Results of RITE's Novel Water-lean Solvent for Energy Efficient CO_2 Capture

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Today’s Presentation

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1. An introduction
2. Water-lean solvent development plan
3. Water-lean solvent selection methodology
4. Selected water-lean solvent optimization
5. Research summary

RITE Liquid Solvent Development Projects

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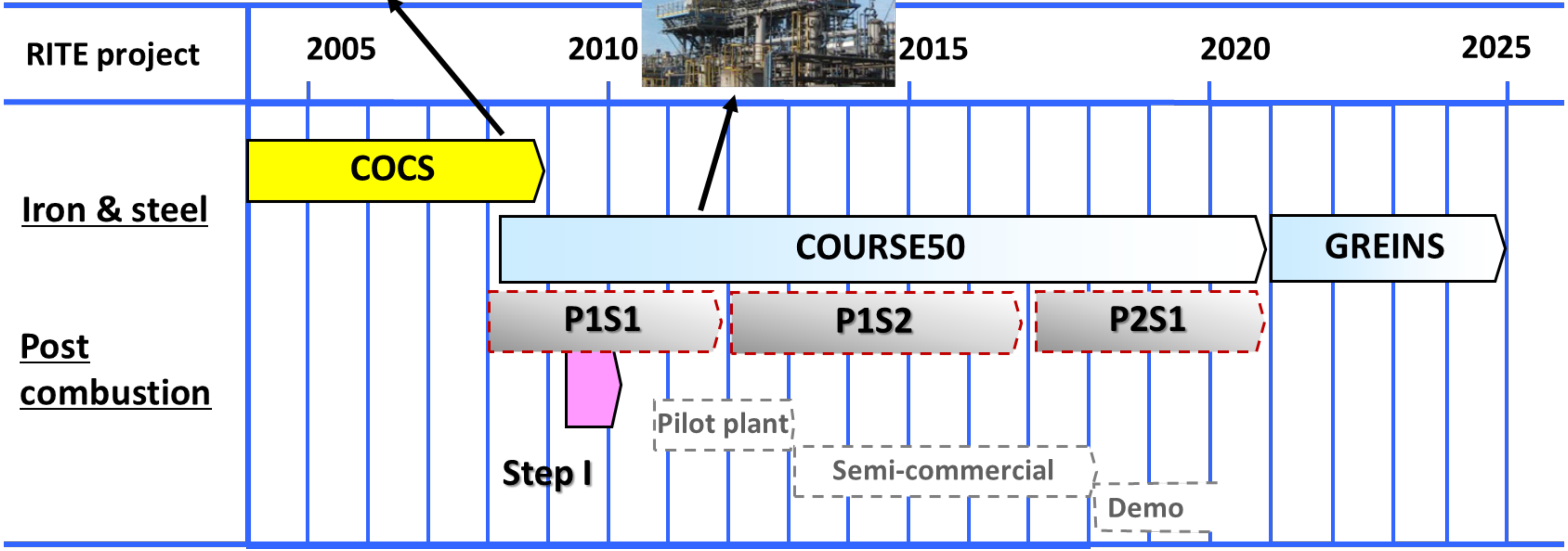
1t/d test plant

New solvents also evaluated @ 30 t-CO_2/d pilot plant.



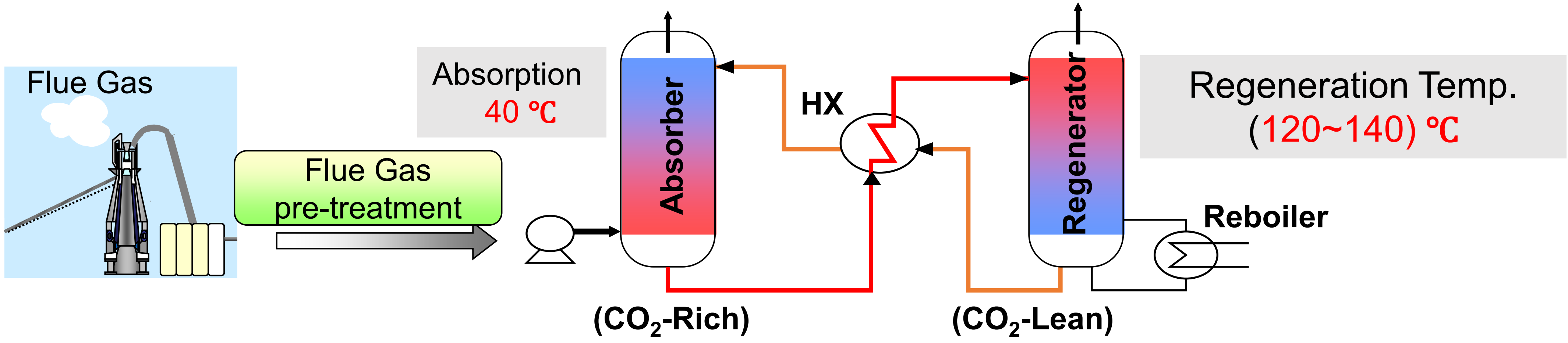
Introduction

Reaction in the absorber:

$$2R\text{-}NH_2 + CO_2 + H_2O \leftrightarrow R\text{-}NHCOO^- + R\text{-}NH_3^+ + HCO_3^-$$

Reaction in the regenerator:

$$R\text{-}NHCOO^- + R\text{-}NH_3^+ + HCO_3^- \leftrightarrow 2R\text{-}NH_2 + H_2O$$



Typical chemical absorption Process

($Amine\text{-}CO_2\text{-}H_2O$) vs ($Amine\text{-}CO_2\text{-}ROH$) solvent

Present Chemical Absorbent	Amine based aqueous solvent system	High specific heat	High evaporation latent heat	Abs. - Reg. Temperature (40~120)℃
Alternative Chemical Absorbent	Amine based water-lean solvent system	Low specific heat	Low evaporation latent heat	Abs. - Reg. Temperature (40~90)℃

Introduction

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Reaction with aqueous amine solution

