

REVIEW OF COMPOSITE DESICCANTS AND THEIR PROPERTIES FOR ROTARY DEHUMIDIFIERS

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Abstract: Background: The rotary dehumidifier's performance largely depends on the desiccant used in the wheel. Composite desiccants are the state-of-the-art sorption agents used in adsorption dehumidifiers as they have higher moisture uptake capacity than pure physical desiccants. Different types of composite desiccants used in rotary dehumidifiers are mainly of four kinds Silica-gel based, Mesoporous silicate-based, natural-rock based, and carbon-based. A review of work done in the past with these desiccants has been reviewed in this paper. The selection of composite desiccant material for dehumidifiers depends not solely on any one parameter but various. Surface properties like specific surface area, pore volume, and the desiccant's pore size have also been proved as vital parameters in the performance of the dehumidifiers and the higher adsorption capacity. Surface properties and operating parameters like the temperature of adsorption and desorption for different composite desiccants were summarized in this paper which will help the new researchers to analyse other composite desiccants. Composite desiccants regenerated well below 100 °C will gain more attention from researchers in the coming years as solar energy prevails compared to conventional heat sources.

Keywords: Composite desiccants, Rotary dehumidifiers, Adsorption, Regeneration, Silica-gel

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INTRODUCTION

In recent years, electrical power consumption has skyrocketed because of modern society's growing industrial needs and comfort requirements. Conventional power plants are dominant players in the energy sector, dependent on fossil fuel sources for power generation. Meanwhile, fossil fuel scarcity and the risk of global warming have pushed the air conditioning sector to identify innovative cooling or dehumidification technologies to support or perhaps replace traditional vapor compression systems. As а result, different potential dehumidification technologies, like

desiccant-operated dehumidification systems, have been developed to replace conventional systems.

The amount of electrical power consumed by the compressor is directly proportional to the load on the RAC system. Air conditioners working on the vapor compression refrigeration cycle must handle dehumidification by reducing the supply air's temperature below its Dew Point Temperature. It is passed through the heating system later to bring the supply air temperature as per human comfort requirements. Here, electrical energy is consumed in both compressors and the heating system. A desiccant dehumidifier is a new way to remove moisture from the supply air. It can be coupled with VCRS for human comfort applications too. The performance of rotary dehumidifiers largely depends on the desiccants incorporated in the dehumidifier. [1]

Desiccants are solid (or liquid) media, wellknown sorption agents. Solid desiccants can be filled in the rotary wheel for moisture adsorption. A Desiccant has a porous structure that provides a large specific surface area for adherence of water vapor molecules [2-4]. Suitable Desiccants should adsorb a large amount of adsorbate under lower temperature conditions and desorb many water molecules at the minimum expense of thermal energy. Also, a good Desiccant should have higher latent heat adsorption than sensible. It should not quickly deteriorate with age after excessive use. It should be non-toxic when it comes in contact with air. It should be cheap and readily available [5-7]. Van der Wall's forces attract and hold the adsorbate molecules at the surface of physical Desiccants. The Mesopores on the surface of physical desiccants retain the moisture in consecutive layers, filling the volume with an adsorbate.

On the other hand, chemical Desiccants were not focused because of having critical problems like salt swelling and agglomeration [8,9]. A suitable desiccant should have less value of moisture not adsorbed, as it indicates that less water is trapped inside the pores of the desiccant [10]. The merits and demerits of physical desiccants and Hygroscopic salts are discussed in table 1.

