

Effects of Pore Structure and Surface Property on Adsorption Performance of New Composite Adsorbing Material for Low Grade Heat Storage

Jun Cheng¹, Dongsheng Zhu¹, Zhaoxi Yang², Huijun Wu¹, Chao Liu¹

¹The Key Laboratory of Enhanced Heat Transfer & Energy Conservation of Ministry of Education, The School of Chemical and Energy Engineering, South China University of Technology, Guangzhou, China

²The School of Chemical Science, South China University of Technology, Guangzhou, China

Abstract: A new composite adsorbing material for low grade heat storage — $\text{SiO}_2 \cdot x\text{H}_2\text{O} \cdot y\text{CaCl}_2$ which is composed of macro-porous silica gel and calcium chloride is introduced. The effects of pore structure and surface property on adsorption performance of adsorbing material are investigated. Pore structure parameters such as BET surface areas and pore diameter distributions of macro-porous silica gel and four composite adsorbing materials with different CaCl_2 content are measured using SEM and Asap2010 apparatus. According to the measured results, the pore structures of macro-porous silica gel, composite adsorbing materials and the CaCl_2 stuff characteristics in pore are analyzed. An open cycle adsorptive heat storage system with composite adsorbing material-water working pair was developed to carry out the experiment test about adsorptive capacity and heat storage density. In the light of the above data tested, the main factor of effect on adsorption performance is analyzed, which offers the reference basis for developing the new-type absorbent further.

Keywords: heat storage, composite adsorbing material, silica gel, adsorption performance

NOMENCLATURE

SG	Macro-porous silica gel
AM	Composite adsorbing material
AM10	Composite adsorbing material with 10% CaCl_2 content
AM20	Composite adsorbing material with 20% CaCl_2 content
AM30	Composite adsorbing material with 30% CaCl_2 content
AM40	Composite adsorbing material with 40% CaCl_2 content

1. INTRODUCTION

For the last two decades, a huge amount of work has been done on developing efficient systems for both accumulation and recovery of low- and middle-temperature industrial heat waste as well as for utilization of renewable sources of thermal energy. Basically, many systems developed to date operate on the principle of heat storing by using either the intrinsic heat capacitance of the storing medium or the latent heat of a phase transition inside this medium. Unfortunately, some parameters of these physical process cannot satisfy potential customers, especially from the viewpoint of the amount of heat stored per unit mass of the storing material as well as the possibility to obtain a long-term storage of accumulated heat[1]. The adsorption heat storage

technology is a new type of one for its high-quality energy storage density in accordance with the present environmental protection requirements.

In this paper, the author has prepared a new composite adsorbing material— $\text{SiO}_2 \cdot x\text{H}_2\text{O} \cdot y\text{CaCl}_2$, which employs chemical dehydration of water molecules tightly coupled to an appropriate lattice material and is composed of macro-porous silica gel and calcium chloride. Existing specimens of these storage media have demonstrated heat storage density approaching 2000kJ/kg.

In order to make use of the composite adsorbing material, it is necessary to study its adsorption mechanism. Pore structure and surface property of porous material are critical elements affecting adsorption mechanism. In this work, macro-porous silica gel and two composite adsorbing material samples are tested by SEM, and macro-porous silica gel and four composite adsorbing material samples with different CaCl_2 content are measured by Asap2010 adsorption equipment, including BET specific area and pore diameter distribution. According to the measured results, the pore structures of macro-porous silica gel, composite adsorbing materials and the CaCl_2 stuff characteristics in pore are analyzed. An open cycle adsorptive heat storage system with composite adsorbing material-water working pair is developed to carry out the experiment test about adsorptive capacity and heat storage density. And then in the

light of the above data tested, the main factor of effect on adsorption performance is analyzed, which offers the reference basis for developing the new-type absorbent further.

