Thermochemical district networks

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Abstract

Thermo-chemical networks are a new technology for district networks, which can provide heating, cooling and drying in one heat loss-free multiservice network. The innovation is the use of thermo-chemical fluids as transport medium, e.g. in the form of concentrated salt solutions, rather than water. Due to the hygroscopic characteristics of the salt solutions, a chemical potential is transported and not thermal energy as in conventional networks. The chemical potential is used to generate useful heat or cold from ambient heat at the place and time of demand or to dehumidify air for drying or air conditioning processes. An important advantage of this novel technology is that the technology is heat loss–free, which means the thermochemical potential stored in the fluids degrade neither in the piping infrastructures nor in storages. In comparison to conventional district heating networks, thermo-chemical networks can be realized with less investment (no insulation is required) and over longer distances (no heat losses occur). The aspect of heat loss-free storage is also interesting for applications of seasonal thermal storage. In particular with solar energy, allowing shifting the energy available in summer to the wintertime. Thermo-chemical district networks and the possibility of long-term storages will improve the efficiency and profitability of the use of solar energy in district heating networks. The demonstrators, realised in Canton Zurich, are part of the project "H-DisNet" funded by the European Program Horizon2020 (Agreement No. 695780).

Keywords: thermochemical network, liquid desiccant, syn- disproportion, absorption, desorption, anergy, exergy, chemical potential

1. Introduction

The statement of the first law of thermodynamics initiated a debate which continues till today - energy cannot be created nor destroyed. This statement does not mention the quality and form of energy, which is then part of the second law of thermodynamics. The conversion of energy requires a state of non-equilibrium (potential difference). Another aspect for the energy is also the availability at the right place and time. The energy storage became more important due to the increase demand of renewable energy.

In the last years, the district heating networks became more popular especially in densely populated areas. Heat losses during the transport are generally accepted up to 20%, whereby the losses can be reduced depending on the consumer density (local component) (Jenni, 2013 [1]).

Thermochemical networks can be an alternative to conventional district heat networks. They can also be integrated in conventional district heating network. They transport a chemical potential, e.g. in the form of concentrated salt solutions instead of thermal energy in form of hot/warm water. This chemical potential can be transported over long distances as well as stored for long time without losses (of course energy is required for the transport). Thermochemical networks can also be used to recover excess heat that cannot be economically used with conventional systems. Another advantage of thermochemical networks is the high energy density of the transport medium. Approximately ten times higher than in conventional systems (Gaegauf, 2016 [2]).

2. Fundamentals of heat transformation

To raise a material flow from a lower to a higher temperature, another one has to balance out the reduction of entropy. Heat transformation is given, if the reduction of one potential (temperature) is raising another potential. Such heat transformation processes can be classified into syn- and disproportionation (Hebcker, 2000 [3]). Figure 1 shows examples of synproportion processes, such as the absorption heat pump and the compression heat pump, and of disproportion processes, such as the thermal power plant and the heat transformer.

If mechanical work and electrical energy are interpreted as heat of infinite temperature, the electrical drive of a compression heat pump or the mechanical work of a turbine can be integrated into this approach.
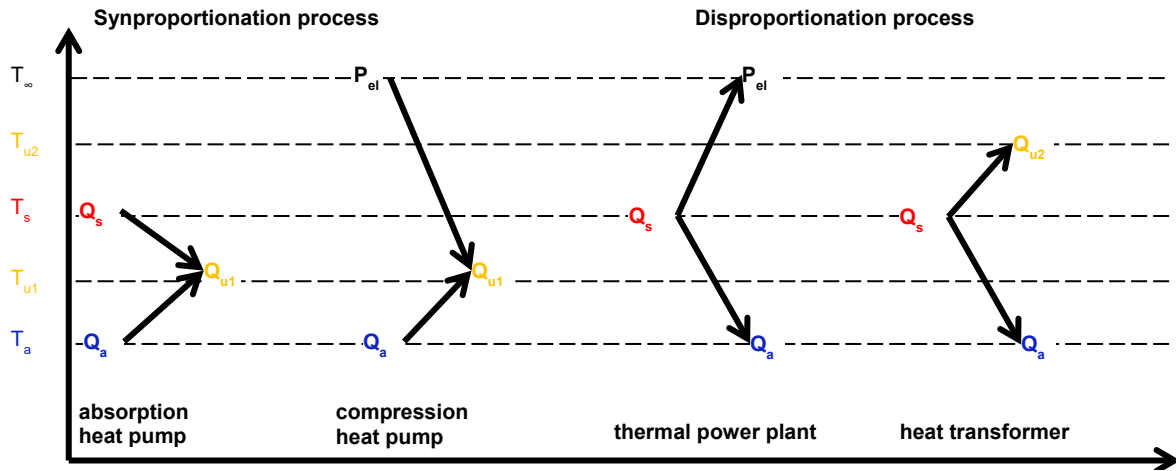