Table 1	1:	Merits	and	Demerits	of	desiccants	[11	1
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Desiccant s	Merits	Demerits
Physical desiccant s (ex silica-gel, activated carbon, natural rocks, etc.)	Good structural stability No swelling and agglomeration Low cost Easy availability in the local markets	Long adsorption/regener ation time Low surface area Low pore volume Weak adsorption isotherm
Hygrosco pic salts (ex- calcium chloride, magnesiu m sulfate, lithium chloride, etc.)	Less adsorption/regener ation time compared to physical desiccants Large surface area Large pore volumes Better adsorption isotherm	Weak structural stability at a high moisture ratio because of lyolysis (the appearance of the very wet surface because of the formation of the hydrates) Swelling and agglomeration Higher cost

Composite desiccants have many advantages over conventional desiccants, as shown in Fig. 1, which brings up various opportunities for researchers in this area. Adsorption cooling technology is currently facing an issue of low COP and uncertain structural stability of desiccants. If we use composite desiccants, this issue can be resolved on a larger scale. In this paper, the composite desiccants are reviewed as they have

high adsorption capacity. Many can be powered using low-grade energy like waste heat or solar energy. The most popular composite desiccants were discussed in the subsequent sections.

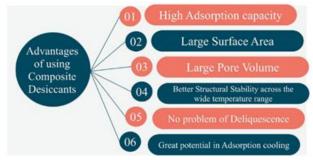


Figure 1: Advantages of Composite desiccants over conventional physical desiccants [11].

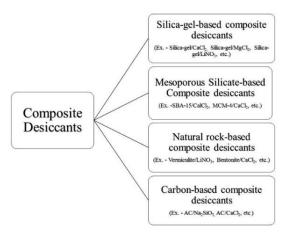


Figure 2: Classification of Composite desiccants [13].

COMPOSITE DESICCANTS

Composite desiccants are mainly synthesized by simple mixing or impregnation (in which physical desiccants are impregnated with hygroscopic salts like Calcium chloride, Magnesium sulfate, Lithium chloride, etc.) process. This chemical addition removes some of the inherits of physical and hygroscopic salts. The structure of pores can change the characteristics of physical desiccants. Adding hygroscopic salt into the physical desiccant helps to increase specific surface area, and hence no. of pores are increased. Chemical adsorbents exhibit swelling, agglomeration, and disintegration problems when exposed to high temperatures. Expanded graphite was added to the physical desiccants as an inert material to avoid agglomeration [12].

Researchers have reported many different types of composite desiccants in recent years. The classification of composite desiccants is shown in Fig. 2.

Silica-gel-based composite desiccants

Many researchers have proven Silica-gel as a well-accepted physical desiccant in applying rotary dehumidifiers. Silica-gel acts as a host providing a specific surface area for the adsorption of hygroscopic salts, which act as a substrate. Silica impregnated with hygroscopic salts has more water adsorption capacity. Many researchers have reported an almost two times increase in the adsorption capacity. Jia et al. [14] reported a two times higher adsorption rate than standalone Silicagel by using Silica-gel/LiCl composite desiccant. The same research has also written a 40% increase in moisture removal rate when the composite desiccant is used in a rotary desiccant wheel.

Along with the higher adsorption capacity, quicker regeneration of composite desiccant was also observed, leading to a decrease in cycle time. Different rates of adsorption and regeneration were marked with other desiccants, but the result is much better than the standalone Silica-gel. Tso et al. [15] prepared a composite desiccant using Silica-gel and CaCl2, which performs very well in adsorption capacity and building its isotherm. The authors concluded it's an excellent pair for lowgrade heat-driven rotary dehumidifiers. Sukhyy et al. [16] studied composite sorbent made of Silicagel and sodium sulfate. This research uses the solgel process to prepare composite material instead of conventional impregnation. Performance analysis was carried out, and it has been noticed that in the future Sol-gel method will serve as a critical process to increase the adsorption capacity of the desiccants. Silica-based composite composite the desiccants have great potential in future because of their structural stability, easy preparation processes, and easy availability.

