International Journal of Greenhouse Gas Control 113 (2022) 103513

Contents lists available at ScienceDirect

International Journal of Greenhouse Gas Control

journal homepage: www.elsevier.com/locate/ijggc

Development and testing of a new post-combustion CO_2 capture solvent in pilot and demonstration plant

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ARTICLE INFO

Key words:
CO_2 capture
Coal-fired flue gas
Regeneration heat consumption
Capture ratio
Absorption solvent
True heat flux
Reaction heat
Alkanolamine

ABSTRACT

Post-combustion CO_2 capture for coal-fired power plants is an important technical option to mitigate greenhouse gas emission from coal-based power generation. CO_2 capture based on chemical absorption is currently the dominant technology for large-scale capture unit. The main obstacle of commercial application is the high cost and high energy consumption, innovation of new absorption solvent is one of the keys to the performance improvement. Based on the characteristics of flue gas, combined with the analysis and comparison of potential amine components, the formula of blended amines are developed, which is further screened by true-heat flux calorimetric test combined with vapor-liquid equilibrium test, HNC-5 is selected through the lab test, because of its lower heat of absorption and higher capture performance. The test on a 1000 t/a CO_2 capture pilot plant under real flue gas conditions shows that the performance index of HNC-5 is consistent with the lab test results. The CO_2 capture ratio is higher than 90%, and the heat consumption during regeneration is reduced by about 20% compared with MEA. The continuous operation results of the 120,000-ton/year CO_2 capture unit show that heat duty of regeneration of HNC-5 is about 2.8GJ/tCO_2, the cost per ton of CO_2 captured is reduced by about 63 CNY, the usage life is longer, helping improve the system availability and reliability.

1. Introduction

The climate change poses a major challenge to sustainable development of human society. One of the most important tasks for addressing the climate change is to substantially and continuously reduce the emission of greenhouse gas carbon dioxide (IPCC Climate Change, 2014). Carbon capture, utilization and storage (CCUS) technology is one of the options with potential of reducing emission significantly. The relevant research of the International Energy Agency (IEA) has shown that (Agency International Energy, 2016), CCUS technology must be adopted for achieving the goal of controlling the average temperature rise around the globe within 2°C compared with the pre-industrial level because its emission reduction contribution rate ranges from 10% to 20%, and it is the main way to achieve direct emission reduction against the backdrop that the marginal emission reduction contributed by renewable energy substitution and energy efficiency improvement tends to decline with time. China's coal-based energy structure will sustain for a long time and, therefore, CCUS technology is essential for the sustainable utilization of coal-based energy in the future.

The power system is characterized by concentrated emission sources and high CO_2 emission intensity. For example, in 2019 (Liu et al., 2018), the CO_2 emissions from the power system in China are about 3.8 Gt, accounting for 38% of the total carbon emissions generated from the energy utilization process around the country. Capturing CO_2 generated from power plants is one of the most effective ways to achieve carbon emission reduction. Three methods are available for capturing CO_2 in power systems: post-combustion capture, pre-combustion capture and oxy-fuel combustion (Metz et al., 2005). The flue gas emitted from the existing power plants is mainly treated using post-combustion capture method based on chemical absorption technology. As the CO_2 gas source, flue gas emitted from coal-fired power plants is featured with large volumetric flow, low CO_2 partial pressure (<15kPa), and complex composition (including H_2O, O_2, SO_x, NO_x, particulate matters) (Xu and Gao, 2009). Generally, in the chemical absorption method, alkaline absorbent reacts with the acid gas CO_2 to separate CO_2 from the gas phase. The chemical reaction occurs at a large rate. As compared with adsorption method, membrane separation method, the chemical absorption method can achieve quick absorption of CO_2 and larger absorption capacity even under low CO_2 partial pressure condition,

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https://doi.org/10.1016/j.ijggc.2021.103513
Received 24 December 2020; Received in revised form 28 July 2021; Accepted 17 October 2021

making it possible for utilizing a small-capacity equipment to treat a large amount of flue gas. The chemical absorption method has been widely used in power plant CO_2 capture projects. Based on this process, coal-fired power plants in Canada and the United States have implemented pilot projects with a CO_2 capture scale of one million tons/year (Preston et al., 2018, Mantripragada Hari et al., 2019).

A typical chemical absorption process is shown in Fig. 1. As shown in the Fig., the flue gas enters the absorption tower after cooling, and contacts the alkaline absorbent lean solution in counter flow. Through a series of processes including mass transfer, diffusion and reaction, CO_2 becomes unstable compounds that are dissolvable in water under the effect of the absorbent. The resulting rich solution flows into the regeneration tower and exchanges heat with high-temperature steam. As a result, the unstable compounds are heated and decomposed, which is a reverse reaction of CO_2 absorption reaction. This desorption process produces regeneration gas which contains CO_2 and steam. Through the subsequent cooling and purification, CO_2 with a high purity can be obtained, and the regeneration of absorbent performance can be achieved.

The entire process draws on the difference of the CO_2-absorbent-water reaction balance at different temperatures, which is a function of the difference in the CO_2 absorption capacity of the absorbent at different temperatures. Although the balance of the CO_2 chemical absorption/regeneration process is theoretically reversible, additional energy is required to overcome the energy barrier of the regeneration reaction, thereby inducing the reaction to occur. In addition, energy is required to maintain the reaction rate. The absorbent regeneration process consumes the largest amount of heat in the CO_2 capture cycle, mainly involving reaction enthalpy in dissociation of the intermediate compounds, the sensible heat of the absorption solution during the heating process, and the latent heat of water vaporization. Although a portion of the heat can be recovered through the optimization of the heat recovery and regeneration device, most amount of the heat is difficult to be reused due to heat dissipation of the equipment and pipelines and deteriorated quality of the heat recovered in the cooling process of the regenerated gas. During operation, acid gases, such as SO_2 and NO_x, contained in the flue gas will first react with alkaline absorbents, and the resulting products cannot be regenerated at the operating temperature of the CO_2 regeneration tower. Such reaction products are called heat stable salts which accumulate continuously, resulting in continuous loss of active ingredients in the absorption solution. Most organic absorbents will react with the oxygen in the flue gas, causing irreversible oxidative degradation or oxidative degradation at high temperatures. The degradation of absorbent is an important reason for the loss of absorbent. In addition, some degradation products are highly corrosive to the equipment, which not only increases maintenance costs, but also affects the reliability of the equipment. The above degradation and corrosion will lead to increased operating costs. Therefore, how to reduce the energy consumption and cost of CO_2 capture technology is a major challenge for the development of this technology, and the solution hinges on the development of new high-efficiency and low-energy absorbents.

