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SOTACARBO
SUSTAINABLE ENERGY RESEARCH CENTRE

POLITECNICO
MILANO 1863

LEAP
Laboratorio Energia e Ambiente Piacenza

Post Combustion CO_2 Capture via Chemical Absorption with Amino Acid Salts Solutions

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INTRODUCTION

Background

- The present work has been carried out in the framework of a collaboration between LEAP (Laboratory of Energy and Environment Piacenza)-Politecnico di Milano and Sotacarbo Research Center

- The activity is partially funded by the Regional Government of Sardinia (FSC 2014-2020) within the “Centre of Excellence on Clean Energy” project (CUP D83C17000370002)

Objective

- Research project on alternative solvents for chemical absorption applied to CO_2 for post-combustion capture applications

- Alternative solvents to be investigated → Amino Acids (green solvents)

- CCS technology applied to Natural Gas Combined Cycle (NGCC) flue-gas

- Reference solvent → 5M MEA solution (30% w/w as from EBTF-CAESAR Project)

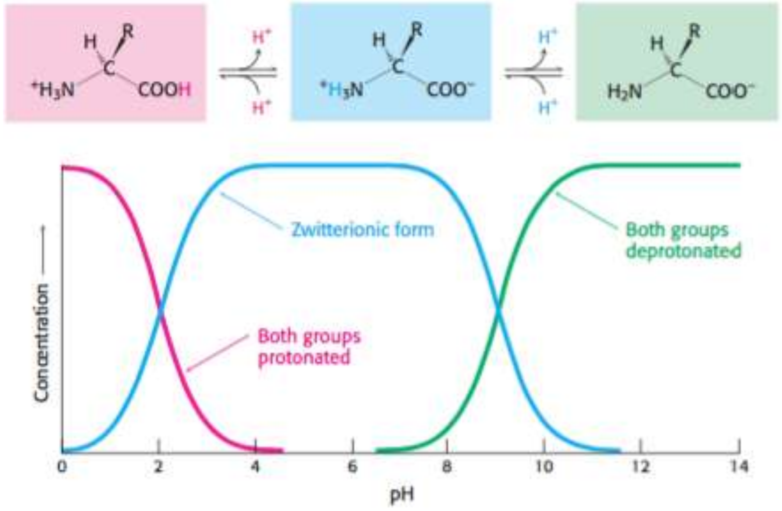
INTRODUCTION

Benefits of Amino Acid Salts and their Potential Impact (Literature Information)

↑ CO_2 Loading and Absorption Rate	↑ Cyclic Capacity	↓ Thermal Oxidative Degradation	↓ Corrosion	↓ Volatility, ↑ Environmental Compatibility
Less circulating solute	Lower circulation rate	Higher solvent life	Longer equipment and accessory life	Lower vapour losses
Lower equipment size (absorber)	Lower energy required (e.g.: pumps)	Reduced make-up and operating costs	Lower equipment cost	Lower solvent make-up
Lower CAPEX	Cost reduction (CAPEX and OPEX)			Reduced health and environmental effects
	Enhanced capacity - solvent precipitation (at high loadings)			

To be verified

INTRODUCTION



- Central carbon atom bonded to carboxyl group, amino group, hydrogen atom, side chain (R)
- R → only difference among the 20 most common amino acids
- R → affects molecular structure, size and electric charge, impacts on water solubility