Mesoporous Silicate based

Advancements in material science allow us to manipulate material properties successfully by controlling its synthesis process. Nanostructured mesoporous silica is the best example of it. The liquid crystal templating approach has increased specific surface area and volume in this desiccant With this advanced type. technique. many mesoporous silicates, such as SBA-15, MCM-48, MCM-50, etc., have been synthesized so far. Ponomarenko et al. [17] have developed Silica-gel impregnated with the solution of CaCl2. It is a novel nanostructured and mesoporous desiccant. It has a 58% ratio by mass of CaCl2. Glaznev et al. [18] also have researched two SBA-15s which are made up of 8.1 nm pore size and another of 11.8 nm pore size. It has been observed that SBA-15 with a large pore size requires less temperature for its regeneration. This regeneration temperature is 6 ٥C less than the necessary regeneration temperature for the SBA-15 with 8.1 nm pore size. Pei et al. [19] also synthesized three types of composite desiccants with core-shell structures. This research work combines mesoporous silica malate with sodium in the amine-functional environment, a state-of-the-art novel desiccant material called (MS-NH2-MAS). Also, MS-NH2-PAAS and MS-NH2-PSS were synthesized in which PAAS stands for Sodium polyacrylate, and PSS stands for sodium polystyrene sulfonate. Because of the higher affinity towards moisture, almost two times higher uptake in adsorption capacity has been observed compared to mesoporous silica. Based on this literature, it has been clear that mesoporous silicate-based desiccants can be adopted in rotary wheels with narrow pore sizes.

Natural rock-based composite

Natural mineral clay can effectively act as a host material for adsorption as they are readily available in the market and cost less. Many natural porous materials combined with chlorine salt have been investigated in past research. Chen et al. [20] have developed a novel series of a composite of attapulgite clay with LiCl solution. The performance of this composite is evaluated using a high vacuum gravimetric method, in which it has been found that the adsorption capacity is 0.51 grams of water per gram of desiccant. This water uptake is more than the pure Silica-gel, but the regeneration temperature required for this composite is more than 100 °C which is unsuitable for solar heat sources. Efforts were also made by Bulut et al. [21] to develop composite desiccants based on Turkish bentonite clay. CaCl2 is used to create a composite that competes with commercial competitors. However, the regeneration temperature required is still high and impossible to attain with low-grade energy like a solar heat source.

On the other hand, to improve the usability of the low-grade energy, efforts were taken by Nakabayashi et al. [22] to develop a new desiccant material based on Wakkanai Siliceous Shale (WSS). This new desiccant is combined with hygroscopic salt solutions like LiCl, CaCl2, and NaCl to improve the adsorption capacity. 5 to 7 times increase in the adsorption capacity was reported compared to the natural shell when treated with the NaCl solution to make a composite. The pressure ratio was kept around 0.5 to 0.7, and the adsorption temperature was about 25 °C. Sapienza et al. [23] have tried to overcome desiccants

adsorption capacity is 0.4 g.g-1 at an adsorption temperature of 36 °C whereas, whereas the regeneration temperature is not more than 66 °C. Such research studies have opened the door for developing new composite desiccants for dehumidifiers based on natural clay.

Carbon-based composite desiccants

Activated carbon is a well-known solid desiccant material for dehumidification. The activated term is used because carbon is treated with chemical agents to enlarge surface characteristics and pore volume. It can be made into powders, microporous molecular sieve structures, granules, and carbon fibers. Activated carbon fiber (ACF) has a better mass transfer rate than granular form because of having a uniform type of pore structure. The heat transfer rate of ACF is larger than granular activated carbon [24]. Type V isotherm shown by activated carbon makes it selective as we can use AC in any environment [25]. Making composites of activated carbon with hygroscopic salts is the best option for further increasing Specific surface area and Pore volume, which leads to improved adsorption capacity. Tso et al. [15] developed a new composite desiccant using activated carbon, silica-gel, and CaCl2. Before making a composite using CaCl2, activated carbon is impregnated by soaking it in a sodium silicate solution for 48 hours. A total of 13 samples were made in this research in which the pure carbon content of activated carbon coexisted with silica and calcium chloride solution. In this research, 0.23 g. g-1 adsorption capacity was reported by sample no. 12 at 0.9 kPa of pressure. More than 93.3% improvement in the adsorption capacity was written in this research. Huang et al. [26] have developed a new composite of silica and activated carbon by

impregnating activated carbon in sodium silicate (Na2SiO3). Higher adsorption capacity than standalone raw activated carbon was obtained at a low-pressure ratio. From these discussions, it has been clear that instead of using pure carbonaceous material for adsorption, we should use activated carbon composites in the rotary dehumidifiers to improve performance. After discovering such novel composite desiccants, researchers have started making new composite desiccant materials. Increased adsorption capacity and good structural stability over standalone physical desiccants were reported by Gordeeva et al. [27] and Simonova et al. [28] in the early years which sets a good platform for other researchers.