Figure 1: Different energy transformation processes. Parameter for : Tu/Qu users ; Ts/Qs source ; Ta/Qa ambient

Figure 2 shows an absorption heat pump process (synproportion). This process can be divided in to two partial processes (fig. 3): synproportion process (consumer of the chemical potential) and disproportionation process (producer of the chemical potential). The synproportion process combines low-temperature heat and exergy (chemical potential) to produce useable heat at a higher temperature. The disproportion process generates exergy by converting heat from high temperature to low temperature heat. A thermo-chemical network can be considered as an absorption heat pump process (or, as a heat transformer if the pressure levels are reversed). (fig. 4)
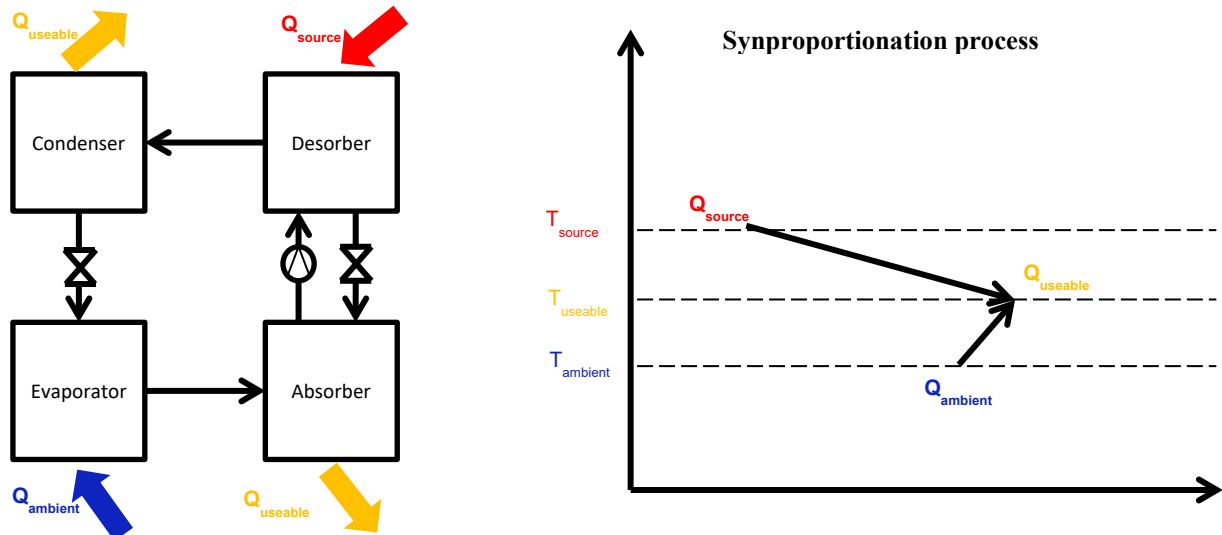

Figure 2: Simplified process of an absorption heat pump

The producers of the chemical potential (source) in the thermochemical network are the sub-system desorber-condenser (transformation of heat into chemical potential) and the generators of useful heat (users) are the sub-system evaporator-absorber (transformation of chemical potential into heat). Many applications can utilise this concept.

3. Applications in thermochemical networks

Generation of chemical potential in an open process:

If excess heat is available at a low temperature level (above approx. 50°C), desorption can be realised as an evaporation process. The condensation heat cannot be used and is transferred to the environment as anergy. Instead of using process excess heat, this process can also be driven by solar thermal energy or excess electrical energy from renewable energy sources (PV, wind).

