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Development and testing of novel Chemisorption Composite using SrCl₂-NEG adding with Carbon coated Ni and Al

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Abstract

This research experimentally investigated the impact of adding Carbon Coated Nickel and Carbon Coated Aluminium on the sorption performance of conventional Strontium Chloride-Natural Expanded Graphite (SrCl₂-NEG) chemisorption composite. In order to evenly distribute Nano particles into the material, manufacture methodology is developed and reported. In this study, experiments were set for testing the sorption performance of applying novel Ni/Al-additive adsorbent with the working fluid of ammonia. Compared with that of SrCl₂-NEG, Ni-additive adsorbent improves the comprehensive heat and mass transfer performance as it reacted faster in both adsorption tests and low temperature desorption tests. By adopting Carbon coated Ni into the chemisorption composite, the overall sorption cycle time and require relatively lower energy for sorption cycles. While Al-additive adsorbent only improves the reaction speed in low temperature desorption tests, and may be applied in negative catalyser for its bad behaviour in adsorption performance tests. This paper reveals that adding Carbon Coated Nickel into conventional chemisorption composite would provide a potential way for improving the overall efficiency of an adsorption system and reducing the overall sorption cycle time.

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Keywords: Carbon Coated Nickel/Aluminum, Strontium Chloride, ammonia, adsorption/desorption performance

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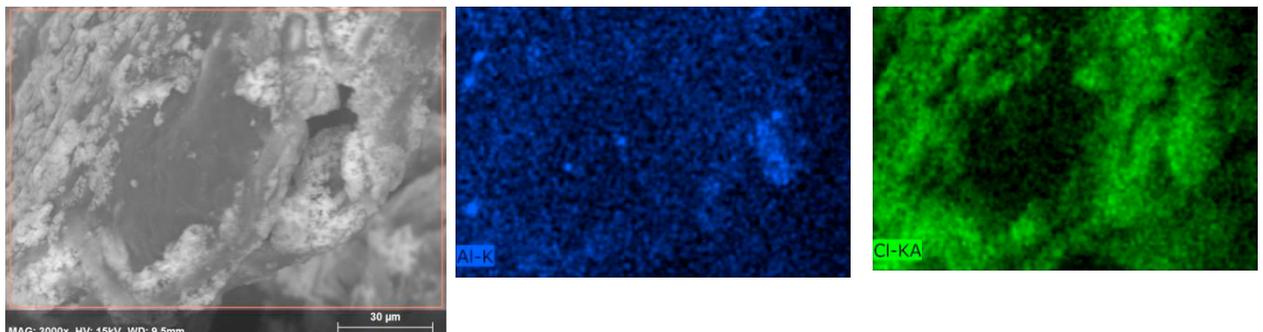
1. Introduction

Solid gas sorption refrigeration technologies, which produce cold for end users by recovering industrial waste heat, solar energy, soil heat and other kind of low grade thermal energy, have been widely investigated in the past few decades [1-4]. To improve the overall performance of adsorption/desorption system, exploitation on new adsorbents raises increasing attractions from researchers [5-8]. The relatively low thermal conductivity of chemical adsorbents and the swelling/agglomeration phenomenon of using chemical adsorbents after several cycle times will lead to low heat and mass transfer performance [9-11]. The composite adsorbents of Chloride salts-porous media-ammonia employ the matrix of porous media expanded graphite [12-14], carbon fibres [15, 16], activated carbon [17, 18], silica gel [19, 20]. These composite adsorbents have higher thermal/mass transfer as they have the high thermal conductivity of chloride salts and the porosity of porous media ensures enough permeability for the mass transfer in the sorbent. The Carbon Coated metal is a potential composite adsorbent as it contains a metal core with high thermal conductivity, high thermal capacity and high electrical conductivity [11, 21], and the coated carbon could prevent metal from reacting with the composite salts and refrigerant. Furthermore, the impact of Carbon Coated metal can act as Nano particle on mass transfer performance could be ignored due to its small volume.