2. EXPERIMENTAL WORK

2.1 Preparation

Using macro-porous silica gel and CaCl_2 as raw materials, composite adsorbents were prepared by the method that matrix granules, macro-porous silica gel are filled with chemisorbent, CaCl_2 solution. Macro-porous silica gel is produced by Qing Dao Hai Yang Chemical Plant and it is of ivory global granule appearance, 4–8mm graininess, 497g/L stacking density; CaCl_2 (analytically pure) is adopted by Tian Jin Bai Shi Chemical Ltd. Co. Consulting the method that Aristov[2] prepared, for letting CaCl_2 into pores of silica gel, the composite adsorbents are prepared as follows:

Firstly, put macro-porous silica gel into electrical heating drying oven for heating 2hrs (the heating temperature is 95°C) until the weight of silica gel has no longer changes in order to get rid of moisture content and other impurity gases in pores of silica gel.

Secondly, put silica gel into vacuum desiccator for cooling to room-temperature for 1hr, then immerse silica gel into CaCl_2 aqueous solution whose mass percent is respectively 10%, 20%, 30%, 40% for 8hrs in order to make CaCl_2 enter adequately into pores of silica gel.

Lastly, put silica gel adsorbed CaCl_2 into electrical heating drying oven for heating (heating temperature is 95°C) until the weight of the sample has no longer changes. Then the needing composite adsorbents with CaCl_2 mass contents 5.74%, 12.86%, 16.04%, 23.35% can be obtained.

Throughout this paper, SG refers to macro-porous silica gel, AM refers to composite adsorbing material, and AM10, AM20, AM30 and AM40 refer to composite adsorbing material samples 1, 2, 3, 4, respectively.

2.2 Microstructure Characterization

Using LEO1530VP SEM equipment, one cross-section of SG and AM30, AM40 are scanned, and direct evidence of pore structures are obtained.

Pore parameters of SG, AMs are measured using an Asap2010 adsorption device made by Micromeritics Co. in USA. The measuring method is N_2 adsorption method. Based on the adsorption theory, under the condition of critical temperature, 77.35K below, results are acquired according to adsorptive capacity of samples to N_2 under different pressure. Measurement results cover BET specific area and pore diameter distribution.

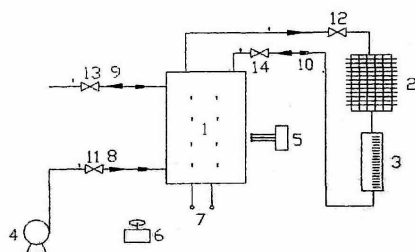
2.3 Experiment with Adsorptive Capacity

Adsorptive capacity of different composite adsorbing materials is tested by using gravimetric method: Dry the adsorbing material samples prepared to be constant weight. 2–3g samples are weighed by flat weighing bottles dried in advance. Then put the bottles in controlled temperature and humidity cabinet to do adsorption experiments with humid air. The

humid air is controlled to maintain 35 degrees Centigrade and relative humidity 50%. Adsorptive capacity datas under different time are gotten.

2.4 Experiment with Heat Storage Density

Schematic of the apparatus for open cycle adsorptive heat storage device is shown in Fig. 1. Heat storage density of composite adsorbing materials can be acquired by packing the materials into the apparatus and doing adsorption/desorption cycle heat storage experiments.



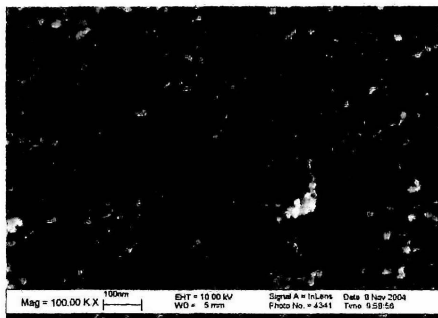
1-adsorbent bed; 2-condenser; 3- liquid trap; 4-fan; 5-data collector; 6-voltage regulator; 7-electric heater; 8-air inlet; 9-air outlet; 10-water inlet; 11–14-valve

Figure 1: Schematic of the apparatus for open cycle adsorptive heat storage device

