coll \rightarrow reac}$). During the morning or cloudy passages, the hot storage provides heat to the reactor ($E_{stor \rightarrow reac}$). At the end of the day when the reactor is cooled down, a fraction of the heat removed is recovered and stored in the hot storage ($E_{reac \rightarrow stor}$). Some thermal losses of the storage E_{stor_loss} and the reactor E_{reac_loss} occur also during all the day and night.

The pilot plant is running since 2006. Figure 5 presents the performances of the thermochemical process over 2007 and 2008 summers. Each point represents a daily performance. The daily solar collector efficiency is defined as the ratio of the total thermal energy collected E_{coll} that is transmitted to the process via the heat transfer fluid, to the total incident solar irradiance E_{sol} :

$$\eta_{coll} = \frac{E_{coll}}{E_{sol}} \quad (3)$$

Comparing the two experimental seasons, a decrease in the collector efficiency is observed. During summer 2007, the daily collector efficiency is about 50 to 60% while in summer 2008 the solar collector efficiency is lower, ranging from 40 to 50% due to aging of the solar collectors.

The coefficient of performance of the process $COP_{process}$, is defined as the ratio of the daily cooling energy E_{cold} produced by thermochemical unit to the total heat solar collected during the day E_{coll} . This definition takes into account the efficiency of the heat storage and that of the thermochemical unit.

$$COP_{process} = \frac{E_{cold}}{E_{coll}} = \frac{E_{cold}}{E_{reac_heating}} \cdot \frac{E_{reac_heating}}{E_{coll}} \quad (4)$$

The daily thermal energy $E_{reac_heating}$ that is supplied to the reactor for its regeneration is equal to the part of the collected solar energy $E_{coll \rightarrow reac}$ that feeds directly the reactor, plus the thermal energy $E_{stor \rightarrow reac}$ that is discharged from the hot PCM storage to the reactor at the beginning of the day or when the collected solar energy is not sufficient. For a same amount of collected energy, the amount of heat that is supplied to the reactor is greater for 2008 summer. Even if the daily heat collected during summer 2007 is mostly greater than in 2008, the daily heating energy of the reactor is somewhat lower during summer 2007. Therefore, daily $COP_{process}$ were generally lower, ranging from 15 to 40% for summer 2007.

This increasing evolution in performance of this solar process is the result of a better control and management of the solar heating loop and of the different components of the sorption pilot plant that have been implemented for summer 2008. This control mainly consisted in the replacement of a defective valve V2 of the hot PCM storage, improvement of the insulations of the reactor and hot and cold PCM storage (insulation increased from 5 to 10 cm thickness), improvement of the Labview control strategies such as the increase of the threshold and hysteresis values of irradiation required for starting/stopping the solar loop. In the end, the total thermal energy that is collected is efficiently used by the reactor, and enables a higher cooling production.

These improvements have counter-balanced the decrease in the solar collector efficiency. The daily process COP for summer 2008 is improved and ranges roughly from 20 to 45%. The daily cooling productivity of such thermochemical process ranges from about 800 to 1200 Wh of cold produced at 4°C per m² of solar collector with a global seasonal productivity of 75 kWh/ m² of collector. Finally, the daily solar coefficient of performance of the whole solar process COP_{sol}, which is defined as the cold produced by solar irradiance varies from 10 to 23%, with a mean value of 0.18 during the hottest summer months (july/august) and 0.11 for the whole functioning period from april to september :

$$COP_{sol} = \frac{E_{cold}}{E_{sol}} = \eta_{coll} COP_{process} \quad (5)$$

4.3 Performances optimization

A modeling of the whole solar process has been performed in order to quantify the optimization potential of the performance over a full season. It follows that the quality of the solar collection (use of more efficient solar collectors such as double glazed collectors, increase of the tilt angle to 35°,...), the management strategy of the solar loop (hot storage management, thresholds and hysteresis switching pumps,...) and of the thermochemical reactor (connection management with the evaporator and the condenser) play an important role on performances. The hot storage in the current configuration has a detrimental effect on the performances and could be avoided. The cooling loop of the reactor and condenser also strongly impact the productivity : the use of more efficient geothermal boreholes could significantly improve the performance. Thus, a cooling productivity gain of 150% could be achieved in comparison to the current configuration by optimizing the design of different components, including the optimization of the heat exchanges with the different thermal loops. By implementing all these potential improvements, the seasonal cooling productivity would increase from 75 to 190 kWh / m².

5. CONCLUSIONS

Solar cooling can become a promising solution for the clean and sustainable air-conditioning of buildings. As the demand for air-conditioning is increasing and, as soft technologies like passive cooling are very difficult to apply in existing buildings, the sorption cooling technology discussed in this paper may provide a competitive alternative to conventional air-conditioning systems. Solar refrigeration is a technology that has a great variety of methods of producing low temperatures; however, very few have demonstrated a technical viability.

The experimental study presented in this paper shows that is possible to develop thermochemical solid-gas sorption process for air-conditioning using only standard flat plate solar collectors operating at a relatively low temperature 70°C. Our results shows that an optimal management and control of the different components of the sorption pilot plant, such as the coupling of the solar collector loop with the hot PCM storage and the reactor or the connection of the reactor with the condenser and evaporator, can result in a substantial increase in the daily cooling production. The mean experimental solar COP of such thermochemical sorption process is around 18% for the summer period (july-august), which is not far from those already obtained (around 22 %) by other more efficient sorption process, e.g. liquid/gas absorption machines. However, it decreases to 11% from april to September.

A modelling of the whole process has been carried out in order to identify ways of improvements of this process. As a result, an improvement of the performances of 10% can be achieved by a better adjustment of the trigger thresholds for the different operating phases. The use of more efficient solar collectors and the change of their tilt angle can provide an improvement of 80% of the yearly performances. The simulations showed also that a better design of the thermochemical reactor and the in-ground cooling loop may provide an improvement of 35 % of the yearly produced cold. By implementing all these potential improvements, the seasonal cooling productivity would increase from 75 to 190 kWh / m².



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ACKNOWLEDGEMENT

The authors wish to acknowledge the French Agency ADEME (“CLIMSOL” project, 2004-2007), the French Research Programs ANR-PREBAT (“ORASOL” project, 2006-2010) and ANR-SEED (“In-STORES” project, ANR-12-SEED-0008-01; 2013-2017) for their financial support.





International Sorption Heat Pump Conference, March 31-April 3, 2014