

A study on the carbon dioxide recovery from 2 ton-CO₂/day pilot plant at LNG based power plant

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Abstract

A pilot plant of 2 ton-CO₂/day for CO₂ recovery from flue gas emitted from 250 MW LNG based power plant was tested with aqueous absorbents. The absorbent tested were of different nature such as primary amine (MEA), blend of primary, secondary, tertiary and sterically hindered amine such as MDEA + HMDA, AEPD + DPTA, and TIPA + DPTA. We have studied the CO₂ recovery as function of temperature, concentration, and flow rate of absorbent, pressure and temperature of stripper, and flow rate and temperature of flue gas. It was observed that while CO₂ recovery increases with increase in flow rate and concentration of absorbent, it decreases with increase in temperature and flow rate of flue gas. The CO₂ recovery ratio increases with increase in stripper temperature and decrease in stripper pressure. CO₂ loading (mol CO₂/mol amine) also decreases with increase in stripper temperature.

For the absorbent flow rate greater than 2.4 N m³/h, the carbon dioxide recovery ratio follows the sequence: MEA > MDEA + HMDA > AEPD + DPTA > TIPA + DPTA.

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1. Introduction

After the Kyoto protocol, CO₂ capture is receiving great attention of scientists over world wide [1,2]. The increasing anthropogenic CO₂ emission and global warming [3,4] have challenged the researchers to find new and better ways to meet the world's increasing needs for energy while mitigating the global warming effect by curtailing the increase in concentration of the major greenhouse gas CO₂ in the atmosphere mainly due to its emission from combustion of fossil fuels [5]. Another goal of CO₂ separation and capture is to isolate CO₂ from its large point sources such as power plants, oil refineries, petrochemical facilities, fertil-

izer and gas-processing plants, steel works and pulp and paper mills and its further utilization in many technological applications including coal conversion, organic synthesis, destructive oxidation of hazardous wastes, enhanced oil recovery, and activated carbon regeneration [6–13]. The CO₂ separation and capture can be achieved through chemical absorption, physical and chemical adsorption, gas-separation membranes, mineralization/biomineralization, and vegetation [14–19]. Fossil-fueled power stations currently account for about one third of global CO₂ emissions.

The most common option for separating CO₂ from flue gases or other gas streams is scrubbing the gas stream using an amine solution. Once the amine solution leaves the scrubber, it is heated to release high-purity CO₂ and the CO₂-free amine that is then reused [20–25]. Among the alkanolamines, monoethanolamine (MEA), diethanolamine

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(DEA), *N*-methyldiethanolamine (MDEA) and di-isopropanolamine (DIPA) and 2-amino-2-methyl-1-propanol (AMP) have been widely used as chemical absorbents, for removal of acid gases (CO_2 , H_2S) [23–27]. Especially, aqueous MEA solution has been used as an industrially important absorbent because of rapid reaction rate, low cost of the solvent, thermal stability and low solubility of hydrocarbons, as well as high alkalinity. It has also some disadvantages such as corrosion, high regeneration energy, and solvent degradation. Tertiary amines such as MDEA and triisopropanolamine (TIPA) do not form carbamate due to the absence of N–H bond. They only act as bases, contributing to the formation of bicarbonate. The advantage of tertiary amines is that the equilibrium is more easily reversed in the stripper. The use of blended amine solvents in acid gas treatment processes is receiving the considerable attention of the researchers [26–29]. Blending of primary, secondary and tertiary amines provide both, the higher equilibrium capacity of the tertiary amine and the higher reaction rate of the primary or secondary amine in one solvent. Presence of bulky groups around amine in sterically hindered amines such as AMP, 2-amino-2-methyl-1,3-propanediol (AMPD), 2-amino-2-ethyl-1,3-propanediol (AEPD) and 2-piperidineethanol (PE) results in the formation of unstable carbamate which leads to the high loading capacity [29–31]. Thus blending of sterically hindered amines with primary or secondary amines would be expected to enhance the loading capacity and absorption rate of CO_2 .

The aim of this paper is to study the CO_2 recovery from a newly constructed pilot plant of 2 ton/day capacity. This pilot plant was constructed near a 250 MW LNG based power plant. The absorbent tested were MEA and blended absorbents containing primary, secondary, tertiary and sterically hindered amine such as MDEA + hexamethylenediamine (HMDA), AEPD + dipropylentriamine (DPTA), and TIPA + DPTA.