Generation of chemical potential in a closed process:

In a close system, the salt solution is regenerated by evaporation of a part of its water (pure water vapour is produced, no humid air). Heat is then released with the subsequent condensation of the water vapour. In the desorption process, a temperature above 100°C is required (at atmospheric pressure). In a close system, unlike the open desorption, no thermal energy is required to concentrate the salt solution, since the heat supplied to the desorber is then almost completely recovered in the condenser: the temperature difference between heat utilisation (warm-water circuit temperature) and the available heat is used. An application for a close system could be realized in motor-driven cogeneration unit (CHP), since the exhaust gas normally has a temperature of approx. 500°C and the warm-water circuit usually is operating at a temperature of approx. 90°C.
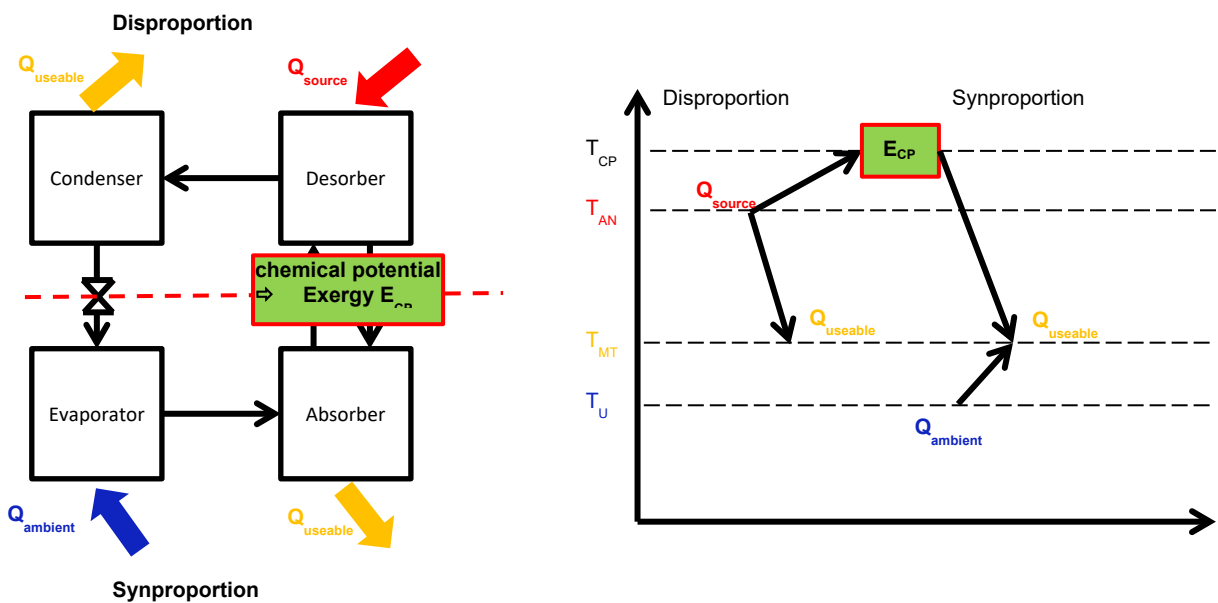

Figure 3: Dis- and synproportion process in a absorption heat pump

Use of chemical potential in open process:

Open sorption processes are a good alternative to support air conditioning systems (e.g. DEC systems: Dessicative and Evaporative Cooling) (Hebecker, 1988; Dai, 2006; Kessling, 1997 [4, 5, 6]). They have a good energy efficiency but require a simultaneous regeneration of the desiccant which can be difficult to realize. This disadvantage can be eliminated by combining the system into a thermo-chemical network. The possibility of accurate air conditioning (temperature and humidity) through an open sorption process is, in addition to building-air-conditioning, particularly interesting for special applications where the air conditions must be strictly adhered. Examples include greenhouses, museums, archives and laboratories. An open absorption process can also be used in industrial drying processes (e.g. low-temperature drying of spices to protect the aromas). The exhaust air leaving the dryer is dehumidified in an absorption scrubber and simultaneously heated by the heat released during absorption. Such a drying process could theoretically be operated energy self-sufficient, i.e. without the supply of additional heat energy.

Open sorption processes are also used to recover excess heat in industrial processes increasing the condensation temperature of combustion gases (Danesi, 2015; Weber, 2008 [7, 8]).