2. Alcohol amine-based chemical absorption method

The commonly used chemical absorbents include alcohol amines, ammonia, amino acid salts, carbonates, etc. (Yang et al., 2014, Guo et al., 2013, Xi et al., 2012, Rochelle Gary, 2009, Jockenhoevel et al., 2009). New types of absorbents include phase-changing absorbents, ionic liquid, nanofluids, etc. (Fang et al., 2015, Xu and Wang, 2018, Huang et al., 2017, Yu et al., 2019). At present, the absorbents used in engineering applications mainly include blended amine absorbent dominated by organic alcohol amines, and composite absorbents containing organic alcohol amines. Monoethanolamine (MEA) is representative of alcohol amine. As one type of organic molecule, its functional group is characterized in that it contains amino and hydroxyl groups. The amino group can be dissociated as basic centers and react with CO_2; hydroxyl group can contribute to increased solubility of molecules in water. In terms of the number of hydrogen atoms around the amino nitrogen atom, alcohol amines can be classified into:

Primary amine (2 hydrogen atoms), such as MEA;

Secondary amine (1 hydrogen atom), such as diethanolamine (DEA), diisopropylamine (DIPA);

Tertiary amines (no hydrogen atoms), such as triethanolamine (TEA), N-methyldiethanolamine (MDEA).

The difference of the substituent group on the amino nitrogen atom can cause changes in the dissociation characteristics of the amino group, which not only affects the absorption reaction path, but also the reaction thermodynamics and kinetic parameters. In terms of reaction mechanism, there are two main pathways for absorption reaction (Conway

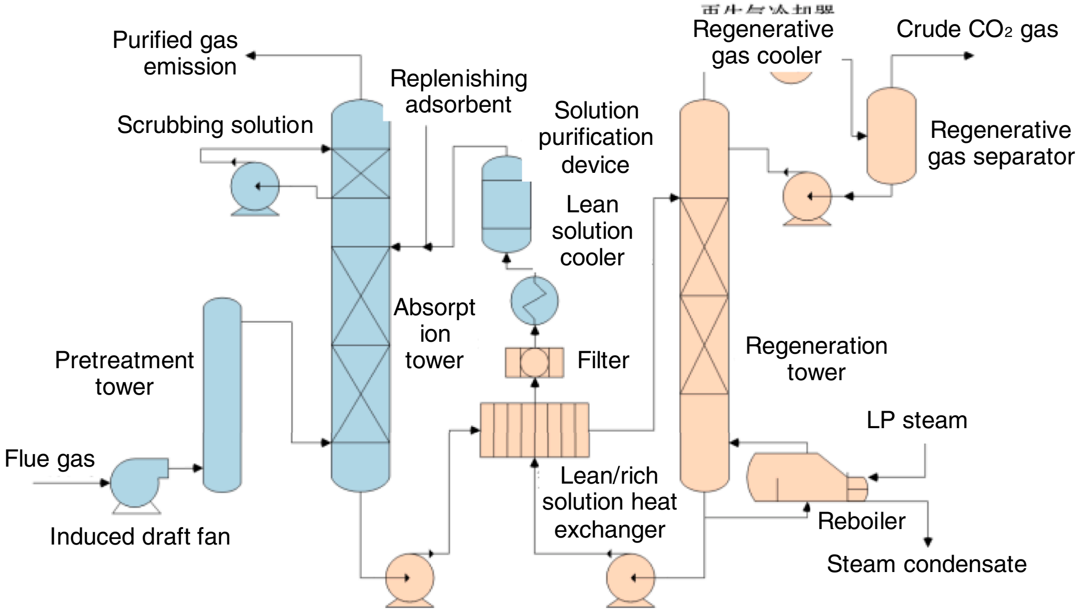

Fig. 1. Diagram of CO_2 chemical absorption process.

et al., 2013): (i) carbamate pathway; (ii) bicarbonate pathway. The reaction speed of pathway (i) is much higher than that of pathway (ii). The absorption reaction of primary and secondary amines takes pathway (i) as the main reaction and proceeds at a stoichiometric ratio of 2:1. As the hydrogen atoms on the tertiary amine amino are completely substituted by the substituent group and cannot be directly hydrolyzed to produce protons, only pathway (ii) is possible. Although the stoichiometric ratio of pathway (ii) is 1:1 and theoretically the absorption capacity per mole is larger, the reaction rate in pathway (ii) is too low under normal pressure and is of no significance in industrial application. As a result, accelerators are required. By changing the geometric characteristics of the molecule, the reaction can be deviated towards pathway (ii) with lower energy consumption. For example, introducing a sterically hindered substituent group on the carbon atom adjacent to the amino group to form a hindered amine can reduce the probability of amino group coming contact with CO_2 molecules, thereby facilitating the progress of reaction pathway (ii).

In respect of the relationship between the reaction kinetic parameters and the geometric characteristics of the alcohol amine molecule, studies have found that the dissociation constant pKa of the alcohol amine molecule in water is proportional to the reaction rate (Nitta et al., 2014, Joback Kevin and Heberle, 2017). pKa is an equilibrium constant that characterizes the alcohol amine molecule's ability of ionizing hydrogen ions. Given the similar mass transfer rate, the greater the pKa, the stronger the alkalinity and the faster the absorption reaction rate. Primary amine, secondary amine and tertiary amine are in descending order in terms of pKa, reaction speed. The application of primary amine and secondary amine is beneficial to shorten the reaction time and even small equipment can achieve the expected capture scale. However, in this case, the enthalpy of formation of the intermediate compound is higher, and the regeneration reaction requires higher temperature and more heat.

The selection of absorbent also needs to take account of the impact of absorbent viscosity and surface tension on gas-liquid mass transfer. Reduced surface vapor pressure of absorbent can avoid absorbent loss and secondary emission of pollutant components caused by absorbent volatilization and reduced corrosion of the absorbent on the capture device (Kittel and Gonzalez, 2014) can reduce the operating cost of the equipment and improve the reliability of the system. Moreover, the selected absorbent shall have stable chemical property, and can be resistant to gas impurities, especially oxygen side reactions, and reduce the degradation loss of absorbent (Liu et al., 2014). In practical applications, the raw materials of the selected absorbent shall be available from a great variety of sources and enjoy lower costs, facilitating the large-scale promotion of the absorbent. In summary, it is necessary to carry out comprehensive design of the physical and chemical properties of absorbent molecules in order to improve the overall performance of absorbents through trade-off and combinations of various factors.