2. Experimental

The chemical absorbents (MEA, MDEA, AEPD, DPTA, TIPA, HMDA) used in this study were obtained from Sigma–Aldrich with a mass purity of >99% and used without further purification. Their aqueous solutions were prepared from the distilled water.

The pilot plant for carbon dioxide recovery is shown schematically in Fig. 1. This pilot plant for carbon dioxide recovery was set up around LNG fired Seoul Thermal Power Plant #5 (capacity 250 MW). Also, removal capacity of pilot plant was 2 ton- CO_2 /day. The pilot plant consists of a chemical absorption based absorber (diameter = 0.46 m, height = 18.8 m) and a stripper or regenerator (diameter = 0.35 m, height = 16.7 m) to regenerate the absorbent along with other equipments such as reboiler, reclaiming, pump, condenser, and lean/rich amine exchanger. Each tower (absorber and stripper) was packed with ring-shaped (~2 cm diameter) stainless steel packing material (IMTP-#25 packing, Norton Co. USA) for increasing retention

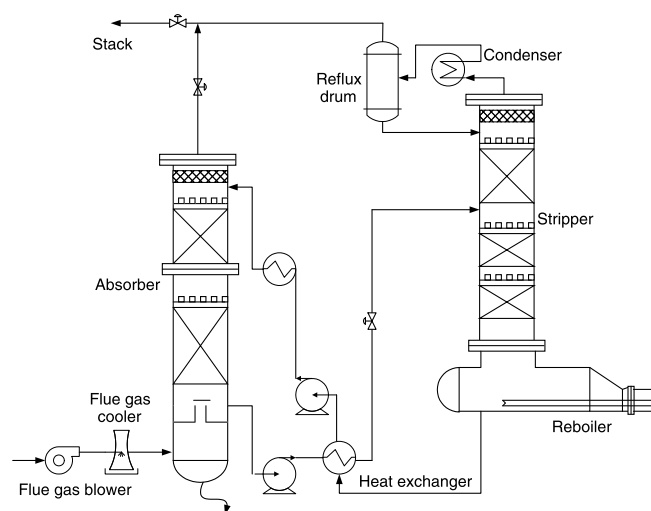


Fig. 1. Process flow diagram of demo pilot plant for carbon dioxide separation.

time and surface area for effective contact between carbon dioxide and absorbent inside tower. The flue gas was cooled to about 40 °C in order to decrease its moisture content prior to introduction into the absorber. The exhaust gas was contacted counter currently with lean solvent in an absorber tower. In the absorber, CO_2 was chemically bonded to the amine at low temperatures between 40 and 50 °C and was thus removed from the flue gas stream. This absorption was based on the reaction between weak base and weak acid that resulted in the formation of water soluble salt. This reaction was reversible and temperature dependent. The remaining gas exits from the top of absorber.

The CO_2 -rich amine was then extracted from the bottom of the absorber and transferred to the regenerator through a heat exchanger in which the solution temperature was raised to between 100 °C and 110 °C. In the regenerator, the CO_2 -rich solution contacted with steam supplied from the reboiler and CO_2 was stripped off the solution. The mixture of steam and CO_2 exits from the top of the regenerator and is cooled in the condenser to separate the CO_2 . The water vapor was sent back to the stripper after refluxing. The purity of the recovered CO_2 was up to 99%. The regenerated CO_2 -lean amine solution was then cooled and recycled back to the absorber for further CO_2 removal from flue gas.

The compositions of flue gases from the plant #5 are shown in Table 1. The lean/rich amine samples in liquid phase were extracted from the absorber tower and stripper and CO_2 was measured by titration method. Each sample

Table 1
Exhaust gas composition

	125 MW (50% load)	187.5 MW (75% load)	250 MW (100% load)
CO_2 (vol%)	8.1	9.7	10.2
O_2 (vol%)	6.4	3.6	2.8
N_2 (vol%)	85.5	86.7	87.0

was analyzed three times and the experimental error in the loading of CO₂ was estimated to be about $\pm 3\%$. The procedure for determining absorbent content in carbon dioxide recovery facility sample assumes that all the alkalinity in the plant solutions is due to the presence of free absorbents.

