

17<sup>th</sup> Sep. , 2013  
Bergen, Norway

# Evaluation of Energy in Precipitating 2-Amino-2-methyl-1-propanol Carbonate Solvent Process for CO<sub>2</sub> Capture

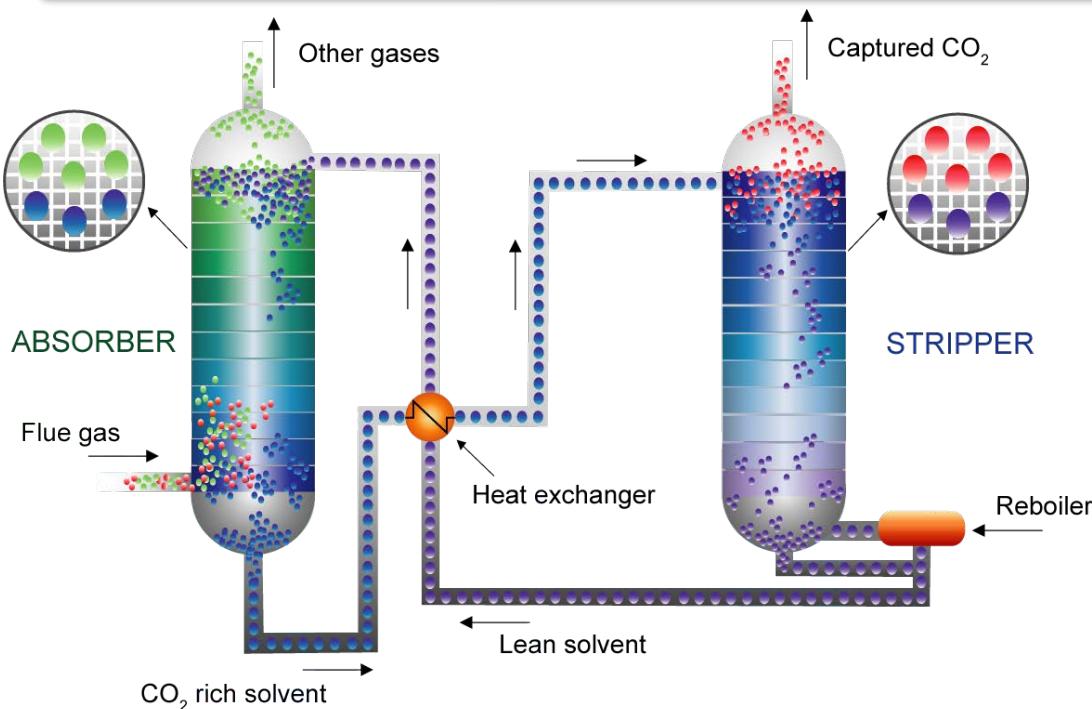
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School of Creative Science and Engineering, Waseda University

# Requirements for PCCS and how to approach



Heat of reaction ↓ (depend on substance)

- $Q_R$**
- Non-ideal mixing <sup>2)</sup>
  - Dissolution of gas into liquid
  - **Chemical reaction**  $\Delta H_r \downarrow$

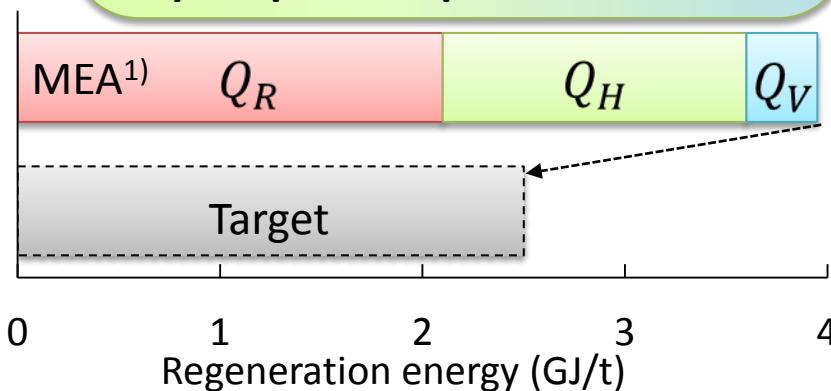
Exploring solvent

- ✓ Novel amine
- ✓ Blend amines

Technologies

- Quantum chemistry
- Organic synthesis

<b><math>Q_H</math></b> (Operating condition)	<b><math>Q_V</math></b>
Sensible heat ↓	Heat of vaporization ↓
<u>Flow rate ↓</u>	<u>Absorption flux ↑</u>
<u>Temperature swing ↓</u>	
✓ Concentration & $\Delta CO_2$ loading ↑	
✓ Multi pressure stripping <sup>3)</sup>	
✓ Rate of reactions	
Fast: RN-COO <sup>-</sup> H <sup>+</sup> ( $pK_a$ )	
H <sup>+</sup> acceptor R'N-H <sup>+</sup> ↘ X ↖ RN-H <sup>+</sup>	
pH ↑ → HCO <sup>3-</sup> ↑ (Low temp. stripping)	
✓ Condensation	
✓ precipitate separation	



1) RITE, COURSE50 NEDO Project report(2006), 2) Kim, I. et. al., Chem. Eng. Sci. 64 (2009)2027-2038,

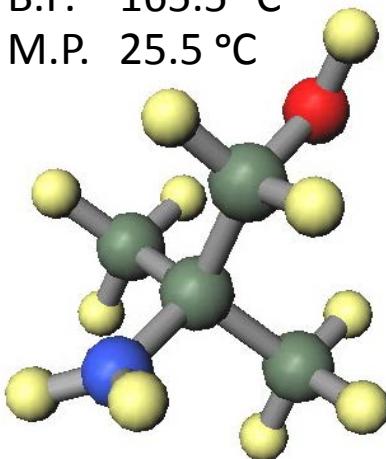
3) Jassim, M., Rochelle, G. Ind. and Eng. Chem. Res. 48 (8)(2006)2465-2472, 4) Oexmann, J., Kather, A., Int. J. of GHG Ctrl. 4 (2010)36-43