Carbamate generation

$2R^1R^2NH + CO_2 \longleftrightarrow R^1R^2NCOO^- + R^1R^2NH_2^+$

absorb CO_2 (1 : 2) ratio

Higher Heat

Regeneration @ ~120 °C

Bicarbonate generation

$2R^1R^2R^3N + CO_2 + H_2O \longleftrightarrow 2R^1R^2R^3NH^+ + HCO_3$

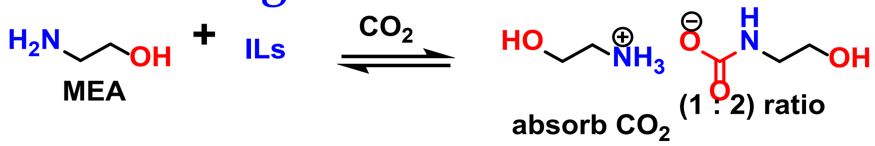
absorb CO_2 (1 : 1) ratio

Lower Heat

@ ~90 °C

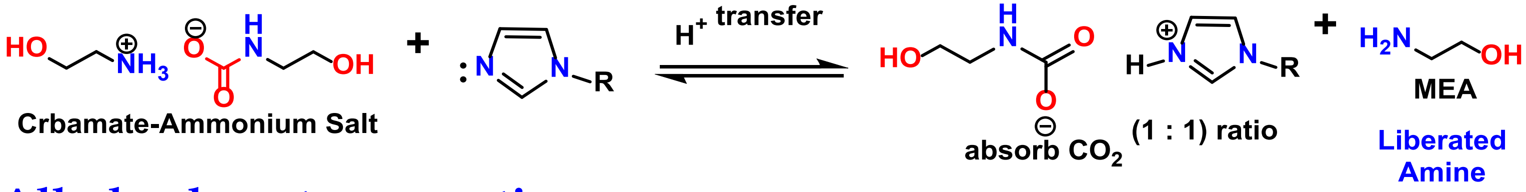
Reaction with non-aqueous amine solution

Carbamate generation

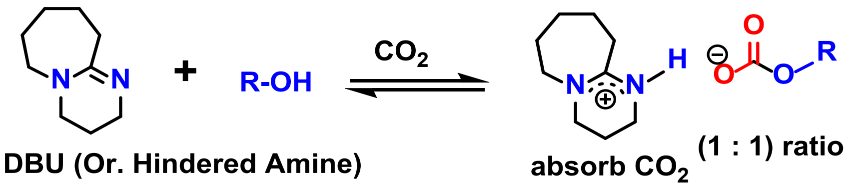


Higher Heat

Regeneration @ ~100 °C



Alkylcarbonate generation



Lower Heat

@ ~90 °C

Aqueous amine scrubbing processes

- High energy consumption for solvent regeneration.
- Environmental and health concerns due to volatile amine loss.
- Corrosion problems.

Non-Aqueous amine scrubbing processes

- Lower specific heat and latent heat of solvent could be reduced reboiler heat duties.
- Primary challenge is the strong and non-linear increase in viscosity that occurs with CO_2 uptake.

Water-lean solvent development plan

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R & D focuses:

- Material that offer lower viscosity.
- Increasing CO_2 rich-lean window.
- CO_2 regeneration at low temperature.

Other important features

- fast absorption kinetics
- high CO_2 cyclic capacity
- low heat requirements for regeneration

Basis (absorb CO_2 1 : 1 ratio)

Carbamate formation (***R-NHCOO⁻***):

$$2R\text{-}NH_2 + CO_2 + Im \leftrightarrow R\text{-}NHCOO^- + Im^+ + R\text{-}NH_2$$

(Carbamate)

Alkylcarbonate formation (***RCO_3^-***):

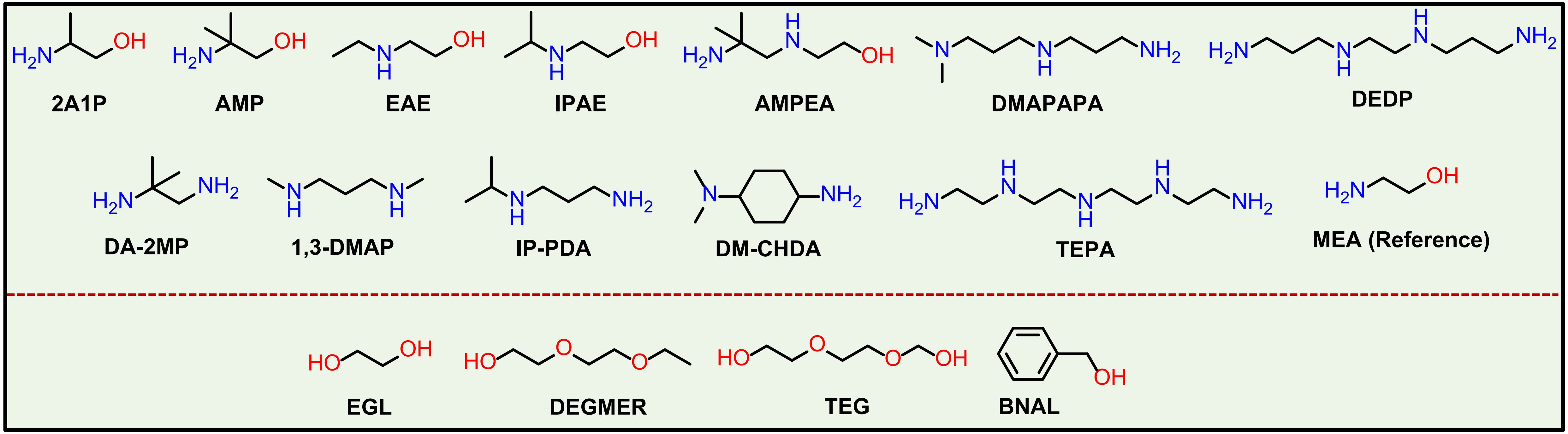
$$R\text{-}NH_2 + CO_2 + R\text{-}OH \leftrightarrow RCO_3^- + R\text{-}NH_3^+$$

(Alkylcarbonate)

Emphasis on

RCO_3^- >> R-NHCOO⁻

Investigated amine absorbents and alcohol solvents



- This work investigated amine absorbents (12) and alcohol solvents (4) short name and their chemical structures
- Monoethanol amine (MEA) used as a reference

R & D Activities

1st step

Laboratory experiments

- Screening test
- Calorimetry
- Vapor-liquid equilibrium
- Spectroscopy

Computational chemistry

- To understand the absorption chemistry for the selection and formulation of amines

