Theoretical investigation of a long-term solar energy storage based on LiBr/H₂O absorption cycle

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Abstract

Sorption thermal energy storage appears to be relevant for long-term solar energy storage because of its low heat loss and high energy density. A long-term solar heat storage based on the absorption of water by lithium bromide is presented. The modelling of the system is detailed and the results of three parametric simulations are discussed. It appears that crystallisation in the solution store could double the storage density and therefore the system competitiveness.

Keywords: thermal energy storage, long term energy storage, solar heat storage, absorption cycles, lithium bromide, dynamic simulation.

1. Introduction

Energy storage is a key component to improve the efficiency of energy systems, especially when the energy source is intermittent, such as solar energy. Heat storage systems based on sorption processes are relevant in case of long-term storage, as storage in physical form (sensible or latent heat) progressively loses thermal energy. However, even though considerable breakthroughs have been made in the past decades, there is no mature long-term sorption heat storage yet [1]. The aim of this project is the development of a long-term solar energy storage device, based on the absorption process, for buildings heating. The modelling and dynamic simulations of the system are presented.

2. Description and operation principle of the process

The system mainly consists of a generator (desorber/absorber), a condenser/evaporator, a solution (lithium bromide (LiBr) aqueous solution) storage tank and a water storage tank (Fig. 1). During sunny periods, especially in summer, the LiBr solution is desorbed in the generator by energy captured by solar thermal collectors. The water vapour which is released, is condensed in the condenser and stored in the water storage tank while the desorbed (concentrated) solution is stored in the solution tank. The sorption heat can therefore be stored with negligible thermal loss, since the heat of this endothermic reaction is kept as a chemical potential. In heating needs periods, particularly in winter, the solution absorbs in the generator water vapour that is evaporated in the evaporator (the same component as the condenser) by a low temperature heat source: the heat of this exothermic phenomenon is used for domestic heating purpose.

Considering some selection criteria [1], especially thermodynamic, technical, economic and ecological, LiBr/H₂O working pair has been chosen. This well known couple in absorption refrigeration processes offers acceptable thermodynamic equilibrium conditions (temperature levels)
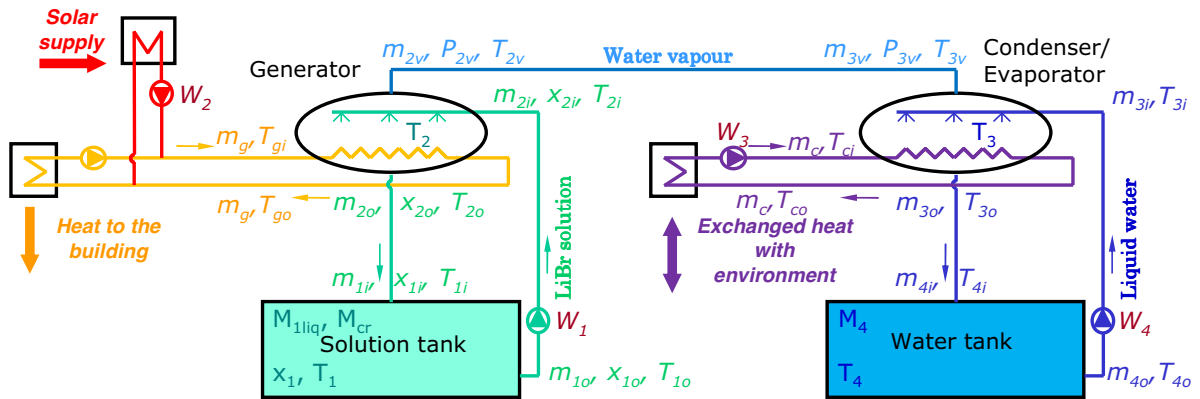
Fig. 1. Schematics of the system for the dynamic simulation.