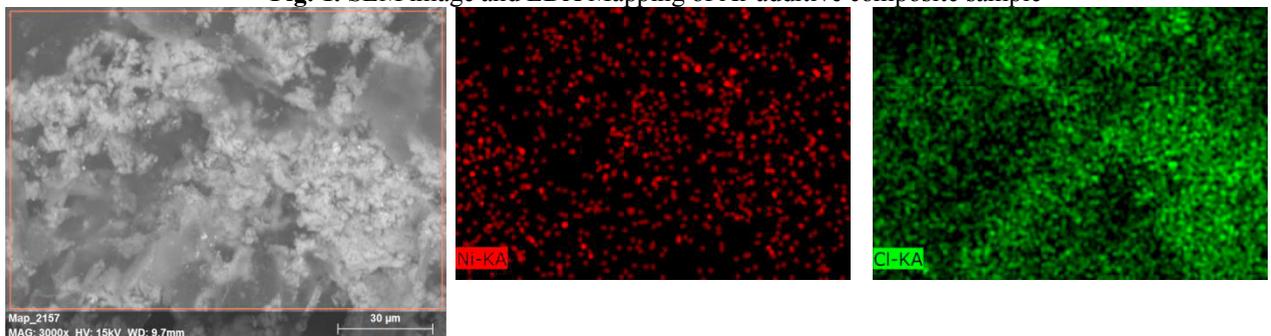
This research utilized Carbon Coated Nickel (Ni@C) and Carbon Coated Aluminium (Al@C) as additives to the conventional Strontium Chloride-Natural Expanded Graphite composite adsorbents. The adsorption/desorption performance with/without the additions was experimentally tested to investigate the performance of conventional chemisorption composite and the novel Nano particles and explore the potential of it for the application in adsorption refrigeration systems.

2. Methodologies

2.1. Preparation of chemisorption composites



(a) SEM image of the Al-additive sample (b) EDX Mapping of the element Al (c) EDX Mapping of the element Cl
Fig. 1. SEM image and EDX Mapping of Al-additive composite sample



(a) SEM image of the Al-additive sample (b) EDX Mapping of the element Ni (c) EDX Mapping of the element Cl
Fig. 2. SEM image and EDX Mapping of Ni-additive composite sample

Chloride strontium (SrCl_2) was selected as the main chemical adsorbent reacting with ammonia. The expanded graphite was used as the matrix of the composite adsorbent. The Ni@C/Al@C has been used as additive into the composite. The mass ratio among SrCl_2 , expanded graphite and Ni@C/Al@C was 40:20:1 referring to the study conducted by Q.Wu et al. [22]. To control the evenly distribution of nanoparticle inside the mixed adsorbents, the nanoparticle was first dispersed into ethanol for 30 minutes ultrasonic bath, which could vibrate and smash the tiny conglomerate of nanoparticle and result in the uniformity. Natural expanded graphite and chloride strontium were poured into this fluid and repeat ultrasonic bath for another 30 minutes. When finished the ultrasonic bath, the mixture was placed into the beaker on the magnetic stirrer and waited for the evaporation. The final step was to dry the prepared material in the oven under the temperature of 120 Celsius for 48 hours and stirred it once half an hour during the drying process.

Prepared composite adsorbents were made into samples and sent to Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray spectroscopy (EDX) for observing the surface morphology of the adsorbents as displayed in Fig. 1 and Fig. 2. The little white spots in Fig. 1 (a) and Fig. 2 (a) had the same shape with the little green spots (elements of Cl) in Fig. 1 (c) and Fig. 2 (c) respectively. This reveals that the little white spots are chloride salts. Moreover, the grey material with sheet structure was expanded graphite. Besides, red and blue particles in Fig. 1 (b) and Fig. 2 (b) displayed the distribution of element of Al and Ni separately. This could indicate the almost evenly distributions of Nano-additives as the little green spots in Fig.1 (b) and the little red spots in Fig.2 (b) illustrate the distributions of the element Al and Ni separately.

2.2. Description of the adsorption test rig

A rational adsorption/desorption system was designed for the new chemisorption composite adsorption and desorption performance tests. This system could test dynamic kinetics relationships and measure the sorption performance simultaneously by using volumetric calculation methodologies.