3. Results and discussion

The CO₂ recovery in the demo pilot plant were studied in aqueous solutions of pure and blended absorbents such as MEA (1.637, 2.456 and 4.039 mol/m³), MDEA (2.182 mol/m³) + HMDA (1.635 mol/m³), TIPA (0.784 mol/m³) + DPTA (0.381 mol/m³), and AEPD (1.423 mol/m³) + DPTA (0.381 mol/m³) at the various absorbent temperature, flue gas temperature, absorbent flow rate, stripper temperature and stripper pressure.

3.1. The effect of absorbent (MEA) concentration and temperature

The effect of absorbent flow rate on CO₂ recovery ratio for different concentrations and temperature of MEA is shown Fig. 2. The concentration of aqueous MEA solutions were 1.637, 2.456, and 4.039 mol/m³ and flow rate of absorbent was varied from 2 to 3.5 N m³/h. The input temperature and flow rate of flue gas were 40 °C and 574 N m³/h, respectively. The temperature of absorbent in absorber and stripper were 40 and 113 °C, respectively. It was found that carbon dioxide recovery ratio increases with increase in absorbent flow rate as well as with increase in concentration of monoethanolamine. The carbon dioxide recovery ratio at absorbent flow rate 3.0 N m³/h in 4.039 mol/m³ MEA is about 22% higher than that in

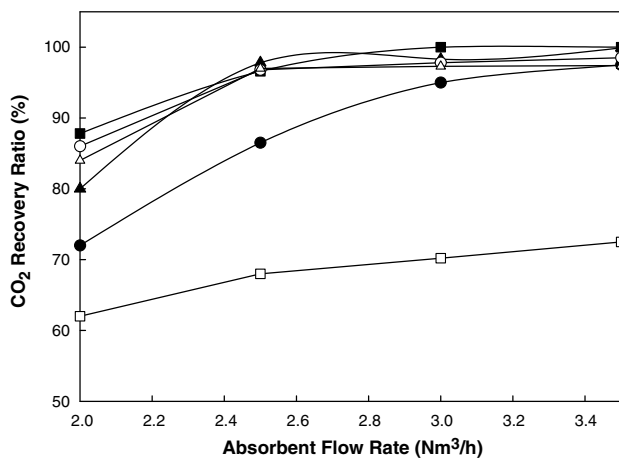


Fig. 2. The effects of absorbent flow rate on CO₂ recovery ratio in MEA at different concentration and different absorbent temperature: (●) MEA (1.637 mol/m³), (▲) MEA (2.456 mol/m³), (■) MEA (4.039 mol/m³), absorbent temperature = 40 °C, flue gas temperature = 40 °C, flue gas flow rate = 574 N m³/h; (○) MEA (45 °C), (△) MEA (50 °C), absorbent concentration = 2.456 mol/m³, flue gas temperature = 40 °C; (□) MEA, (55 °C), flue gas flow rate = 574 N m³/h.

1.637 and 2.456 mol/m³ MEA. But this increase reduces to about 3% at the highest flow rate of absorbent of 3.5 N m³/h.

The effect of absorbent temperature and flue gas temperature on CO₂ recovery ratio for same concentration of MEA (2.456 mol/m³) is also shown in Fig. 2. The CO₂ recovery ratio decreases with increase in absorbent temperature from 40 to 55 °C. The effect of temperature decreases with increase in absorbent flow rate. The carbon dioxide recovery ratio decreases with increase in flue gas temperature and at the maximum absorbent flow rate of 3.5 N m³/h, it is about 27.4% higher at 40 °C than that at 55 °C.

3.2. The effect of flow rate of absorbent and flue gas in different absorbent

Variation in CO₂ recovery ratio with absorbent flow rate for MEA and blended absorbents such as MDEA + HMDA, TIPA + DPTA, and AEPD + DPTA at 40 °C are shown in Fig. 3. The carbon dioxide removal ratio increases with increase in absorbent flow rate in all the absorbents studied. For the absorbent flow rate more than 2.4 N m³/h, the carbon dioxide recovery ratio vary in the following order

MEA > MDEA + HMDA > AEPD + DPTA > TIPA + DPTA.