3rd step

Evaluation of engineering performance

- Corrosion
- Degradation

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2nd step

Plant tests

- 50 kg CO_2/d
- 1 t CO_2/d
-30 t CO_2/d

Process simulation

Laboratory Scale Experiments

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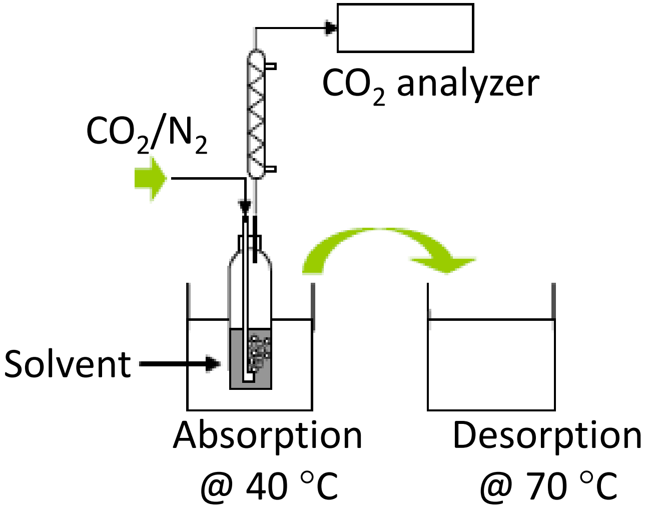
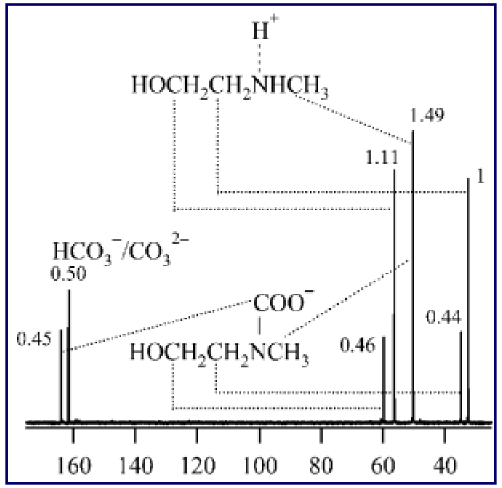
Screening test

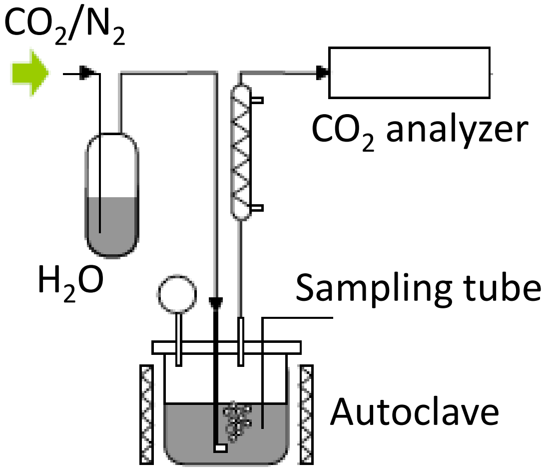


^{13}C NMR



Calorimetry

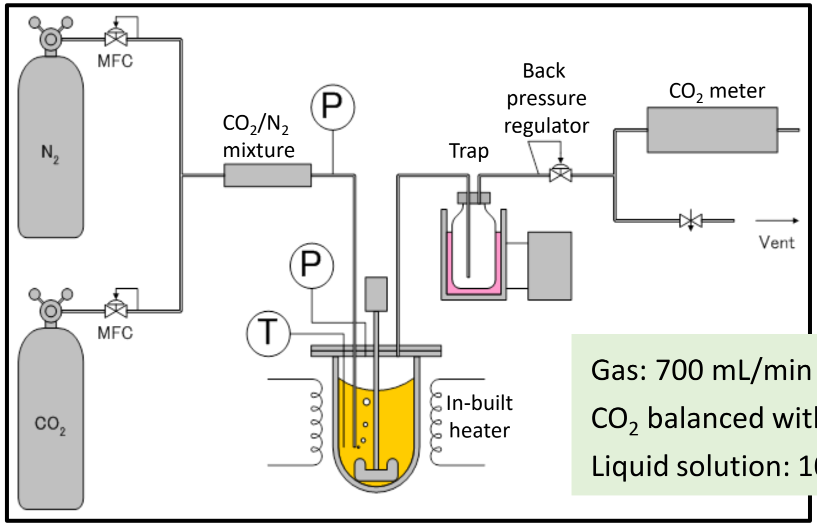
Vapor-liquid equilibrium



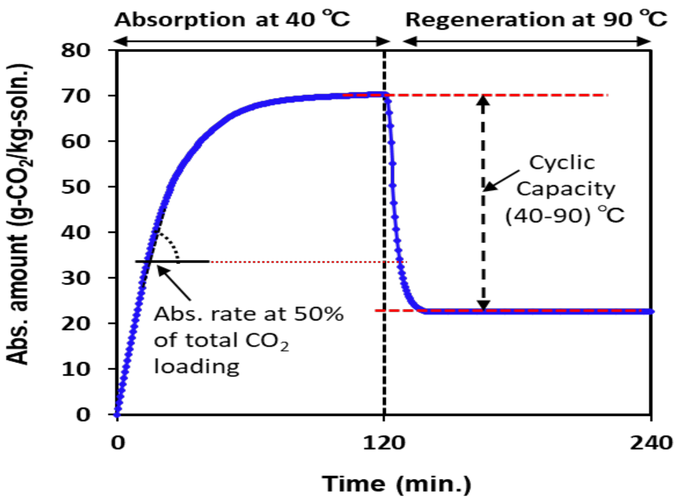
Absorption rate, Desorption rate, Absorption capacity, Heat of reaction, Speciation