DIFFERENT PROPERTIES OF COMPOSITE DESICCANTS

When selecting composite desiccant material for a particular application, it depends not solely on any single property but many. Some properties like a hygroscopic salt percentage in the host matrix, Specific surface area, pore volume, adsorption and regeneration temperature, pressure ratio, and, most importantly, adsorption capacity could be the performance indices that served as a selection criterion. All these essential properties were discussed in the subsequent sections below.

Temperature of regeneration and adsorption

The temperature at which desiccants were reactivated for adsorption is called the temperature of regeneration. Rotary dehumidifiers work on lowgrade energy like waste heat or solar power. The temperature range available in such conditions for desiccant regeneration is roughly 50 - 150 °C. Composite desiccants regenerated in this temperature range are well accepted as we don't need to provide auxiliary heaters. The scatter graph shown in Fig. 3 shows that most of the composite

desiccants reported in the past studies were in the temperature range of 50 °C to 125 °C.

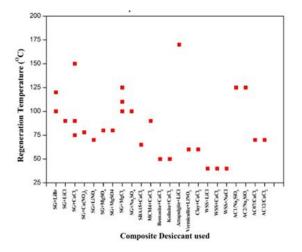


Figure 3: Different Composite desiccants and their Regeneration temperature

Compared to other desiccants, Composite desiccants are well-proven in the temperature range, easily achievable through low-grade energy options like waste heat or solar energy. On the other hand, adsorption temperature is also a crucial property always associated with the adsorption process. Adsorption is an exothermic process in which heat is released from the system and needs to be removed. If the amount of adsorption heat is more, then the COP of the system decreases. The adsorption temperature should be kept low to improve the system's performance is most important. Ideally, if the adsorption heat generated is less, it will be good. Different composite desiccants in the range of accepted adsorption and regeneration temperatures are shown in Fig. 4.

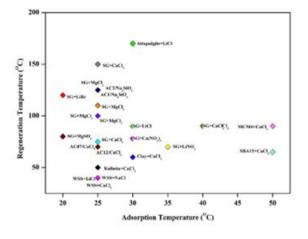
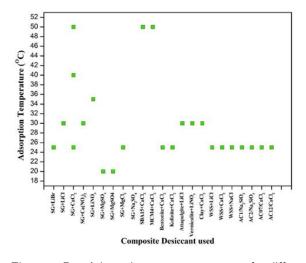
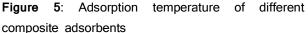


Figure 4: Different desiccants at regeneration and adsorption temperature

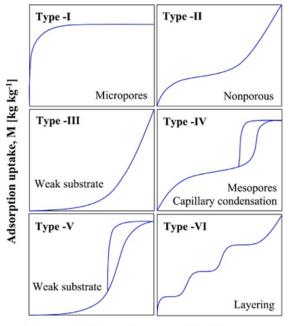




Composite desiccants release less adsorption heat, and many researchers report that removing adsorption heat is not an issue that prevents using composite desiccants. As shown in Fig. 5, the adsorption temperature by different reported composite desiccants in the studies reported by researchers is nearby in the atmospheric temperature range.

Adsorption capacity and type of lsotherms

The ability of a desiccant substance to adsorb water in its pores is referred to as its adsorption capacity. The adsorption capacity or water uptake capacity of desiccants is evaluated against the pressure ratio and the resulting curve, known as the Adsorption isotherm. The performance of the rotary dehumidifier is tied to the desiccants, which must be carefully monitored in terms of adsorption capacity and isotherm. The adsorption isotherm of desiccants is critical in the usage of desiccants for various applications. Initially, IUPAC (International Union of Pure and Applied Chemistry) provided certain basic types of adsorption isotherms, as illustrated in Fig. 6.