Use of chemical potential in closed process:

The possibility of loss-free storage makes thermo-chemical fluids a promising opportunity for seasonal heat storages in solar-heated buildings. Sodium hydroxide solution is recommended as a suitable storage medium in various publications (Weber, 2008; Hui, 2008; Goetz, 2001; [9, 10, 11]), but cannot be used in open processes: the reaction of sodium hydroxide with the carbon dioxide of the air forms a poorly soluble sodium carbonate, which precipitates in solid form during cooling processes and therefore clog pipes and plant components. The plant components for regeneration (desorber-condenser) as well as those for utilisation of the chemical potential (evaporator-absorber) shall operate at a negative pressure specified by the temperature level (vapour pressure of the water). However, the transport and storage of the fluid can be decoupled and can operate at atmospheric pressure allowing the integration to the network (the decoupling can be realised e.g. using a hydrostatic height difference to the storage tank/pipeline of the network).
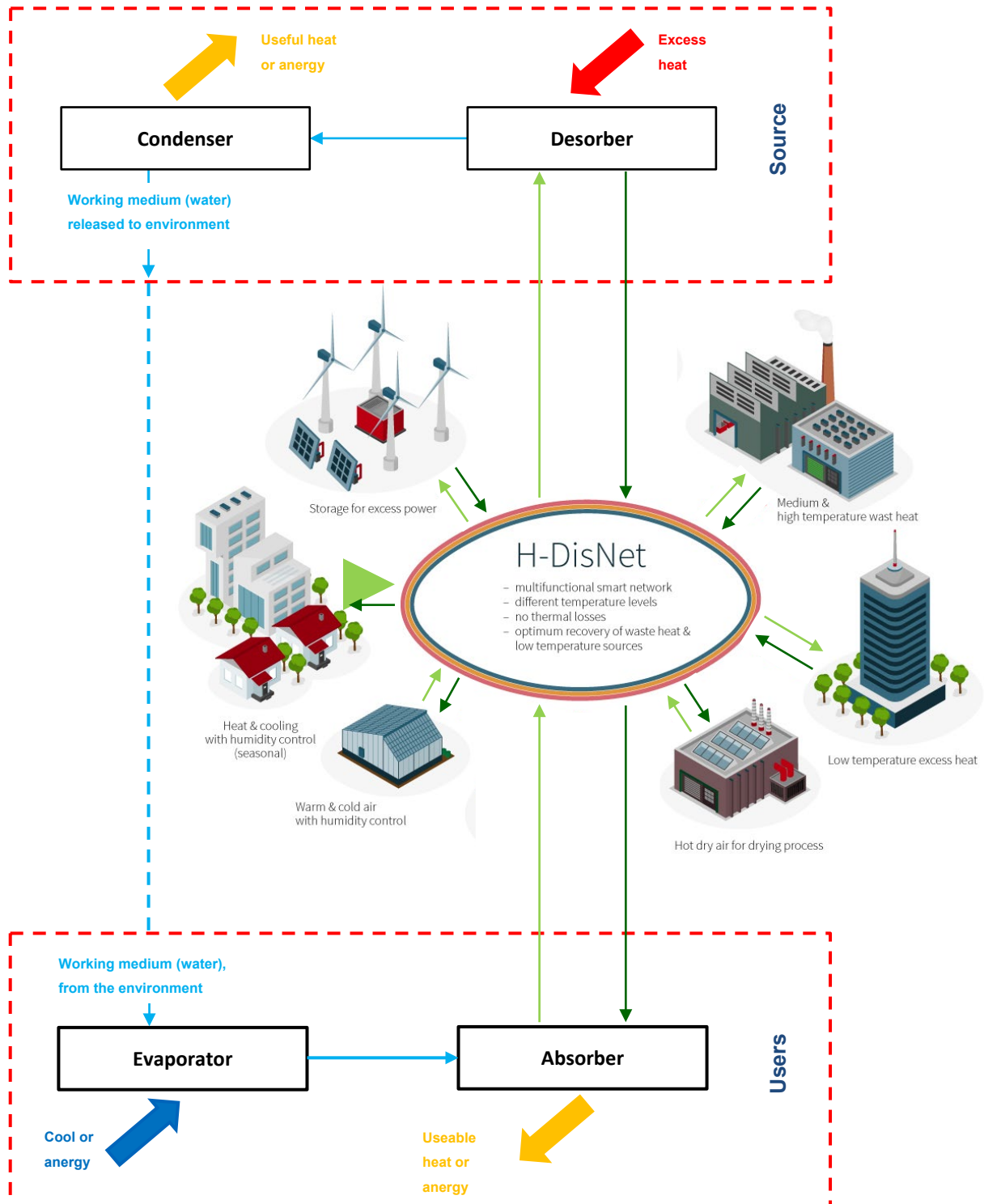

