

A critical review on various desiccant materials used for dehumidification of air

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Abstract: - Some materials like desiccants they have great affinity for water vapour. They are usually group of adsorbent materials. Due to this quality, desiccant materials can produce hot and dry air which can be used for the drying process as well as in air-conditioning applications to minimize the latent heat load. A good desiccant material must have well moisture absorption capability as well as lower regeneration temperature. The water vapour absorption capacity of desiccant material basically depends upon the desiccant characteristics like pore volume, apertures size and void fraction. Depending upon normal physical state, the desiccants can be either solids or liquids. Solid desiccant material such as silica gel, natural zeolites, synthetic zeolite, activated alumina, synthetic polymers etc. are extremely porous in nature and adsorb watervapour by using mechanisms of chemical adsorption. Liquid desiccants such as Calcium chloride, tri-ethylene glycol, and lithium chloride are generally very strong solutions of ionic salts and their behavior is controlled by changing its temperature and concentration. This paper presents a full study on different solid, liquid and composite desiccants which combine two or more desiccant materials for better properties and performance. This review has a phenomenal importance for the investigation and technical development in the field of desiccant dehumidification and air-conditioning technology.

Keywords: -Solid desiccant, Liquid desiccant, Regeneration, Composite Desiccant, Dehumidification.

1. Introduction

With the improvement of people's living standard and the attention to health condition, human beings put forward higher quality requirements for their work and living environment^[1]. More fresh air is introduced into indoor room, it needs to be cooled and dehumidified in hot and humid regions to meet people's comfort. In addition, some of modern production workshops, for example factories of powder, lithium battery, and pharmaceutical equipment, require constant lowHumidity^[2]. The conventional method for space cooling and dehumidification is mainly using vapour compression refrigeration system. This system can cool the process air below dew point temperature and remove the water vapour from moist air and then process air is reheated as supply air which meets the requirement of advanced design. This approach consumes a lot of high-grade electrical energy^[2]. Desiccant based air-conditioning systems offers a promising alternative to vapour compression refrigeration air-conditioning systems especially, under conditions involving high latent loads. This technique allows the use of low-temperature industrial waste heat or solar power to drive the cooling cycle. Therefore, it attracted increased research attention during the last two decades. Desiccants are chemicals with great affinity to moisture. They absorb/release moisture because of the variation in vapour pressure between the surface of the desiccant and the surrounding air. Dehumidification will occur when the vapour pressure of the surface of the desiccant is less than that of the environmental air^[3,11]. Dehumidification continues till the desiccant material reaches equilibrium with the surrounding air. Regeneration of this desiccant will occur when the vapour pressure of the desiccant is larger than that of the surrounding air, which is usually accomplished by heating the desiccant to its regeneration temperature and exposing it to an air stream. Desiccants can be classified as adsorbents which absorb moisture without considering physical and chemical changes or absorbents which absorb moisture by considering physical or chemical changes. Desiccants can be solids or liquids and can hold moisture through adsorption or absorption^[10]. Most adsorbents are liquids and most adsorbents are solids. Several types of solid desiccants are mostly used in desiccant cooling systems are silica gels, activated alumina and molecular sieves etc.

1.2 Background of study: -

Nowaday's AC became a necessary part of everyday life. The conventional vapor compression type ACs use the HCFC or HFC based refrigerants thus contaminating the globe continuously in European market nearly 1.6 million units of room AC's were sold in 1996.and 3.5 million units were sold in 2005. As of Italy and Spain the yearly additional cooling ability is about 12.6 GW i.e. near 5 GW increase in electric peak demand and owing to heavy growth in cooling demand the deprivation of environment is also large However, the DAC is an environment friendly AC technology which can be operated by thermal energy somewhat than electricity. Progress of desiccant technology was started by Shelpuk and Hooker in 1979 under the scheme of US solar heating and cooling program. Until now many developments have been made in the solid, liquid and hybrid DAC system through experiments and simulations the application of desiccant are also expanding widely and showed higher potential as compare to VAC system.

