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## RESEARCH ABSTRACT

The phenomenon of water evaporation and condensation is a fundamental pillar on which natural and anthropic processes are built. The energy density associated to the phase change from liquid to vapor, and vice versa, is one of the highest among many different substances and, for sure, the highest occurring at low temperatures. This characteristic confers to the water liquid/vapor phase transition a role of main character in the field of thermoregulation processes. For example, the human body temperature regulation works on the phenomenon of evapotranspiration of water through the skin. A similar approach is present in most of the mammals and animals. The same role is played at planet level. Evaporation from free water surface, and condensation in the upper layers of the troposphere, are fundamental phenomena influencing the temperature of the planet.

Despite its positive relevance, the presence or absence of water vapor has a dichotomous nature. Too much water vapor in the air is a problem, especially for the indoor environment, negatively affecting thermal comfort of people. At the same time, the presence of water vapor in the air it has to be considered as a resource, especially for those regions affected by drought. The response to the problem of thermal comfort is an intensive power solution called air conditioning. The forecasted increase of energy demand for cooling in the next future defined the new term "cold crunch", to identify a dangerous scenario in which 2/3 of the world's households could have an air conditioner. The consequences will be a further intensive use of fossil fuels to satisfy this incremented energy demand for thermal comfort. On the contrary, the prospective of using atmospheric water vapor is a fascinating solution, especially for that country lacking any access to conventional fresh water sources. Machines converting water vapor into liquid fresh water are typically called atmospheric water harvesting generators. Again, the biggest share of technological solutions is occupied by very power intensive systems.

In both cases, the most applied solution is to use vapor compressing units to cool down the air up to the dew point, obtaining then the condensation of water vapor and the separation from treated air streams. Main energy consumptions are generated from the vapor compressor, resulting in an intensive use of electric power.

The alternative solution explored within this research his based on the iteration between water vapor and hygroscopic materials. The use of sorbents translates the problem of water vapor treatment, from an original consumption of electrical energy to the need of heat.

The alternative approach here investigated considers the use of hygroscopic materials through the phenomenon of physic sorption. The thermal power, required for the regeneration of the material to activate cycle of sorption/regeneration, if provided at temperature below 90°C, enables the use of cheap technology and sustainable sources such as solar energy and waste heat. The alternative solutions here explored aim to shift the request of electrical power for the separation of water vapor from air to a thermal power need, with potential benefits in terms of carbon footprint and for the electric network. However, the competition with conventional

technologies is not only a matter of energy saving, problems related to cost of materials and components manufacturing, together with maintenance issues, are usually the bottle neck for that kind of systems.

Theoretical studies, numerical modelling and experimental activities carried out in this research are strongly grounded in the set of sustainable development actions for the sectors of cooling and clean water solutions, enclosed in the set of action called Sustainable Development Goals (SDG 6 and 7).

Chapter 2 focuses on the fundamental characteristics of physical adsorption. These are the main pillars of the phenomena and applications investigated in this research project. Functional hydrophilic groups such as hydroxyl, silanols and carbonyl are the basic bricks that builds the water uptakes curves of materials such as Silica gel and Zeolites. The knowledge of intrinsic properties together with equilibrium thermodynamic behaviour are fundamental for the correct exploitation of these materials in air dehumidification and water harvesting sectors. A particular effort was carried out to investigate water uptakes of a silica gel provided by the Oker-Chemie producer, and a very performing zeolite SAPO-34, provided by the ITAE-CNR of Messina. The equilibrium curves obtained from the fitting of the silica gel equilibrium tests is useful for the numerical model realized in the next chapters.

Peculiarity of adsorption materials is the possibility to reversibly switch between adsorption and desorption within the dehydration operative zone, without affecting its properties. The limit is defined by the critical temperature  $T_B$  that, most of the case, doesn't exceed 200°C. To invert the mass transfer during desorption an external energy input is required, supporting the break of the attractive interaction between the adsorbed molecules with the sorbent surface traps (hydroxyl; silanol; silicate, etc...) first, and second to assist the diffusive transportation of water molecules through the internal porosity of the material up to the external bulk side. The way the adsorption/desorption cycles are operated gives typically the name of the category. Thermal swing adsorption use the heat as energy source, and regenerate the sorbent rising the temperature. Pressure swing adsorption uses the gradient pressure of gas species as unique driving force for the process, and regeneration is carried out reducing the total pressure within the sorbent bed. In addition to these two methods, sorbent regeneration may also be assisted by ultrasounds. This technique is mostly experienced at research level, with the advantage to increase the diffusion transport of the sorbate through the pores of the sorbent. Among different applications in the chemistry sectors for gas separation and chemical removal, or in the petroleum sector as a more efficient alternative to standard distillation, air conditioning sector had different example of experimental and industrial/commercial applications. In this case the adsorption/desorption swing belongs to the thermally driven category. The rationale is quite simple: the application of adsorption phenomena in air conditioning and refrigeration rises as potential competitor to electrically driven vapor compression units. The use of pressure swing and ultrasounds require, necessarily, mechanical energy generated from an electrical conversion, failing then the original scope to be an alternative solution. In the following chapter the experimental testing of improved solutions shows the advantages of the application of *conjugated heat and mass transfer* for air dehumidification