for the process [2]. However, contrarily to the case in refrigeration systems and in order to increase the energy storage density, the solution is aimed to be concentrated up to the crystallisation curve, and stored with crystals. Indeed, the amount of heat that is stored is roughly proportional to the amount of water that is desorbed. The higher the amount of water absorbed, the higher the heat of sorption that can be got back. So, during desorption, the more water extracted from the diluted solution, the more heat stored. When the solution is desorbed so that its concentration reaches the solubility limit, crystals appear in the storage. The crystallisation ratio r, that is the solid to liquid mass ratio in the solution tank, is an indicator of crystallisation level in the solution tank. $r_{max} = 4$ means that the maximum mass fraction of solid in the solution tank during a whole cycle is 80%. A solution tank without crystallisation leads to $r = 0$. The storage density increases with the maximum crystallisation ratio but this leads to some technological difficulties such as the complication of the solution circulation by pumps when crystals are present in the storage.

The annual cycle of the process is presented in Fig. 2. At the beginning of the charging period, in summer, the solution is at the temperature T_{tank} of the environment in which the tanks are stored (point 1).When solar supply is available, the diluted solution is pumped from the solution tank to the generator (desorber). It is then heated by the solar loop and increases in pressure until the liquid/vapour
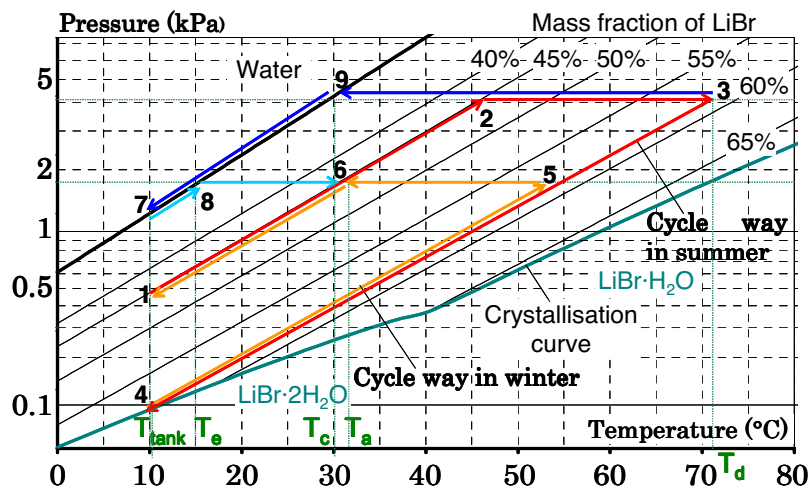

Fig. 2. Duhring chart of lithium bromide / water cycle in annual absorption heat storage process.

pressure equilibrium in the condenser is reached (point 2). As the heat supply continues and the temperature level is sufficient, the solution desorbs water vapour, becomes concentrated (point 3) when the released water vapour is condensed in the condenser (point 9): it is the effective phase of desorption. The condensed water that leaves the condenser is collected in the water tank (point 7). The concentrated solution, which exits the generator, returns to the solution tank (point 4) where it gets cold as the tank is not insulated. In winter, the concentrated solution is pumped to the generator that operates then as an absorber. The water vapour is absorbed by the solution until the pressure equilibrium in the generator and the evaporator (point 5) is reached. Then the absorption takes place at constant pressure (5→6) maintained by the vapour produced in the evaporator and the produced useful heat is evacuated by the heating loop fluid. The diluted solution (point 6) goes back to the solution tank (point 1).

3. System modelling

The sizing in statics conditions does not consider the transient characteristics of the system pertaining to the operating conditions of the process that change year-round: daily fluctuations of the solar source, the environment (heat sink or source) and the heat demand for heating, variation of solution concentration in the storage, crystals formation, etc. Its is also important to take into account thermal loss to the ambient, walls thermal inertia, heat and mass transfer limitations in various components and the energy consumption by auxiliary equipments (especially circulating pumps).

Therefore, the aim of the dynamic modelling is to evaluate the system actual performances and to propose an optimal design as function of the climatic conditions. In addition, it aims to find optimal control of the process.