In the development of absorbents, new molecules can be designed and developed based on the structure-activity relationship between the structure and chemical properties of a single molecule. On this basis, several types of absorbents can be blended to comprehensively utilize the characteristics of different absorbent components, thus obtaining a combination of absorbents with the highest overall efficiency of the absorption/desorption cycle and the lowest energy consumption for CO_2 capture. This is also a commonly used strategy in the development of absorbents. In the previous research on evaluating the performance of mixed amine absorbents, the researchers mostly focus on the measurement of vapor-liquid equilibrium (VLE) and reaction rate. Some studies focus on the enthalpy of CO_2 absorption/regeneration. As the measurement of reaction enthalpy is affected by the blending method, measuring principle and equipment difference, the reported reaction enthalpy values vary greatly. Moreover, there is also a lack of measuring devices and methods that combine thermodynamics, kinetics, and reaction enthalpy. This results in a certain deviation in the comprehensive evaluation of absorbent performance.

In view of the important role of CO_2 absorbents in improving the performance of CO_2 capture technology, the heat flux method and thermodynamic equilibrium integrated reactor are used in this paper to carry out comprehensive performance test of compound mixed amine absorbents, in order to screen out new type of absorbent with desirable performance, and demonstrate such performance through pilot test. Further, the new type of absorbent has been used in engineering applications to verify its long-term performance and economy.

3. Performance analysis in laboratory

Planar molecules with desirable structural rigidity are selected based on absorption capacity, cycle capacity, reaction rate, molecular stability, volatility, viscosity and other parameters of alcohol amine monomer. They are combined and compounded with tertiary amines, sterically hindered amine s and accelerator molecules to form four kinds of alternative combinations. Each of the combinations comprises 3-4 kinds of alcohol amine monomers, supplemented by carbonate for adjustment purpose. A real heat flux reaction calorimeter is employed to test the four combinations for absorption reaction air-liquid equilibrium curve and reaction enthalpy. And the test results are compared with the relevant parameters of MEA.

3.1. *Real heat flux reaction calorimeter*

The CPA201 real heat flux reaction calorimeter manufactured by ChemiSens is employed. The components of the calorimeter are as shown in Fig. 2, mainly comprising reactor, thermostat, air/liquid inflow controller, temperature and pressure sensor, control unit and human-computer interaction interface. The reactor is the component where the reaction occurs and is the core unit for parameter measurement. It is immersed in the constant temperature medium in the thermostat. The structural schematic diagram of the reactor is shown in Fig. 3. The top cover and base of the reactor are made of 316L stainless steel, and the top cover is provided with a sensor and a stirring device which can record the temperature and pressure of the gas phase medium inside the reactor. The reactor wall is in form of a double-layer glass jacket which provides a thermal insulation layer. The heat transfer between the reactor and the external constant temperature environment only occurs through the base. The base is provided with a thermocouple to measure the temperature of the liquid. The Peltier element in the base receives the signal from the control unit to heat or cool the medium, allowing the liquid temperature inside the reactor to reach the set temperature. Inside the reactor, a heat flow sensor is provided on the heat transfer path between the liquid and the Peltier element to record the heat flux value of the heat transfer process in real time.

The main technical indicators of the calorimeter are as follows: constant-temperature heating bath capacity 13L, reactor capacity 250 mL, liquid measurement volume: 10~180mL; reactor test pressure range: from vacuum to 2MPa; test temperature range: -10℃ to 160℃; test modes: constant temperature, temperature scanning, constant heat flux, variable temperature, ambient constant temperature; heat detection limit: 5J; power resolution: 0.03W. It can be used to accurately measure the heat change in the reaction system. The reactor has been subjected to calorimetric check within its test temperature range before the experiment.

3.2. *Test method with calorimeter*

During the CO_2 absorption reaction measurement process, add about 100 mL of absorbent solution into the reactor, and immerse the reactor into a constant temperature medium (propylene glycol). When the reactor reaches a constant temperature, that is, the solution temperature reaches the set value and maintains at it for 200 seconds, while the heat flux change is less than 0.05W, inject CO_2 into the reactor at fixed flow and in batches. In the experiment, the control steps of the injecting gas in

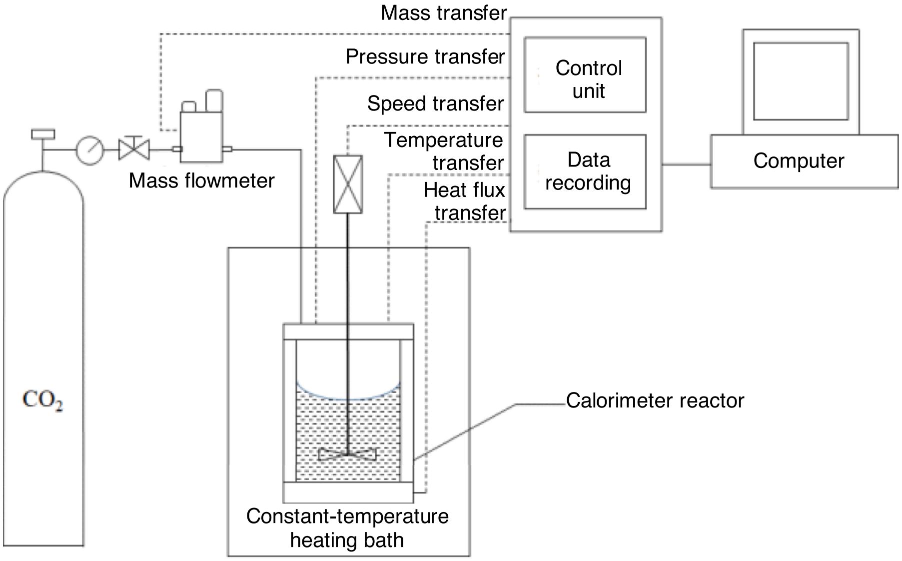

Fig. 2. Diagram of reaction calorimeter apparatus.