Figure 4: Thermo-chemical network

4. Thermo-chemical fluids

Only water-based fluids are considered in this paper. Different groups of substances such as salts, alkalis, acids, organic compounds and ionic liquids can be used as absorbents (Bittrich, 2001; [12]).

In addition to thermodynamic properties, the following criteria must be considered for the selection of the thermos-chemical fluid:

Availability / Price

Environmental compatibility / Recyclability / Toxicity

Chemical stability

Aspects of secondary importance in stand-alone application such as absorption chillers (price, availability, toxicity) can have a huge impact in thermo-chemical networks which requires a massive volume of these fluids. As a result of these circumstances, the following fluids were investigated as transport fluid in thermo-chemical networks:

Table 1: Selection of different desiccant

Desiccant	Comments
Lithium bromide (LiBr)	common in absorption plants (chillers), but not suitable in thermo-chemical network due to the high price. Used as reference
Lithium chloride (LiCl)	common in dehumidification systems, but not suitable in thermo-chemical network due to the high price. Used as reference
Calcium chloride ($CaCl_2$)	High efficiency
Magnesium chloride ($MgCl_2$)	High efficiency
Calcium nitrate $Ca(NO_3)_2$	Not corrosive. Low efficiency at low temperatures and high efficiency at high temperatures.
Sodium hydroxide (NaOH)	Very high efficiency. Not suitable in open processes.

Coefficients have been defined to describe the properties of interest for thermo-chemical networks in the entire range of solubility as function of mass fraction of the absorbent (ξ) and the temperature (T). The following substance properties were considered:

Table 2: Desiccant properties

Solubility	$T^{SL}(\xi)$	Density	$\rho(\xi,T)$
Phase equilibrium	$p^{LV}(\xi,T) / T^{LV}(\xi,p)$	**Dynamic viscosity**	$\eta(\xi,T)$
Specific enthalpy	$h(\xi,T)$	**Thermal conductivity**	$\lambda(\xi,T)$
		Surface tension	$\delta(\xi,T)$

An open-access database has been created for the aqueous solutions of the salts in table 2 and is available on the website[1] of the Institute of Energy Systems and Fluid Dynamics (IEFE) of the Zurich University of Applied Sciences (ZHAW). The database provides material data functions for Excel™ and Matlab™.

The diagram of the phase equilibrium (Log(p)-1/T) (fig. 5) reports the crystallisation line as function of temperature and vapour pressure. Furthermore, the humidity of the air is plotted. The diagram is a valid instrument for the selection of fluid for specific applications.

For example, in an open sorption process with the calcium nitrate absorbent it is not possible to achieve a relative humidity less than 50% at a temperature of 20°C, while it would be possible with the other thermo-chemical fluids. In general, the lowest temperature in the entire network limits the concentration. With the information about the aimed air quality and the tempeture of the network, the maximum and minium concentration can be determined. The

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[1] (https://www.zhaw.ch/de/engineering/institute-zentren/iefe/energiespeicher-und-netze/thermische-speicher/)

transport quantity is defined according to the network and process boundaries conditions.