in the indoor environment. Three different studies published by the author report performances, advantages and drawbacks of the application of sorption techniques to manage the latent part of a typical air treatment carried out for ventilation of buildings. Most of the content on this subject are reported on Chapter 3. The experiments presented in this paper explored the feasibility of operating a fixed sorption bed for air dehumidification and cooling. Tested sorption beds are based on air/water finned coil heat exchanger, with two sorbent configurations: coated with a surface thin layer of Zeolite SAPO-34; a packed bed filled with silica beads of 3 mm. A flow of hot/cold water in the coil activates the two phases of non-adiabatic adsorption and regeneration. Cold water at 18°C is used to refrigerate the adsorption process to combine a conjugated dehumidification and cooling, providing a direct process that doesn't require to reach dew points temperatures. This enables the use of chilled water at higher temperature than in standard air conditioning systems, increasing the efficiency of cold sources. Regeneration is driven at relative low temperature and compatible with solar thermal systems at low temperature. Different configurations offer different properties: a massive sorbent configuration gives higher latent cooling power, but the increase of surface area for the mass transfer increases the power consumptions needed to overcome air pressure drop through the ADS-HX. Conversely, a coated coil configuration is more responsive, but reaches saturation conditions faster, requiring lower switching times between the regeneration and the adsorption. In both cases, the power consumptions were substantially low if compared with the cooling power exchanged with the process air stream and as a result the demonstrated Coefficient of Performances (electric) has reached numbers as higher than 20.

The interesting outcome of regeneration tests reported in Chapter 3, is the possibility to generate very high and consistent peaks of humidity, overcoming values of 60 g kg<sup>-1</sup>, and dew points much higher than 40°C. The exploitation of this phenomenon led to the second investigated application in the Chapter 4: the Atmospheric Water Harvesting. The fundamental principle behind this application is that if the dew point of the hot and humid stream resulted from the regeneration is sufficiently higher than ambient temperature, considerable amount of water can be tapped out of the air without the use of any refrigeration system. This approach reduces drastically energy demand and can be a potential solution for regions with drought problems and in which the problem of access to freshwater resources is a limiting factor for the economic and social development.

This study demonstrates the possibility of the effective use of the most spread renewable sources for water production: the water vapor atmosphere as primary source of water and the sun as primary source of energy. A water harvesting prototype built and tested in the Lab demonstrated how also the inexpensive and less performing silica gel can be used if combined with an efficient cycle. Lab environmental conditions reproduced hot and arid climates (dew point below 10°C and ambient temperature above 30°C), demonstrating that water can be extracted from silica gel at a regeneration temperature of 57°C and condensed at ambient temperature with high thermal efficiencies and using solar grade thermal energy. The adopted solution is compared also with different studies at prototype level, aiming to solve the problem mostly with improvement on the material side,

