Recent progress on hygroscopic materials for indoor moisture buffering

Xu Zhang\textsuperscript{1,2}, Menghao Qin\textsuperscript{1} and Kan Zu\textsuperscript{1}

\textsuperscript{1} Department of Civil Engineering, Technical University of Denmark, Lyngby, Denmark
\textsuperscript{2} School of Gemology and Materials Technology, Hebei GEO University, Shijiazhuang, Hebei, China
Corresponding email: menqin@byg.dtu.dk

Abstract. Once in contact with the indoor air, hygroscopic materials can moderate the indoor humidity fluctuation by adsorbing or releasing water vapour, and then improve the moisture regulation and thermal management of buildings. It is desirable to explore the characterized properties of these materials about moisture buffering behaviour. In this regard, we review various hygroscopic materials used for the built environment control. The hygrothermal properties of hygroscopic materials often can be characterized by some parameters, such as water vapour adsorption/desorption capacity, water vapour adsorption/desorption rate, water vapour diffusion coefficient, and so on. To provide an insight on the existing research on humidity control materials, different research studies and the recent progress on humidity control materials have been summarized. The materials include traditional and conventional building materials, some natural materials, and novel humidity control materials. Besides, the relevant parameters are considered as well as the improvement suggestions to enhance the application of humidity control materials in building environments. Finally, new multifunctional materials and intelligent moisture control materials together with the corresponding systems are collated to summarize the latest research trends. The overview of the application of hygroscopic materials can provide current and future researchers guidelines for the science-oriented design of moisture control systems for new energy-efficient buildings.

1. Introduction

The indoor environmental quality has been widely concerned in the recent 30 years. The indoor relative humidity is an important factor to determine indoor climate conditions, which is closely related to people’s health, occupants’ thermal comfort, and building energy consumption [1,2]. To maintain an indoor comfortable environment, the American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) recommends that indoor relative humidity should be maintained between 40% and 65%, which is the desired comfort relative humidity range for human beings [3]. The main methods to the humidity regulation highly rely on air conditioning technology, but the air conditioning system is not a kind of ecological control method to control indoor humidity. The traditional air conditioning systems require spending a large amount of energy on dehumidification, especially in high-performance buildings. Some materials can absorb or release moisture to positively mitigate the humidity fluctuation in the built environment. The utilization of humidity control materials to reasonably control indoor humidity with low energy consumption is a topic of research in hygrothermal conditions for buildings.

Humidity control materials (hygroscopic materials) can automatically regulate the relative humidity with the change of temperature and humidity of the air in the regulated space with their moisture...
absorption and desorption capacity. Some traditional building materials, natural materials, high-performance hygroscopic materials, and composite humidity control materials are often used in modern buildings. Many traditional and conventional building materials, such as concrete, drywall, brick, and plywood, have moisture buffering capacity for indoor humidity control [4, 5]. Many natural materials such as natural minerals and plant fibers have been studied to achieve the humidity control purpose [6,7]. They can adsorb water out of the air through the pores and functional groups on the surface to achieve humidity regulation, such as diatomite, sepiolite, vegetal fibers, stem fibers, and so on. Synthetic desiccants, such as silicates, aluminophosphates, zeolites, and inorganic salt, tend to have strong moisture absorption capacity and are widely used in civil engineering [8, 9]. To achieve the purpose of indoor comfort and health, it is often necessary to use composite humidity control materials or a multi-material assembly system to control the temperature, humidity, and indoor air pollutants of the building environment.

With people's attention to the indoor living environment, more materials and new technologies are studied, which may be applied to the building environment. But there are still many challenges in the application of humidity control materials in buildings, i.e. how to use hygroscopic materials with other functional materials to realize the multi-function adjustment and the energy saving of the built environment. This paper summarizes the existing research on humidity control materials, different research studies, and the recent progress on humidity control materials. First, several kinds of humidity control materials and their characteristics will be introduced systematically. Secondly, many humidity control materials using in the corresponding systems are collected to summarize the latest research trends. The overview of the application of hygroscopic materials can provide current and future researchers’ guidelines for new buildings.