The test rig consisted of an adsorbent bed, a condenser/evaporator containing ammonia, one oil bath for the adsorbent bed and one for the condenser. A differential pressure sensor lies the bottom of the condenser/evaporator, testing the pressure difference between the top and the bottom of condenser. And five temperature sensors were set for monitoring the temperature of the inlet and outlet oil pipes of both adsorbent bed and condenser and the inner temperature of the adsorbent bed. Besides, an electric heating wire was inside the condenser to prevent the condensation of the ammonia in the connected pipe line or in the condenser itself as shown in Fig.3. The chemisorption composite held density of 450 kg/m^3 , in which 66% is Strontium Chloride and 2% is Carbon coated Nickel/Aluminium.

3. Evaluation methods

3.1. The gross mass of the ammonia inside condenser/evaporator

The gross mass of the ammonia (m_{am}) inside condenser/evaporator could be calculated by equation (1)

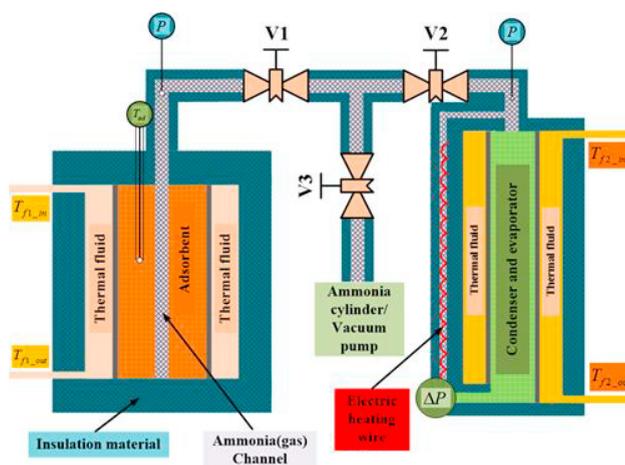


Fig.3. Schematic diagram of the test rig [23, 24]

m_{am} - the gross mass of the ammonia inside condenser/evaporator;

$$m_{am} = \left(1 - \frac{v_l}{v_g}\right) \times \Delta p \times \frac{A_c}{g} + \frac{V_c}{v_g} \tag{1}$$

v_g and v_l - The specific volume of the vapour phase

ammonia and saturated liquid ammonia under the controlled temperature of the condenser/evaporator, respectively;

Δp - The pressure difference between the top and the bottom of the condenser/evaporator;

V_c and A_c - The internal volume and the internal cross sectional area of the condenser, respectively.

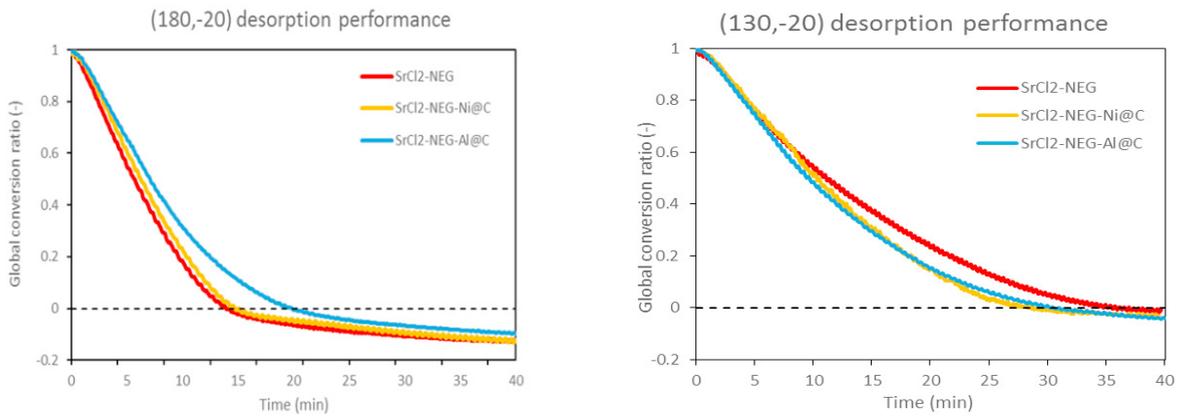
3.2. The global adsorption conversion ratio

$$X = \frac{m_{am(SrCl_2 \cdot NH_3)} - m_{am}}{m_{am(SrCl_2 \cdot NH_3)} - m_{am(SrCl_2 \cdot 8NH_3)}} \tag{2}$$

The global adsorption conversion ratio (X) of this adsorption/desorption performance test rig could be calculated by equation (2).