3.1. Assumptions and basic equations

The model is based on the energy and mass balance equations and the properties of the LiBr/H_2O couple [3]. It rests on the assumption that mass transfers do not limit phenomena at issue. Most of the studies on absorption systems and supported by experiments use that assumption [4]. It is also admitted that the pressure in the generator is equal to the pressure in the condenser and the amount of water vapour desorbed (respectively absorbed) in the generator is completely condensed (respectively evaporated) in the condenser. The internal temperature in the generator is assumed to be uniform even if it varies along the heat exchanger due to the variation of the concentration of the solution. Crystal is considered to be in equilibrium with the saturated solution when it appears in the solution storage tank. An equilibrium factor α [5, 6], which is used in equation (**13**), is introduced to take into account the fact that the solution leaving the generator is not in equilibrium conditions because of the short solution residence time in the generator (when $\alpha = 1$, the solution is supposed to be in equilibrium in the generator $x_{2o} = x_{2oeq}$).

The main inputs of the model are the incident solar radiation and the area of the solar collector surface, the ambient temperature and the heating demand, the flows rate of the solution and water, the overall heat transfer UA of the heat exchangers, and so on. Different variables such as components pressures or temperatures, the mass of water in the water tank, the mass of solution and of crystal of LiBr hydrate in the solution store, the circulating pumps consumptions, heat losses … can be predicted.

Solar collectors

A simplified model of flat-plate solar collector with area A_{sc} is used by writing the useful energy Q_{sc} received by the heat transfer fluid in the form:

$$Q_{sc} = I \cdot A_{sc} \cdot \eta_{sc} = m_g \cdot C_{pw} \cdot \left(T_{go} - T_{gi}\right)$$ (1)

The collector efficiency η_{sc} is given by [7]:

$$\eta_{sc} = \eta_o - a_1 \cdot \left(\frac{T_m - T_{ext}}{I}\right) T_m - a_2 \cdot I \cdot \left(\frac{T_m - T_{ext}}{I}\right)^2$$ (2)

with $T_m = \dfrac{T_{go} + T_{gi}}{2}$. (3)

Expression (1) suggests that the solar collector is under steady state conditions and does not consider the thermal inertia of the collector.

Heat exchangers: generator and condenser

The generator and condenser are modelled as heat exchangers based on the logarithmic mean temperature difference approach. The exchanged heat, in the generator for example, is therefore:

$$Q_2 = \left(UA\right)_2 \cdot \frac{T_{gi} - T_{go}}{\ln\left(\dfrac{T_{gi} - T_2}{T_{go} - T_2}\right)} = m_g \cdot C_{pw} \cdot \left(T_{gi} - T_{go}\right)$$ (4)

Heat losses to the ambient are evaluated under the assumption that shells covering the exchangers are isothermal and the ambient temperature T_{ref} is constant during a simulation step. So, for the generator:

$$\left(MCp\right)_2 \cdot \frac{dT_{sh}}{dt} = \left(UA\right)_{2\,surf\,int} \cdot \left(T_2 - T_{sh}\right) - \left(UA\right)_{2\,surfext} \cdot \left(T_{sh} - T_{ref}\right)$$ (5)

is solved to calculate the heat loss that will be used in the components equations (11) to (38).

$$Q_{2loss} = \left(UA\right)_{2\,surfin} \cdot \left(T_2 - T_{sh}\right)$$ (6)

Interconnecting tubes

Heat losses of tubes that connect the system component are also. It is admitted that the specific heat of the fluid in the tube is constant along the tube. For example for the connection tube between the generator and the solution tank:

$$T_{1i} = T_{ref} + \left(T_{2o} - T_{ref}\right) \cdot \exp\left(\frac{-\left(UA\right)_{1\to2}}{m_{1i} \cdot Cp_{sol}}\right)$$ (7)

$$Q_{21loss} = m_{2o} \cdot \left(h_{2o} - h_{1i}\right)$$ (8)

