



GHGT-10

CO₂ Capture by Improved Hot Potash Process

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Abstract

Global climate warming caused by emission of greenhouse gas including CO₂ is one of serious problems nowadays. In an effort to mitigate CO₂ emissions, one of most effectively clean energy plan is to produce power from coal using the integrated gasification combined cycle (IGCC). However, the cost of existing CO₂ capture technologies is still too high. Utilization of large-solubility and low-cost absorbent for CO₂ capture in IGCC can effectively reduce the electricity price increase caused by addition of CO₂ removal unit. As it needs to trap CO₂ before combustion under high pressure in IGCC absorption is considered to be a better choice.

HPP (Hot Potash Process) uses aqueous solution of potassium carbonate as the absorbent. Compared to physical solvent absorption method Rectisol and Selexol, HPP has relatively low investment and relatively high CO₂ recovery. Even in comparison with other chemical absorbent amine method HPP still has advantages as good chemical stability and low vapor pressure.

In this paper several activators piperidine, piperazine, pyrazine, morpholine, imidazole, N-hydroxyethyl piperazine, N-aminoethyl piperazine, AMP was tested respectively at 70°C. As a result, piperidine activation works best, followed by N-(2-hydroxyethyl)piperazine, N-(2-aminoethyl) piperazine, 2-amino-2-methyl-1-propanol and piperazine, pyrazine and imidazole is at its worst. Among them, N-(2-hydroxyethyl)piperazine is less volatile, more stable and suitable as the activator. Absorbing capacity and absorbing rate of CO₂ in carbonate aqueous solution with HPZ increases by 5% or more than those with PZ.

An improved HPP process is presented adopting the new activator. In this process two de-absorption two columns is designed operating at different pressure. This makes it possible to reuse the heat of condensation during high pressure de-sorption in re-boiler of low pressure de-sorption. By preliminary calculating the novel process can save energy consumption obviously. The steam consumption, cooling water consumption and power consumption declines by 43.30%, 31.81% and 10.57%, respectively. It is expected to develop a low-cost technology for capture CO₂ from IGCC in the future.

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Keywords: Type your keywords here, separated by semicolons ;

1. Introduction

Global climate warming caused by greenhouse gas emission is one of serious problems nowadays. It had been point out in Nature that once earth was beyond the limit not clear currently dramatic change of climate would occur. A number of data shows that main cause resulted in global warming is excessive emission of greenhouse gas including CO₂ by human activity¹⁻³. Manifesto of UNITED NATIONS CLIMATE CHANGE CONFERENCE COPENHAGEN emphasized that climate change is one of great challenge for mankind we should make effort to stabilize the atmospheric concentration of greenhouse gas and restrain the deterioration of global climate⁴.

In the future for a long period time China is still using coal as the main fuel. As the CO₂ emissions from thermal plant accounts for 60% of all CO₂ emissions in China, it is particularly important to reduce CO₂ emissions from the existing and new coal-fired plant. In view of higher power generation efficiency and better environmental compatibility IGCC(Integrated Gasification Combined Cycle)^{5,6} is a promising clean coal power generation technology.

Although IGCC with pre-combustion CO₂ capture technology has advantage of high pressure and low consumption, there are still some shortcomings for existing capture technologies, such as Rectisol, Selexol and PC process⁷. It is urgent to further develop low-cost CO₂ capture technologies.

CO₂ capture methods are mainly as follows: absorption, adsorption, membrane separation, biological transformation and hybrid of two or three separation technologies.

Since absorption has such advantages as large capacity, high efficiency and good industrial performance, it always has been favored by researchers. Currently there is an urgent need to address is how absorption is reasonable applied in thermal power and how to further reduce the cost of CO₂ capture⁸⁻¹⁶.

HPP (Hot Potash Process) uses aqueous solution of potassium carbonate as the absorbent^{7,17-19}. Compared to physical solvent absorption method Rectisol and Selexol, HPP has relatively low investment and relatively high CO₂ recovery.

Even in comparison with other chemical absorbent amine method HPP still has advantages as good chemical stability and low vapor pressure.

HPP was presented early in the 1950s and has continuously improved to raise absorption rate and increase the corrosion resistance. Arsenic trioxide and glycine, boric acid and alkyl alcohol amine was ever used to improve effect of HPP. Sterically hindered amine once became a hot topic using as absorption activator. Recently a very long period time piperazine compounds attracted wide concern from researchers. As piperazine compound has cyclic di-amine structures it is helped to fix CO₂ by forming carbamate. And the absorption capacity increases due to adding piperazine, energy consumption will be greatly reduced²⁰⁻²⁴.