The carbon dioxide recovery ratio for MEA, MDEA + HMDA, AEPD + DPTA, and TIPA + DPTA at the maximum absorbent flow rate (3.5 N m³/h) were about 98%, 93.5%, 92.5% and 84%, respectively. The rich amine CO₂ loading was determined by titration method for these absorbents and shown in Fig. 4. It also increases with absorbent flow rate and found to be maximum for MEA and minimum for TIPA + DPTA.

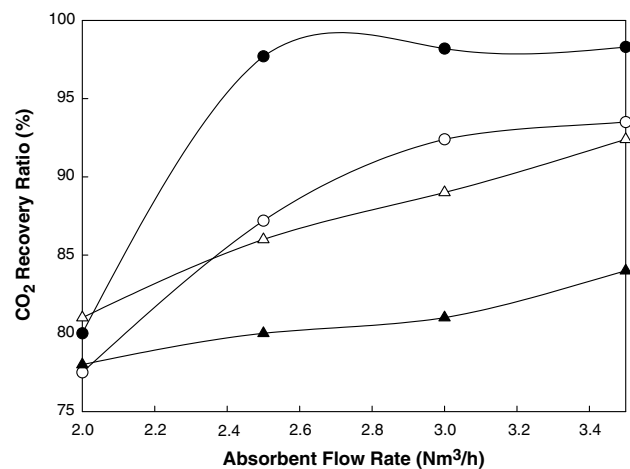


Fig. 3. The effects of absorbent flow rate on CO₂ recovery ratio: absorbent and flue gas temperature = 40 °C, flue gas flow rate = 574 N m³/h, stripper pressure = 0.45 kg/cm², stripper temperature = 113 °C; (●) MEA (2.456 mol/m³); (○) MDEA + HMDA; (▲) TIPA + DPTA; (△) AEPD + DPTA.

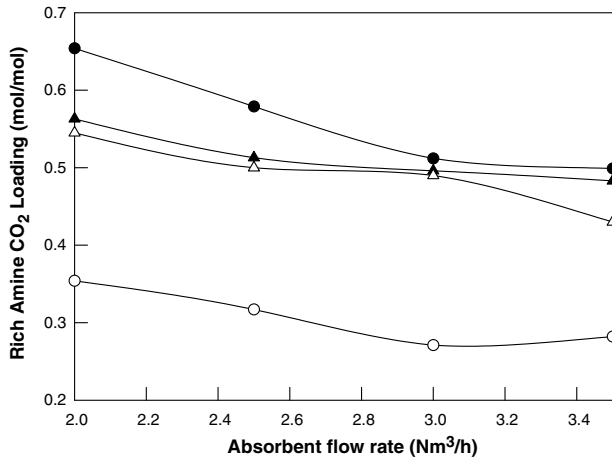


Fig. 4. The effects of stripper temperature with rich amine carbon dioxide loading: MEA (2.456 mol/m^3); (○) MDEA + HMDA; (▲) TIPA + DPTA; (△) AEPD + DPTA, absorbent temperature = 40°C , flue gas temperature = 40°C , flue gas flow rate = $574 \text{ N m}^3/\text{h}$, absorbent flow rate = $2.5 \text{ N m}^3/\text{h}$.

The influence of flow rate of flue gas in these absorbents (MEA, MDEA + HMDA, AEPD + DPTA, and TIPA + DPTA) at 40°C on CO_2 recovery ratio is shown Fig. 5. The flow rate of absorbents and stripper pressure were kept constant at $3.0 \text{ N m}^3/\text{h}$ and 0.45 kg/cm^2 , respectively, while flow rate of gases was varied from 574 to $697 \text{ N m}^3/\text{h}$. As shown in Fig. 5, the carbon dioxide removal ratio decreases with increase in flow rate of flue gas. The carbon dioxide recovery ratios for these absorbents follow the order

MEA > MDEA + HMDA > AEPD + DPTA > TIPA + DPTA.