Gas Scrubbing Test

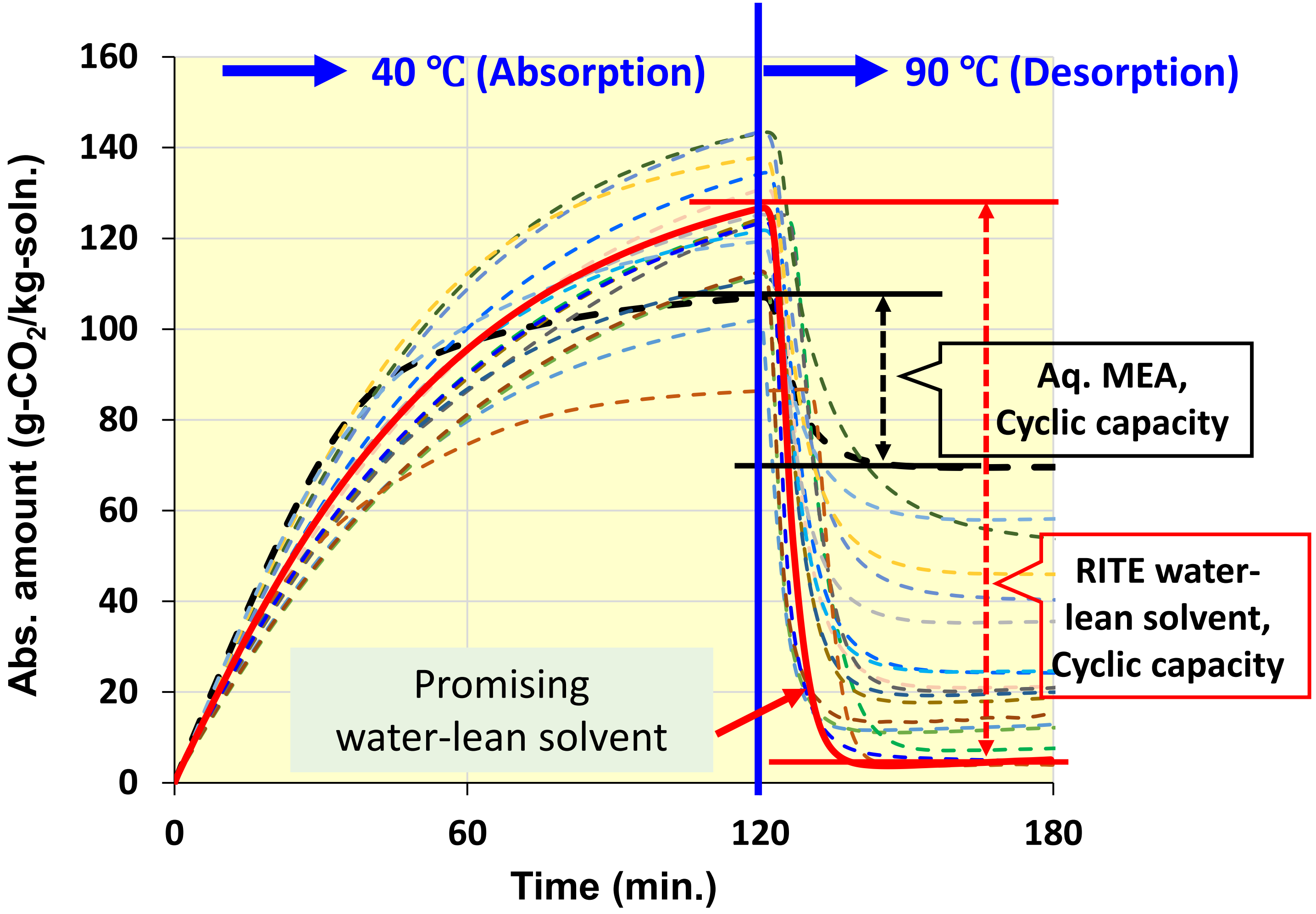
Gas scrubbing test apparatus



Gas: 700 mL/min 20% CO_2 balanced with N_2
Liquid solution: 100g

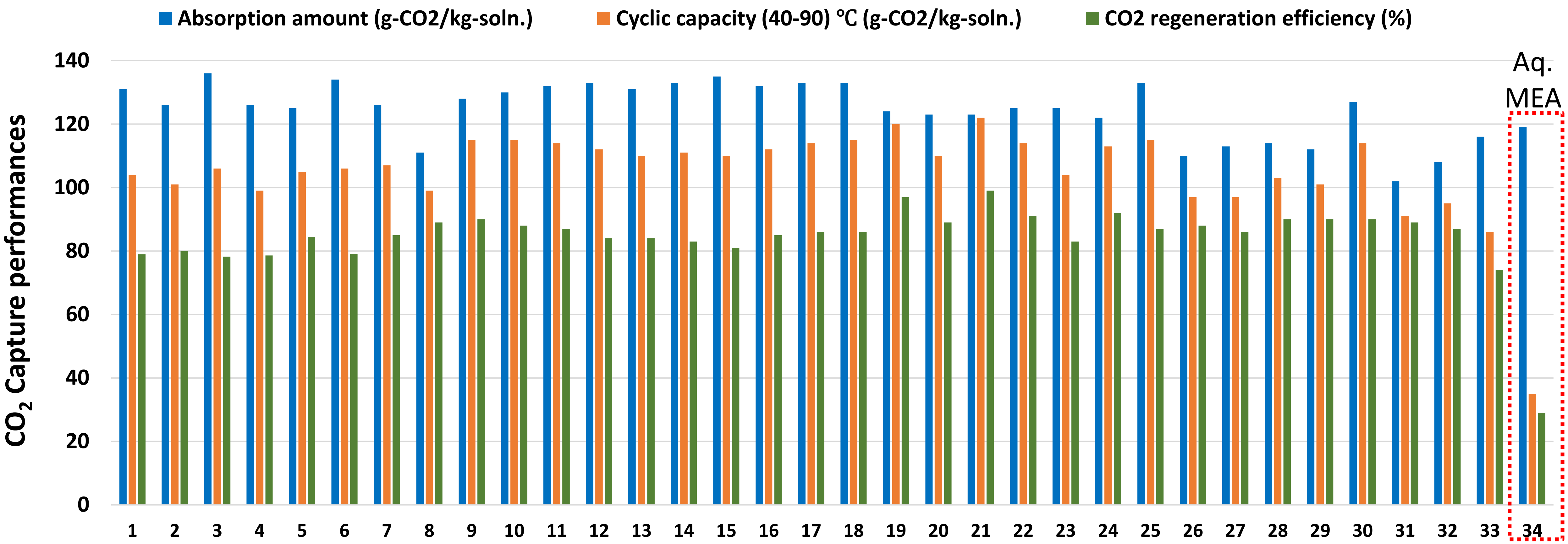


Typical example of a gas scrubbing test



Points of focus: High absorption/desorption rate, low reaction heat, high CO_2 recovery capacity

Screening Test Results



- Absorption amount (g-CO_2/kg-soln.) = 120 min. CO_2 loading at 40 °C
- Cyclic capacity (g-CO_2/kg-soln.) = difference between CO_2 loadings at (40 – 90)°C
- CO_2 regeneration efficiency = (Cyclic capacity/Absorption amount) x100%