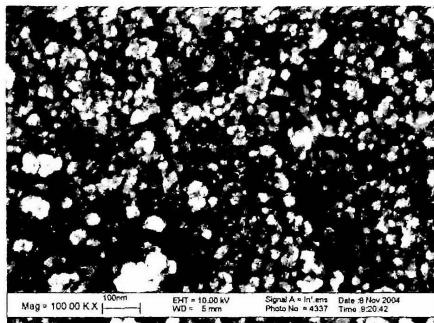
3. RESULTS AND DISCUSSION

3.1 SEM Test

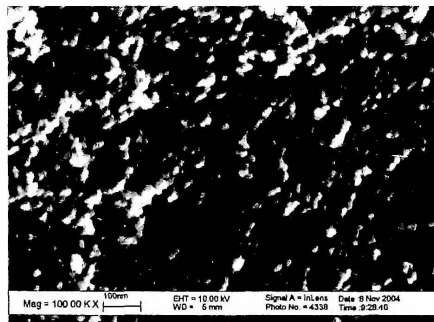
The results of SEM test of macro-porous silica gel and AM30, AM40 are presented in Fig. 2. The objects with the white powder form are packed to the pores of composite adsorbing materials, that is to say CaCl_2 molecules enter into the pores of silica gel. Through the comparison, packing quantity of CaCl_2 in composite adsorbents increases gradually with the increase in CaCl_2 solution concentration.



(a) SG



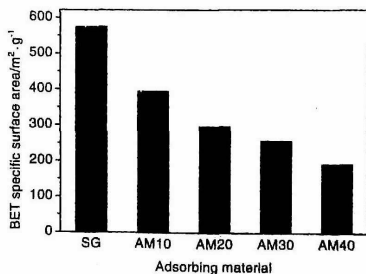
(b) AM30



(c) AM40

Figure 2: SEMs of composite adsorbing material samples

3.2 BET Specific Surface Area

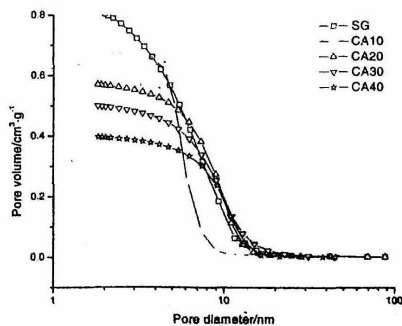

Figure 3: BET surface area of different adsorbing materials

Pore structures of adsorbing materials can be reflected by BET specific surface area. Specific surface areas of SG and AMs are shown in Fig.3. Specific surface area of SG, the greatest is 575m²·g⁻¹. Specific surface area of AM10 is 395 m²·g⁻¹. Specific surface area of AMs decreases with the increase in CaCl₂ content. Specific surface area of AM40 is only 192 m²·g⁻¹. The reason is as follow: the higher CaCl₂ concentration is, the higher CaCl₂ content filled in pores of macro-porous silica gel is, resulting in the decrease in specific surface area.

3.3 Pore Diameter Distribution

According to the size of aperture, the pores of solid porous materials are divided into three kinds by IUPAC[3]: micropore whose aperture is smaller than 2.0nm; macropore whose aperture is greater than 50.0nm; mesopore whose aperture is between the former. Pore diameter integral and differential distributions are shown in Figs.4, 5. Pore diameter differential distribution indicates the volume of pore diameter (corresponding abscissa). Pore diameter integral distribution is the integral of pore diameter differential distribution and indicates that the pore volume of pore diameter is not less than the value of corresponding abscissa. Because the pore diameter distribution is concentrative, in order to display pore diameter distribution clearly, the abscissa in pore diameter distribution is expressed in logarithmic coordinates.

It can be learned that there are a large amount of macro and meso pores in adsorbents. The fact that SG has an apparent peak at about 6.0nm pore diameter shows pore diameter distribution of SG is comparatively narrow. However, pore diameter distribution of AM10 is comparatively wide. With the increase in CaCl₂ content, pore diameter distribution of AMs turns wide, and furthermore, it changes along the increase in pore diameter.