In view of the above reasons some nitrogen-containing heterocyclic compounds few reported previously was tested further in this paper to improve HPP²⁵. Solubility of CO₂ in potassium carbonate aqueous solution coupling activators was determined to evaluate the absorption performance under high pressure.

2. Experimental and data Processing

2.1 Materials

Specifications and sources of reagents used in experiment are listed in Table 1.

Table 1 specifications and sources of reagents

Regent	Specification	Source
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CO ₂ (gas)	>99.95% (vol)	Beijing APBAIF Gases Industry Co
Potassium carbonate	99.5%(wt)	Shanghai International Aladdin Regent Inc.
Piperidine	99.5%(wt)	Shanghai International Aladdin Regent Inc.
Piperazine	99%	J&K China Chemical Ltd, Beijing
Morpholine	99%	Shanghai International Aladdin Regent Inc.
Imidazole	99%(wt)	J&K China Chemical Ltd, Beijing
Pyrazine	99%(wt)	J&K China Chemical Ltd, Beijing
N-hydroxyethyl piperazine	98.5%(wt)	J&K China Chemical Ltd, Beijing
N-aminoethyl piperazine	99%(wt)	Shanghai International Aladdin Regent Inc.
2-Amino-2-methyl-1-propanol	99%(wt)	J&K China Chemical Ltd, Beijing

The water used in experiment was de-ionized water.

2.2 Apparatus and experimental procedures

2.2.1 Description of the Apparatus

A constant-volume method was used to determine the solubility of CO₂ in solvent, which was described in detail by Ning Ai^{26,27}. In this work, integral ball valve was replaced and leakage of apparatus was effectively prevented. Accuracy of measurement has been improved further.

Compared with other measure techniques, the constant-volume method can be used to measure the VLE data simply and precisely. Further more, this method can also avoid the accumulate errors caused by the decompression stage in the direct measurement.

2.2.2 Experimental procedures

As described by Ning Ai^{26,27}.

2.2.3 Screening of activators

0.05 Mol different activators piperidine, piperazine, pyrazine, morpholine, imidazole, N-hydroxyethyl piperazine, N-aminoethyl piperazine, AMP were added in potassium carbonate solution and evaluated CO₂-absorbing capacity according to the above method in 2.2.2 at 70°C,. Results were listed in Figure 1.

2.2.4 Determination of series of VLE data at different temperature

Since hydroxyethyl piperazine had better activation effect it was chosen as the activators in further experiments. At a certain temperature and a certain pressure the moral concentration of CO₂ in solution was obtained according to the above method in 2.2.2. Changing temperature and pressure and repeating the above data processing a series of VLE data could be available at different temperatures and pressures, as shown in Figure 3.

2.3 Data processing

As described by Ning Ai^{26,27}.

3 Results and Discussion

3.1 Reliability test of experimental setup

The solubility of CO₂ in water was measured at high pressure to verify the reliability of apparatus used in this study. In this paper, it is assumed that pressure has little effect on the value of Henry's constants. As shown in Table 2, the Henry's constants measured are in the range of 0.2 to 1.4 MPa,

Table2 Comparison of Henry's constant from work and from literatures

H(MPa, this work)	H(MPa , literature	Relative errors
184.7	186.0 ^[28]	-0.699%
	183.9 ^[29]	0.435%

Compared with the literature data ^{28,29}, the deviations are in the allowable range. It means that the experimental method in this work is valid for the measurement of gas solubility at high pressure. Moreover, the possible error generated in this work can be decreased further by measuring the solubility of a solvent with high CO₂ loading.

3.2 Influence of activator on VLE

Different activators were added in potassium carbonate solution and were evaluated CO₂-absorbing capacity according to the above method in 2.2.2 at 70°C. Results were listed in Figure 1.

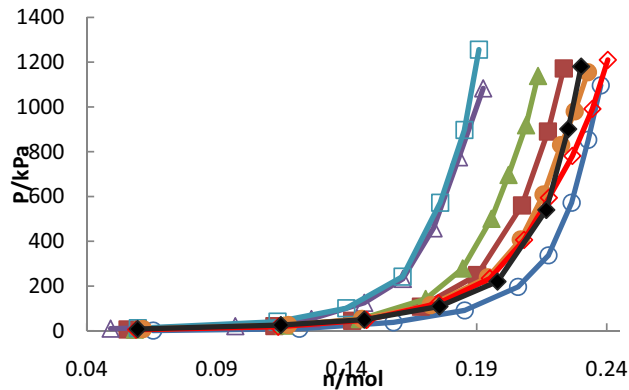


Fig 1. Vapor-liquid equilibrium data of CO₂-potassium carbonate solution with activators at 70 °C