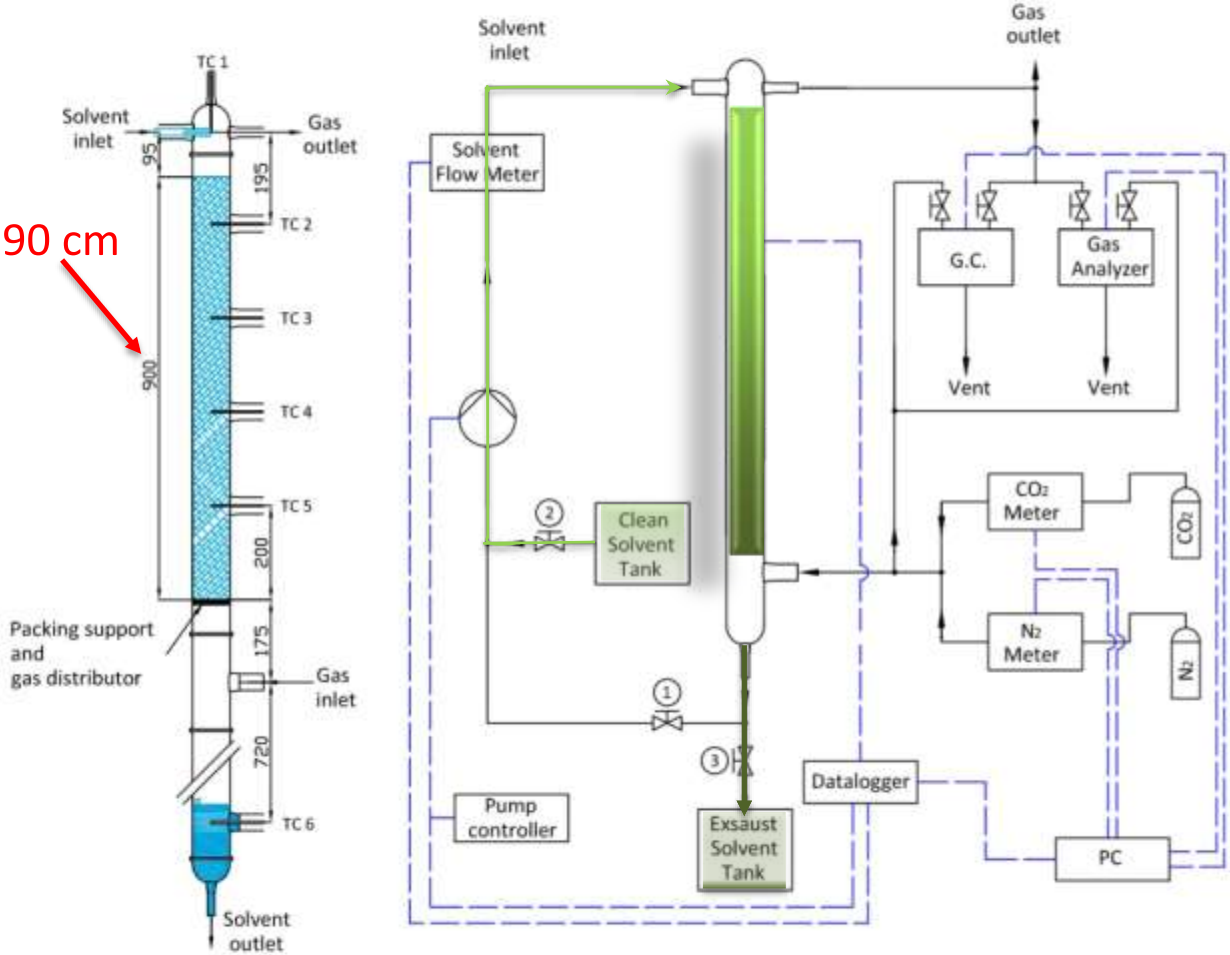
- In water solutions, the following equilibrium is established (pH environment):

$$\underset{(I)}{HOOC-CHR-NH_3^+} \overset{-H^+}{\longleftrightarrow} \underset{(II)}{^-OOC-CHR-NH_3^+} \overset{-H^+}{\longleftrightarrow} \underset{(III)}{^-OOC-CHR-NH_2}$$