X - the global adsorption conversion ratio of the chemisorption composite;

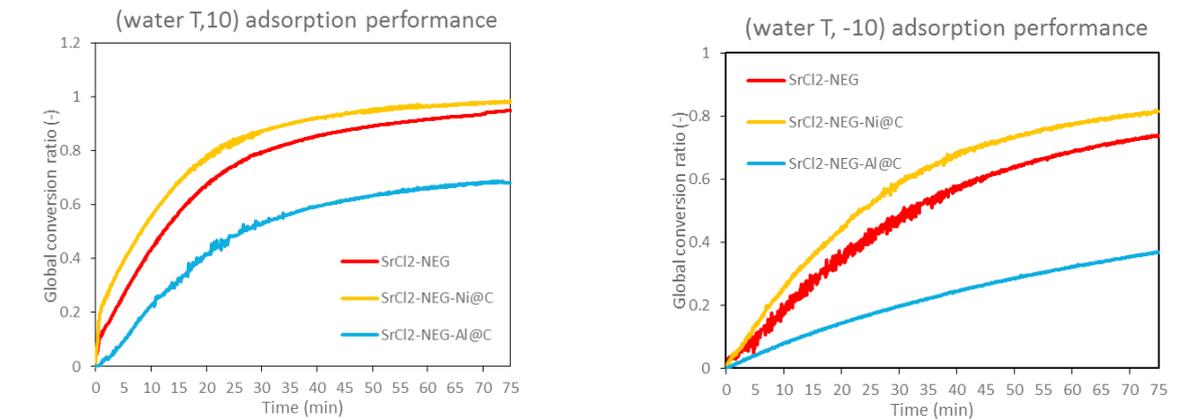
$m_{am(SrCl_2 \cdot NH_3)}$ and $m_{am(SrCl_2 \cdot 8NH_3)}$ - the gross mass of ammonia in the condenser/evaporator when the adsorbent absorbs 1 portion of ammonia and 8 portions of ammonia, respectively.



(a) Desorption performance under 180°C

(b) Desorption performance under 130°C

Fig.4. Comparison of the desorption performance of the SrCl₂-NEG, SrCl₂-NEG-Ni/Al@C



(a) Adsorption performance under water cooling and restricting cryostat at 10°C

(b) Adsorption performance under water cooling and restricting cryostat at -10°C

Fig.5. Comparison of the adsorption performance of SrCl₂-NEG and SrCl₂-NEG-Ni/Al @C

4. Results and discussion

The desorption performance were tested when controlling the heat source from the oil bath near the adsorbent bed at the temperature of 180 °C/130 °C and keeping the condenser/evaporator at the temperature of -20 °C (Cryostat at 1.91 bar). The Red, yellow and blue curves in Fig.4 refer to the evolution of global conversion ratios of no-additive, Ni-additive and Al-additive adsorbents respectively.

It can be observed that conventional chemisorption composite possessed the best desorption performance with the fastest reaction speed and the lowest equilibrium global conversion ratio, while Aluminium-additive composite obviously held the worst desorption performance, when the adsorbent bed was controlled under the constant heat source of 180°C from oil bath. This contributes to the density of Carbon Coated Nickel/Aluminium, under the high temperature with the enough thermal activated energy, as all the compressed composite had the same density in the adsorbent bed, the Nano-additive composites were less in the amounts of SrCl₂-NEG which absorbs ammonia. The fully adsorbing adsorbent condition is the same as the beginning with the same cryostat pressure and high enough heat source temperature, but the conventional adsorbent adsorbed more ammonia, and then accelerated the desorption. And this also explains the less global conversion ratio of no-additive composite as the Nano-additive adsorbent did not adsorb the same amount ammonia as the traditional one did. Besides, the density of Nickel and Aluminium are 8.9g/cm³ and 2.7g/cm³ respectively, and the addition of the Nano-Ni and Nano-Al are the same, which means SrCl₂-NEG-Al@C had much more volume in Nano particle and less SrCl₂-NEG than Nickel-additive and slowed down the desorption process. Moreover, when the global conversion ratio was over zero the curves showed the reaction of equation (3), as well as this, the further reaction of equation (4) was related to the global conversion ratio that was under zero.