Water-lean solvent performances

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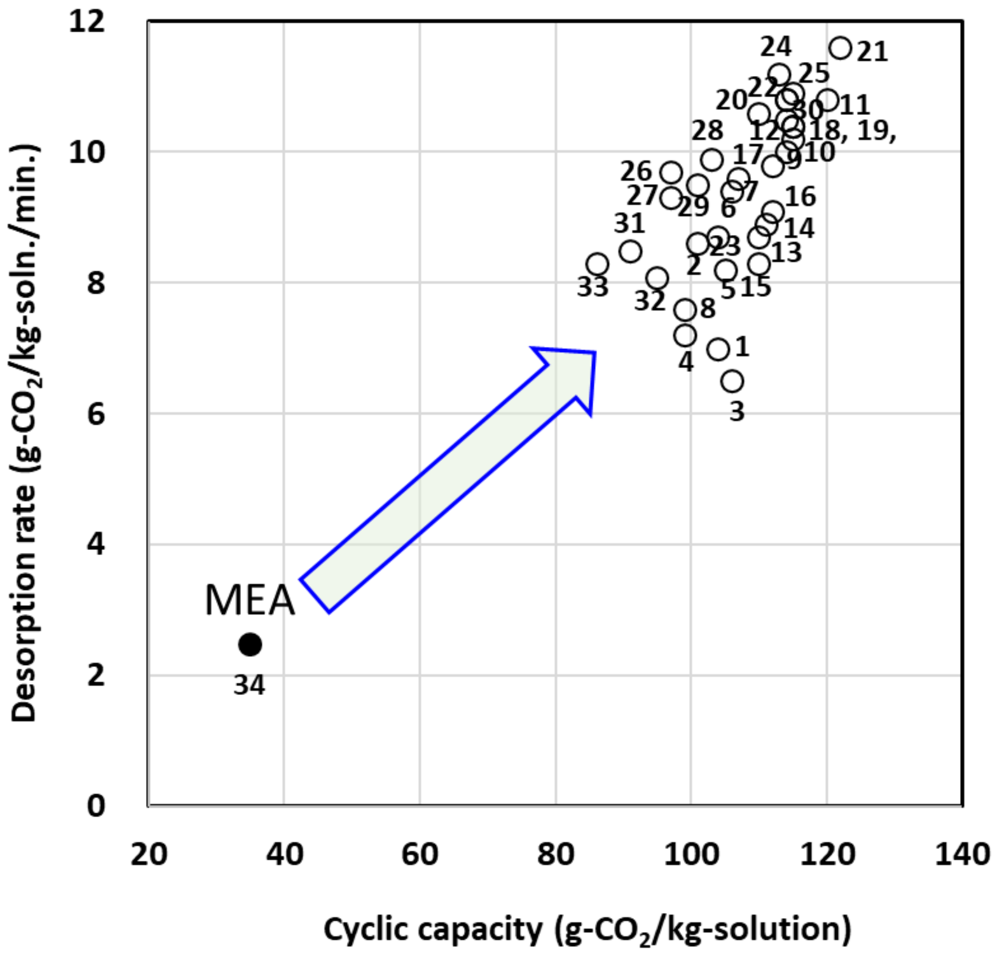

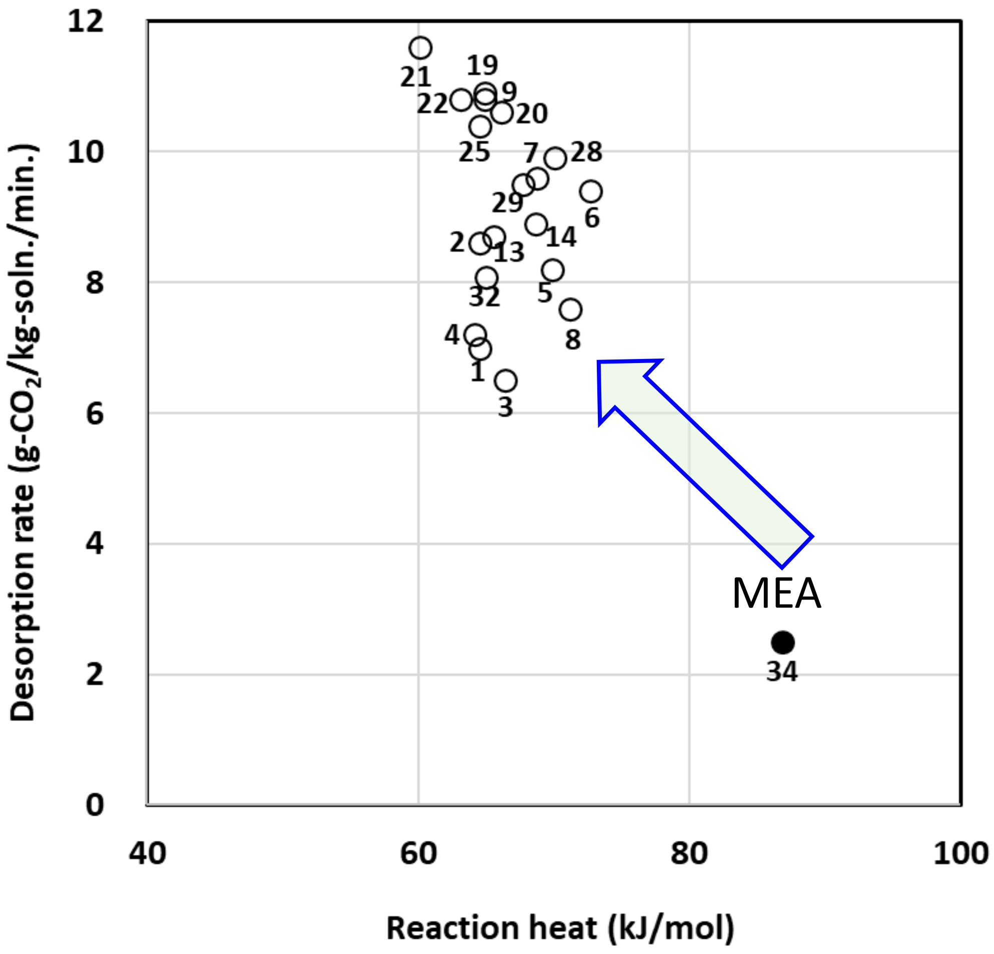

- Succeeded in increasing cyclic capacity by increasing desorption rate ➡ Contributes to improving CO_2 recovery capacity.
- Succeeded in reducing reaction heat while increasing desorption rate ➡ Contributes to reducing thermal energy