2. Humidity control mechanism and performance parameters of hygroscopic materials

The indoor humidity is mainly affected by the temperature and humidity of the surrounding environment. Hygroscopic materials can absorb/release water vapor from/to the space according to the variations of ambient temperature and humidity, and then affect the relative humidity of indoor environment [10]. Generally, there are two main principles for humidity control materials to regulate humidity. First, the properties of some solid porous humidity control materials are mainly decided by the pore structure, the diffusion of water vapor in the pores, and the material surface. The water vapor in the air interacts with the pore surface of the material so that the vapor pressure in the micro space structure is higher than that in the indoor environment, and the water vapor gathers or condenses into liquid water in the pores. Secondly, such as some inorganic salts can absorb and release water vapor from space by chemical reaction. The humidity control mechanism of hygroscopic materials is shown in Figure 1. According to the humidity control mechanism of humidity control materials, a series of parameters have been introduced to characterize the multiple humidity control performance. Generally, the amount of moisture adsorption and the rate of moisture adsorption are important evaluation parameters of hygroscopic materials.

![Figure 1. The humidity control mechanism of hygroscopic materials: (a) working principle of hygroscopic materials and (b) moisture adsorption of hygroscopic materials.](image-url)
3. **Hygroscopic materials**

3.1. **Traditional building materials**

With the development of science and technology, some traditional materials are still widely used in construction, such as various types of brick, wood, gypsum, and concrete. These materials also have a certain adsorption and storage capacity for the water vapour in a space and can regulate the indoor humidity properly. Some researchers have studied the moisture buffering capacity of wood, brick, gypsum, and concrete for the built environment, and the specific parameters are listed in Table 1. Though these traditional building materials have a certain buffering effect on the humidity in the space, their moisture adsorption capacity and buffering value is significantly lower than some novel humidity control materials and can be combined with other materials or special processes to achieve its effective humidity control function [11]. Therefore, the development of functional humidity control materials based on traditional building materials is a research hotspot in recent years.

| Materials                  | Test conditions                                      | Moisture adsorption capacity (g/g×100%) | References |
|---------------------------|-----------------------------------------------------|----------------------------------------|------------|
| Concrete                  | Temperature 4-30 °C, Relative humidity range 30-90%, Air speed 0.1-0.3 m/s | 0.95% | [4] |
| Brick                     | Temperature 4-30 °C, Relative humidity range 30-90%, Air speed 0.1-0.3 m/s | 0.24% | [4] |
| Unfiered brick            | Relative humidity range 40-60%, Air speed 0.2-1.2m/s | 0.98% | [12] |
| Gypsum board              | Relative humidity range 45-60%                       | 0.5% | [13] |
| Pine wood                 | Relative humidity range 40-60% Air speed 0.2-1.2m/s  | 1.6% | [12] |
| Beechwood                 | Relative humidity range 40-60%, Air speed 0.2-1.2m/s | 1.5% | [12] |
| carbon-gypsum-cement compound | Average temperature23 °C, Relative Humidity range 30-95% | 6.9% | [9] |

3.2. **Natural hygroscopic materials**

In the natural environment, many natural materials can adsorb moisture in the air and regulate the surrounding environment. Natural porous minerals and plant fibers can buffer moisture in the air and can be used as humidity control materials. The natural porous minerals are usually a series of silicate solid materials with layered or micropore structures. The minerals take advantage of their hydrophilic and pore structure to adsorb and condense water molecules in a certain space, such as sepiolite, montmorillonite, zeolite, diatomite, bentonite, and so on. The diatomite, a naturally occurring porous mineral, can adsorb water content to about 10% in 80% RH [14]. Diatomite pore structure and surface further affect the humidity control performance of diatomite and diatomites from different areas show different properties in the process of humidity control. Therefore, diatomite usually requires simple chemical treatments to further improve its moisture absorption performance. Most natural porous minerals are used as a filling material with other building materials to realize the humidity control function.
function of building materials. The minerals are mixed as a filler with cement, gypsum, or wood to form humidity control materials. Some researchers have shown that the humidity is lower by 20% to 30% using the zeolite composite humidity control materials in the room [15]. Plant fiber is generally considered as a kind of environmentally friendly biobased material with wide sources. Plant fibers are mainly composed of sugar-based polymers and have a multi-scale structure [16, 17]. Due to the chemical composition and microstructure of the plant fiber, the strong hydrophilic behaviour of such reinforcing fibers leads to a high level of moisture absorption in wet environments. Some researchers who have studied the water absorption in cellulose showed that the amorphous phase and the highly polar carboxyl functions in plant fibers can create hydrogen bonds with the air-water [18, 19]. The moisture absorption characteristics of natural minerals and plant fibers are shown in Table 2.