# 2-Amino-2-methyl-1-propanol (AMP)

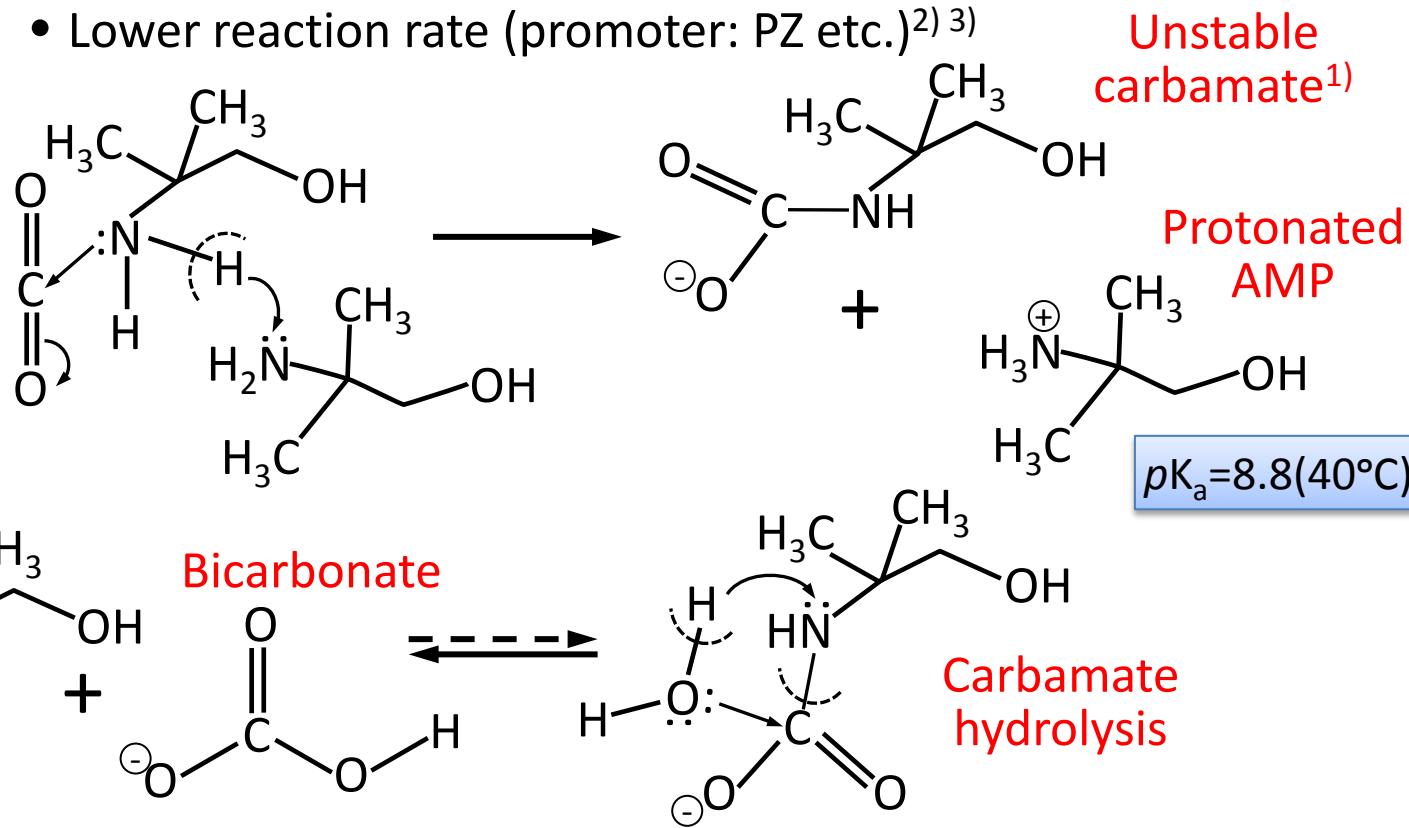
M.W. 89.14 g/mol

B.P. 165.5 °C

M.P. 25.5 °C



- One of promising candidates
- Moderately, sterically hindered primary amine
- Lower corrosiveness
- Lower reaction rate (promoter: PZ etc.)<sup>2) 3)</sup>

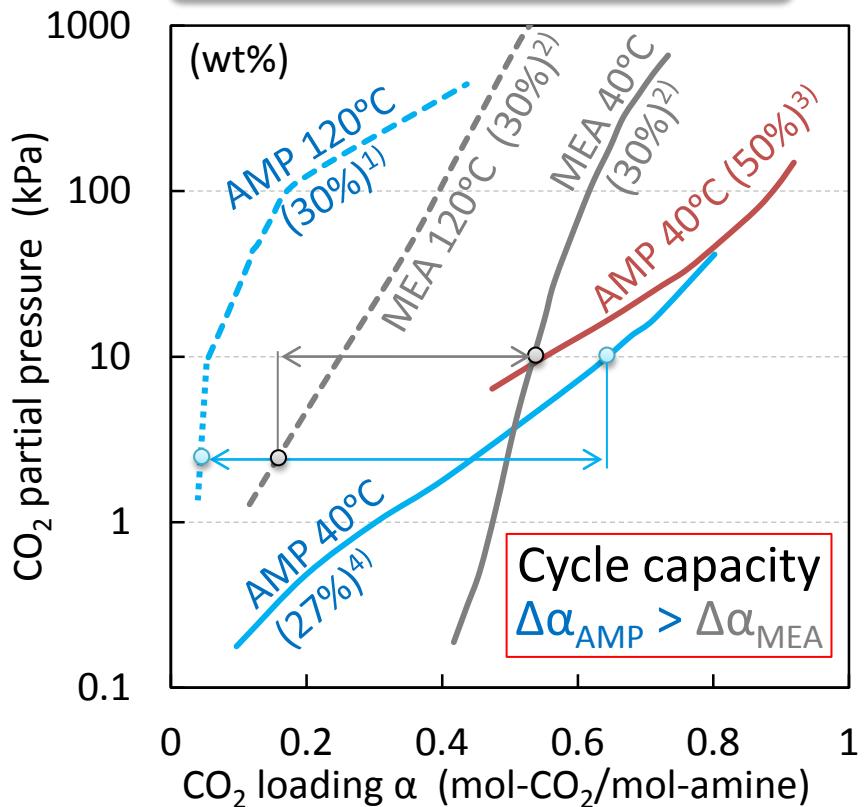


$$K_c = [\text{AMPCOO}^-]/[\text{AMP}][\text{HCO}_3^-] < 0.01$$

1) Barzaghi, F., ChemSusChem , 5, (2012)1724-1731, 2) Puxty, G., Rowland, R. Environmental Sci. & Tech. ACS 45 (2011)2398-2405,  
3) S.S. Bandyopadhyay, Chem. Eng. Sci. 64 (2009)1185-1194

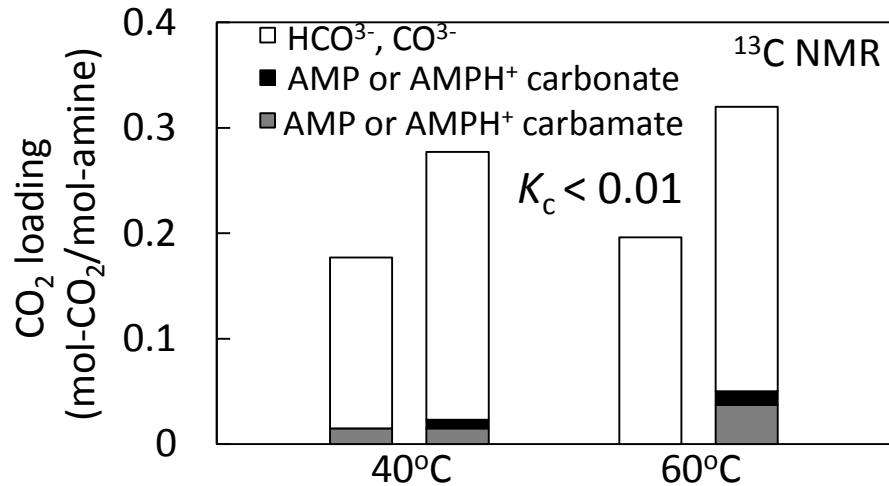
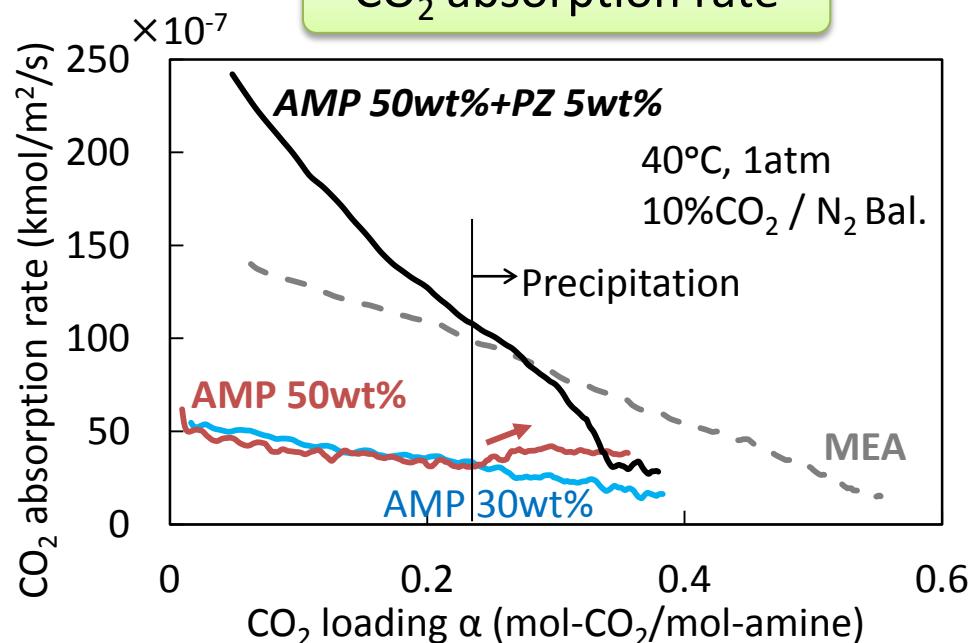
# VLE and absorption rate: AMP and MEA