cationic (I), zwitterionic (II) or anionic (III) form

- Form III: CO_2 reactive, zwitterionic mechanism → + strong base, basic pH

MATERIALS and METHODS



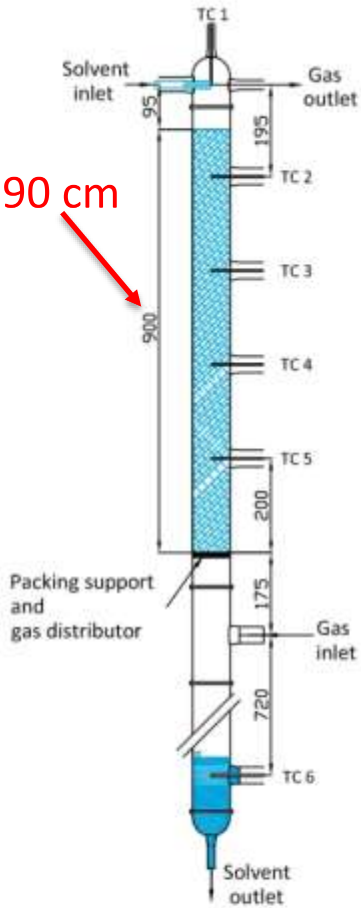
Equipment

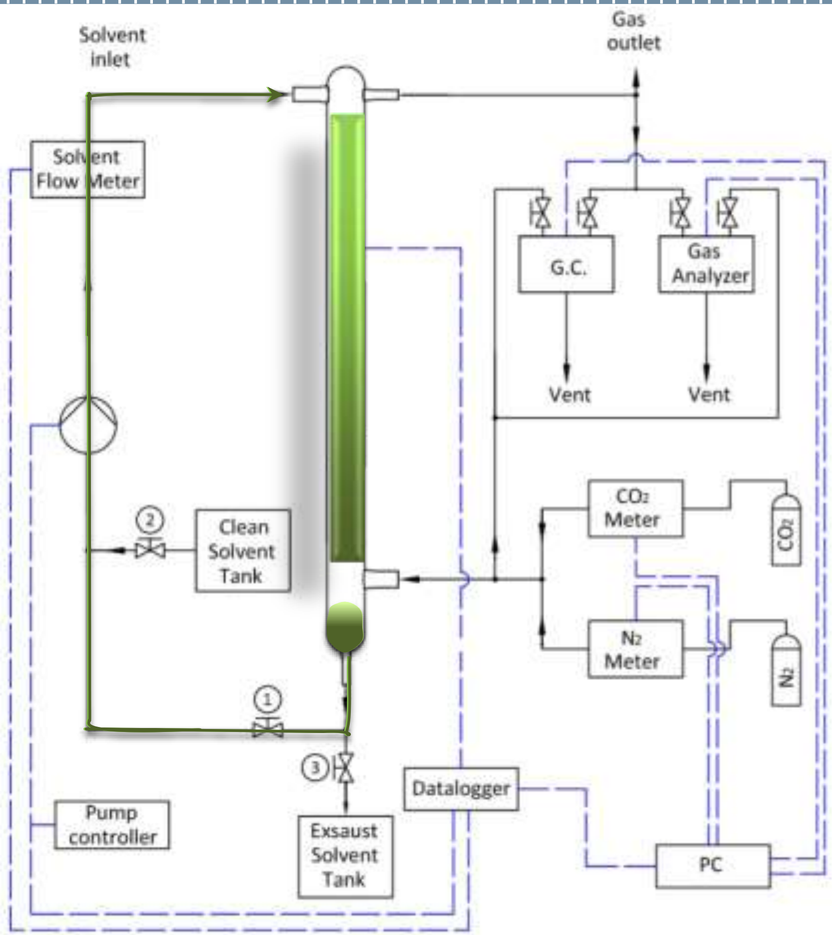
- Glass column (adiabatic)
- 90 cm packed bed (metallic Raschig rings)
- Online analyser and micro GC for CO_2 gas concentration
- Mass flowmeter (gas side) and volumetric flowmeter (liquid side)

Open Cycle

- Counter current absorption of 4% CO_2 rich gas (open cycle) with tested solution at given concentration
- **Rich loading** over 90 cm absorption
- **Removal** calculation over 90 cm absorption

MATERIALS and METHODS





Equipment

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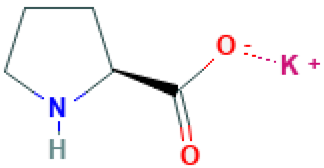
Closed Cycle

- Counter current absorption of 4% CO_2 rich gas (open cycle) with tested solution at given concentration
- Test duration → until **saturation**
- **Loading curves**, maximum loading, **capacity**
- Identification of an **Open Cycle Equivalent time lapse** and related figures of merit (e.g.: removal, partial capacity)