Figure 4: Pore diameter integral distributions of SG and AMs

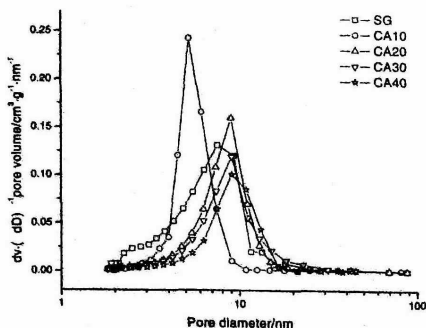


Figure 5: Pore diameter differential distributions of SG and AMs

3.4 Research on Adsorption Performance of Adsorbing Materials to Vapour

Research on fundamental property of adsorption is concentrated on quantity and heat equilibrium property mainly. Among them, adsorptive capacity and heat storage density are two important parameters which can measure adsorption process.

3.4.1 Adsorptive Capacity

Adsorption curves of SG and AMs are shown in Fig. 6. Adsorptive capacity of composite adsorbing materials is better than the one of pure silica gel. For example, AM40 balanced soakage reaches 0.5kg/kg, which is 3.1 times of quantity for the pure silica gel. Furthermore, with the increase in CaCl_2 solution concentration during preparation process, balanced adsorptive capacity increases. For instance, balanced adsorptive capacity of AM40 has been improved by 1.2 times than the one of AM10.

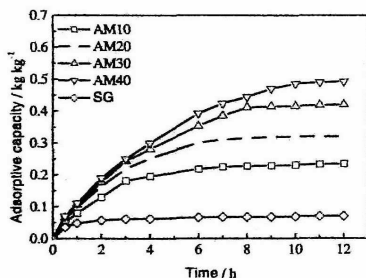


Figure 6: Influences of CaCl_2 solution concentration on adsorptive capacity

3.4.2 Heat Storage Density

Heat storage density of different adsorbing materials in open-cycle heat accumulator is shown in Fig. 7. It is obvious that with the increase in CaCl_2

content, heat storage density increases, the highest one can be up to 1170kJ/kg, far greater than silica gel.

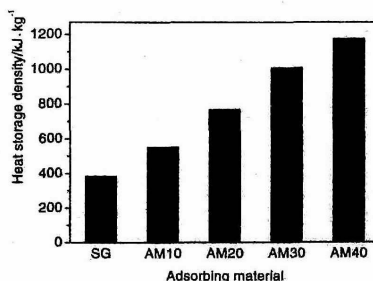
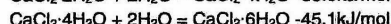
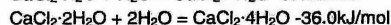
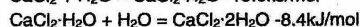


Figure 7: Heat storage density of different adsorbing materials

3.5 Research on Adsorption Mechanism and Influence Factor

There are two kinds of adsorption action of adsorbing materials to vapour: one is physical adsorption which is of silica gel with great specific surface area to vapour, H_2O molecules are compressed into adsorbing materials owing to the function of adsorption potential field, and the order of magnitude of heat of physical adsorption is only for

$\Delta H_a^p \leq 0.2 \text{ eV/mol}$ (equivalent to 20J/mol); the other is chemical adsorption which is produced by reversible chemical reaction between CaCl_2 and vapour. One CaCl_2 molecule can absorb 6 H_2O molecules at most:



It is obvious that in the adsorbing materials, surface area is not a decisive factor that determines to adsorption performance, but chemical adsorption of CaCl_2 plays a significant role. Therefore, with the increase in CaCl_2 solution concentration during preparation process, CaCl_2 content in composite adsorbing materials increases, and then composite adsorbing materials are of greater adsorptive capacity and heat storage density.

4. CONCLUSION

(1) With the increase in CaCl_2 content, specific surface areas of AMs decrease, pore diameter distributions of AMs turn wide, and furthermore, they change along the increase in pore diameter, making average pore diameter increases.

(2) The function which CaCl_2 packs into silica gel makes specific surface areas of composite adsorbing materials decrease, accordingly adsorptive capacity and heat storage density produced by physical

adsorption decrease. However, because of chemical adsorption of CaCl_2 to water, the total adsorption performance increases greatly and is in direct proportion to CaCl_2 content. Adsorption performance of adsorbing materials to water is determined mainly by specific surface area, pore diameter distribution and CaCl_2 content, etc, among which CaCl_2 content plays a leading role.

5. ACKNOWLEDGMENTS

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