### Table 2. Moisture adsorption characteristics of natural minerals and plant fibers.

| Materials        | Test conditions                                      | Moisture adsorption capacity (g/g×100%) | References |
|------------------|------------------------------------------------------|----------------------------------------|------------|
| Diatomite        | Temperature 20-30 ℃, Relative humidity range 11-90%, Air speed 0.1-0.3 m/s | 1-3% | [20] |
| Nature zeolite   | Temperature 20℃, Relative humidity 0-80%             | 3.9% | [21] |
| Nature zeolite after modifying | Temperature 20℃, Relative humidity 0-80%             | 6.4% | [21] |
| Sepiolite        | Temperature 20℃, Relative humidity range 30-90%     | 10% | [22] |
| Heat-treated sepiolite | Temperature 23-40℃, Relative humidity range 30-90%, surface area 145 m²/g | 15% | [22] |
| Modified Bentonite | Relative humidity range 33-75%                     | 10% | [23] |
| Fiber of sisal   | Temperature37℃, Relative humidity range 0-98%      | 15.4% | [24] |
| Fiber of hemp    | Temperatperse37℃, Relative humidity range 0-98%    | 14.4% | [24] |
| Fiber of nut     | Temperature37℃, Relative humidity range 0-98%      | 14.5% | [24] |

3.3. Some synthetic and novel humidity control materials

Although some natural materials can regulate the humidity in the environment, the amount of moisture absorption is limited. Some synthetic materials have good adsorption capacity and adsorption rate and can be used as hygroscopic materials for built environment. Silica gel is a kind of amorphous silica with a porous structure, which is considered an effective material for humidity control. FUMIHIKO OHASHI made some mesostructured silica products, and these materials possess a sharp increase in adsorption of water vapour when the relative water vapour pressure is located at 40–60% [25]. Wang demonstrated a full-solid-state humidity pump using the silica gel materials, which showed a humidity transfer rate of 28.38g/h for small-space humidity control application [26]. In addition, some inorganic salts can also be used as hygroscopic materials, such as LiCl•6H₂O, CaCl₂•6H₂O, NH₄Cl, NaNO₃, Pb(NO₃)₂ and so on[27]. Because different concentrations of the salt solution have different saturated vapour pressure, the humidity of the surrounding space can be controlled by changing the concentration of the salt solution. Silica gel and hygroscopic salt can usually be assembled as composite humidity control
materials to enhance water adsorption characteristics. Some silica gel-host composites and their properties are shown in Table 3. Organic polymer materials are also the humidity control materials reported with high humidity control capacity. In recent years, there is more and more research on polymer humidity control materials, mainly focusing on the development of materials with high moisture adsorption capacity and rapid adsorption and release of humidity to adapt to different applications. Recently, mesoporous materials such as metal-organic frameworks (MOFs) have emerged as an effective candidate for the currently used desiccants. MOFs have open frameworks with ordered structure and high surface area, which make these materials promising desiccants in the sorption-based their variable chemical structure. Many studies have been reported about the utilization of MOF materials on the humidity regulation in buildings, such as MOF-801[28], MOF-841[29], MIL-160[30], MIL-100 (Cr, Fe, Al) [11, 31] and so on. Moisture adsorption characteristics of synthetic and novel humidity control materials are shown in Table 3.