Relative Pressure, P/P. [-]

Figure 6: Adsorption Isotherms given by IUPAC [11]

Desiccants with type III isotherms are not acknowledged among the five isotherms given since they absorb moisture from the air at very high-pressure ratios. Types I, II, and IV are also less appropriate because they adsorb more moisture at lower pressure ratios, which may result in the hydrophilicity of desiccants and structural instability at high regeneration temperatures [29]. According to Zheng et al.[13], perfect desiccant material should adsorb at pressure ratios less than or equal to 0.5 atm, and regeneration should happen at pressure ratios greater than or equal to 0.6 atm. Figure 7 represents various desiccants and their operating pressure ratio range as stated in different studies. Sultan et al. [30] investigated the adsorption capacity of desiccants. It has been discovered that desiccants of type III isotherm are different environmental well acceptable under when the relative humidity of scenarios the environment is greater than 80%. For mild humidity conditions, type V isotherm desiccants are a common choice. Desiccants of type I and II isotherms are particularly fit for desert areas.

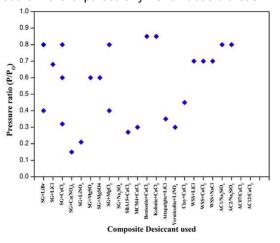


Figure 7: Composite desiccants and their pressure ratio

Various composite desiccants inhibit good adsorption capacity over standalone physical desiccant systems. Some researchers have incorporated composite desiccants in their studies and reported values of adsorption capacities in a gram of moisture per gram of desiccants, as shown in Fig. 8. Silica-gel-based desiccants have good adsorption capacity compared to others. Bu et al. [31] prepared three types of desiccant material by soaking three different Silica-gel into a solution of CaCl2. Three different samples of Silica-gel are 2-3 nm, 4-7 nm, and 8-9 nm pore size. The adsorption capacity and moisture removal rate are observed to

increase with the increasing CaCl2 content. Sample with 2-3 nm pore size has no enhancement in the adsorption capacity, and moisture removal rate as partial blockage of pores was observed. In their research, Gordeeva et al. [32] and Cortes et al. [33] also observed an increase in adsorption capacity. Cortes et al. [33] Concluded that the adsorption capacity is more when Silica-gel is prepared by soaking into CaCl2 compared to LiBr and MgCl2. Gordeeva et al. [27] have reported more Adsorption capacity for Silica-gel/MgSO4 when the percentage of MgSO4 has been increased in the Silica-gel.

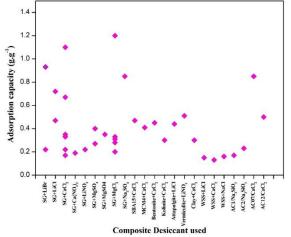


Figure 8: Adsorption capacity of different composite desiccants

• Structural properties

The structure, orientation and configuration of composite desiccant play an essential role. Hydrophilic nature, stability across the wide range of adsorption and regeneration temperatures, and stability at various pressure ratios affect the dehumidification system's performance. Structural properties were determined using SEM (Scanning Electron Microscope) and BET (Brunauer, Emmett and Teller) methods. SEM images of some desiccants were as shown in Fig. 9. Bu et al. (Bu, Wang, and Huang 2013) prepared three types of desiccant material by soaking three different Silicagel into a solution of CaCl2. Three different samples of Silica-gel are 2-3 nm, 4-7 nm, and 8-9 nm pore size. The adsorption capacity and moisture removal rate are observed to increase with the increasing CaCl2 content. Sample with 2-3 nm pore size has no enhancement in the adsorption capacity, and moisture removal rate as partial blockage of pores was observed.