RESULTS

Solvent Selection: Potassium Prolinate vs. MEA

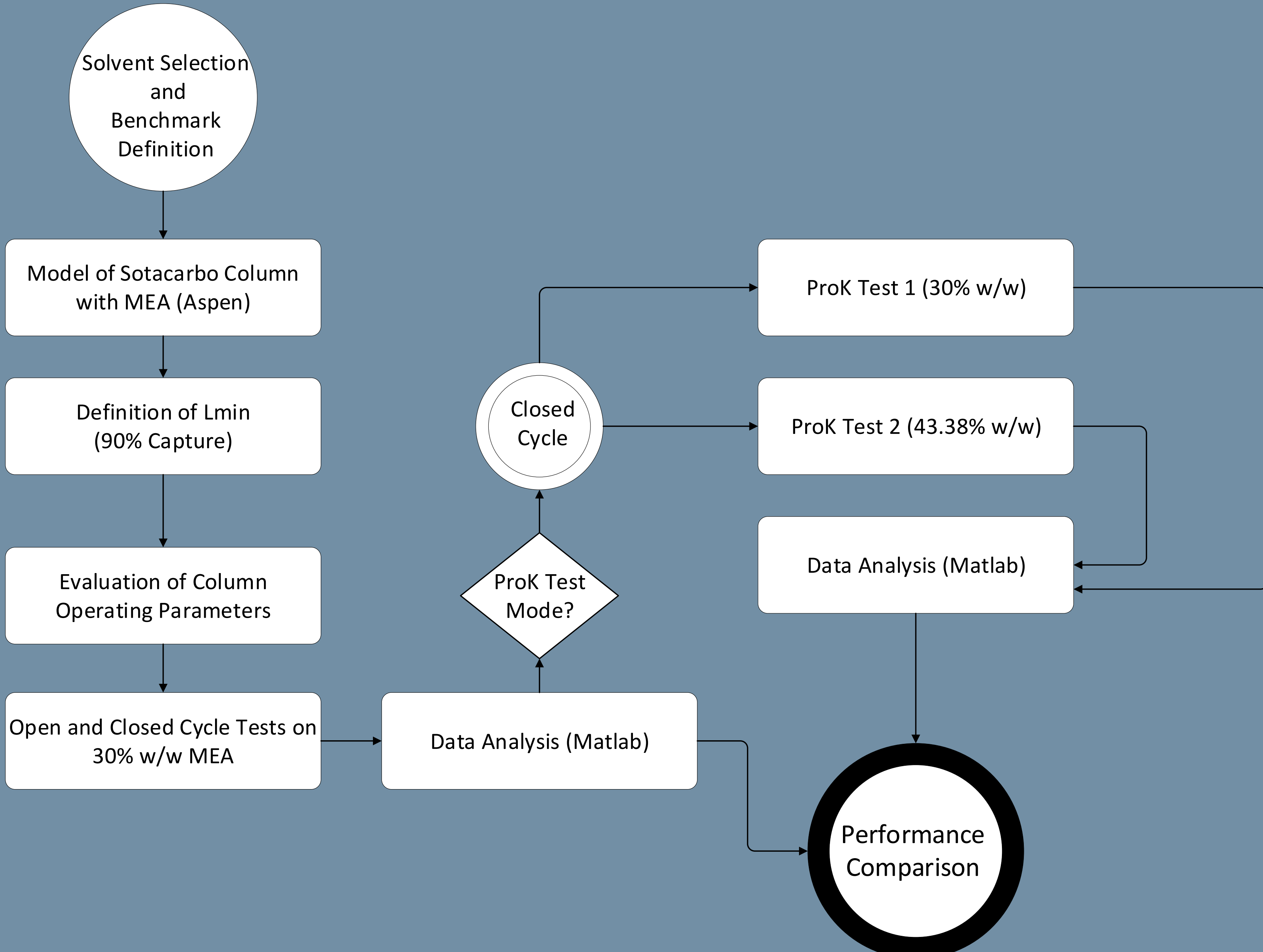


FOCUS ON: non-precipitating solvents

	C [M]	T [K]	Density [kg/m³]	Viscosity [mPa*s]	H_{CO2} [kPa*m³/kmol]	p_{CO2} [kPa]	N_{CO2} 10^{-3} [mol/m²s]	kov [s^{-1}]	D [10^{-9}m²/s]	pKa [-]	Reference
ProK	0.97	303	1058.6	1.27	4384	2.92	4.00	26632	1.08		(Hamborg et al., 2008; Paul and Thomsen, 2012)
	2.00	303	1118.8	2.00	5806	3.09	4.58	71940	0.988		
	3.03	303	1167.8	3.46	7854	3.19	4.05	130855	0.819	10.64	
MEA	5.00	298	1010.6	2.48	3320	4.00	1 (@ 3M, 40°C)	90800	1.65	9.5	(Amundsen et al., 2009; Bui et al., 2014; Feron, 2016; Freguia, 2002; Hall, 1957; Luo et al., 2015)

- Higher AA viscosity and Henry constant
- Higher AA kinetic constant and N-CO_2
- Lower AA diffusivity

→ Solvent screening to include energy performance (e.g.: heat of regeneration)