3.3. The effect of stripper pressure and stripper temperature

The effect of stripper pressure on CO_2 recovery ratio for different absorbent (MEA, MDEA + HMDA, AEPD +

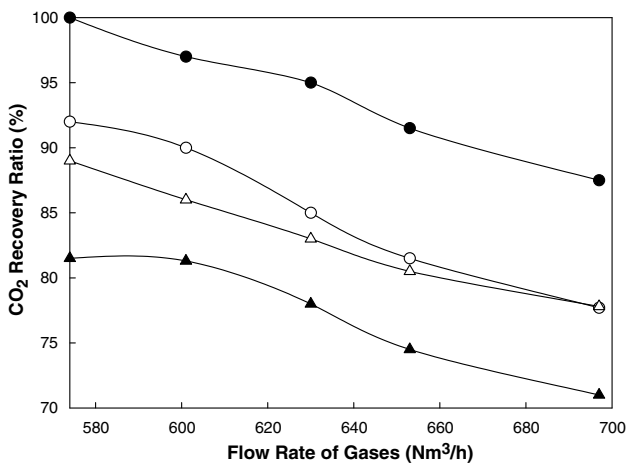


Fig. 5. The effects flue gas inflow amount on CO_2 recovery ratio: (●) MEA (2.456 mol/m^3); (○) MDEA + HMDA; (▲) TIPA + DPTA; (△) AEPD + DPTA, absorbent flow rate = $3.0 \text{ N m}^3/\text{h}$, absorbent temperature = 40°C , stripper temperature = 113°C , stripper pressure = 0.45 k/g cm^2 .

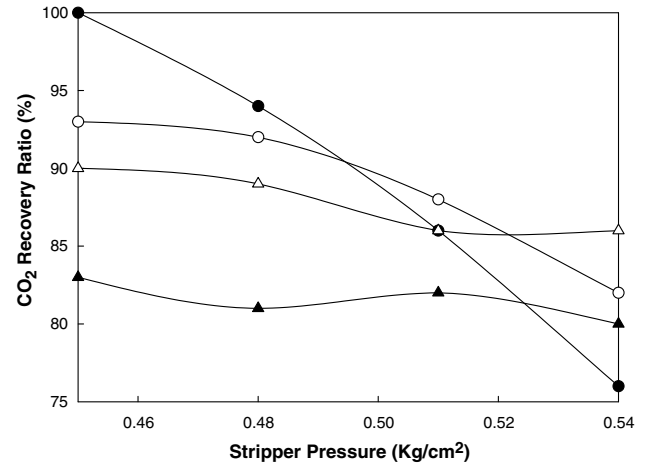


Fig. 6. The effects of stripper pressure on CO_2 recovery ratio: (●) MEA (2.456 mol/m^3); (○) MDEA + HMDA; (▲) TIPA + DPTA; (△) AEPD + DPTA, absorbent flow rate = $3.0 \text{ N m}^3/\text{h}$, absorbent temperature = 40°C , stripper temperature = 113°C .

DPTA, and TIPA + DPTA) is shown Fig. 6. The flow rate of flue gas, input temperature of absorbents, and inside temperature of stripper were $3.0 \text{ N m}^3/\text{h}$, 40°C , and 113°C , respectively. Fig. 6 shows that carbon dioxide recovery ratio decreases with increase in stripper pressure. The carbon dioxide is completely recovered in MEA (2.456 mol/m^3) at about stripper pressure 0.45 kg/cm^2 . In case of blended absorbent, carbon dioxide removal ratio vary in the order

MDEA + HMDA > TIPA + DPTA > AEPD + DPTA.

At stripper pressure 0.45 kg/cm^2 , CO_2 recovery ratio for MEA, MDEA + HMDA, TIPA + DPTA, and AEPD + DPTA were about 100%, 93%, 90% and 83%, respectively.

Fig. 7 shows the effects of stripper temperature on carbon dioxide recovery ratio in aqueous MEA and blended