Circulating pumps

The energy transferred to the solution and water by the circulating pumps (W_1 and W_2) is estimated by considering an isentropic efficiency for each pump and that the density of the fluid is almost constant between the considered points. Thus, as illustration, equation (9) gives the work w_1 provided by W_1 to the solution.

$$w_1 = v_{1o} \cdot \frac{\left(P_2 - P_1\right)}{\eta_{isW_1}} \tag{9}$$

3.2. Equations of the global process

Generator

$m_{2i} = m_{1o} = v_{1o} \cdot \rho_{sol}\left(T_1, x_{1liq}\right)$	mass continuity equation	(10)
$m_{2i} = m_{2o} + m_{2v}$	global mass balance	(11)
$m_{2i} \cdot x_{2i} = m_{2o} \cdot x_{2o}$	LiBr mass balance	(12)
$x_{2i} - x_{2o} = \alpha \cdot \left(x_{2i} - x_{2oeq}\right)$		(13)
$m_{2i} \cdot h_{2i} + Q_2 = m_{2o} \cdot h_{2o} + m_{2v} \cdot h_{2v} + Q_{2loss}$	energy balance	(14)
$P_2 = P_{2v} = P_{3v} = P_3$		(15)
$P_2 = P_{sol}\left(T_2, x_{2o}\right)$	state equation	(16)
$T_2 = T_{2o} = T_{2v} = T_{3v}$		(17)
$m_{1i} \cdot h_{1i} + w_1 = m_{2i} \cdot h_{2i} + Q_{1 \to 2loss}$	energy balance on tube 1→2	(18)
$h_{2o} = h_{sol}\left(T_2, x_{2o}\right)$	state equation	(19)

Condenser/evaporator

$m_{3i} = m_{4o} = v_{4o} \cdot \rho_{wliq}\left(T_4\right)$		
$m_{3i} + m_{3v} = m_{3o}$	global mass balance	(20)
$m_{3i} \cdot h_{3i} + m_{3v} \cdot h_{3v} = m_{3o} \cdot h_{3o} + Q_{3loss} + Q_3$	energy balance	(21)
$P_3 = P_w\left(T_3\right)$		(22)
$T_3 = T_{3o}$		(23)
$m_{4i} \cdot h_{4i} + w_4 = m_{3i} \cdot h_{3i} + Q_{4 \to 3loss}$	energy balance on tube 4→3	(24)
$h_{3o} = h_{wliq}\left(T_3\right)$	state equation (saturation)	(25)
$h_{3v} = h_{wv}\left(T_2, P_2\right)$	state equation	(26)

Solution tank

$M_1 = M_1' + \left(m_{1o} - m_{1i}\right) \cdot dt$	global mass balance	(27)
$M_1 \cdot x_1 = M_{1liq} \cdot x_{1liq} + M_{cr} \cdot k = M_{LiBr}$	LiBr mass balance	(28)
$M_{1liq} \cdot h_{1liq} + M_{cr} \cdot h_{cr} = M_{1liq}' \cdot h_{1liq}' + M_{cr}' \cdot h_{cr}' + \left(m_{1i} \cdot h_{1i} + Q_{1loss} - m_{1o} \cdot h_{1o}\right) \cdot dt$ energy balance		(29)
$h_{1o} = h_{1liq} = h_{sol}\left(T_1, x_{1liq}\right)$	state equation	(30)
$P_1 = P_{sol}\left(T_1, x_{1liq}\right)$	state equation	(31)
$m_{1i} \cdot h_{1i} + Q_{2 \to 1loss} = m_{2o} \cdot h_{2o}$	energy balance on tube 2→1	(32)
$h_{cr} = h_{1liq} + \Delta h_{cris}$	$h_{cris} \approx 64.5$ kJ·kg^{-1} [8]	(33)