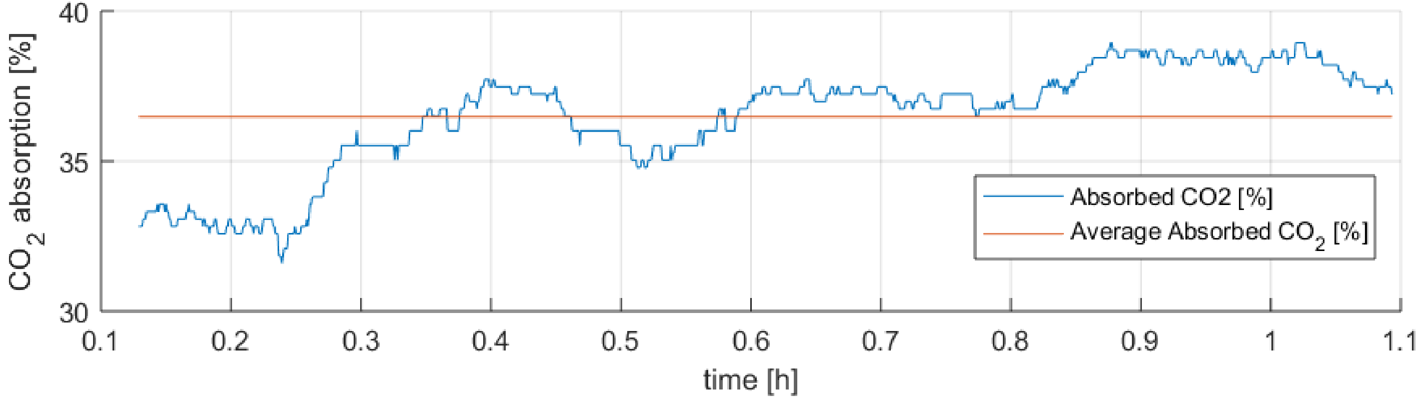

Solvent Selection and Benchmark Definition
Model of Sotacarbo Column with MEA (Aspen)
Definition of Lmin (90% Capture)
Evaluation of Column Operating Parameters
Open and Closed Cycle Tests on 30% w/w MEA
Data Analysis (Matlab)
ProK Test Mode?
Closed Cycle
ProK Test 1 (30% w/w)
ProK Test 2 (43.38% w/w)
Data Analysis (Matlab)
Performance Comparison

RESULTS

		OPEN CYCLE	CLOSED CYCLE			UNIT
		MEA	MEA	ProK-test 1	ProK-test 2	
Gas flow rate		111.71	111.86	111.79	111.81	mol/h
- molar	CO_2	4.63	4.78	4.71	4.72	mol/h
	N_2	107.08	107.08	107.08	107.08	mol/h
- volumetric						
	CO_2	0.1	0.1	0.1	0.1	Nm^3/h
	N_2	2.4	2.4	2.4	2.4	Nm^3/h
Liquid flow rate		3.5	3.5	3.4	3.8	l/h
- mass		3.5	3.5	3.8	4.4	kg/h
- mol		155	155	155	155	mol/h
Solvent concentration		30%	30%	30%	43.38%	w/w
- molar		5.0	5.0	2.2	3.2	mol/L
Tgas in		9	12.5	9.4	8.2	°C
Tliquid in		22	18	18	19	°C
L/G		1.39	1.39	1.39	1.39	mol/mol

RESULTS

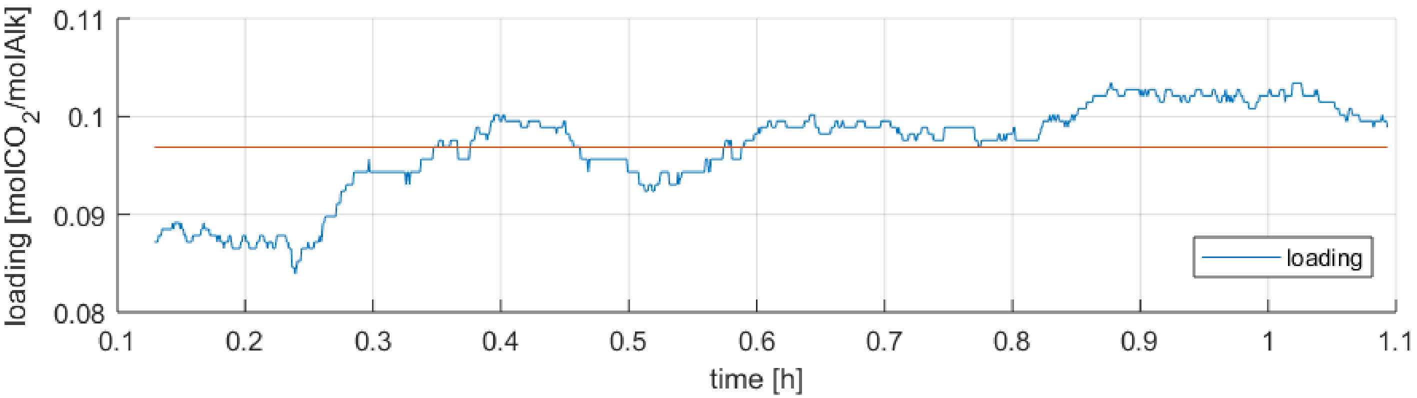
MEA Open Cycle Test (from Data Analysis)