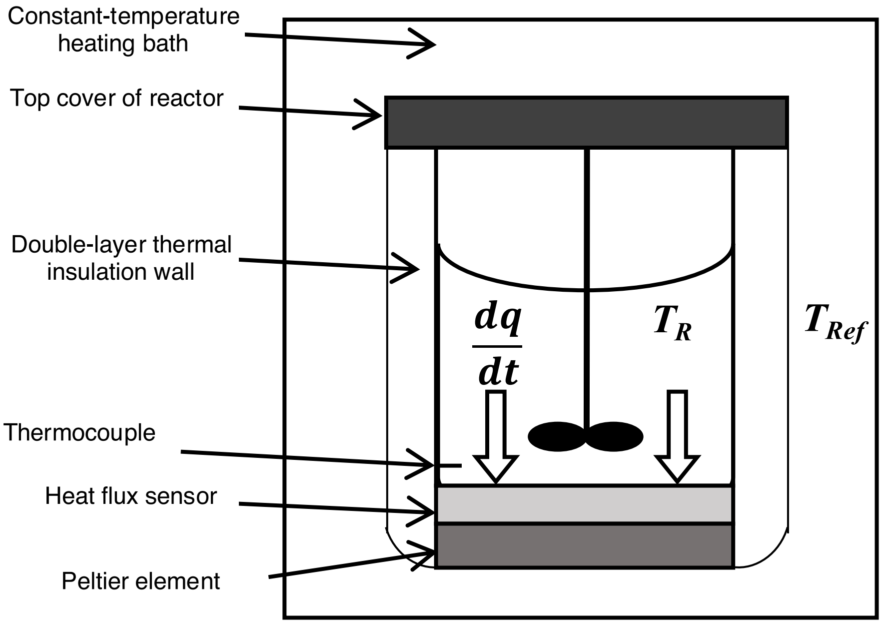

Fig. 3. Diagram of calorimeter reactor (arrow indicating the heat transfer direction).

batches are as follows:

Step 1: Set the temperature to 40°C, and heat up the reactor and the constant-temperature heating bath at the same time;
Step 2: Once the reactor reaches the above constant temperature, open the CO_2 inlet valve to control the inflow rate, and close the inlet valve when the single inflow amount reaches the preset value;
Step 3: Wait for the reactor to reach the constant temperature again, indicating that the single inlet gas reaction has reached equilibrium;
Step 4: Return to Step 2 to repeat the cycle, until the total mass of inlet CO_2 reaches the set value or the gas pressure inside the reactor reaches the set value;

Some original data obtained directly during the experiment is shown in Fig. 4 (only two dosing cycles are shown here).

The measurement method of real heat flux and the calculation method of absorption enthalpy are detailed in reference (Xu et al., 2015, Guo et al., 2016).

3.3. Test results

The performance test of absorbent is based on the MEA solution. Fig. 4 shows the change of absorption enthalpy of MEA solution (30% by weight) loaded with CO_2 and CO_2 partial pressure in the gas phase as a function of CO_2 molar load of the absorbent at 40℃. In the figure, the differential enthalpy (ΔH_{diff}) is defined as the ratio of the heat released by the absorption reaction after a single CO_2 inlet to the amount of CO_2 added at a time, kJ/mol; the integral enthalpy (ΔH_{int}) is defined as the ratio of the total amount of heat released by the reaction system starting from the initial CO_2 inlet to the total amount of CO_2 absorption, kJ/mol. Conventionally, reaction enthalpy is measured by adding CO_2 into the solution continuously until the saturation condition is achieved, and

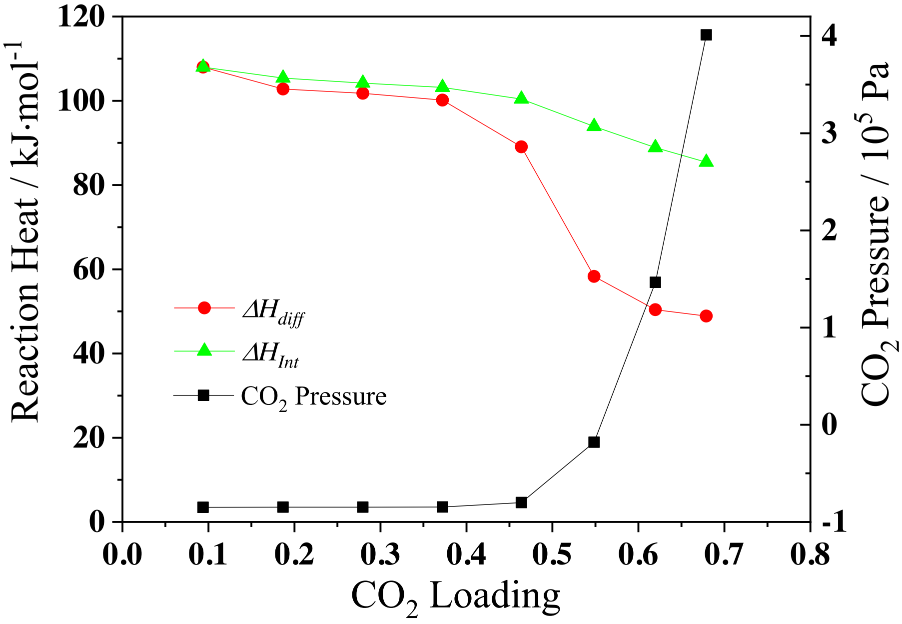

Fig. 4. VLE and reaction heat diagram of absorption reaction between 30% by weight MEA and CO_2 at 40℃.

then calculating the average absorption enthalpy based on the total amount. Thus, the integral enthalpy is obtained. Repeat the measurement for at least twice, and the data deviation shall be within 5%.

At a molar load smaller than 0.5, MEA absorbent (30% by weight) has a differential absorption enthalpy, ΔH_{diff}, of about 100 kJ/mol, which is close to the theoretical calculation value (Gupta et al., 2013), and slightly higher than the values measured by calorimeters in the previous literature, 80-95 kJ/mol (Kim and Svendsen Hallvard, 2007, Kim et al., 2009). The gas inlet rate, gas phase pressure in the absorption reaction, reaction temperature, pre-calibrated value of the heat flux sensor, etc., all have an impact on the measured value of the absorption enthalpy. Therefore, with the same instrument, condition and operation method, the difference of absorption enthalpy between different absorbents can be obtained in a unified system, thereby measuring the regeneration enthalpy of the regeneration reaction.

Figs. 5–8 show the change of absorption enthalpy of four alternative mixed amine solutions (30% by weight) and CO_2 partial pressure in the gas phase as a function of CO_2 molar load of the absorbent at 40℃.