**Table 3. Moisture adsorption characteristics of synthetic and novel humidity control materials.**

| Materials                        | Test conditions                     | Moisture adsorption capacity (g/g×100%) | References |
|----------------------------------|-------------------------------------|----------------------------------------|------------|
| Silica gels                      | Temperature 24℃, Relative humidity 0-80%, Pore diameter 10nm | 30% | [21] |
| Mesostructured silica            | Relative humidity 40-60%, Surface area 1200 m²/g, Pore diameter 2.6 nm | 35% | [25] |
| Silica gel–lithium chloride      | Temperature 25℃, Relative Humidity 30-80% | 55% | [33] |
| Silica gel–calcium chloride      | Temperature 25℃, Relative Humidity 30-70% | 32% | [33] |
| Silica gel–lithium bromide       | Temperature 20℃, Relative Humidity 10-80% | 43% | [33] |
| konjac glucomannan-acrylic acid copolym | Temperature 25℃, Relative Humidity 0-90% | 110% | [34] |
| MOF-303Al                        | Temperature 25℃, Relative Humidity 0-40% | 33% | [35] |
| MIL-100Fe                        | Temperature 30℃, Relative Humidity 30-90% | 30% | [35] |
| MIL-101Cr-NO3                    | Temperature 20℃, Relative Humidity 20-90%.Surface area 1245 m²/g | 38% | [36] |
| MIL-101Cr-NH3                    | Temperature 20℃, Relative Humidity 20-90%, surface area 2690 m²/g | 90% | [36] |
| MIL-160Al                        | Temperature 30℃, Relative Humidity 0-30%, surface area 1070 m²/g | 35% | [37] |
| Y-shp-MOF-5                      | Temperature 25℃, Relative Humidity 30-80%, surface area 4549 m²/g | 39% | [38] |
| Cr-soc-MOF-1                     | Temperature 30℃, Relative Humidity 30-90%, surface area 4549 m²/g | 190% | [39] |

4. Development trend of humidity control materials used in indoor environment
Since the living environment can be affected by indoor temperature, humidity, air quality, and other aspects, more new functional materials or new systems have been developed to realize the integrated control of indoor environment. Considering that a large amount of heat transferred during the process of adsorption and desorption by hygroscopic materials, the research of phase change humidity control materials (PCHCM) has become a hot spot in recent years [40]. Some composite materials such as fabric-sodium sulfate-silica gel, metal-organic frameworks-octadecane composite, and vesuvianite/sepiolite/zeolite-hydrochloric acid were reported to be used as humidity control phase change materials in some papers [41]. Qin made use of a combined HAMT (heat, air and moisture transfer model) and enthalpy model to evaluate the performance of PCHCM. The results have shown that up to 20% of the potential energy could be saved when using PCHCM in the buildings [42]. In order to further promote the use of interior decoration materials, more functional materials and humidity control materials are combined to form multi-functional composite building materials. Zhang used sepiolite and nano-TiO₂ to prepare a multifunctional powder coating material for the interior wall [43]. Qiu prepared a cemented by hydrothermal synthesis of sepiolite and calcium silicate to function both in humidity regulation and volatile organic compound removal [44]. This material can not only regulate the indoor humidity but also inhibit the growth of bacteria in the indoor air and remove formaldehyde in the air. As many new materials are reported, humidity control materials also can be integrated with new materials to form a new integrated system. For example, Qin reported a new dehumidification system, which can utilize the energy highly effective during the process of water vapor adsorption and desorption by using the assembly of the refrigeration silicon chip and hygroscopic materials [45].

5. Conclusion
To date, many new hygroscopic materials have been studied and applied in building environment. Humidity control materials are developing in the direction of being intelligent, multifunctional, high performance and practical systems, which can improve the building environment and save energy to a certain degree. On the basis of current materials and various technologies, the assembly of hygroscopic materials with other technologies can not only promote the practical applications of hygroscopic materials in the built environment, but also expand the application of hygroscopic materials in agriculture, food and daily chemical products.