## Vapor Liquid Equilibrium



- 1) Tong, D. et. al., Int. J. GHG Ctrl, 6 (2012)37-47
- 2) Jou, F. Y. et. al., Canadian J. Chem. Eng. 73 (1995)140-147
- 3) Kundu, M. et.al., J. Chem. Eng. Data 48 (2003)789-796
- 4) Roberts, B. E. et. al., Chem. Eng. Comm. 64 (1988)105-111

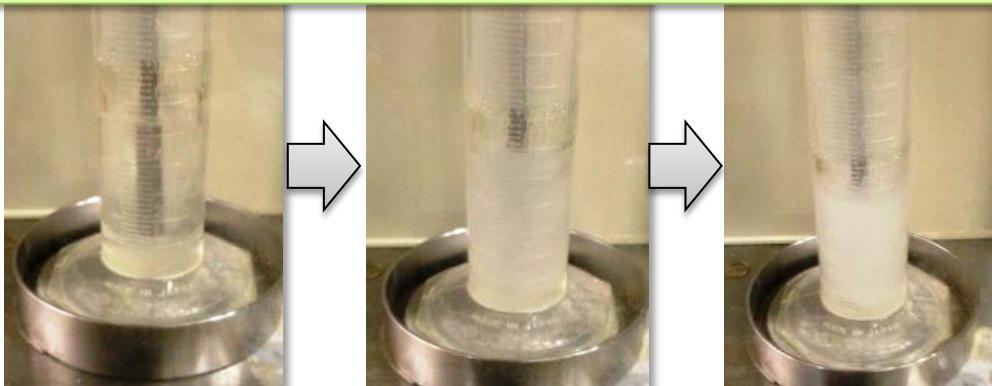
## CO<sub>2</sub> absorption rate



# Experimental: Precipitation of AMP

AMP 50wt% (5.6M) at 40°C

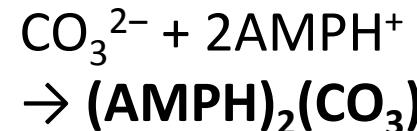
→ getting whitely turbid by precipitation of salt



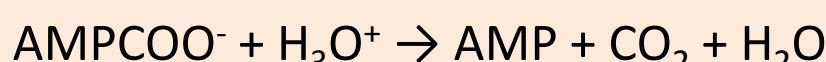
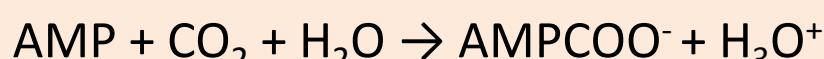
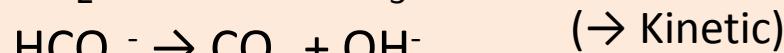
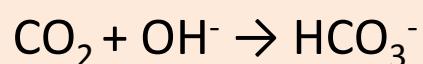
Chemical structure  
by Raman spectroscopy

Cation: Protonated AMP

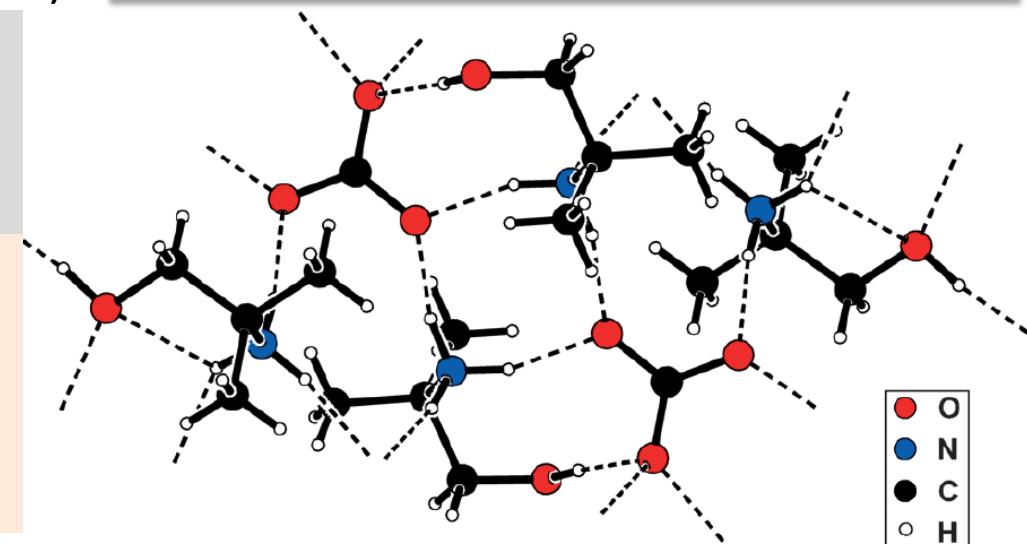
Anion: Carbonate ( $1068\text{ cm}^{-1}$ )



Reaction model in AMP-REA (ASPEN PLUS)\*



Separation of concentrated carbonates  
reduces regeneration energy?



Legend:  
● O  
● N  
● C  
○ H

\*Jamal, A., et al., Chem. Eng. Sci. 61 (2006) 6571-6603

Barzagli, F., ChemSusChem, 5, (2012) 1724-1731

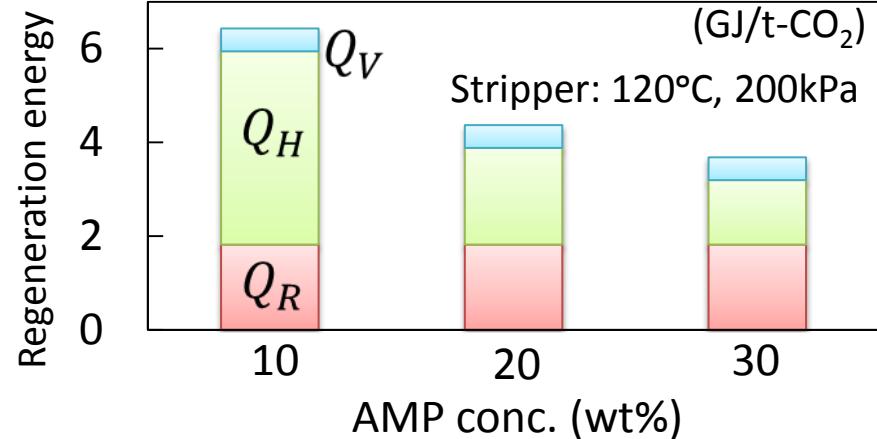
# Advantage of Solid-Liquid phase separation process

Higher concentration :

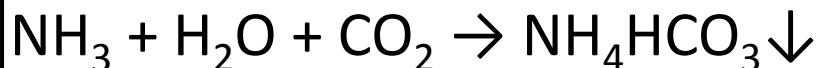
- ✓ Absorption capacity ↗
- ✓ Sensible heat ↘