In industrial applications, the CO_2 molar load of alcohol amine absorbent is obtained through simulation and operation optimization. On the one hand, it is necessary to increase the difference of molar load between rich solution and lean solution, namely, to increase the capacity of the absorption/regeneration cycle; and on the other hand, it is also necessary to control the regeneration temperature and time and hence the heat consumption of regeneration. Generally, the CO_2 load of rich solution is 0.5-0.6; that of lean solution is 0.2-0.3. Therefore, the use of absorbents with a smaller reaction enthalpy for CO_2 load less than 0.6 is more conducive to reducing heat consumption. Through comparison, it follows that, among the four formulas above, Formula 4 has the lowest absorption enthalpy, which is more than 20% lower than that of MEA.

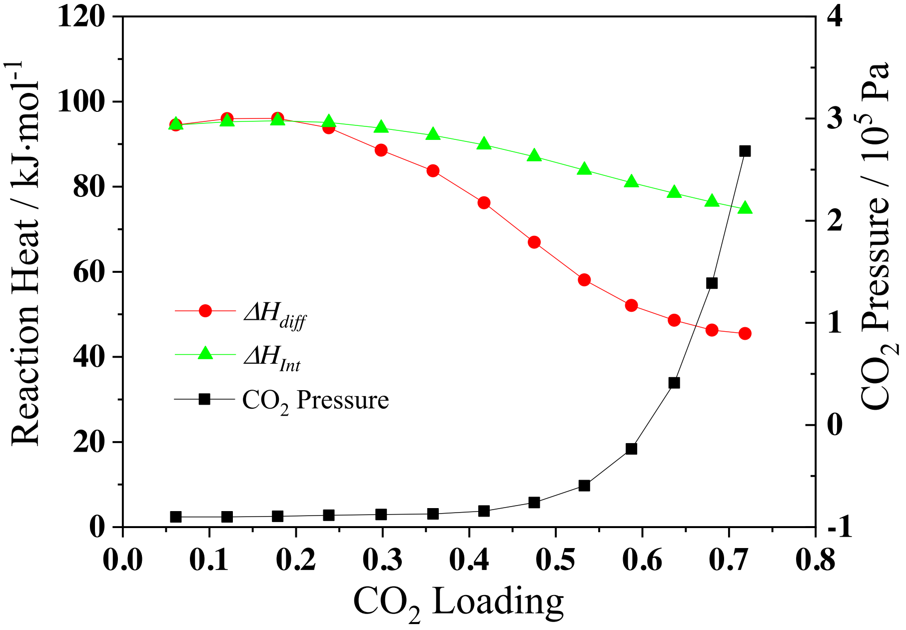

Fig. 5. VLE and reaction heat diagram of absorption reaction between Formula-1 (30% by weight) solvent and CO_2 at 40℃.

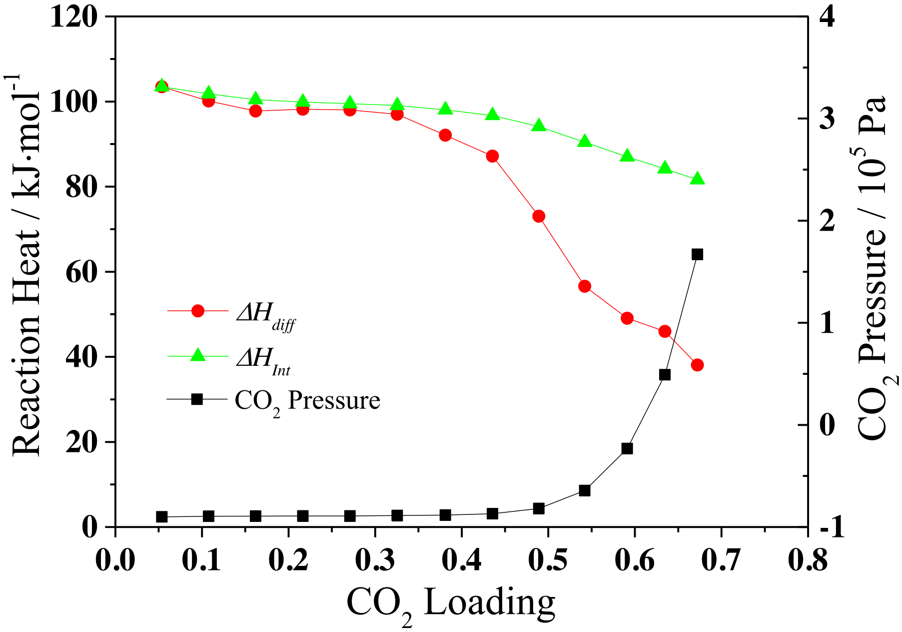

Fig. 6. VLE and reaction heat diagram of absorption reaction between Formula-2 (30% by weight) solvent and CO_2 at 40℃.

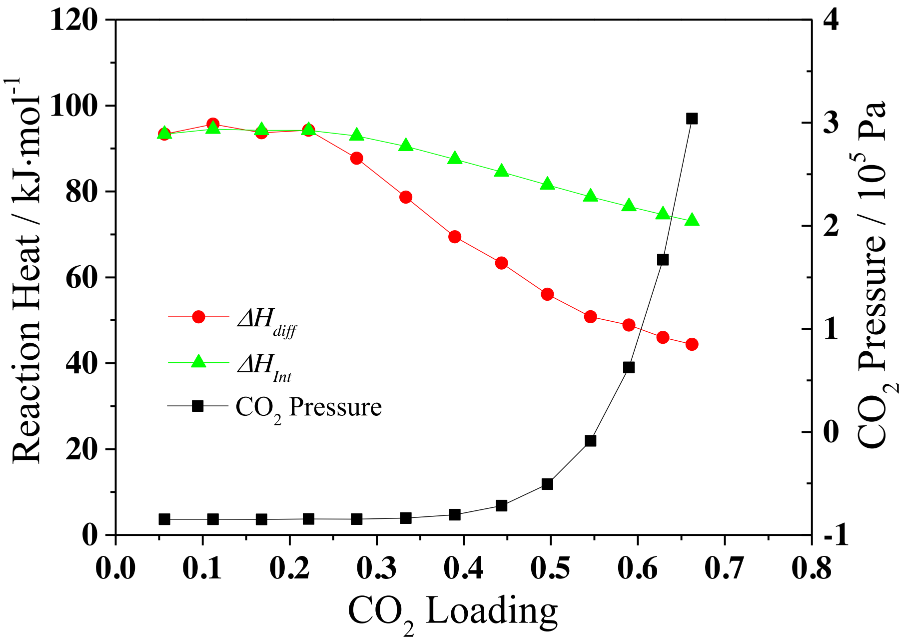

Fig. 7. VLE and reaction heat diagram of absorption reaction between Formula-3 (30% by weight) solvent and CO_2 at 40℃.