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References
[1] Che W, Tso C, Sun L, Lp D, Lee H, Chao C and Laua A 2019 Energy consumption, indoor thermal comfort and air quality in a commercial office with retrofitted heat, ventilation and air conditioning (HVAC) system Energy Build 201 202-15
[2] Zu K, Qin M, Rode C and Libralato M 2020 Development of a moisture buffer value model (MBM) for indoor moisture prediction Appl. Therm. Eng. 171 115096
[3] Zu K, Qin M and Cui S 2020 Progress and potential of metal-organic frameworks (MOFs) as novel desiccants for built environment control: A review Renew. Sust. Energ. Rev. 133 110246
[4] Rode C, Peuhkuri R, Lone H, Time B, Gustavsen A, Ojanen T, Ahonen J, Svennberg K, Harderup L and Arvidsson J 2006 Moisture buffering of building materials (Technical University of Denmark Report) p 11-13
[5] Li Z, Wei F and Liu W 2011 Manufacture on building blocks of humidity-controlling composite materials used in greenhouse International (Conference on Materials for Renewable Energy and Environment) p1125-28
[6] Muguda S, Lucas G, Hughes P, Augarde C, Perlot C, Bruno A and Gallipoli D 2020 Durability and hygroscopic behaviour of biopolymer stabilised earthen construction materials Constr Build Mater 259 119725

[7] Célinó A, Fréour S, Jacquemin F and Casari P 2014 The hygroscopic behavior of plant fibers: a review Front. Chem. 1 43

[8] Singh R, Mishra V and Das R 2018 Desiccant materials for air conditioning applications-A review (Conference Series: Science and Engineering) p 12005

[9] Zha X, Zhang J and Qin M 2018 Experimental and numerical studies of solar chimney for ventilation in low energy buildings Procedia Engineering 205 1612-1619

[10] Hou G, Ji Z, Wang J, Wang J M and Wang X 2008 Domestic and abroad research status of humidity-control materials Materials Review (in Chinese) 8 24

[11] Qin M, Hou P, Wu Z and Wang J 2020 Precise humidity control materials for autonomous regulation of indoor moisture Build. Environ. 169 106581

[12] Padfield T and Jensen L 2011 Humidity buffering by absorbent materials (Proceedings of the Nordic Symposium on Building Physics) p 475-482

[13] Lee J K and Kim T Y 2018 Evaluation of humidity control ceramic coard using gypsum binder Korean J. Mater. Res. 28 62-67

[14] Kong W, Du Y, Bu C and Wang C Study on preparation and performance of diatomite-based humidity controlling materials 2011 Non-Metallic Mines (in Chinese) 34 57-59

[15] Zhou B and Chen Z 2016 Experimental study on the hygrothermal performance of zeolite-based humidity control building materials Int. J. Heat Technol. 34 407-14

[16] Mcdonald M, Kendall A, Tanaka M, Weissman Jand Stubbs G 2008 Enclosed chambers for humidity control and sample containment in fiber diffraction J Appl Crystallogr 41 206-209

[17] Bharadhipa P, Singh M and Mishra S 2019 Influence of graphene oxide on mechanical and hydrophilic properties of epoxy/banana fiber composites JOM 71 838-843

[18] Alix S, Philippe E, Bessadok A, Lebrun L, Morvan C and Marais S 2009 Effect of chemical treatments on water sorption and mechanical properties of flax fibres Bioresour. Technol. 100 4742-49

[19] Bessadok A, Marais S, Gouanvé F, Colasse L, Zimmerlin I, Roudesli S and Métayer M Effect of chemical treatments of Alfa (Stipa tenacissima) fibres on water-sorption properties 2007 Compos Sci Technol 67 685-97

[20] Hu Z, Zheng S, Sun Z, Chen Y and Yan Y 2017 Influence of pore structure on humidity control performance of diatomite Sci Technol Built Environ 23 1305-13

[21] Wan H, Huang H, Wang X and Hu J 2013 A review on structure and properties of humidity controlling materials Materials Review (in Chinese) 27 60-63

[22] Caturla F, Sabio M and Reinoso F 1999 Adsorption–desorption of water vapor by natural and heat-treated sepiolite in ambient air Appl Clay Sci 15 367-80

[23] Castrillo N, Mercado A and Volzone C 2015 Sorption Water By Modified Bentonite Procedia Materials Science 8 391-96

[24] Saikia D and Bora M 2003 Study of hygroscopic properties of some plant fibres under thermal condition Indian J. Pure Appl. Phys. 41 484-87

[25] Ohashi F, Maeda M, Inukai K, Suzuki M and Tomura S 1999 Study on intelligent humidity control materials: Water vapor adsorption properties of mesostructured silica derived from amorphous fumed silica J. Mater. Sci. 34 1341-46