Water tank

$M_4 = M_4' + \left(m_{4o} - m_{4i}\right) \cdot dt$	global mass balance	(34)

$$M_4 \cdot h_4 = M_4^{'} \cdot h_4^{'} + \left(m_{4i} \cdot h_{4i} + Q_{4loss} - m_{4o} \cdot h_{4o} \right) \cdot dt \qquad \text{energy balance} \qquad (35)$$

$$h_{4i} = h_4 = h_{wliq}\left(T_4 \right) \qquad \text{state equation (saturation)} \qquad (36)$$

$$P_4 = P_w\left(T_4 \right) \qquad \text{state equation (saturation)} \qquad (37)$$

$$m_{4i} \cdot h_{4i} + Q_{3 \to 4loss} = m_{4o} \cdot h_{4o} \qquad \text{energy balance on tube } 3 \to 4 \qquad (38)$$

4. Process dynamic simulation

4.1. Inputs and operating conditions of the system simulation

Three simulations have been performed for a single family house of 120 m² that meets Passive house standards [9] in order to achieve 100% solar fraction. Therefore, the annual heating need that must be met by the storage is about 1800 kWh with a peak heat load of 1.2 kW.

Since the aim of this work is not an accurate modelling of a building, but that of the storage, the building heating needs are estimated based on a simplified method. They are estimated by considering a base temperature T_{base} (the outside temperature above which a building needs no heating) and an overall heat loss coefficient for the building:

$$Q_b = UA_b \cdot \left(T_{base} - T_{ext} \right) \qquad (39)$$

Calculations in static conditions show that a decrease of the heating temperature (heating floor loop) from 35°C to 25°C could double or more the storage density. The improvement of the system efficiency thus requires a discharge temperature as low as possible but sufficient for heating purpose. The mean supply temperature needed for the heating floor loop is thus set to 33°C.

The meteorological data, solar radiations and outdoor temperature, are those of Chambéry, in the alpine region of France. The thermal collector efficiency parameters are those which are suggested for simulation studies within the IEA-SHC Task 32 [10].

Simplified models for the heat sink (condenser) and the low temperature heat source (evaporator) have also been assumed: the temperature of the cooling water at the entrance of the condenser T_{ci} is set to 5°C below the outdoor temperature when the latter is higher than 10°C; otherwise, T_{ci} is set to 5°C. The heat transfer fluid temperature entering the evaporator is constant and equal to 10°C. These two evolutions could be those of a geothermal source.

Because of their potential large volumes, both storage tanks are presumed to be buried or stored in a basement where the ambient temperature T_{tank} is assumed to be constant. As for the condenser and the generator, they are in a non-heated space which temperature T_{ref} is supposed to be constant.

Other simulation parameters are summarized in table 1.

Table 1. Parameters and inputs for the simulations.

η_0	0.8	α	0.95	$UA_{2surfint}$, $UA_{3surfint}$	4 000 W·°C⁻¹
a_1	3.5 W·m⁻²·°C⁻¹	η_{isW1}, η_{isW2}	0.8	$UA_{2surfext}$, $UA_{3surfext}$	0.4 W·°C⁻¹
a_2	0.015 W·m⁻²·°C⁻²	dt	10 s	MC_{p2}, MC_{p3}	9 000 J·°C⁻¹
v_{1o}*	3·10⁻⁶ m³·s⁻¹	$UA_{1 \to 2}$, $UA_{2 \to 1}$	10 W·°C⁻¹	T_{tank}	5°C
v_{4o}	5·10⁻⁶ m³·s⁻¹	$UA_{2 \to 3}$, $UA_{3 \to 2}$	0 W·°C⁻¹	T_{ref}	15°C
v_g, v_c	4·10⁻⁴ m³·s⁻¹	$UA_{3 \to 4}$, $UA_{4 \to 3}$	10 W·°C⁻¹	T_{base}	10°C

*The solution flow rate v_{1o} during absorption is the half of the flow rate during desorption

4.2. Simulations results

The required sizes of the system components and the achieved performances are summarized in table 2. In the first simulation (n°1), the process is run without crystallisation in the solution store. In both following simulations (n°2 and n°3), LiBr hydrates crystals are admitted up to 67m% and 80m% of the solution storage content during the year.