Water-lean solvent performances

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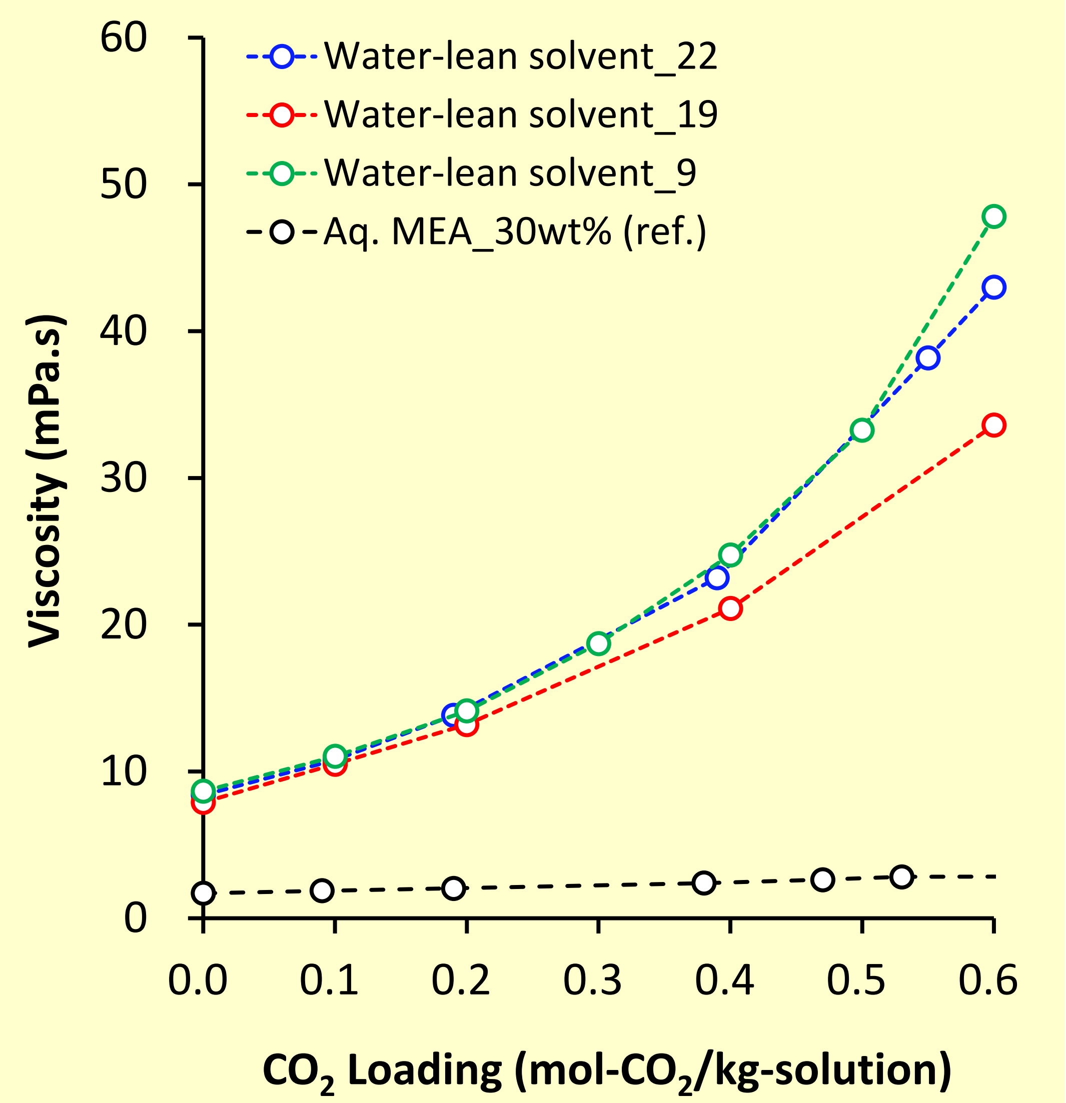
Selected three water-lean solvent performances

Selected Water-lean Solvent	Absorption[a]/ Desorption[b] Rate (g/kg/min.)	CO_2 Loading[c] @ 40 °C (g/kg)	Cyclic Capacity[d] @ (40-90) °C (g/kg)	CO_2 Recovery[e] (%)	Heat of Absorption[f] (kJ/mol-CO_2)	Specific Heat[g] (J/gK)
Water-lean solvent_22	1.35/10.8	125	114	91	63.1	3.1
Water-lean solvent_19	1.40/10.8	124	120	97	64.9	3.0
Water-lean solvent_9	1.32/10.6	123	110	89	66.1	2.9
Aq. MEA_30wt% (Ref.)	2.38/2.38	119	35	29	86.9	3.75

[a]CO_2 absorption rates were calculated at 50% of the 120-min CO_2 loading at 40 °C and [b]desorption rates were calculated at the average of the initial 10-min CO_2 loading at 90 °C; [c]120-min CO_2 loading at 40 °C; [d]difference between CO_2 loadings at 40 and 90 °C; [e](c/b) ×100%; [f]Heats of reaction were measured at 40 °C and atmospheric pressure; [f]Specific heats of all water-lean solvent and aq. 30wt% MEA solutions were measured at 40 °C and atmospheric pressure.

Viscosity: Selected Water-Lean Solvent



- All water-lean solutions viscosity as a function of CO_2 loading was measured at 40 ^oC.
- As expected, the viscosity increases with increasing CO_2-loading.
- This work selected water-lean solutions can keep lower viscosity if we compared to global NAS/water-lean solvents.
- All CO_2 loaded water-lean solutions showed higher viscosity in comparison to aq. 30wt% MEA.