As such, Formula 4 is superior to MEA in terms of both reaction rate and reaction enthalpy. The further physical parameter measurement shows that the viscosity of Formula 4 is comparable to that of MEA, and the absorbent phase is stable during the reaction process. Therefore, Formula 4 is selected as the preferred component to carry out subsequent scale-up test and demonstration, and it is named with HNC-5.

4. Pilot test

4.1. Pilot test plant

In order to verify the capture performance of the novel absorbent HNC-5 under the real flue gas conditions of coal-fired power plants, an operational test of 1,000-ton/year CO_2 capture pilot test plant of Huaneng Changchun Thermal Power Plant was performed, plant photo see Fig. 9. The test result has been compared with the previous basic performance test of MEA solution as well as the laboratory test data.

The structure of the pilot plant and the basic operation test of MEA are detailed in references (Wang et al., 2015; Feron et al., 2017). The feedstock gas of the pilot plant is draw from the scrubbed flue gas through FGD (Flue Gas Desulfurization). A flue gas pretreatment unit is installed in front of the absorption tower to control the inlet gas temperature and acid gas composition. The design flow of inlet gas is 500Nm^3/h, the design capture capacity is 100~125 kg/h, the design specific surface area of the packing is 250m^2/m^3, the design absorption temperature is 40~60℃, and the design regeneration temperature is 115-125℃.

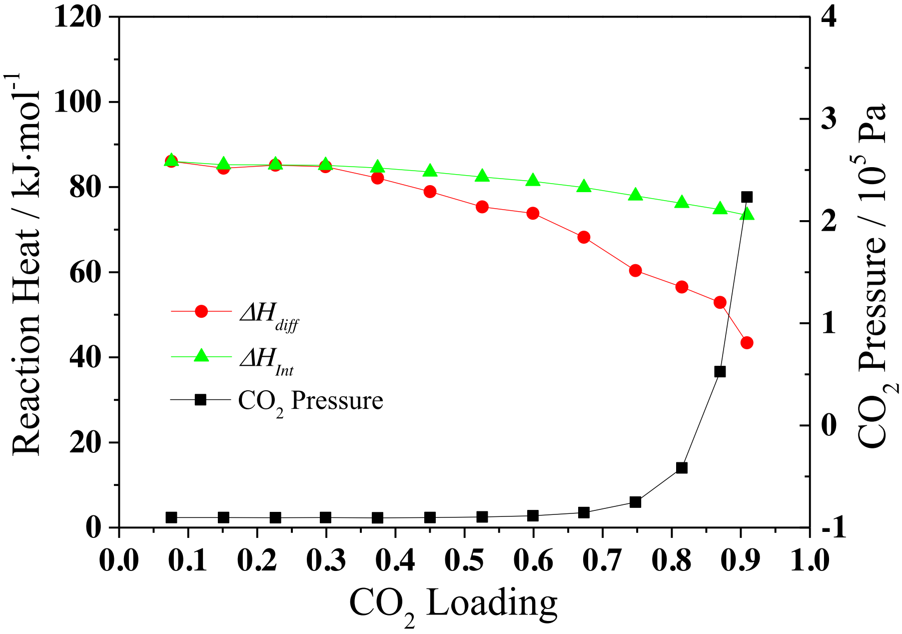

Fig. 8. VLE and reaction heat diagram of absorption reaction between Formula-4 (30% by weight) solvent and CO_2 at 40℃.

Fig. 9. Photo of 1000t/a CO_2 capture pilot plant in Changchun Thermal Power Plant.

4.2. *Pilot test results*

The main operating parameters during the performance test of HNC-5 absorbent are as follows: the flue gas flow at the inlet of the absorption tower is maintained at about $450 Nm^3/h$, and the volume fraction of CO_2 in the flue gas is maintained in the range of 11.0-11.5%, as shown in Fig. 10.

Through operation optimization, the HNC-5 aqueous solution (lean solution) with a mass fraction of 25% was added from the top of the absorption tower to react with the flue gas at a liquid-to-gas ratio of 2.5. The volume fraction of CO_2 in the flue gas at the outlet of the absorption tower is reduced to about 1.0%. The capture rate of the absorption plant for CO_2 in the flue gas is maintained above 90%. The operating temperature of the reboiler at the bottom of the regeneration tower is maintained at about 110°C. Through calculating the steam consumption rate, it is found that the heat load of the reboiler during operation, namely, the heat consumption for regeneration of HNC-5 in producing per unit of CO_2, is about $3.0 GJ/tCO_2$. The uncertainty of the data result is about 5%, see Fig. 11.

In the previous benchmark performance test of MEA solution under the same conditions of the plant, when the liquid-to-gas ratio of the MEA lean solution to the flue gas in the absorption tower is 4.0, the energy consumption of the system during optimized operating condition is the lowest, and the MEA regeneration heat consumption is $3.6 GJ/tCO_2$. Fig. 12 reflects the change of the gas pressure in the reactor, while inject the same amount of carbon dioxide into the 30wt.% MEA and 30wt.% HNC-5 solution system of the same quality respectively. The curve shows that HNC-5 absorbent has a faster absorption reaction rate than MEA, therefore, the system can operate at a lower liquid-to-gas ratio, while maintaining the specified CO_2 capture rate and CO_2 yield. At 90% capture rate, the regeneration heat consumption of HNC-5 absorbent for CO_2 capture is about 20% lower than that of MEA, which is basically consistent with the experimental measurement.

5. Engineering application

5.1. *Capture system*

After the pilot performance test is completed, HNC-5 absorbent was officially used in the industrial capture plant: 120,000 tons/year CO_2 capture system of Huaneng Shanghai Shidongkou Second Power Plant. It is constructed as a supporting project for Shidongkou Second Power Plant Phase II 2x660MW domestic ultra-supercritical units. With a design flow of $66000 Nm^3/h$, it comprises a capture area and a refining area, and can produce food-grade purity CO_2 products. It was completed in 2009. Afterwards, the system has been subjected to development and demonstration of several new technologies, including flue gas pre-treatment, waste liquid disposal, new types of equipment as well as system anti-corrosion. After renovation, it has an operating time of more than 2000h per year since 2015, making it the largest post-combustion CO_2 capture device with the longest cumulative operating time in China today (Wang and Xu, 2014).