The storage efficiency represents the useful heat provided to the building divided by the useful solar energy supplied to the generator for desorption. It is about 35% in all the cases considered and denotes significant heat losses. Those heat losses occur mainly when the generator outlets (water and solution) cool down in the tanks and the condenser. It can be noticed that the storage density is increased more than four times when crystallisation is accepted. However, increasing the maximum crystallisation ratio above 2 does not significantly increase storage density but could increase difficulties (solution circulation) and decrease a little the storage efficiency since the heat required for desorption increases with the solution concentration. The mass of water that must be desorbed and stored in the charging period to meet the heating need is almost the same, regardless of the presence or absence of crystals in the storage. Indeed, the highest part of the absorption heat is provided by the evaporation heat of water in the evaporator and the process behaves like a thermally driven heat pump.

Table 2. Main results of the process dynamic simulation for a Passive House (1800 kWh/year heating need).

Parameters	Unit	n°1	n°2	n°3
Surface of flat solar collector	m²	14	14.5	14.5
Total mass of anhydrous LiBr salt in the storage	t	43.6	8.1	7.4
Useful volume of the solution of LiBr storage tank	m³	46.9	9.2	8.4
Useful volume of the water storage tank	m³	2.9	2.9	2.9
Maximum mass fraction of LiBr in the store	m%	58.1	66.6	68.2
Maximum crystallisation ratio	-	0	2	4
Mean supply temperature of the heat transfer water to the building	°C	33	33	33
Storage efficiency	%	35	35	35

4. Conclusion

Crystallisation appears to be necessary for the competiveness of the process. Even though the storage density of lithium bromide is quite high (200 kWh/m³ as against 50 kWh/m³ for water between 35°C and 80°C), 100% solar fraction achievement requires large storage volumes. Lithium bromide is expensive so that it is difficult to imagine the process competiveness without further improvements. Economic analysis is required to choose the optimal maximum crystallisation ratio combining the optimal collector surface, storage efficiency, material cost and easy solution circulation. The solution recirculation in the solution tank leads to a lot of heat losses; so its better management would significantly enhance the storage efficiency. The theoretical results derived from this modelling have to be compared with experimental results from a prototype that is presently under construction.

Acknowledgements

Nomenclature

General

A	surface area (m²)	3	condenser or evaporator

A surface area (m²)

a_1 first order collector heat loss coefficient (W·m^{-2}·°C^{-1})

a_2 second order collector heat loss coefficient (W·m^{-2}·°C^{-2})

C_p specific heat (J·kg^{-1}·°C^{-1})

dt simulation step duration (s)

h specific enthalpy (J·kg^{-1})

Δh_{cris} specific enthalpy of solution of lithium bromide dihydrate (J·kg^{-1})

I incident solar radiation (W·m^{-2})

k mass fraction of anhydrous LiBr in the crystal hydrate

m mass flow rate (kg·s^{-1})

M mass (kg)

(MC_p) heat capacity of heat exchanger shell (J·°C^{-1})

M_{LiBr} initial mass of LiBr anhydrous (kg)

P pressure (Pa)

Q heat (w)

t time (s)

T temperature (°C)

T_m mean collector fluid temperature (°C)

T_{tank} ambient temperature around the storage tanks (°C)

U heat transfer coefficient (W·m^{-2}·°C^{-1})

v volume flow (m^3·s^{-1})

w work (w)

x mass fraction of lithium bromide in the solution (m%)

Subscripts/Superscripts

1   solution storage

2   generator

3   condenser or evaporator

4   water storage

1→2   tube connecting 1 to 2

'   value from previous time step

b   building

c   condenser external loop water

cr   crystal

ext   exterior (outside)

g   generator external loop water

i   inlet

is   isentropic

liq   liquid

loss   loss

max   maximum

o   outlet

ref   surrounding

sc   solar collector

sol   solution

surfext   external side of heat exchanger

surfint   internal side of heat exchanger

v   vapour phase

w   water

Greek symbols

α   absorption percentage

η   efficiency

η_0 optical efficiency of the solar collector

ρ   density (kg·m^{-3})

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