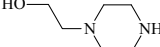
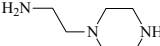
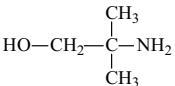
○, Piperidine; ●, N-(2-Hydroxyethyl)piperazine; □, Pyrazine; ■, Piperazine; ▲, Imidazole; ▲, Morpholine; ◊, N-(2-Aminoethyl) piperazine; ◆, 2-Amino-2-methyl-1-propanol

Shown in Figure 3 and Table 2, piperidine activation works best, followed by N-(2-hydroxyethyl)piperazine, N-(2-aminoethyl) piperazine, 2-amino-2-methyl-1 -propanol and piperazine, pyrazine and imidazole is at its worst.

As a weak base the pKa values of the above activators are listed as in Table 3.

Table 3 pKa values of activators used in this work ^[30,31]

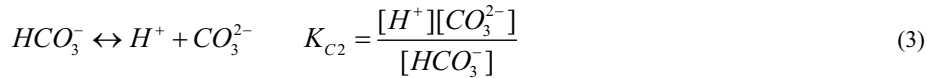
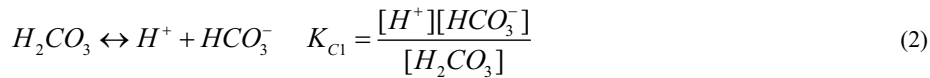
Activator	Molecular formula	pKa value
piperidine	<chem>C1CCNCC1</chem>	11.123
piperazine	<chem>C1CCNCCN1</chem>	9.781
morpholine	<chem>C1CCNCCO1</chem>	8.492

imidazole		7.03
pyrazine		0.6
N-(2-hydroxyethyl) piperazine		9.27
N-(2-aminoethyl) piperazine		10.12
2-amino-2-methyl-1-propanol		9.694

Based on Figure 1, at the same pressure (0.6Mpa) liquid molar fraction x6 with different activators and pKa values are drawn in a same as in Figure 2. It can be seen from Figure 2, with the pKa value activation effect show an approximately increasing trend.

As pKa value reflects the basic strength of activator. With the increase of pKa value, basic enhanced activation effect also enhanced. This phenomenon can be explained by the following process^{32,33}.

As CO₂ absorbing by potassium carbonate, phase-equilibrium meet Henry's law on the vapor-liquid interface.



Total carbon concentration in the liquid phase equals to:

$$C_C = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \quad (4)$$

$$C_C = \frac{P_{CO_2}}{H} \left(1 + \frac{K_{C1}}{[H^+]} + \frac{K_{C1}K_{C2}}{[H^+]^2} \right) \quad (5)$$

Taking into account of ionization of water:



By electrically neutral principle and ignoring item $\frac{K_{C1}K_{C2}}{[H^+]^2}$ (secondary ionization is weak), it can be obtained:

$$C_C \approx [K^+] + [H^+] - \frac{K_w}{[H^+]} + \frac{P_{CO_2}}{H} \quad (7)$$

Clearly, compared with CO₂ absorbing by water [see formula (9)], because addition of potassium ion, the solubility of CO₂ increased sharply ($[K^+] \gg [H^+]$).

$$C_c \approx [H^+] - \frac{K_w}{[H^+]} + \frac{P_{CO_2}}{H} \quad (8)$$

When activator A is added in potassium carbonate aqueous solution, it ionizing as the following ways:



$$\text{As } C_A = [AH^+] + [A] \quad (10)$$

$$\text{So } [AH^+] = C_A \frac{[H^+]}{[H^+] + K_A} \quad (11)$$

By electrically neutral principle:

$$[K^+] + [H^+] + [AH^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \quad (12)$$

$$[K^+] + [H^+] + C_A \frac{[H^+]}{[H^+] + K_A} = \frac{K_w}{[H^+]} + \left(\frac{K_{C1}}{[H^+]} + 2 \frac{K_{C1}K_{C2}}{[H^+]^2} \right) \frac{P_{CO_2}}{H} \quad (13)$$

The solubility of CO₂ in liquid solution approximately equals to:

$$C_c \approx [K^+] + [H^+] + C_a \frac{[H^+]}{[H^+] + K_a} - \frac{K_w}{[H^+]} + \frac{P_{CO_2}}{H} \quad (14)$$

It can be drawn from the above with the activator adding the solubility increases, and solubility increases with decrease of the Ka value. This shows as an active agent, alkaline enhances activation.