[26] Li B, Hua L, Tu Y and Wang R 2019 A full-solid-state humidity pump for localized humidity control Joule 3 1427-36

[27] Ge G, Xiao F and Niu X 2011 Control strategies for a liquid desiccant air-conditioning system Energy Build 43 1499-1507

[28] Choi J, Lin L and Grossman J 2018 Role of structural defects in the water adsorption properties of MOF-801 J. Phys. Chem. C 122 5545-52

[29] Staschiak J 2020 Solar Air Conditioning with Metal Organic Frameworks (The Ohio State
[30] Permyakova A, Skrylny O, Courbon E, Affram M, Wang S., Lee U., Valekar A, Nouar F, Mouchaham G, Devic T, et al 2017 Synthesis optimization, shaping, and heat Reallocation evaluation of the hydrophilic metal-organic framework MIL-160 (Al) ChemSusChem 10 1419-26

[31] Feng X, Qin M, Cui S and Rode C 2018 Metal-organic framework MIL-100 (Fe) as a novel moisture buffer material for energy-efficient indoor humidity control Build. Environ. 145 234-42

[32] Qin M, Hou P, Wu Z and Wang J 2020 Precise humidity control materials for autonomous regulation of indoor moisture Build. Environ. 169 106581

[33] Rafique M, Gandhidasan P and Bahaidarah H 2016 Liquid desiccant materials and dehumidifiers-A review Renew. Sust. Energ. Rev. 56 179- 95

[34] Li W, Wang C, Chen G, Zhan X, Zhou J, Huang J and Jiang F 2007 Study on the SAP'S moisture-absorption characteristics of konjac glucomannan-acrylic acid copolymer Journal of Material Science and Endineering (in Chinese) 25 276-300

[35] Vivekh P, Kumja M, Bui D and Chua K 2018 Recent developments in solid desiccant coated heat exchangers-A review Appl. Energy 229 778-803

[36] Khuwia A, Rammelberg H, Schmidt T, Henninger S and Janiak C 2013 Water sorption cycle measurements on functionalized MIL-101Cr for heat transformation application Chem. Mater. 25 790-98

[37] Cadianu A, Lee J, Borges D, Fabry P, Devic T, Wharmby M, Martineau C, Foucher D, Taulelle F, Jun C, et al 2015 Design of hydrophilic metal organic framework water adsorbents for heat reallocation Adv. Mater. 27 4775-80

[38] AbdulHalim R, Bhatt P, Belmabkhout Y, Shkurenko A, Adil K, Barbour L and Eddaoudi M 2017 A fine-tuned metal-organic framework for autonomous indoor moisture control J. Am. Chem. Soc. 139 10715-22

[39] Abtab S, Alezi D, Bhatt P, Shkurenko A, Belmabkhout Y, Aggarwal H, Weselinski L, Alsadun N, Samin U., Hedhili M N, et al 2018 Reticular chemistry in action: A hydrolytically stable MOF capturing twice its weight in adsorbed water Chem. 4 94-105

[40] Hou P, Qin M, Cui S and Zu K 2020 Preparation and characterization of metal-organic framework/microencapsulated phase change material composites for indoor hygrothermal control J. Build. Eng. 31 101345

[41] Asim N, Amin M, Alghoulce M, Badieid M, Mohammadid M, Gasaymeh S, Amin Nasd Sopiana K 2019 Key factors of desiccant-based cooling systems: Materials Appl. Therm. Eng. 159 113946

[42] Qin M, Belarbi R, Mokhtar A and Nilsson L 2009 Coupled heat and moisture transfer in multilayer building materials Constr. Build. Mater. 23 967-75

[43] Jiang Z 2006 Research progress of humidity-controlling materials Materials Review (in chinese) 10 8-11

[44] Qiu P, Guo L, Qi Y, Cheng M and Jing Z 2020 Hydrothermal solidification of sepiolite into a cemented sepiolite aggregate for moisture regulation and formaldehyde removal Clay Minerals 55 320-328

[45] Yang J, Fu H and Qin M 2015 Evaluation of different thermal models in EnergyPlus for calculating moisture effects on building energy consumption in different climate conditions Procedia Engineering 121 1635-1641