Quantitative ^{13}C-NMR Experiment

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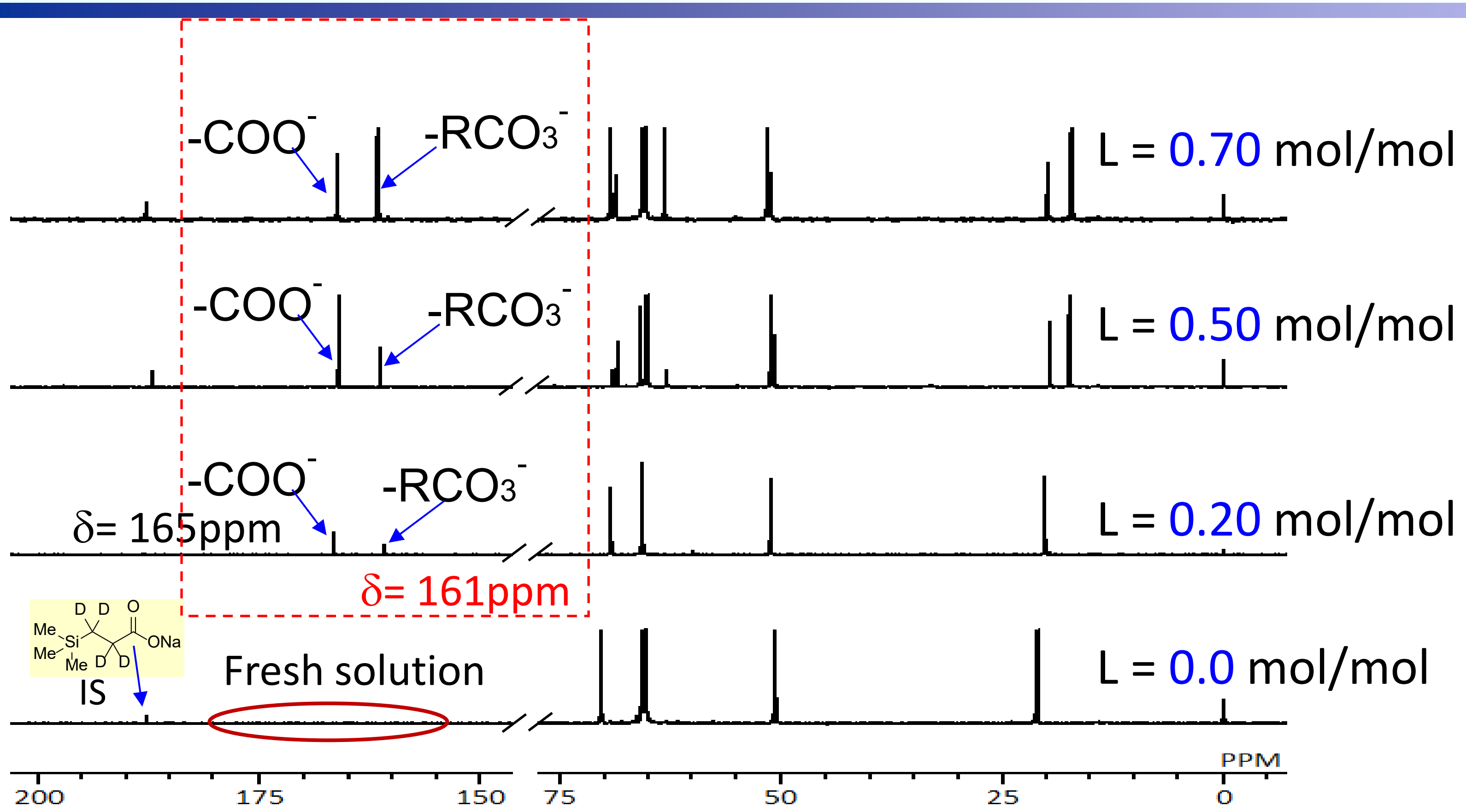


Emphasis on

RCO_3^- >> $R\text{-}NHCOO^-$

Carbamate formation (minor):

$$2R\text{-}NH_2 + CO_2 \leftrightarrow R\text{-}NHCOO^- + R\text{-}NH_3^+$$

(Carbamate)

Alkyl carbonate formation (major):

$$R\text{-}NH_2 + CO_2 + R\text{-}OH \leftrightarrow RCO_3^- + R\text{-}NH_3^+$$

(Alkylcarbonate)

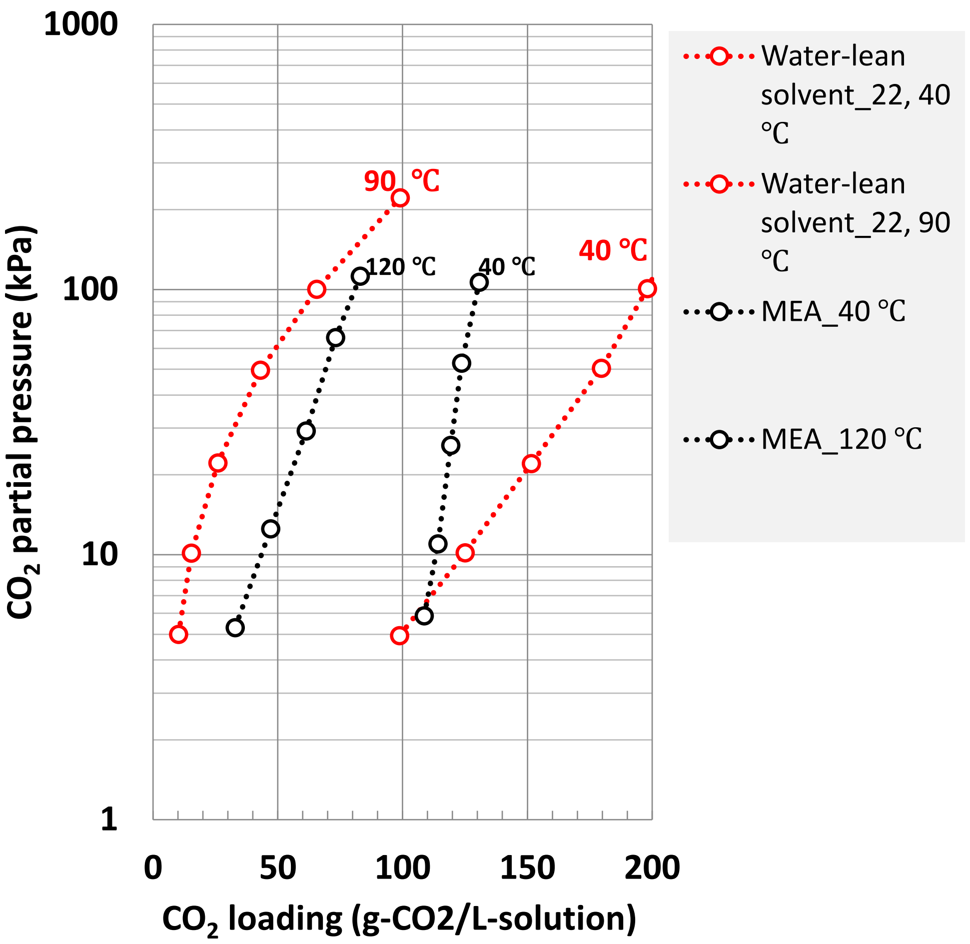
Validation of ^{13}C-NMR analysis

CO_2 Loading mol-CO_2/mol-amine		Anion ratio ^{13}C NMR	
TOC	^{13}C NMR	-COO $^-$	-RCO_3^-
0.20	0.20	0.90	0.10
0.50	0.49	0.79	0.21
0.70	0.69	0.42	0.58