✓ Keeping higher pH & driving force

✗ Additional energy of phase change



Alstom<sup>1)</sup> Ammonia bicarbonate



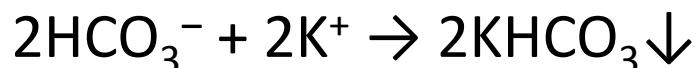
SINTEF<sup>3)</sup>

Potassium salt of sarcosine (KSar)

## Prior researches

Shell<sup>2)</sup>

Potassium bicarbonate



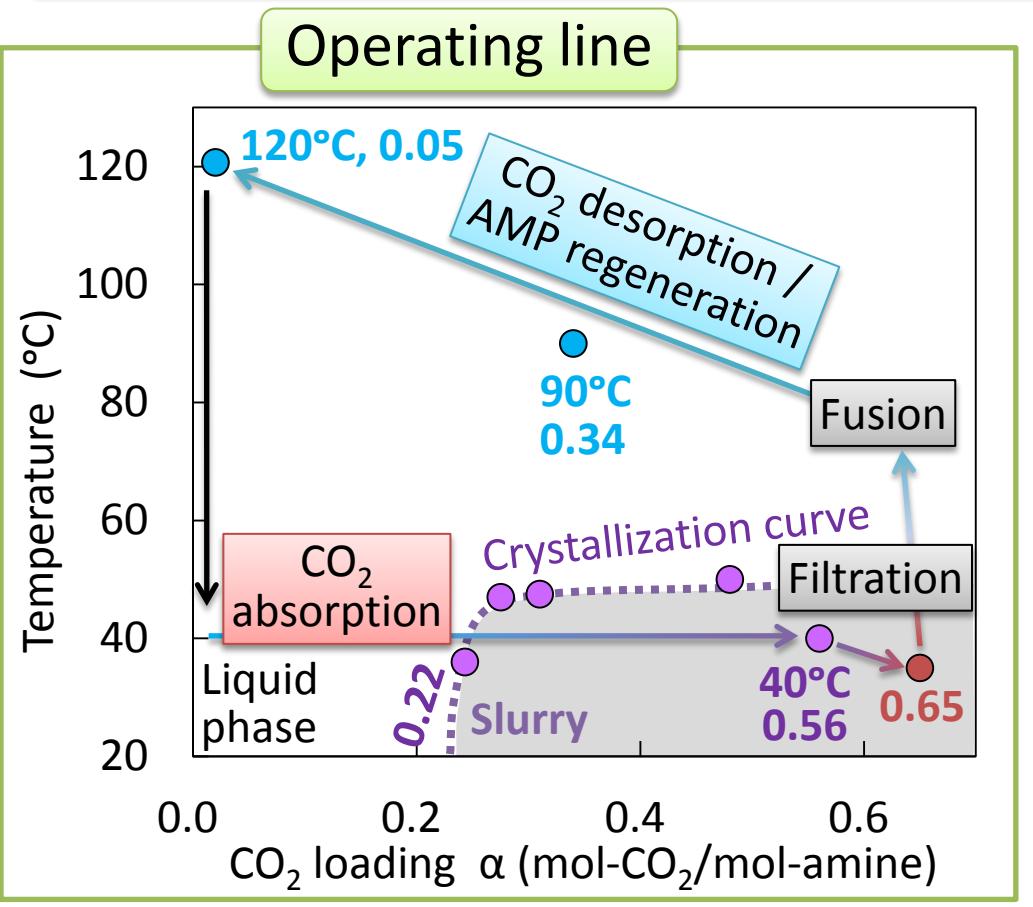
Solid separation: 35°C

Stripper: 90°C, 1.1 bar

1) Alstom DOE/NETL report 2007; No.401/021507 2) Moene, R., Schoon, L., Straelen, J., Geuzebroek, F., Proc. GHGT11 (2012)

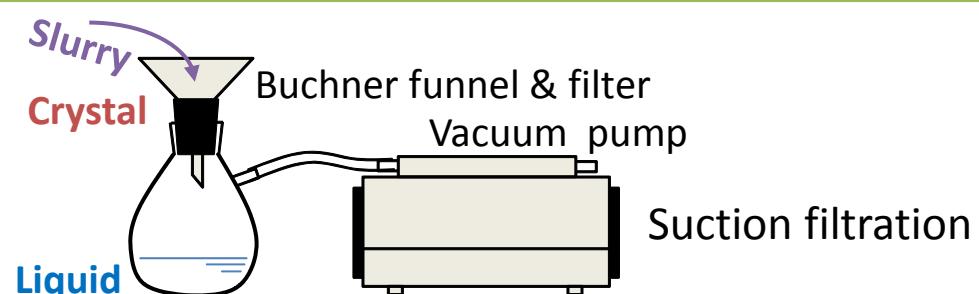
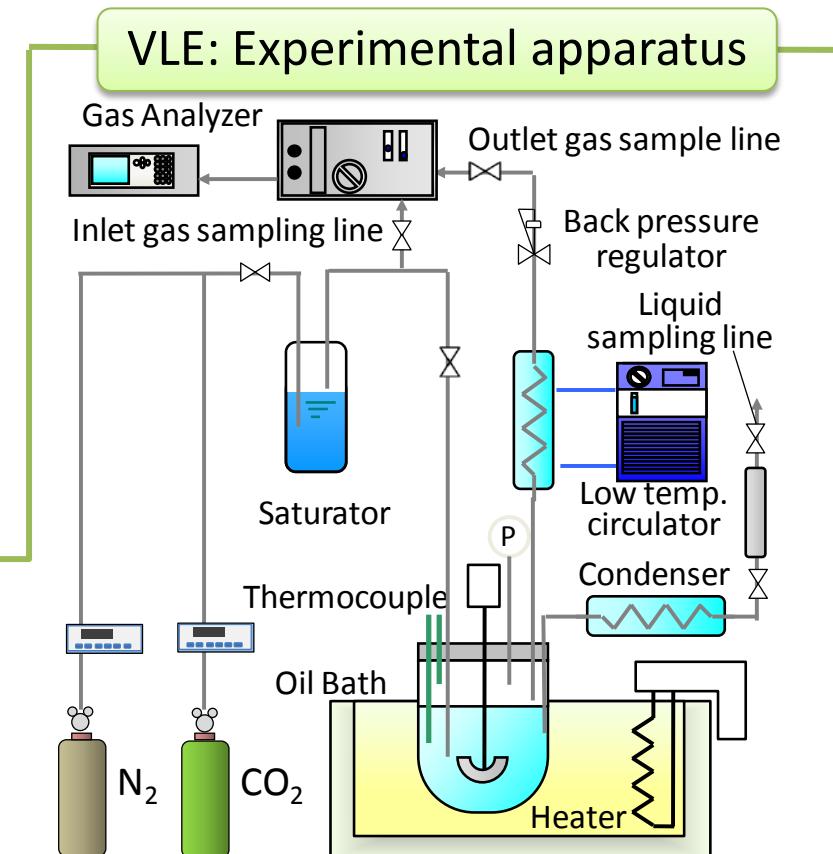
3) Ma'mun, S., Kim, I., Proc. GHGT11 (2012)