Absorption

36.5%

CO_2 absorption (av.)

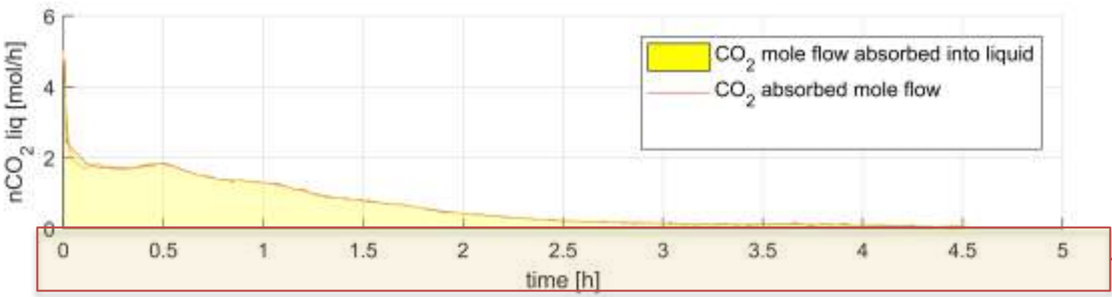


Loading

~0.1 $molCO_2/molALk$

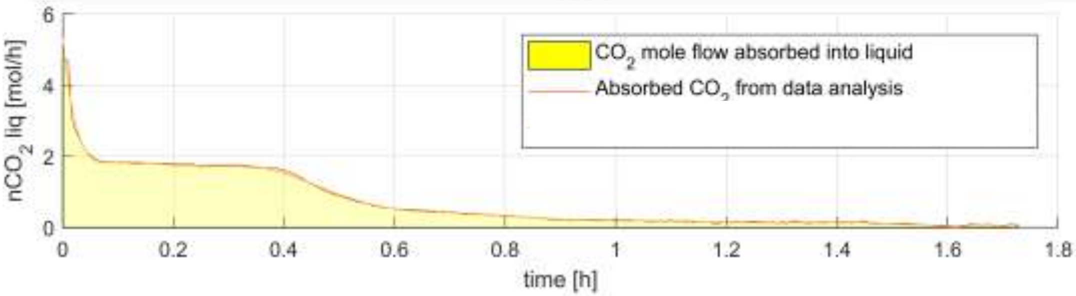
RESULTS

MEA vs. ProK Closed Cycle Test (from Data Analysis)