showing as an effective cycle led to comparable and even improved performances, in the same operational range. Experimental results demonstrated that the performance of the device reduces as the water uptake reduces and the severity of the climatic environment. In particular, the latter has a considerable effect on the first four hours of operation. This analysis has been carried out with help of some performance indicators, investigating on water production capacity and energy performances. Further on, a 1d numerical model of the packed bed ADS-HX used in this application has been developed based on different solution adopted in literature and checked with experimental data to demonstrate its accuracy. The thermal energy required is comparable with the typical output of a solar thermal collector: a daily production of up to 2 L/day per square meter of the solar field is achievable with regeneration temperatures below 60°C, ambient temperature up to 35°C, and a consumption of thermal energy between 1-3 kWh per liter of harvested water. Global water vapor availability varies during the year, reaching higher values during the period of July-September, and a total volume higher than 12000 km<sup>3</sup>. Most of the water is concentrated within the ICZ, but a discrete availability can be found in zones that recently have experiencing a water stress situation with occasional drought events: in north America, south Europe, the Asiatic and the MENA region. The definition of a good performing cycle, as what studied in this research, enable the use of poor performing materials such as silica gel, with water uptake as much as lower of 0.1 kg<sub>w</sub> kg<sub>SiO<sub>2</sub></sub><sup>-1</sup>, and compatible with most of the conditions of water stressed regions. The realized prototype produced between 3.3 and 1.5 L of water, with low initial water content of silica (<0.1 kg<sub>w</sub> kg<sup>-1</sup>SiO<sub>2</sub> typical of dry environments), regeneration temperature of 57°C, over an operational time of ten hours. Compared to existent prototype in literature, this configuration is one of the most efficient at the liter-scale dimension. Despite these evidences, it is clear that silica gel, given its intrinsic properties, is not suitable for all the climates. In very dry environments, with dew points lower than 0°C, silica gel cannot exhibit any sufficient Δw to be applied in a cycle to produce water. At the same time, very dry climates are not necessary connected to a water stress condition. Further development will be carried out to apply this cycle with more performing material, without increasing the regeneration temperature. The theoretical model, based on the LDF theory, is in good agreement with experimental, in both adsorption and regeneration. The estimated average errors on air temperature, air moisture and silica water content are below 10%. Depending on weather condition (temperature and humidity), regeneration time with a minimum thermal efficiency of 50% should not overcome 3-5 hours of functioning with initial water uptake between 0.1-0.2 kg<sub>w</sub> kg<sub>SiO<sub>2</sub></sub><sup>-1</sup>. The developed model is a suitable tool for the design optimization of an engineered system according to the climatic condition of a location. Further on, with a tuned calibration to overcome the errors generated with the LDF, thanks to the very low computational costs (10 hours of real process simulated in less than 1 minute) this model will be implemented on a new prototype version(Figure 4.28). This has been implemented to have an all in one configuration, with all the components below two solar thermal panels. This model will be used as management tool to establish control logic for the switch between to ADS-HX, according to the variation of climatic conditions.

Main issues related to the application is its low water content in very dry environment. This drove the research interest on new solutions. In Chapter 5 physical and chemical properties of various types of polymeric systems, possessing hydrophilic characteristics, have been investigated with the purpose of developing alternative configurations of a heat and mass exchanger to capture moisture from ambient air and convert it into fresh water. In the following sections, the different types of organic materials studied will be described, analyzing in detail the adsorption properties of the materials under well-defined atmospheric conditions, defined by the couple of T and RH. Last, it will be described prototypes of ADS-HX that can be used to produce fresh water by exploiting the performance of various organics materials. Two were the field of analysis: liquid polymers, and bio-hydrogels. Most of the research was carried out in the framework of the PrinceTo project attaining promising results from the application of liquid polymers and biological hydrogels in the water harvesting sector. This step of the research, driven by the need for more performing materials in condition of drought, aims to overcome the low capacity resulted from the WAT-AIR Lab, identified as the main limiting factor for the increase of the water density of the SAWG prototypes. Among the different analyzed liquid polymers, the copolymer PDMS-b-PEO showed very interesting performances, especially for its very rapid dynamics on absorbing and releasing water vapor. A small prototype has been tested to verify the possibility of regenerating, with dynamic conditions, at temperature between 55-65°C. Results are very promising and push further research interests on that direction. Improvement of performances is also achievable on the static configuration, with using smarter and biocompatible material giving the possibility of realizing ADS-HX configurations with hybrid geometry respect to classical the coating or the packed bed solutions as in the chapter 3. The use of a composite hydrogel, based on calcium bentonite clay and alginate biopolymer, give the possibility to print configurations combining moulding techniques and ionotropic gelation.

The composite hydrogel resulted in very high performances in terms of water uptakes. Figure 4 shows the water absorption capacity of the polymer at different temperatures and pressures of the water vapor in equilibrium. During the adsorption phase (operated at temperature between 20-35°C and pressure of water vapor between 0.8-1 kPa, typical of a dry environment) the water uptake can reach values as much as 80% of the dry basis (the water uptake of silica gel, the most common hygroscopic material, at the same operative condition is 10-15%). The regeneration can be carried out at temperature as low as 60°C, that can reduce the water content up to 10%. The total amount of water released (mass variation of 70%). This, combined with a good density of the polymer (650 kg m<sup>-3</sup>), increases the total specific density of a machine based on this component, extracting up to 480 liters of water per cubic meter of composite.