# Development of operating line of precipitation process



**Experimental condition**

	$T$ (°C)	$P_{\text{CO}_2}$ (kPa)
Absorber	40~50	10
Stripper	90 ~ 120	10 ~ 100

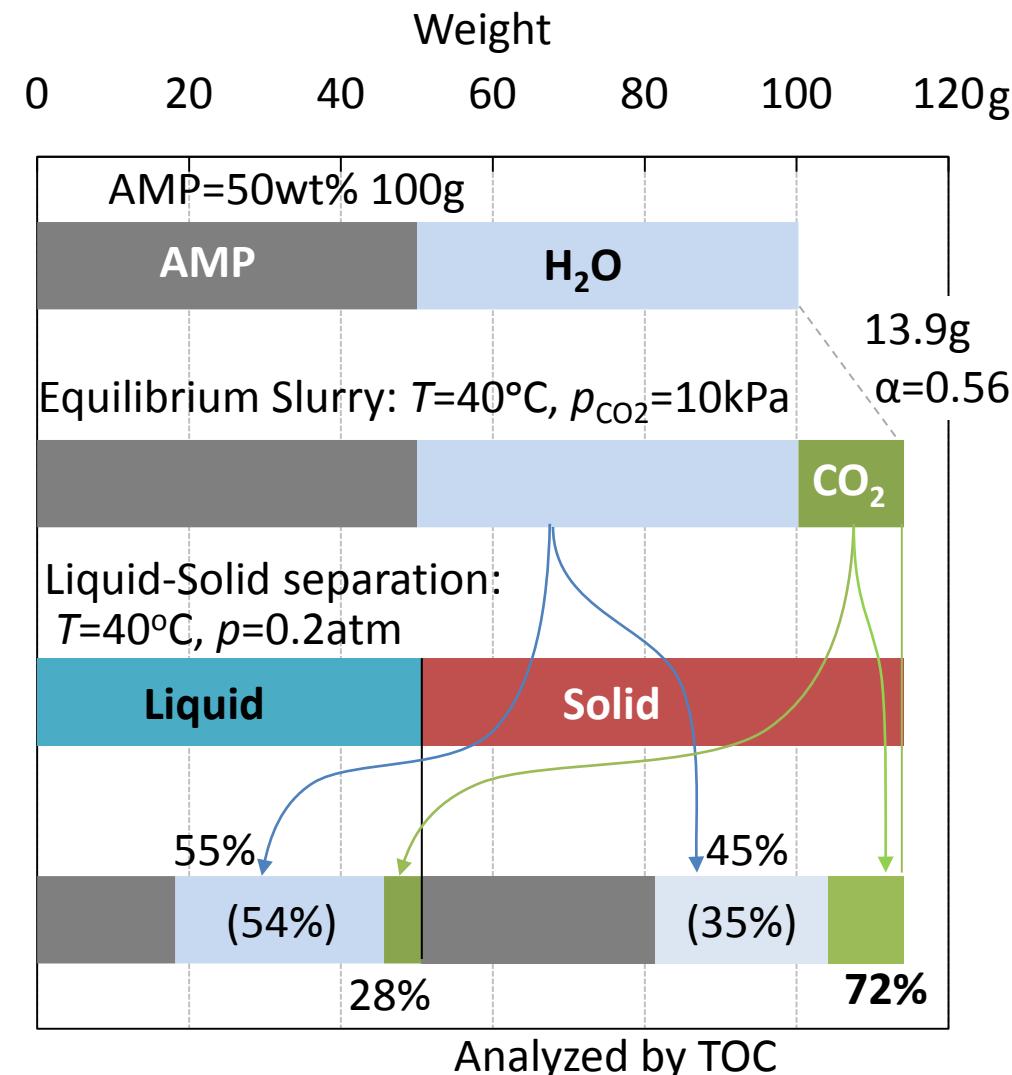


# Slurry separation and crystal recovery

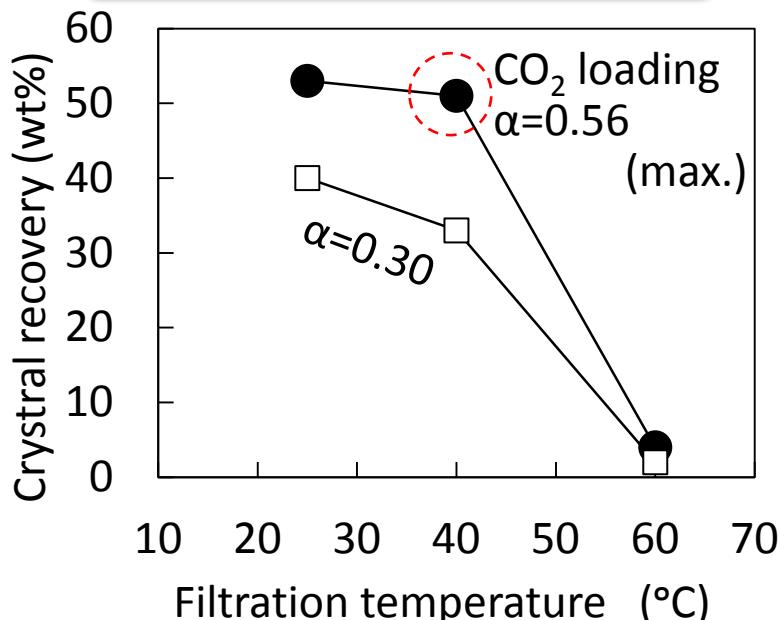
## Condition of suction filtration

Filtration Temp. (°C)	25~60 ±5
Filter diameter (μm)	8~10
Suction Pressure (kPa)	80
Suction time (min./g)	0.1

## Estimation of CO<sub>2</sub> recovery

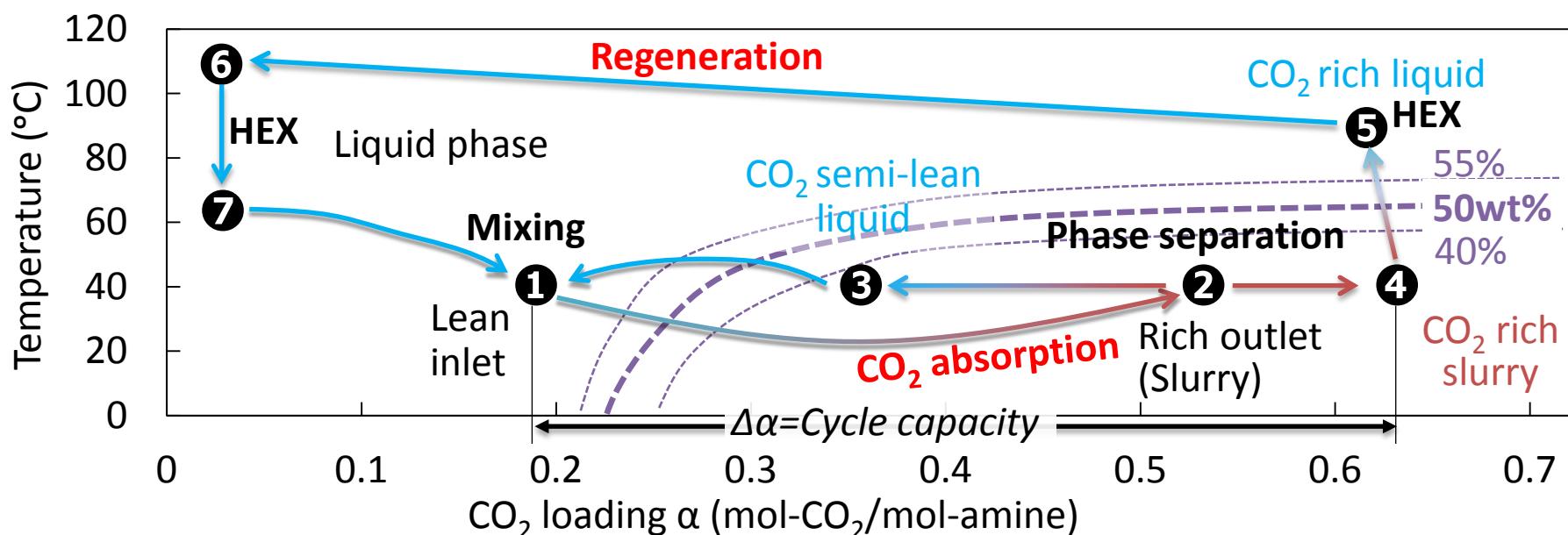
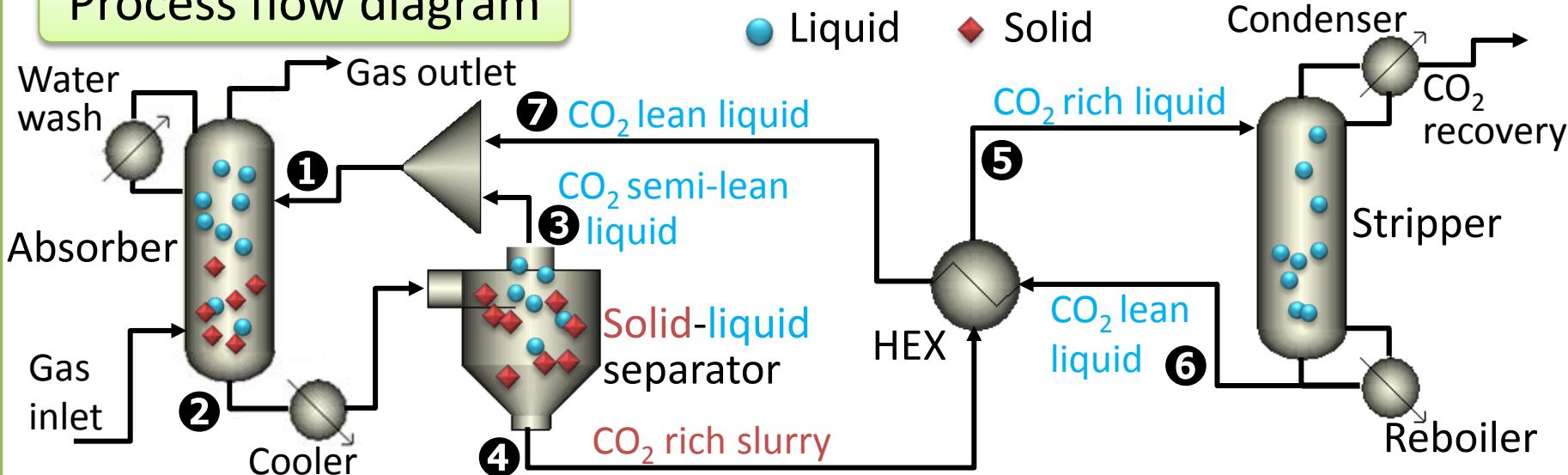