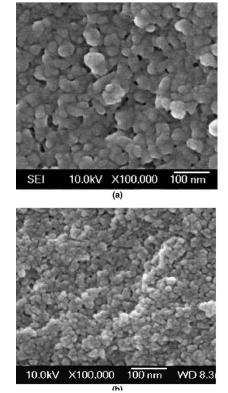


Figure 9: SEM images of (a) Silica-gel (b) Silicagel - LiCl Composite Desiccant [14]

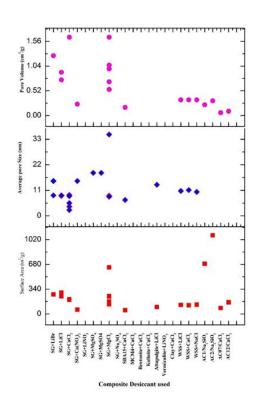


Figure 10: Structural properties of different desiccant materials reported so far in the past research work

The Specific Surface area (m^2/g) , Average pore size (nm), and pore volume (cm^3/g) of desiccant) values for different composite desiccants are reported in the past research studies are shown in the scatter graph in Fig. 10.

CONCLUSIONS

Dehumidification achieved using desiccants is benign environmental technology that has gained many researchers' attention in the last two decades. The working of the dehumidifiers largely depends upon the desiccants incorporated in the system. Desiccants are state-of-the-art sorption agents used in the system to remove moisture from the incoming air. Desiccants can be incorporated into the rotary wheels for adsorption and regeneration. Development in material science has triggered the use of novel composite materials in rotary dehumidifiers as they provide improved heat and mass transfer rates. This research explains some widely used composite desiccants, which can be integrated into the dehumidifiers to uplift moisture from the flowing air. When selecting composite desiccant material for а particular application, it depends not solely on any single but many. Some properties like a property hygroscopic salt percentage in the host matrix, Specific surface area, Pore-volume, Adsorption and regeneration temperature, Pressure ratio, and, most Adsorption capacity importantly, could be the performance indices that served as a selection criterion. This paper mainly discusses four types of composite desiccants: Silica-gel-based, Mesoporous Silicate-based, Natural rock-based, and Carbonbased. Various desiccants of these types were discussed in this paper. Amongst all these desiccants, it has been observed that adsorption capacity is notably increased when desiccants are synthesized with the impregnation of hygroscopic salts. This regeneration process can be achieved at temperatures as low as 40 °C. Despite these advancements in composite desiccants, we can't say that only one composite material satisfies all requirements of effective and improved the dehumidification. Every composite desiccant has some plus points and also has its shortcoming. A good trade-off must be made per merits, demerits, cost and availability of the composite desiccants. A tailor-made novel composite desiccant is always a need to improve dehumidification. According to this research, some conclusive comments were made as follows -

 Silica-gel-based composites are most widely used in rotary dehumidifiers as they have good structural properties and can regenerate at low temperatures, which can be easily achieved using solar energy. The impregnation method of preparing silica-gel-based composite needs improvement, or the Sol-gel process needs to be adopted to increase the Adsorption properties further.

- 2. Carbon-based desiccants have shone in the past few years as promising results were obtained. Surface properties measurement techniques in the analysis of carbon-based composite desiccants are more cost-consuming, and it requires a thorough knowledge of chemistry and material science. In the upcoming future, more research is expected in this area.
- Mesopore silicate-based composite desiccants have more opportunities to improve methods of pore generation and their effective distribution to increase adsorption capacity.
- 4. Natural rock-based desiccants have good adsorption capacity, but the availability of such desiccants is limited to some locations only. Also, the Regeneration temperature of these desiccants is above 150 °C, which makes it not a good choice for solar-operated dehumidification technology.
- Structural properties like Specific surface area, pore volume, pore size, pore distribution, etc., significantly improve moisture uptake capacity. Hence, it needs to be evaluated before the actual use of desiccants.

The advancement in the composite desiccant will overcome the low COP and Specific cooling power (SCP) when incorporated into the refrigeration system. And hence, more research is expected. Comments mentioned through this research work are a step forward to help the new researchers who want to undertake this area as their research interest and seek the knowledge of different composite materials that many researchers in the past are using.

CONFLICTS OF INTEREST

The authors have no conflicts of interest to declare.

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