Activation effects of piperidine, N-(2-hydroxyethyl)piperazine, N-(2-aminoethyl) piperazine, 2-amino-2-methyl-1-propanol are all better than that of piperazine. Among them, N-(2-hydroxyethyl)piperazine is less volatile, more stable and suitable as the activator.

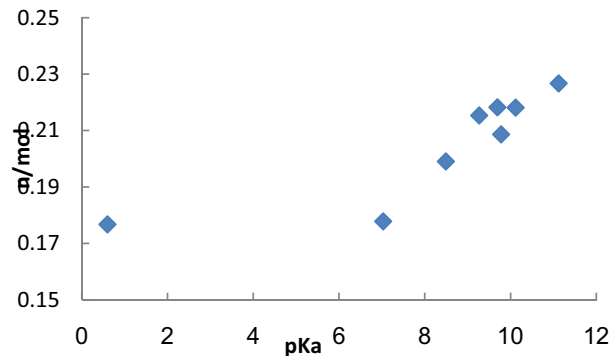


Figure 2 Correlation analysis of pKa values and absorbing effect

(n is the molar amount of CO₂ in the liquid phase at 0.6MPa)

3.3 VLE data at different temperature

After activator screening, it is found that hydroxyethyl piperazine (HPZ) had better activation effect. It was chosen as the activators in further experiments. VLE data of CO₂-K₂CO₃-H₂O-HPZ at different temperature is listed in Figure 3.

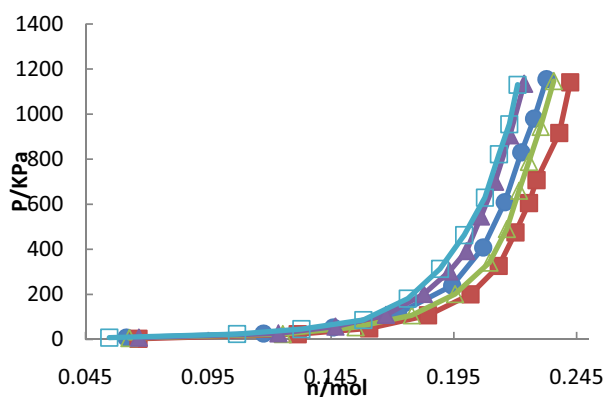


Fig 3. Vapor-Liquid Equilibrium Data of CO₂, potassium carbonate, H₂O and N-(2-Hydroxyethyl)piperazine

□,80°C; ▲,75°C; ●,70°C; △,65°C; ■,60°C

By Fig.6 in the temperature range of 60°C–80°C, CO₂ solubility in the liquid phase decreases with increasing temperature, absorption rate accelerates with increasing temperature. Overall considering the solubility and absorption rate, 70°C is more appreciate choice. Meanwhile according to literature data absorption temperature in industrial HPP process is always 70°C. For this work the same temperature can be considered to be suitable temperature.

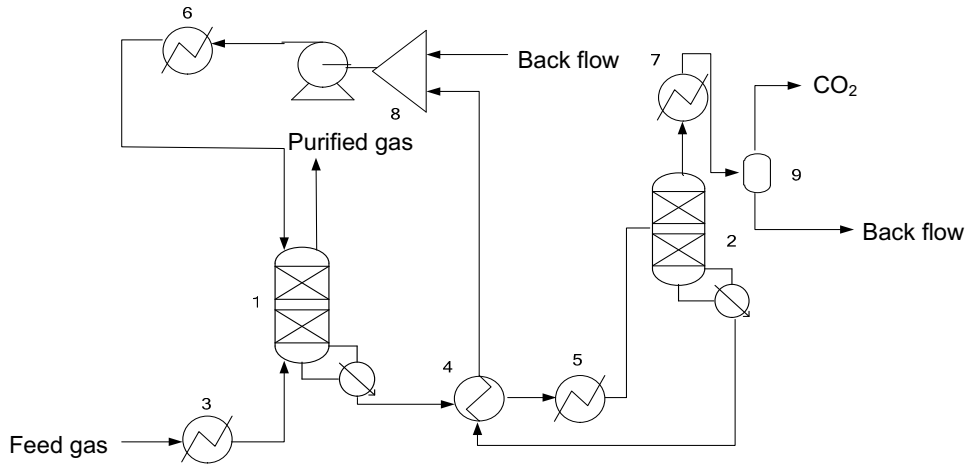
Next, an improvement process using NPZ is developed.