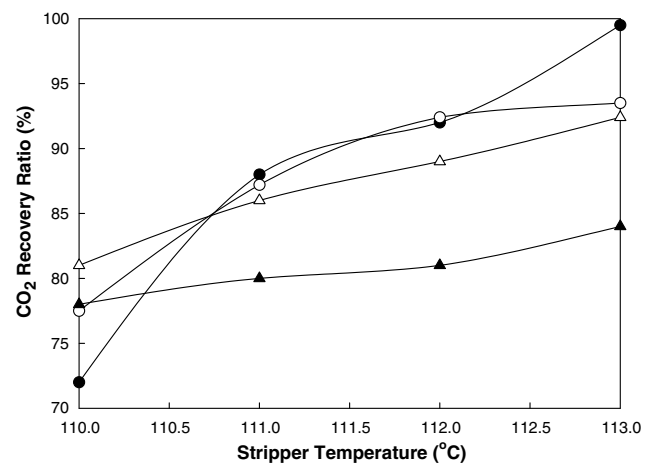


Fig. 7. The effects of stripper temperature on CO_2 recovery ratio: (●) MEA (2.456 mol/m^3); (○) MDEA + HMDA; (▲) TIPA + DPTA; (△) AEPD + DPTA, flue gas flow rate = $574 \text{ N m}^3/\text{h}$, absorbent flow rate = $3.0 \text{ N m}^3/\text{h}$, absorbent temperature = 40°C , stripper pressure = 0.45 kg/cm^2 .

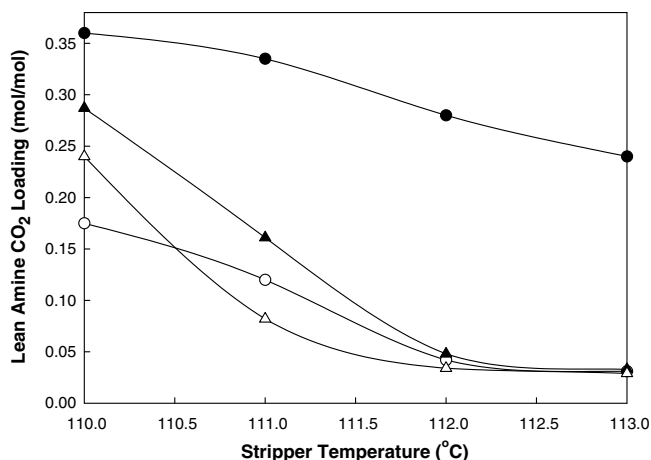


Fig. 8. The effects of stripper temperature on lean amine carbon dioxide loading; (●) MEA (2.456 mol/m^3); (○) MDEA + HMDA; (▲) TIPA + DPTA; (△) AEPD + DPTA, flue gas flow rate = $574 \text{ N m}^3/\text{h}$, absorbent flow rate = $3.0 \text{ N m}^3/\text{h}$, absorbent temperature = $40 \text{ }^\circ\text{C}$, stripper pressure = 0.45 kg/cm^2 .

absorbents solution. The absorbent flow rate, stripper pressure, and flue gas flow rate were kept constant at $3.0 \text{ N m}^3/\text{h}$, 0.45 kg/cm^2 , and $574 \text{ N m}^3/\text{h}$, respectively. The carbon dioxide recovery ratio increases with increase in reboiler temperature from $109 \text{ }^\circ\text{C}$ to $113 \text{ }^\circ\text{C}$. The carbon dioxide recovery ratio in MEA at reboiler temperature $113 \text{ }^\circ\text{C}$ was found to be higher than those for other blended absorbents such as MDEA + HMDA, TIPA + DPTA, and AEPD + DPTA.

The lean amine CO_2 loading ratio ($\text{mol CO}_2/\text{mol absorbent}$) in aqueous MEA (2.456 mol/m^3) and in other blends at the reboiler temperature from $109 \text{ }^\circ\text{C}$ to $113 \text{ }^\circ\text{C}$ was measured and shown in Fig. 8. It was observed that loading ratio decreases with an increase in reboiler temperature.

4. Conclusion

The CO_2 recovery as a function of temperature, concentration, and flow rate of absorbent, pressure and temperature of stripper, and flow rate and temperature of flue gas were studied in a 2 ton- CO_2/day pilot plant in MEA, MDEA + HMDA, AEPD + DPTA, and TIPA + DPTA. It was observed that while CO_2 recovery increases with an increase in flow rate and concentration of the absorbent, it decreases with an increase in temperature and flow rate of the flue gas. The CO_2 recovery ratio increases with increase in stripper temperature and decrease in stripper pressure. For the absorbent flow rate greater than 2.4, the carbon dioxide recovery ratio follows the sequence: MEA > MDEA + HMDA > AEPD + DPTA > TIPA + DPTA.

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