2. Desiccant material: -

Generally, the materials which have the ability to attract and hold other gases or liquids are termed as sorbents. These sorbents are mainly used in chemical separation processes and are used for absorbing gases or liquids other than water vapour. Desiccants are a subset the sorbents, which specifically have affinity for water. ^[3]This process of absorbing and holding water vapour by the desiccants may be defined as either absorption or adsorption depending on whether the desiccant material undergoing chemical change on attracting moisture (absorption) or not (adsorption). Materials like wood, natural fibres, clay sand various synthetic materials can also attract and hold water vapour, but they have less holding capacity. Generally, a desiccant attracts between 10 to 1100% of its dry mass of water vapour depending on the moisture content available in the surroundings and the type of desiccant material used. Desiccants continuously attract moisture, even from the dry air, until it reaches equilibrium with the environment. Moisture is removed by heating the desiccant material to temperatures from 50° to 150° C ^[4] and exposing to a regeneration air stream. After the desiccant is completely dried, it should be cooled so that it can attract water vapour again ^[4]. The desiccants are available either as solids or liquids, namely, solid desiccants and liquid desiccants. Mostly adsorbents are solids and absorbents are liquids.

3. Solid desiccants: -

Solid desiccants are highly porous materials which adsorb water by various mechanisms like chemical adsorption onto the walls of pores or consecutive layered physical adsorption of water molecules or capillary condensation into the pores ^[5]. These have large internal surface area per unit mass, as large as 4600 m² and the surface area which attracts water is always in the crystalline structure of the material ^[7]. These materials attract moisture because of electrical field present at the desiccant surface, which utilizes the atomic and electrostatic forces to attract water molecules into the microscopic pores of the desiccant surface. Solid desiccants are generally classified into following classes.

3.1 Silica gel

Silica gel is silicon dioxide (SiO₂ xH₂O), a naturally occurring mineral that is processed and purified into granular or beaded form with amorphous micro-porous structure. It has the surface area of 650m²/g with pore size ranging from 2–3 nm (type A) to about 0.7nm (type B) and heat of adsorption nearly equals 2800kJ/kg^[5]. It is considered an important desiccant material due to the strong affinity towards moisture and commonly used in DAC systems. Many silica gel based composite materials have also been developed which perform better than pure silica gel.

Advantages

1. Moisture removal capacity: Titanium silica gel can hold up to 40% of its dry weight in water when in equilibrium with air at saturation.
2. Non-overloading desiccant because titanium silica gel is a solid, insoluble desiccant, it is not possible to “wash out” the desiccant from the wheel. This means no special precautions are necessary even when it is exposed to air at 100% relative humidity.
3. Stability: Silica gel does not undergo any chemical or physical change during the adsorption process. It is inert, stable, and non-toxic.
4. Chemical resistance: Titanium silica gel is a steady material and is resistant to most chemicals. In particular, it is resistant to acids and sulfur products which might be found in the combustion products of a direct fired gas burner.

3.2 Zeolites

Zeolites are alumina silicate minerals of alkali and alkaline earth metals like sodium, potassium and calcium. They have crystalline lattice which are wide open that makes ease of holding water vapour like in a cage and have porous structure to accommodate the alkali and alkaline earth metal ions. Water vapour can be removed by heating the material, leaving unchanged alumina silicate skeleton with a void fraction ranging from 0.2 to 0.5. After heating, the size of apertures of the skeleton ranges from 3 to 8 Å for further adsorption of water vapour. Generally, zeolites will be contacted with aqueous solutions of appropriate cations (practically 0.1M) at a temperature of 60-70°C at solid to liquid (S/L) weight ratios ranging from 1/20 to 1/50, for cation exchange. Clinoptilolite, analcime, Natrolite, Heulandite, Phillipsite and Stilbite are some of the common zeolite minerals [21]. These zeolites are also used in some of the industrial chemical processes like gas separations, ion exchanges, water treatment and catalysis ^[8].