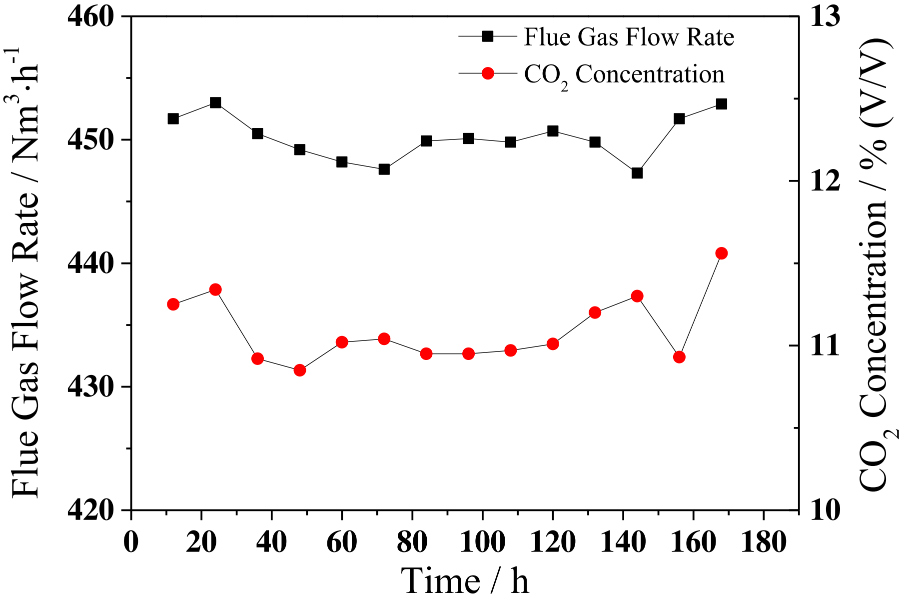

Fig. 10. Flue gas parameters during pilot test of HNC-5.

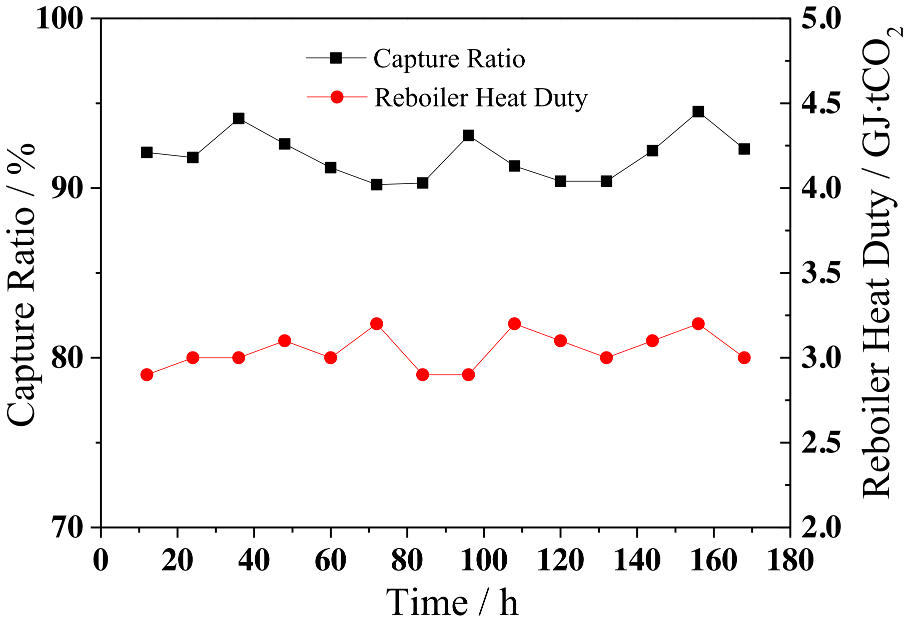

Fig. 11. Capture performance of HNC-5 during pilot test.

5.2. Test results

In the demonstration operation of HNC-5 absorbent, the initial concentration comparable to the previous MEA-based absorbent operation is adopted, with a mass fraction of 25%-30%. The comparative test is mainly intended to investigate the tolerance and reliability of the absorption solvent under actual industrial flue gas conditions and obtain the loss data of the absorbent in the long-term operation of the industrial-scale plant, and to measure the regeneration heat consumption based on the steam consumption rate. Table 1 summarizes the typical comprehensive performance data and economic indicators of HNC-5 absorbent and MEA-based absorbent.

It follows from the above table that, when HNC-5 absorbent is used, the cost of raw material consumption per ton of CO_2 produced by the capture system is reduced by CNY 25.02, a decrease of 29.6%; the steam consumption is reduced by 0.63GJ, a decrease of 18.4%. Assuming that the cost of steam per GJ is CNY 60, the operating cost can be reduced by CNY 37.8 due to the reduction of steam consumption. As such, the total production cost per ton of CO_2 by the system is reduced by CNY 62.82 when HNC-5 absorbent is used. The absorbent regeneration heat consumption measured on the demonstration plant is even lower because that the heat dissipation of the packed tower and pipeline is relatively less due to increased size of the capture equipment, which is more conducive to reducing the energy consumption for capturing each ton of CO_2.