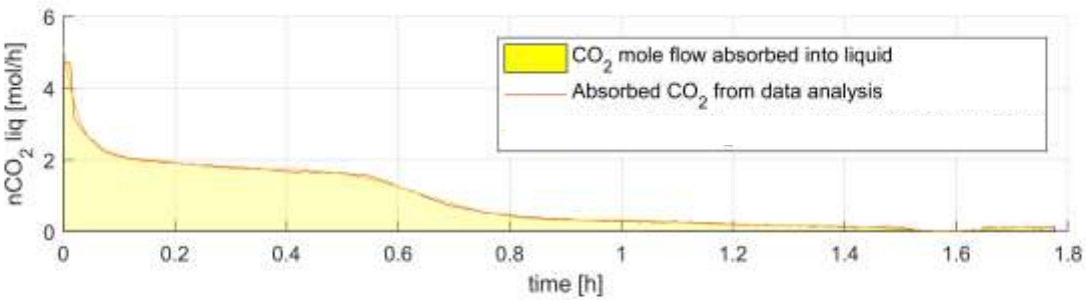


Absorbed flow rate-30% w/w MEA solution

Longer test duration



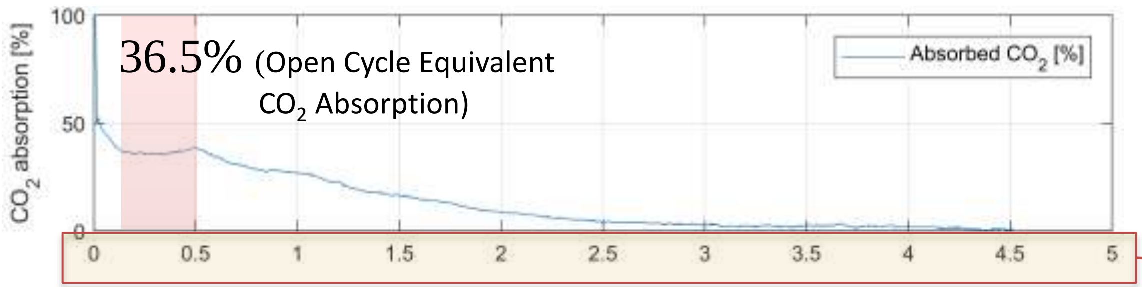
Absorbed flow rate-30% w/w ProK solution



Absorbed flow rate-43.38% w/w ProK solution

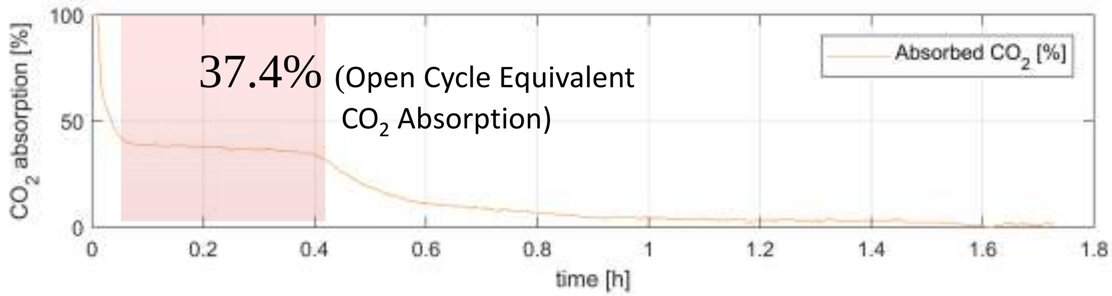
RESULTS

MEA vs. ProK Closed Cycle Test (from Data Analysis)