The density and viscosity determinate the energy required for the transport. A high concentration difference between supply and return line means a high energy density and therefore a small fluid quantity has to be transported. Considering the viscosity, which increases as a function of the concentration, a high concentration can be detrimental, because the energy required for the transport is increasing also.
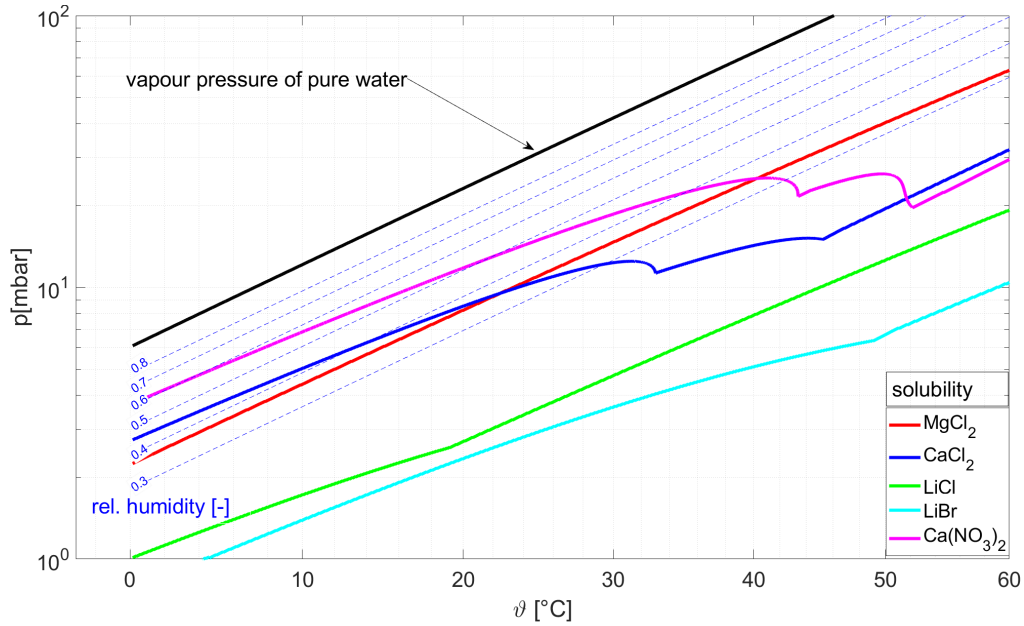

Figure 5: Different desiccant and their solubility boundaries within the log(p)-1/T- diagram

The efficiency of the system ("energy storage density" of the transport medium) is given by the caloric material properties, while the parameters for the design of the ab-/desorber are the thermal conductivity, surface tension and diffusion coefficients.

5. Characteristic Numbers

The usable heat (ΔH) of the network is defined through the mass balance between the concentrated and diluted solution, since the difference is proportionally to the absorbed water (Δm_w). In relation to the mass of the concentrated solution ($m_{sol,1}$) a **mass specific "energy density" (k_E)** is given.

$$\mathbf{k_E} = \frac{\Delta H}{m_{sol,1}} = \frac{\Delta m_w \, \Delta h_v}{m_{sol,1}} = \frac{\xi_2 - \xi_1}{\xi_2} \, \Delta h_v \qquad (1)$$

The formula (1) is valid for an isothermal process, mixing effects were neglected.

The heat of vaporization (Δh_v) can be assumed as constant within the temperature range of application. Therefore, the dimensionless number **(k_e)** can be defined:

$$\mathbf{k_e} = \frac{k_E}{\Delta h_v} = 1 - \frac{\xi_1}{\xi_2} \qquad (2)$$

The kinematic viscosity ν (dynamic viscosity divided by density) is a function of temperature and concentration and can be used as a reference for energy required for the transport (**k_T**).

$$\mathbf{k_T} = \nu = \frac{\eta}{\rho} \qquad (3)$$

6. Demonstrator

The absorption process will be tested as air conditioning system in the Horizon2020 project H-DisNet. A demonstrator is installed in Switzerland in a greenhouse (approx. 600 m^2), owned by Meyer Orchideen AG. Here a new air distribution system will be also tested. The conditioned air is injected direct under the plant tables. The advantage of this new air distribution system is that only the air around the plants is heated or cooled and not the air of the entire greenhouse. A considerable energy saving is expected, which will be validated during the project. Orchids are cultivated in different growth phases, which require different climatic conditions (leaf growth approx. 30°C and flower formation approx. 20°C at 65% humidity each). The energy balance over one year shows a positive energy demand (heat). However, on warm days with high solar radiation, heat must be dissipated. Based on measurements in the greenhouse, a heating and cooling load of 75 kW was determined.