3.3 Activated Alumina

Activated aluminas are hydrides and oxides of aluminium, generally prepared by thermal dehydration or activation of aluminium tri-hydrate or gibbsite. The structural characteristics of alumina can be controlled either by temperature and duration of the thermal process or by the gases used for producing them. Activated alumina, like silica gel, has greater capacity for water vapour than zeolites and surface acidity is the important property for adsorption as well as catalysis. Because of this surface acidity, Lewis acid sites (sites that accept electrons) are abundant on alumina and for fully hydrated alumina, Bronsted acid sites (OH groups that don't proton) are present. This activated alumina has surface area ranging from 150 - 500 m²/g and heat

adsorption capacity as high as 3000kJ/kg^[9]. The pore configuration of the activated alumina mainly depends on the conditions of heat treatment and will be of size ranging from 1.5 – 6 nm. Because of its high sorbent properties, it has been prominently used in desiccant dehumidification and cooling applications and also in removal of oxygenates, Lewis bases, polar organic compounds and hydrogen fluorides from gases and liquids. Depending on the degree of hydration, the high temperature forms of alumina are θ -alumina and δ -alumina having only Lewis acid sites and γ -alumina and η -alumina having both type of acid sites (both Lewis and Bronsted).

3.4 Magnesium Sulfate

Magnesium sulfate (or magnesium sulphate) is an in-organic salt (chemical compound) and contain magnesium, sulfur and oxygen, with the formula $MgSO_4$. It is often encountered as the emphydrate sulfate mineral epsomite ($MgSO_4 \cdot 7H_2O$), commonly called Epsom salt^[13]. Anhydrous magnesium sulfate is frequently used as a drying agent. The anhydrous form is hygroscopic (readily absorbs water from the air) and is therefore difficult to weigh accurately; the hydrate is often preferred when preparing solutions (for example, in medical preparations. Anhydrous magnesium sulfate is generally used as a desiccant in organic synthesis due to its great affinity for water. During work-up, an organic stage is saturated with magnesium sulfate until it no longer forms clumps. The hydrated solid is then removed with filtration or else decantation. Other inorganic sulfate salts such as sodium sulfate and calcium sulfate may also be used in the same way^[13]

3.5 Molecular sieve/synthetic zeolite

Molecular sieve also known as synthetic zeolite can adsorb moisture strongly hence considered for different moisture removal and AC application. Zeolite prepared from fly ash has shown significant potential for solar cooling application. Composites desiccants are developed from synthetic zeolite and silica gel to obtain favorable adsorption characteristics under lower and higher relative humidity which enables deep dehumidification^[15]

3.6 Calcium oxide

Calcium oxide (CaO) is calcinated or recalculated lime having a dampness adsorptive limit of at the very least 28.5% by weight. The distinctive highlights of calcium oxide (otherwise called Quick Lime) are: it will adsorb a considerably more prominent measure of water at low relative mugginess than different materials. It is powerful in holding dampness at high temperatures; and it is moderately modest when contrasted with numerous different desiccants^[13]

3.7 Calcium sulphate

Calcium sulphate ($CaSO_4$), better referred to monetarily as Diorite, is an economical option accessible in reasonable bundling shapes. Calcium sulphate is made by the controlled drying out of gypsum, going about as a universally useful desiccant designed for the most part for research centre utilize. It is synthetically steady, non-breaking down, nontoxic, non-destructive, and does not discharge its adsorbed water when presented to higher surrounding temperatures. The ease of calcium sulphate must be weighed against its similarly low adsorptive limit: it adsorbs just up to 10% of its weight in water sulphate. Calcium sulphate additionally has recovery attributes that tend to restrict its helpful life. Albeit accessible, it isn't typically sold in bundle frame^[14]