4 Process improvements

The classical HPP process includes mainly two columns absorber and stripper. In the absorber CO₂ of feed gas is absorbed by potassium carbonate solution and purified gas emits from the top of tower. The loaded liquor absorbed CO₂ is regenerated in the stripper by thermal desorption and recycling reused in absorption column. The classical process, the largest drawback is that energy consumption is too high, especially desorption energy percentage is too large, is in dire need of improvement.

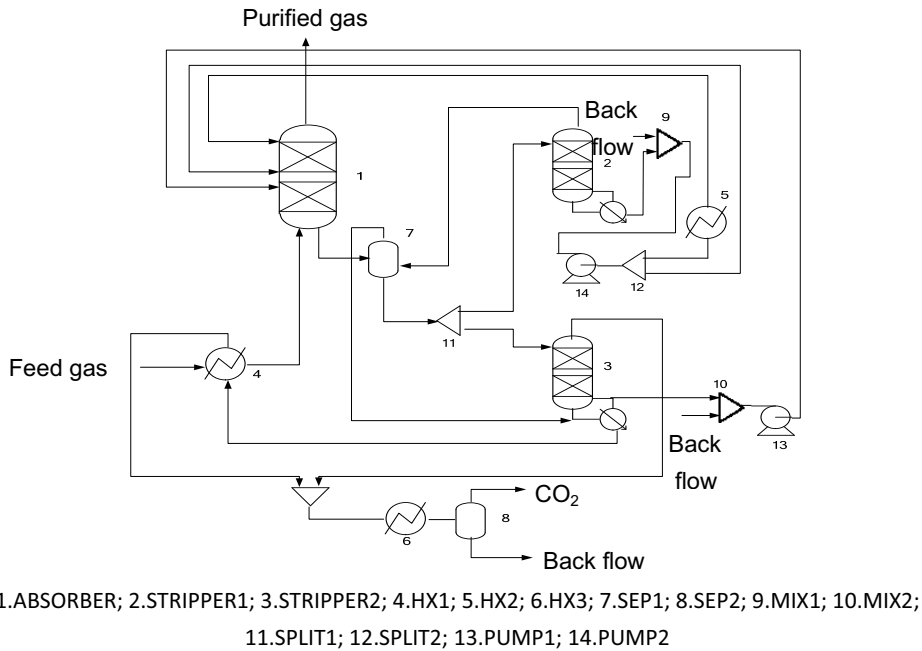
Based on new activator a improved process is presented. A couple of desorption columns with different operating pressure is adopted in the new process. One runs at a high pressure the other runs at atmosphere pressure. Thus condensation latent heat of the former can be used in the reboiler of the latter. Applying several absorbents feed recycled with different desorption degree from two strippers into the different feed stage of absorber, taking advantage of sensible heat of lean liquid to heat feed gas, are all valid in saving energy in improved process.

According to Table 4, compares with the classical process, the improvement process obviously reduced desorption heat consumption, after using the activator, the energy consumption further reduces.



1.ABSORBER; 2.STRIPPER; 3.HX1; 4.HX2; 5.HX3; 6.HX4; 7.HX5;
8.MIX; 9.SEP

Fig.7 Sketch of classical process of HPP²²



1.ABSORBER; 2.STRIPPER1; 3.STRIPPER2; 4.HX1; 5.HX2; 6.HX3; 7.SEP1; 8.SEP2; 9.MIX1; 10.MIX2;
11.SPLIT1; 12.SPLIT2; 13.PUMP1; 14.PUMP2

Fig.8 Sketch of improved process of HPP

Table 4 Energy comparison between the classical process and improved process

	EE(kJ/s)	EH(kJ/s)	EC(kJ/s)
classical process	4811	941836	957174
improve process without activator	4747	748635	634380
improved process with activator	4501	712373	616790

4 Conclusions

(1).By comparison of pre-combustion CO₂-trapping technologies, absorption is a economically viable methods. As HPP method has comprehensive advantages in device investment, absorption efficiency and operational stability, it is necessary to conduct a in-depth study;

(2).Experiments studies have showed that activation of NPZ has better performance. It is expected to use in HPP process to improve the absorption effect;

(3)An improved process is presented and two desorption columns with different operating pressure is adopted in the new process. One runs at a high pressure the other runs at at atmosphere pressure. Thus condensation latent heat of the former can be used in the reboiler of the latter. The new process is expected to soon be pilot;

(4)If waste heat from IGCC could be recovered fully, the effect of energy-saving of improved HPP process is more obvious.

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