Figure 6: Application in the greenhouse

Air-conditioning

The absorbers are counter-flow with random packings. The air is simultaneously tempered (cooled or heated) and humidified or dehumidified by a hygroscopic salt solution. The temperature ϑ_Z and the humidity φ_Z of the conditioned air (point 2 in figure 7 and figure 8) can be set exactly through the temperature ϑ_L and the salt concentration ξ_L of the solution, because the thermodynamic equilibrium is nearly reached at the top of the absorber.
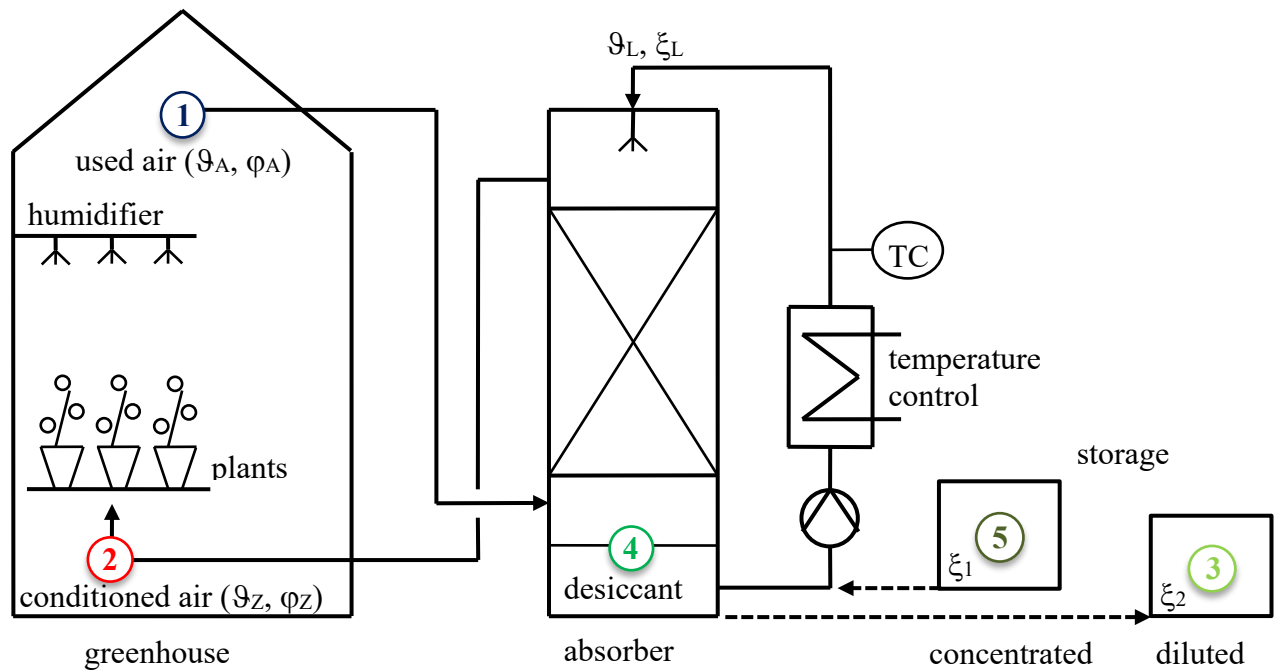

Figure 7: climate-concept within the greenhouse

An exact climate condition can be realised with minimum technical effort. The absorption process for cooling in the greenhouse is illustrated in the log(p)-1/T diagram with calcium chloride as working fluid (figure 8). The measurements have been carried on in laboratory for an absorption scrubber. They show a maximum deviation of