## Crystal recovery from slurry



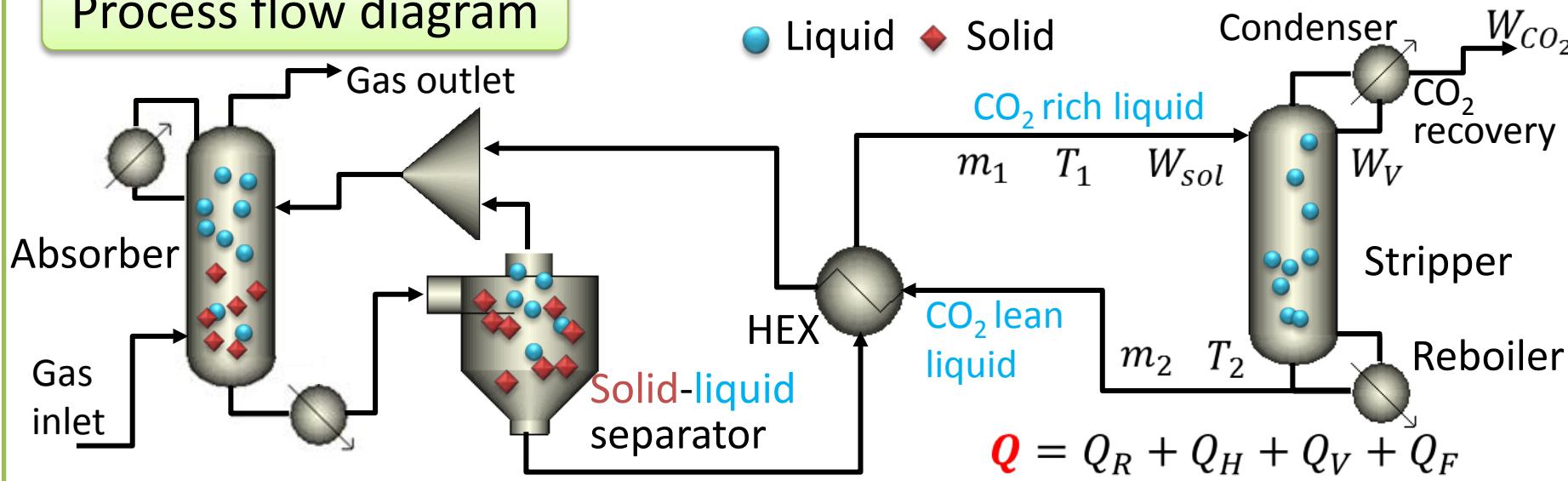
# Conceptual PFD and operating line (AMP 50%)