4. Composite desiccant material

Composite materials are generally formed by the impregnation of hygroscopic salts into the pores of the host, i.e., a porous desiccant material in this case. The hygroscopic salts (nitrates, sulphates and haloids etc.) possess high water adsorption characteristics but they are unstable at higher humidity ratios due to lyolysis, so porous desiccant materials with stable characteristics like silica gels, activated carbon, mesoporous silicates and natural rocks are used as host material^[17]

4.1 Liquid and polymer desiccants

Liquid desiccant has been used in many DAC systems and yield decent COP. common liquid desiccant are lithium chloride, lithium bromide (LiBr), CalciumChloride ($CaCl_2$), and triethylene glycol. The liquid desiccant can be regenerated at lower temperature (60 to 75 °C) which gives an opportunity to utilize low grade waste heat. Polymer desiccant enables 2-3 times higher absorption ability as compared to silica gel and the result are more exciting when operated on higher relative humidity conditions and low regeneration temperature^[11,12,20].

4.2 Bio desiccant and activated carbons

Many hydrophilic desiccants are produced from biomass with an appropriate water vapour adsorption ability. In a study dry coconut coirs gave interesting performance with lower heat of adsorption as compared to silica gel. Biomass is also used for activated carban production^[19]. E.g. almond shell, coconut shell, oil palm shell, pistachio shell and walnut shell: cherry stones and

coffee endocarp. Usually the activated carbons are considered as hydrophobic substance but with some treatment it can absorb water vapours at higher relative pressure. Studies shows that activated carbon can yield 2-3 times higher water vapour adsorption as compared to silica gel^[21]

4.3 Bentonites clay: -

Clay is naturally occurring porous adsorbent which holds high moisture adsorption affinity. It is inexpensive and can work within the normal ranges of temperature and humidity. Many kinds of clay are used for water sorption applications after some treatments. The performance of certain clay depends on its source and the type of activation. Studies shows that the water vapour holding capacity of bentonites clay can be increased by 20% when chemically treated with hygroscopic material^[3, 5, 6]

4.4 Mesoporous silicate-based composite

A new family of ordered mesoporous silicates, prepared by hydrothermal formation of SGs in the presence of long-chain surfactant templates, have attracted intensive attention since the discovery of MCM-41 and FSM-16 in 1990s. Then, a variety of mesoporous silicates with different pore sizes have been developed, such as MCM-48, MCM-50, KIT-1, SBA-15 and so on^[17].

These mesoporous silicate exhibits better adsorption characteristics over ordinary SGs as a result of regular structures, large surface areas, abundant silanol groups and narrow pore size distribution.^[23]

4.5 Binary salt impregnated composites

The research works mentioned above were based on the composite desiccants with single salt impregnations. Recently composite desiccants with double hygroscopic salts impregnation became more prominent in research. Synthesized two composite desiccants by permeating Lithium chloride+ Lithium bromide and $\text{CaCl}_2 + \text{CaBr}_2$ into silica pores and found that the water vapour can be desorbed at 70°C by increasing the chlorine salt concentration in the binary salts. These binary salts impregnated composite desiccants were found to be having higher water adsorption characteristics when compared to single salt composite desiccants and low regeneration temperatures less than 100°C. The water adsorption characteristics of these composite desiccants mainly depends on the concentration and categories of salts, fabrication processes and pore distribution of host material. By varying these above characteristics, composite desiccants with desired and required adsorption characteristics can be synthesized^[14].

5. Liquid desiccant

Liquid Desiccants are generally strong ionic salt solutions whose behaviour can be controlled through varying their concentration, temperature or may be both. The control of temperature is handled by coolers or heaters, whereas concentration is handled by heating the desiccant to remove water vapour into the atmosphere or a scavenger airstream. In air washer, when air is passed through it, the dew point of the air supplied approaches the water temperature with which the machine is supplied. In this process, more humid air gets dehumidified and less humid air humidified. In the same way, the air is brought into contact with the liquid desiccant solution^[4]. Generally, the vapour pressure of liquid desiccant solution is lower than that of water at same temperature and the air gets dehumidified due to this vapour pressure difference^[12].