At lower bath temperature (130°C), both Nano-additive composite showed faster desorption rate than traditional SrCl₂-NEG, and adsorbents with Aluminium held the fastest desorption speed in the first 20 minutes while chemisorption composite with Nickel became the most active after 20 minutes reaction. This is because the activating heat source temperature is relatively lower than 180°C and thus could not supply enough energy to boost the reaction process. On this occasion, Carbon Coated metal does much better in compounding heat transfer with mass transfer than conventional composite does. This could be utilized to potentially increase the desorption speed at relatively low temperature and thus reduce both the adsorption cycle time and the overall energy consumption. And all global conversion ratio at heat source temperature of 130°C higher than that at heat source temperature 180°C, which reveals that the desorption process is exothermic in nature.

The adsorption performance tests were also set for investigating the effect of adding Nano particles into SrCl₂-NEG as well. After finishing a fully desorption process, close both V1 and V2 valves on the top of the rig, and cool the adsorbent bed by running water to environmental temperature (20°C). Meanwhile, control the temperature of the ammonia inside the condenser/evaporator by cryostat at a desirable level (10°C and -10°C) and keep it stable. Then open V1 and V2 to start the adsorption performance tests. In these tests, the adsorption performance of this novel chemisorption composite with Nickel is the fastest among all three kinds of chemisorption composite, while Al-additive composite possesses the slowest adsorption performance reaction in both conditions as the consequence shown in Fig.5. It indicates that adding Carbon Coated Nickel into conventional chemisorption composites improves the overall performance of heat and mass transfer by inheriting the desirable thermal conductivity of Ni. While the Al-additive adsorbent reveals that the additional metal may react with SrCl₂ as described in equation (5).



This could result in the consumption of the SrCl₂ and cause the lowest reaction speed and the lowest equilibrium global conversion ratio. The adsorption performance also shows the feasible solution to reduce the sorption cycle time by adding Carbon Coated Nickel into conventional chemisorption composite to boost the reaction speed. Besides, Carbon Coated Aluminium may be employed as negative catalyser in some circumstances where slow but stable adsorption process is in need.

5. Conclusions

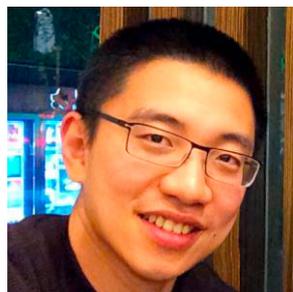
The novel chemical composite adsorbents, the blend of Carbon Coated Nickel or Carbon Coated Aluminium with Strontium Chloride–Natural Expanded Graphite, were formulated and analysed in this research. The conclusions are shown below:

- And by this method, Carbon Coated metal could be evenly distributed into the mixture materials using the methodology aforementioned as it has been proved by SEM and EDX analysis, and could therefore increase the overall thermal conductivity of the adsorbents.
- The Carbon Coated Nickel in the adsorbents improves the overall energy efficiency of the adsorption/desorption system and reduces the cycle time of the system.
- The Carbon Coated Aluminium could just reduce the desorption time at lower temperature (130°C) and may be applied as negative catalyser in adsorption process due to its higher speed in low temperature desorption test and lower speed in adsorption test compared with SrCl₂-NEG respectively.

This research puts forth new chemical composite adsorbents and provides fundamental data for developing more additives for adsorption system. Further research could focus on other metal-additive chemisorption composite using different candidate Carbon Coated metals to enhance the sorption.

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Biography

Dr Yiji Lu, born in June 1989, is currently a research associate in Newcastle University. He graduated from Shanghai Jiao Tong University in 2011 for his bachelor degree, he conducted his M.Phil. and Ph.D. in Newcastle University in 2012 and 2016. His Ph.D. program was fully sponsored by EPSRC and was awarded the '2015 Chinese Government Award for Outstanding Self-financed Students Abroad' from China Scholarship Council. His research interests include but not limited to advanced waste heat recovery technologies, engine thermal management, advanced engine development, engine emission technologies, chemisorption cycles and expansion machines for power generation system. He has been regularly invited to review the manuscripts for the scientific journals including Applied Energy, Applied Thermal Engineering, Energy (the International Journal), and Energy for Sustainable Development.

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