Process flow diagram



# Equilibrium-based estimation of regeneration energy

Process flow diagram

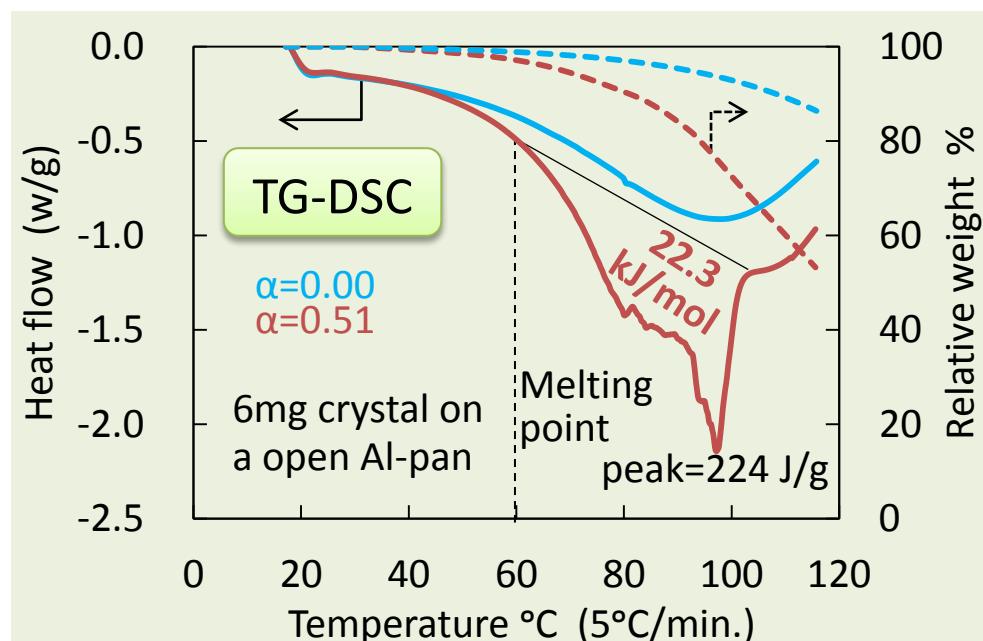
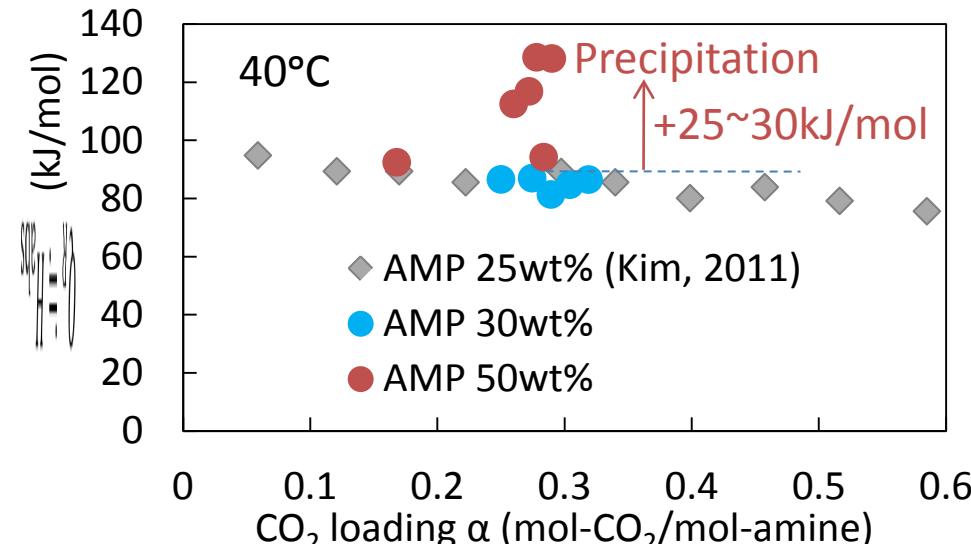
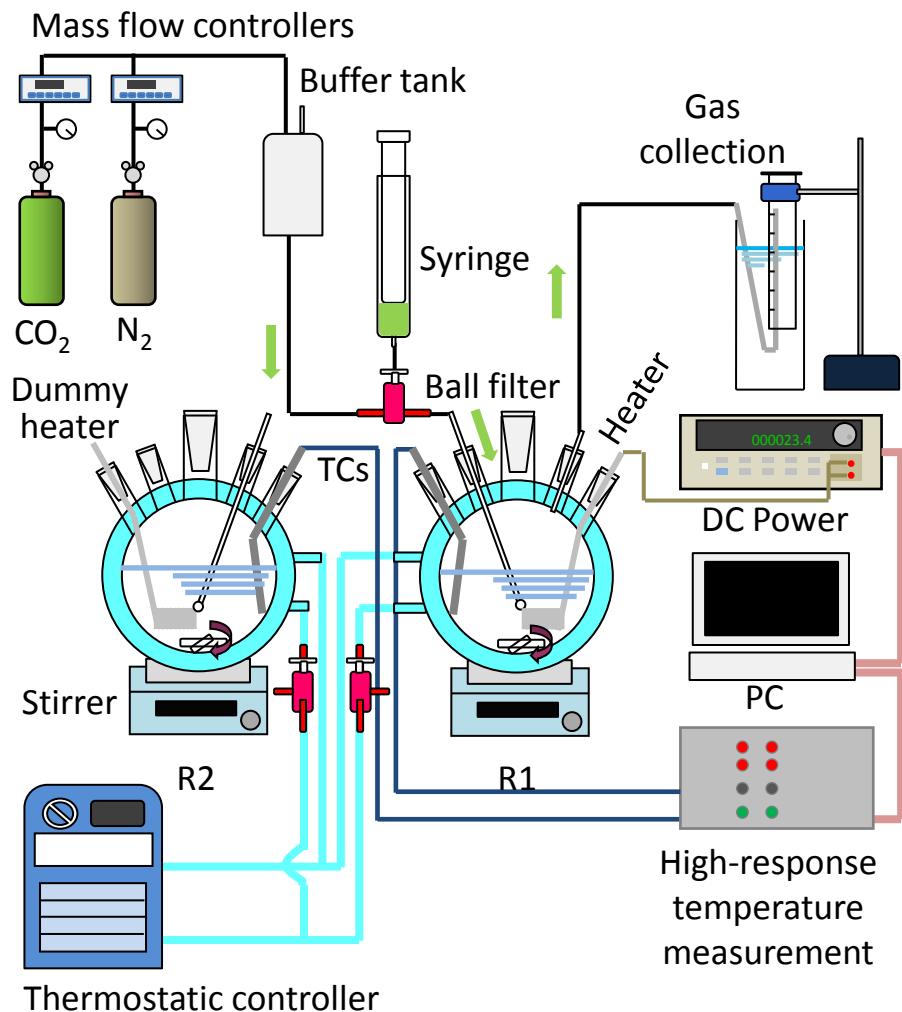


Heat	Formula	Experimental
Dissolution	$Q_R = f(m_1, m_2, H_{abs})$	DRC
Sensible	$Q_H = \left( \int_{T_1}^{T_F} C_{pS} dT + \int_{T_F}^{T_2} C_{pL} dT \right) \cdot W_{sol}/W_{CO_2}$	DRC, VLE
Vaporization	$Q_V = H_V \cdot W_V/W_{CO_2}$	VLE
Fusion	$Q_F = f(m_F, H_F)$	DRC, TG-DSC

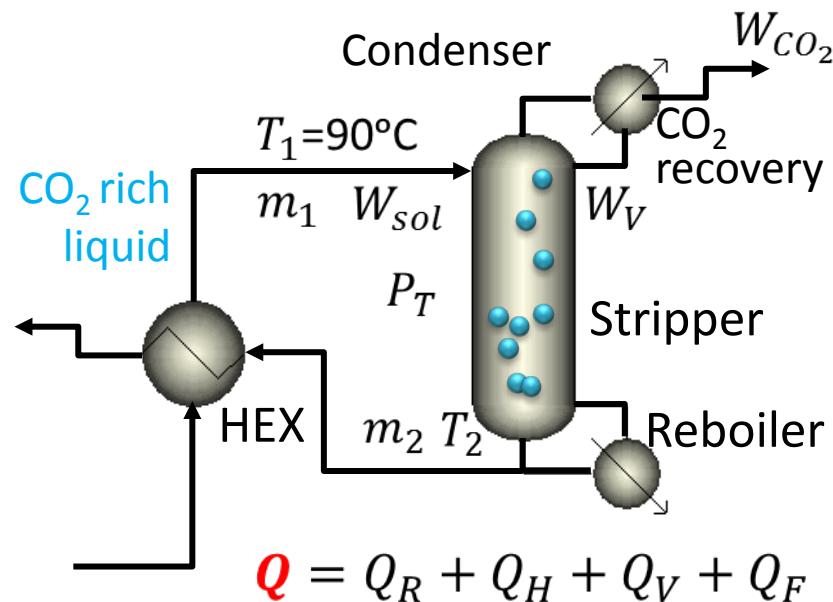
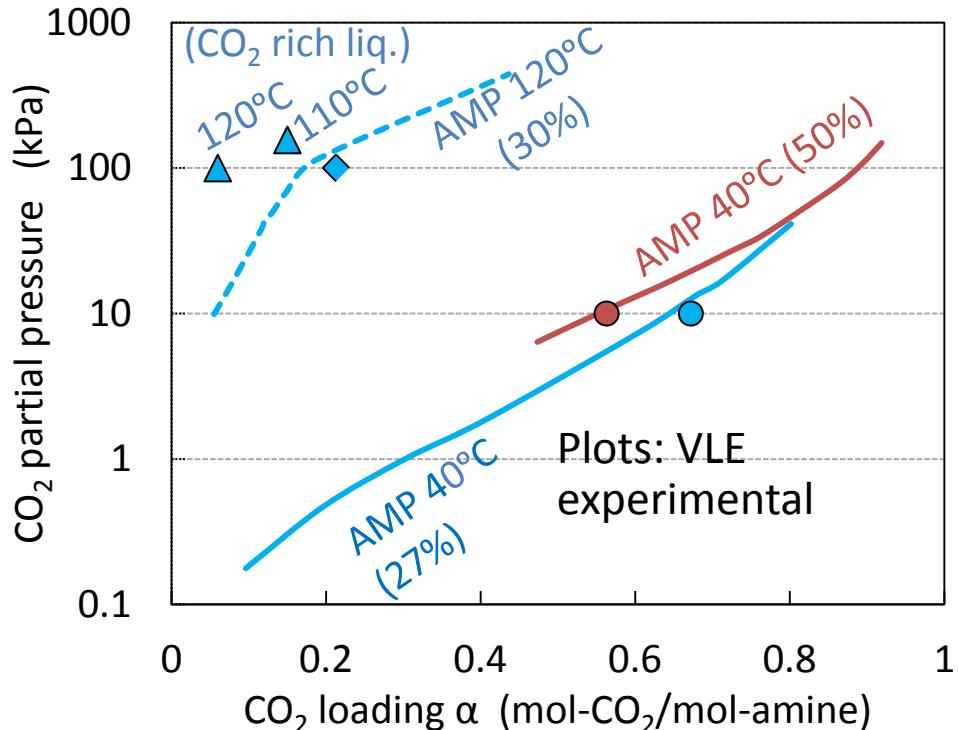
\*RITE, COURSE50 NEDO Project report(2006)