The selection of liquid desiccants depends on many parameters like density of energy storage, thermo-physical properties, vapour pressure, availability, regeneration temperature, boiling point temperature, cost, etc. and of all the above parameters, vapour pressure of the surface is of main concern. Some of the commonly used liquid desiccants, because of their low surface vapour pressure at low temperature and high concentration, are calcium chloride, lithium chloride, and lithium bromide and triethylene glycol^[18].

5.1 Calcium chloride

Calcium chloride is an ordinary ionic halide which serves calcium practical in watery arrangement and at room temperature it is a strong^[11]. It is generally produced by direct reaction of limestone with hydrochloric acid but in large quantities it is produced as a byproduct of Solvay process. It has a boiling point temperature of 1395°C with 2.15 g/cc density^[12]. In $\text{CaCl}_2\text{-H}_2\text{O}$ solutions, the crystallization line is complex because of the formation of α and β tetrahydrates.

Calcium chloride can serve as a source of calcium ion in an aqueous solution, as calcium chloride is soluble in water. This property can be useful for displace ions from solutions. Calcium chloride have a very high enthalpy change of solution. A considerable temperature rise accompanies its dissolution in water. The anhydrous salt is deliquescent. It can accumulate adequate water in its crystal lattice to form a solution. Drying tubes are frequently packed with calcium chloride [18]. Kelp is dried out with calcium chloride for use in producing sodium carbonate. Adding solid calcium chloride to liquid can remove dissolved water. These hygroscopic properties are additionally connected to keep a fluid layers on the outside of the roadway, which holds dust down^[20].

5.2 Lithium Chloride

Lithium chloride is an ionic salt that is widely used in air-conditioning systems. It has better hygroscopic properties and amazing solubility of about 83g/100 ml at 20°C in polar solvents. It has a boiling point temperature of 1382°C with 2.068 g/cc density. The crystallization line of LiCl-H₂O solution is an increasing mass fraction of LiCl and reducing water content^[12, 20].

5.3 Lithium Bromide: -

Lithium bromide is another lithium salt that is widely used as desiccant in air-conditioning applications. It is generally produced by treating lithium carbonate with hydrobromic acid and it can also be produced as a precipitate in water by treating lithium hydroxide with hydrobromic acid^[20]. It generally forms many crystalline hydrates comparative to other bromides of alkali metals. It is quite soluble in water, methanol, ethanol, ether and also slightly in pyridine. It has a boiling point temperature of 1265°C with a density of 3.464 g/cc^[25].

5. Conclusions: -

The ability of a desiccant to attract water vapour depends on the difference in vapour pressure between its surface and the process air. All desiccant materials attract moisture until they touch equilibrium point with the surrounding air. The absorbed water vapour is usually removed from the desiccant by regeneration in which desiccant is exposed to a regeneration airstream having temperature between 50 and 150°C.

Generally, the capacity of solid desiccant is less than the capacity of liquid desiccant but the use of composite desiccant materials may improve the moisture adsorption capacity. In case solid desiccant for air dehumidification with low grade waste heat as driving energy silica gel always performs better than another solid desiccant. Where as in case of liquid desiccant the most suitable is LiCl because of its lower vapour pressure but the major problem with LiCl is its high cost, this issue can be solve by combining it with cheapest desiccant CaCl₂. At the same time the composite desiccant of silica gel and LiCl has adsorption capacity 2-3 times higher than that of pure silica gel. The limitation faced by desiccant system is availability of regenerating heat to regenerate desiccant material. But the use of solar energy and waste heat for regeneration of desiccant material will make the system more economical. The use of desiccant system can solve lot of environmental problems well, as it can also minimize the high demand of electrical energy for conventional air-conditioning system and poor indoor air quality.

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