Conditions: Quantitative ^{13}C NMR

^{13}C-NMR : inverse-gated decoupling (90 ℃ pulse, 60 s delay, 600 scans); Internal Standard: $(CH_3)_3Si(CD_2)_2COONa$ in D_2O; Temp: 296-297 K

VLE CO_2 Solubility: Water-lean Solvent



Water-lean Solvent_22 vs aqueous MEA

Tested Sample	40 ℃ P_{CO2} [kPa]	40 ℃ CO_2 rich [g-CO_2/L-soln.]	90 ℃ P_{CO2} [kPa]	90 ℃ CO_2 lean [g-CO_2/L-soln.]	Cyclic capacity (**40-90**) ℃ [g-CO_2/L-soln.]
Water lean solvent_22	13	132.2	13	18.3	113.9
	20	148.3	20	24.4	123.9
	100	197.8	100	65.6	132.3
Aqueous MEA_30wt% (Reference)	13	114.7	13	71.6	43.1
	20	118.2	20	78.7	39.5
	100	134.2	100	83.1	51.1

- Under equilibrium condition at any CO_2 partial pressure and temperature this work water-lean solvent remarkably increased cyclic CO_2 capacity compared to reference aqueous MEA solution.

Evaluation at 5kg$_{-CO2}$/d bench plant

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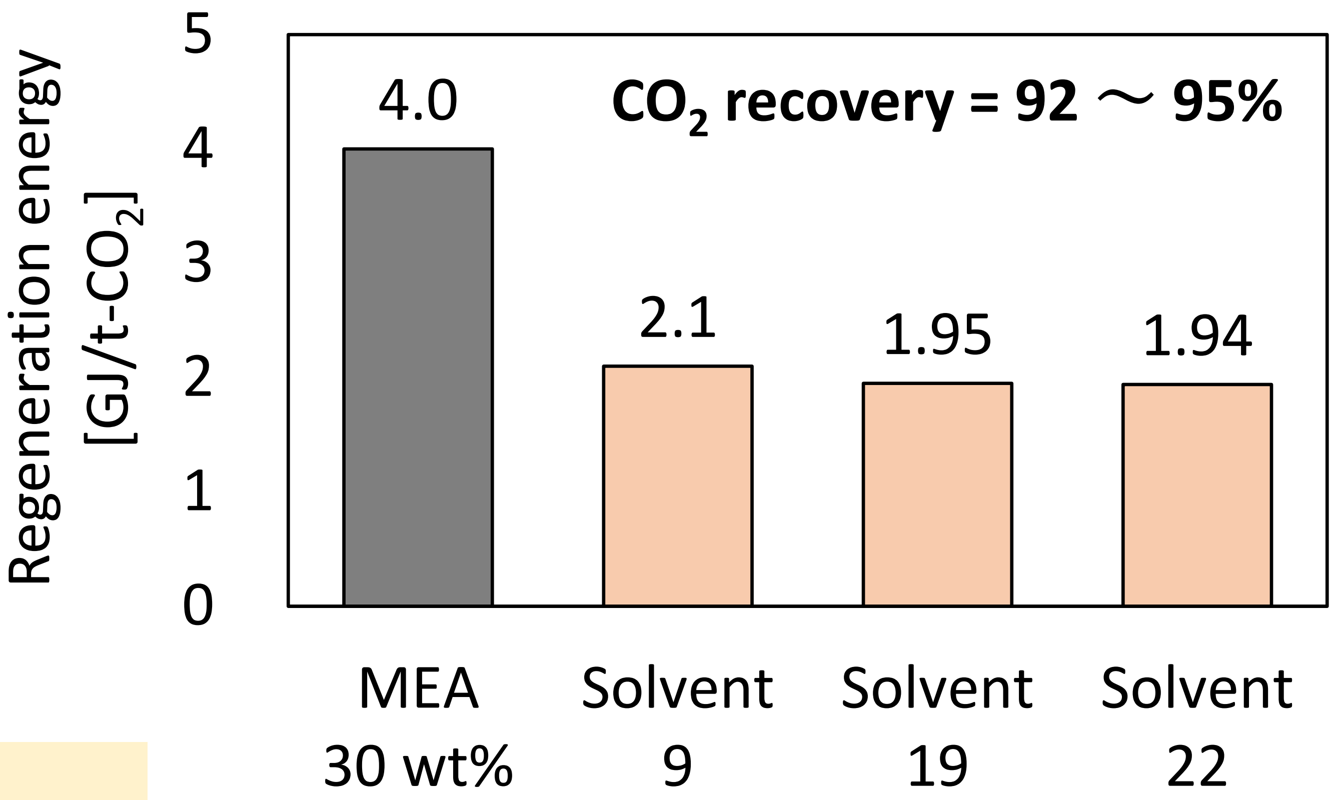
CAT-LAB

CAT: Chemical Absorption Test plant



CAT-LAB test conditions and equipment specifications

Gas: Blast furnace gas (20%$_{CO2}$)

CO_2 capture capacity: 5 kg$_{-CO2}$ / d

Absorber [mm]: 1,500H x 50ϕ

Stripper [mm]: 1,200mm x 50ϕ

Gas flow rate [L/min.] = 10

Column filling: Dixon packing (6 mm)

This work water-lean solvents significantly lower regeneration energies than conventional aqueous MEA.

Research Summary

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- RITE developed new water-lean solvents to establish a low-cost CO_2 capture system for integrated steelworks.
- Amines for new water-lean solvents were selected based on experimental and computational methods, and formulated by optimizing concentration, blending, etc.
- New solvents showed excellent performance. The regeneration energies of the solvents are $\sim$ 2.0 GJ/t-CO_2.

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Thank you for your attention.

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