# Measurement of heat of fusion

## Heat of $\text{CO}_2$ absorption by DRC



# Operating condition of stripper



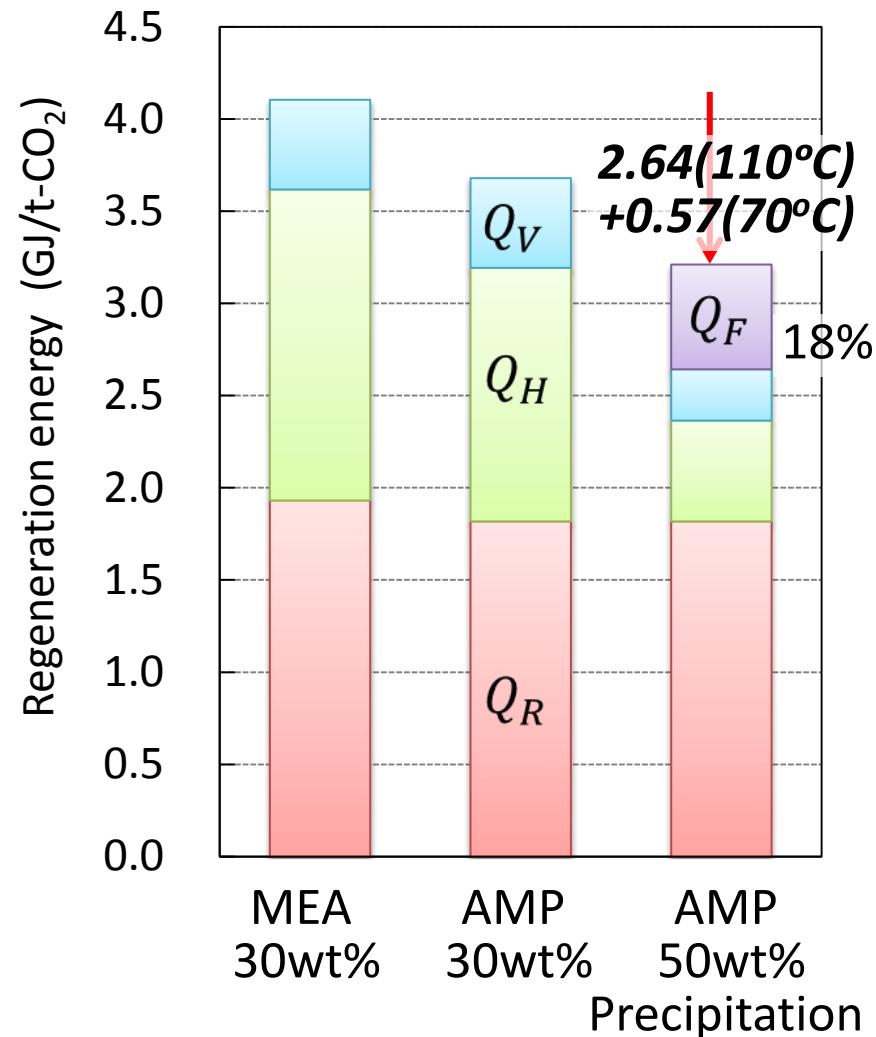
CO<sub>2</sub> rich liquid (derived from separated solid) kept a low CO<sub>2</sub> loading (0.15) at 110°C

- ✓ Lower  $T_2 \rightarrow Q_H = \left( \int_{T_1}^{T_F} C_{ps} dT + \int_{T_F}^{T_2} C_{pL} dT \right) \cdot W_{sol}/W_{CO_2}$  decrease
- ✓ Higher  $P_T \rightarrow Q_V = H_V \cdot W_V/W_{CO_2}$  decrease

Operating condition of stripper for CO<sub>2</sub> rich liquid (Solid with 45% moisture):  
 Reboiler temperature  $T_2 = 110^\circ\text{C}$       Total pressure  $P_T = 300\text{kPa}(\text{abs.})$

# Result: regeneration energy estimation

	M	30% MEA	30% AMP	50% AMP
$P_T$	kPa	200	200	300
$T_2$	°C	120	120	110
$P_{H_2O\_2}$	kPa	198.5	198.5	143.3
$P_{CO_2\_2}$	kPa	1.5	1.5	156.7
$m_1$	mol-CO <sub>2</sub> /mol-amine	0.52	0.6	0.65
$m_2$	amine	0.2	0.02	0.15
$H_R$	kJ/mol-CO <sub>2</sub>	85	80	80
$H_v$	kJ/kg	2202	2202	2230
$C_p$	kJ/kgK	3.60	3.75	3.50
$\rho$	kg/L	1.08	1.08	1.08
$W_{CO_2}/W_{sol}$	kg-CO <sub>2</sub> /kg-amine	64.0	81.8	128.1
$W_v/W_{CO_2}$	kg-H <sub>2</sub> O/kg-CO <sub>2</sub>	0.22	0.22	0.12
$Q_R$		1.93	1.82	1.82
$Q_H$		1.69	1.38	0.55
$Q_V$	GJ/t-CO <sub>2</sub>	0.49	0.49	0.28
$Q_F$		(0.00)	(0.00)	0.57
$Q_{total}$		<b>4.10</b>	<b>3.68</b>	<b>3.21</b>



$$Q_{total} = Q_R + Q_H + Q_V + Q_F$$

\*Value of solid paste derived from 50% AMP

# Conclusions

We proposed a precipitating 2-Amino-2-methyl-1-propanol (AMP) carbonate solvent process for CO<sub>2</sub> capture and estimated its regeneration energy by the equilibrium-based method using properties obtained by VLE and calorimetry.

- ✓ At 40°C and 10kPa CO<sub>2</sub>, 50 wt% AMP precipitated in CO<sub>2</sub> loadings of more than 0.22 and equilibrium CO<sub>2</sub> loading of slurry was 0.56.
- ✓ Chemical structure of the crystal was identified as a salt of protonated AMP and carbonate by Raman spectroscopy.
- ✓ The precipitate solid obtained by simple suction filtration contained 35% moisture and 72% of absorbed CO<sub>2</sub>.
- ✓ The precipitate solid completely melted at 70°C and was regenerated down to a CO<sub>2</sub> loading of 0.05 at 120°C and 100kPa CO<sub>2</sub>.
- ✓ The regeneration energy using the precipitating AMP carbonate solvent process was estimated at 3.21 GJ/t-CO<sub>2</sub>, and 18% of which requires only 70°C.