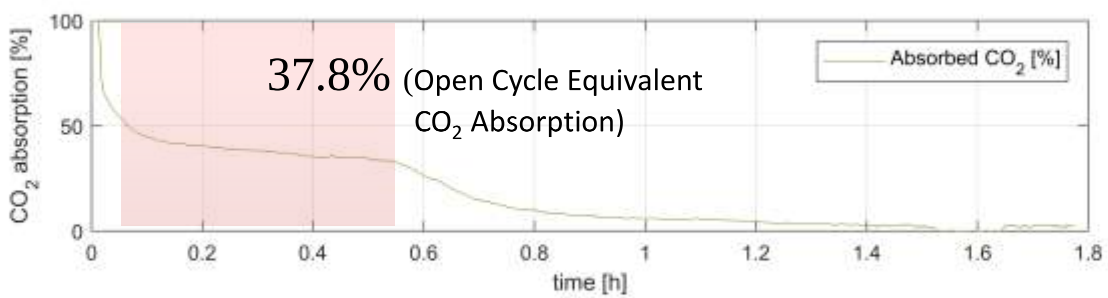


Absorption
30% w/w MEA solution

Longer test duration

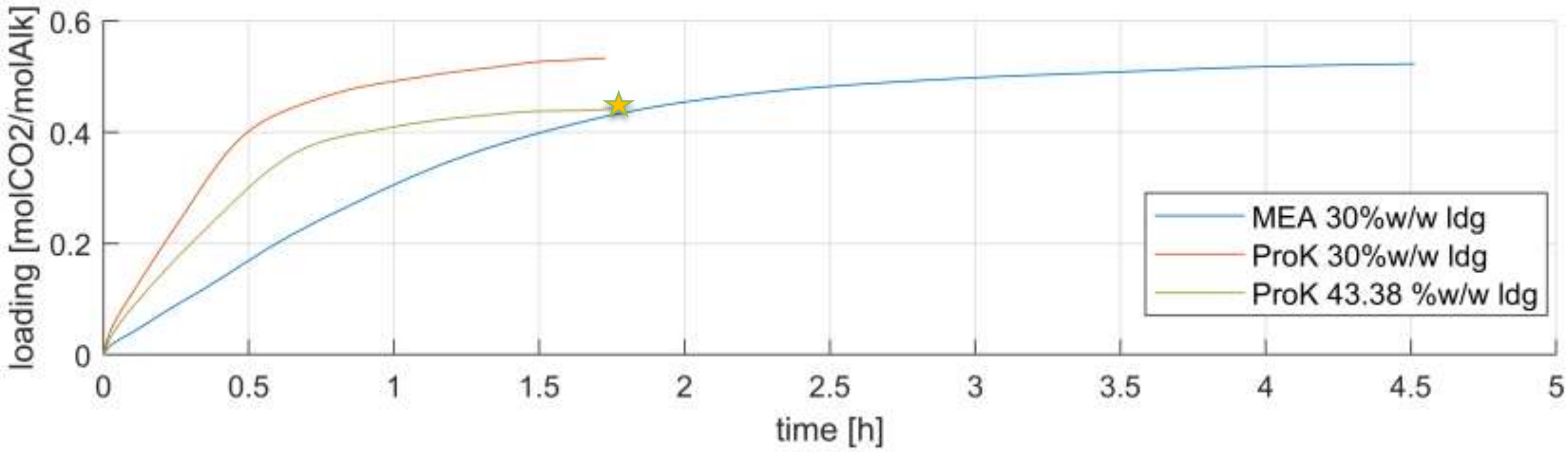


Absorption
30% w/w ProK solution



Absorption
43.38% w/w ProK solution

DISCUSSION



★ Precipitation detected

- From data analysis
- Faster loading increase detected during ProK tests
- Lower maximum loading achieved by 43.38%w/w ProK (**0.44 molCO_2/molAlk**)
- Comparable maximum loading of ProK and MEA 30%w/w (respectively **0.53 vs. 0.52 molCO_2/molAlk**)

DISCUSSION

	MEA-Closed Cycle 30% w/w	ProK-Test 1 30% w/w	ProK-Test 2 43.38% w/w	Unit
Circulating solute $-n_{Alk}$ (MEA/ProK)	5.42	2.23	3.38	mol
Circulating solvent (water+solute)	1.103	1.138	1.193	kg
Mole of CO_2 absorbed	2.83	1.19	1.50	mol
Calculated Loading (end of test)	0.52	0.53	0.44	molCO_2/molAlk
Calculated Capacity	2.57	1.04	1.25	molCO_2/kg solvent
Time period of Open Cycle Equivalent	0-0.48	0-0.39	0-0.54	h
Mole of CO_2 absorbed Open Cycle Equivalent	0.88	0.76	1.09	mol
Partial capacity (end of Open Cycle Equivalent)	0.80	0.67	0.91	molCO_2/kg solvent
Average absorption (Open Cycle Equivalent)	36.5	37.4	37.8	%

CONCLUSION

Final Considerations

- ProK solutions (30% and 43.38%w/w) have been tested at **bench-scale** to investigate CO_2 absorption from synthetic NGCC flue gas;
- **Faster loading increase** of ProK vs. MEA
- **Similar maximum loading** of MEA vs. ProK 30%w/w;
- Calculated **capacity** at the end of the MEA closed cycle test is the **highest** one among the three assessed (2.57 $molCO_2/kg_{solvent}$);
- Open cycle equivalent time-lapse → 43.38% w/w ProK shows higher partial capacity compared to MEA (0.91 vs. 0.80 $molCO_2$/kg Solvent)
- Open cycle equivalent time-lapse → comparable CO_2 removal among the 3 cases

Future Work

- Investigation of other AA for NGCC flue gas decarbonisation
- Modelling and experimental campaigns to estimate the **AA regeneration duty**
- Definition of thermodynamic models and **techno-economic assessment** for a comprehensive evaluation of AA performance

Thank You for Your Attention

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INTRODUCTION

Motivation

- Amines → Primary, secondary and tertiary
- Unhindered (primary or secondary) amines form a fairly stable carbamate → high energy requirement for solvent regeneration
- Hindered (tertiary) amines form an unstable carbamate and have a higher theoretical capacity
- Tertiary amines regeneration is less energy-demanding than unhindered amines
- Low rates of absorption make tertiary amines difficult to be used for CO_2 gas removal

- MEA considered a benchmark in the field of CO_2 capture via chemical absorption → economical technology
- MEA+ CO_2 → high reaction rate and capacity, low molecular weight and cost, high heat of regeneration (~3.5-3.9 GJ/ton CO_2);
- MEA is affected by vaporization losses due to high vapor pressure, it is corrosive and it forms degeneration products (oxidative and thermal degradation), toxicity issues