During the demonstration operation, the HNC-5 absorbent exhibited desirable stability and reliability, which mainly lies in that the loss of the absorbent is significantly less than that of MEA, see Fig. 13. During the test, the mass fraction of MEA in the lean solution was reduced from 25.13% to 13.46%, and its concentration was reduced by about 46.44%, which is attributable to the entrainment of liquid droplets by the flue gas, the evaporation of MEA itself and the degradation loss. As a chain-

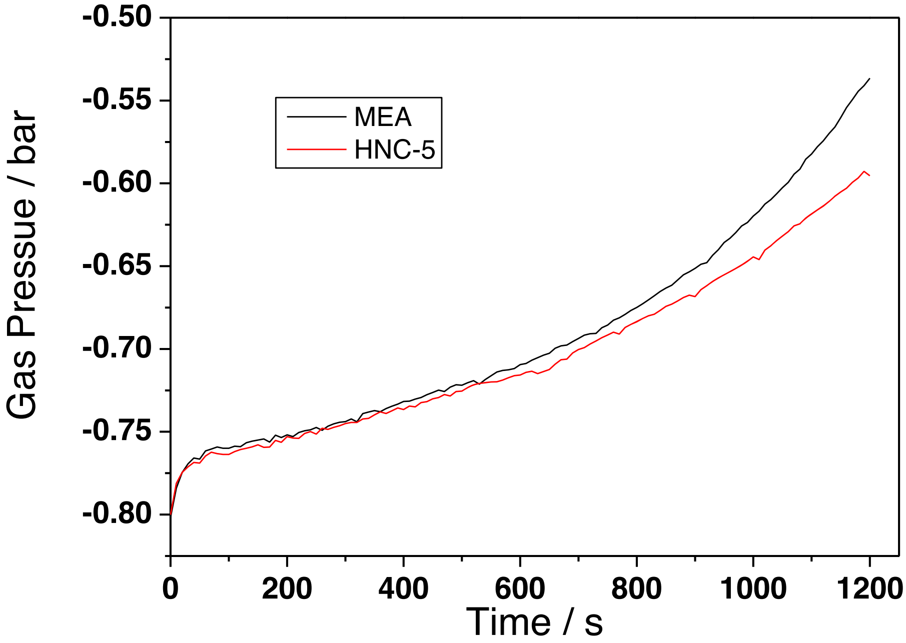

Fig. 12. Partial pressure change curve of carbon dioxide after absorption reaction with MEA and HNC-5.

Table 1
Operation performance index and capture cost using MEA and HNC-5 absorption solvent.

Item	Unit	MEA	HNC-5
Absorbent consumption	kg/tCO_2	4.69	1.32
Unit price of raw material	CNY/kg	18	45
Cost of absorbent raw material	CNY/tCO_2	84.42	59.4
Steam consumption	GJ/tCO_2	3.43	2.8
Heat consumption cost	CNY/GJ	60	60
Steam cost in operation	CNY/tCO_2	205.8	168

shaped small molecule, MEA is prone to oxidative degradation and polymerization reactions. The test on composition of the absorbent also reveals the rapid accumulation of formate, acetate, and oxalate over time, indicating continuous degradation of MEA during operation. Under the same operating conditions, the mass fraction of the active ingredients of HNC-5 absorbent is maintained at a concentration range of 25%-21% for a long time (over 500h), and the accumulation rate of degradation products is only 10%-20% of MEA. This shows that the stability of the chemical structure of absorbent can increase the service life of the absorbent, thereby improving the availability and reliability of the capture system.

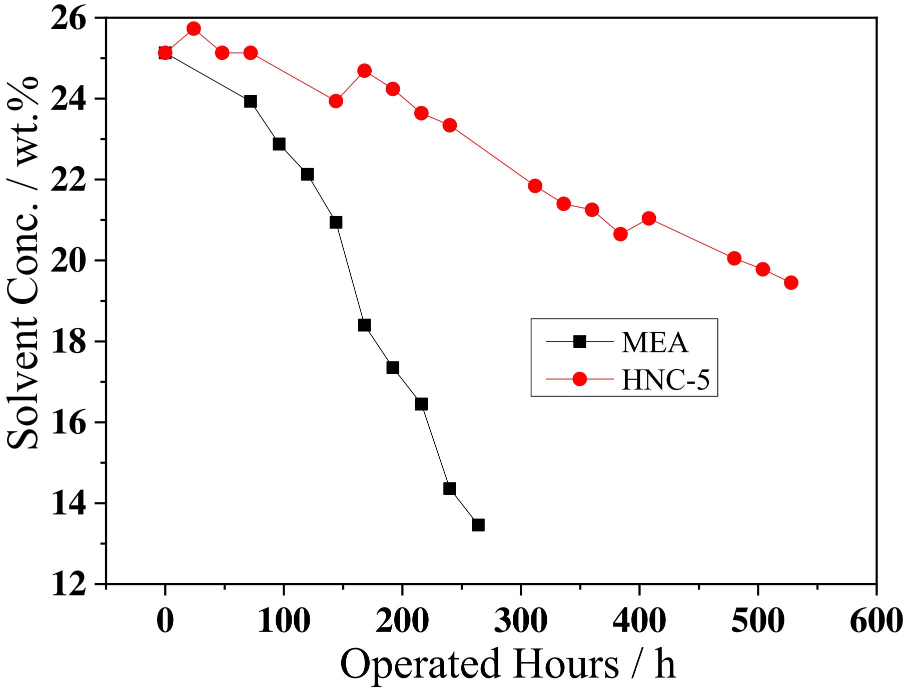

Fig. 13. Solvent concentration (by weight) loss of MEA and HNC-5 during demonstration operation.

6. Conclusions

The post-combustion capture technology based on chemical absorption method is an important technical option for CO_2 emission reduction in coal-fired power plants. To overcome the disadvantages of high capture cost and high energy consumption of this technology, it is necessary to improve its overall performance through innovation of absorbents. Based on the analysis of the alcohol amine absorbent monomer, this study has optimized four compound mixed amine absorbent combinations. Through comparison test with MEA as the reference and heat flux calorimeter, it is found that Formula 4 enjoys more desirable performance, which is named HNC-5. HNC-5 absorbent was applied to the 1,000-ton/year CO_2 capture device of Changchun Thermal Power Plant to test and compare the capture performance of MEA and HNC-5 absorbent. As compared with MEA absorbent, HNC-5 absorption solution can maintain a capture rate of CO_2 in flue gas larger than 90% during operation of the plant, and the regeneration heat consumption is about 3.0GJ/t CO_2, which is about 17% lower than that of MEA. By applying HNC-5 absorbent in the 120,000 tons/year CO_2 capture demonstration device, it is found that, under the same operating conditions, the capture performance and anti-degradation performance of HNC-5 absorbent have been greatly improved, and the heat consumption for capture is about 2.8GJ/tCO_2, contributing to a save of CNY 63 for capturing each ton of CO_2. The performance parameters of the pilot test and demonstration operation agree with the laboratory results well, indicating that the integrated reaction equilibrium and calorimetric test is a new type of comprehensive and reliable CO_2 absorbent development test method.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge the financial support of National key R&D program of China (2019YFE0100100, 2018YFE0116800) and Huaneng S&T Project (HNKJ20-H58)

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