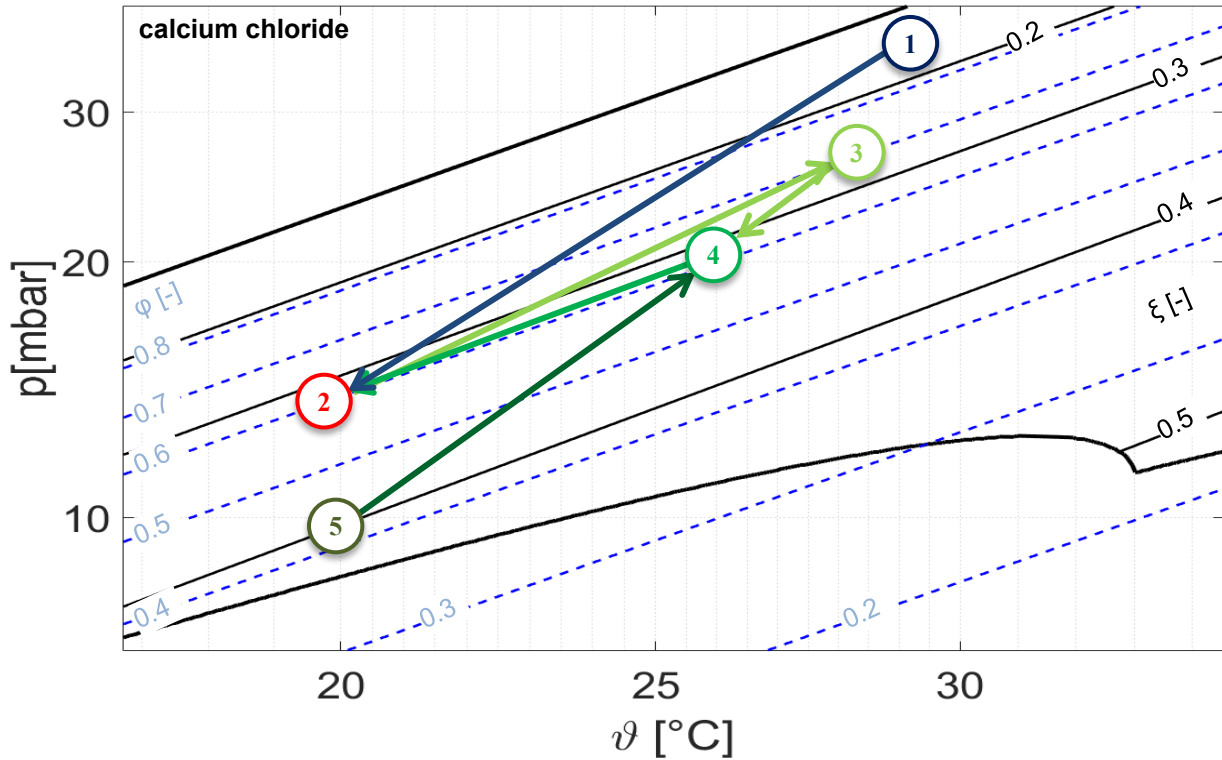the conditioned air (point 2) from the desired target value (phase equilibrium) of ±1K and ±5% relative humidity.

Figure 8: climate process in the greenhouse (cool load)

The tolerance range of the optimum growth conditions of the plants are ±2.5 K and ±15% relative humidity.

The analysis shows that $CaCl_2$ and $MgCl_2$ have different characteristic numbers, even though they share the same difference in concentration. This is a result to the different position (ξ_2) of the diluted solution in the solution field. For a high benefit/effort ratio, the position of the diluted solution is much more important than the difference in concentration. Since these properties are in no way linear, each process must be considered and evaluated separately.

Table3: Assessment of the working materials using the greenhouse as an example of application

Salt solution	ξ_1 [-]	ξ_2 [-]	k_E [kJ/kg]	k_e [-]	k_T [mm²/s]
Lithium bromide (LiBr)	0.59	0.30	2450	1.00	2.2
Lithium chloride (LiCl)	0.43	0.19	3062	1.25	5.6
Calcium chloride (CaCl$_2$)	0.40	0.28	1470	0.42	6.7
Magnesium chloride (MgCl$_2$)	0.35	0.23	1283	0.52	9.1
Calcium nitrate Ca(NO$_3$)$_2$	0.53	0.45	544	0.18	7.1

7. Conclusions

The technology is already under test in the greenhouse which is the Swiss demonstrator of the H-DisNet project. The plan is to extend the demonstrator in future projects with a fully automatic control system and with the integration in a small district network.

The absorption technology is also very promising for other application as for example in drying process in food industry and for the climatization of museums and historic archives, where self-sufficient systems can be designed using renewable energy or excess heat as driving source for the regeneration.

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Appendix: Unites and Symbols

Table 1: Symbols

Quantity	Symbol	Unit
Specific enthalpy	h	$J\ kg^{-1}$
Thermal conductivity	λ	$W\ m^{-1}\ K^{-1}$
Mass concentration	ξ	-
Density	ρ	$kg\ m^{-3}$
Surface tension	σ	mNm^{-1}
Heat flux	Q	W
Thermal diffusivity	α	$m^2\ s^{-1}$
Dynamic Viscosity	η	Pa s
Vapour pressure	p^{LV}	mbar
Mass	M	Kg
Kinematic viscosity	ν	m^2s^{-1}