Sustainable CO_2 Capture Using Recovered Silica-PEI: Capacity, Efficiency, and Economic Viability

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- Optimisation of silica- alkoxylated polyethyleneimine (APEI) for post-combustion capture and DAC.
  - Organic reagent-free preparation
- Recently completed ABSALT ACT3 project,
- Regenerating spent Si-APEI/PEI adsorbents.
  - Valuable liquid products and silica for re-use

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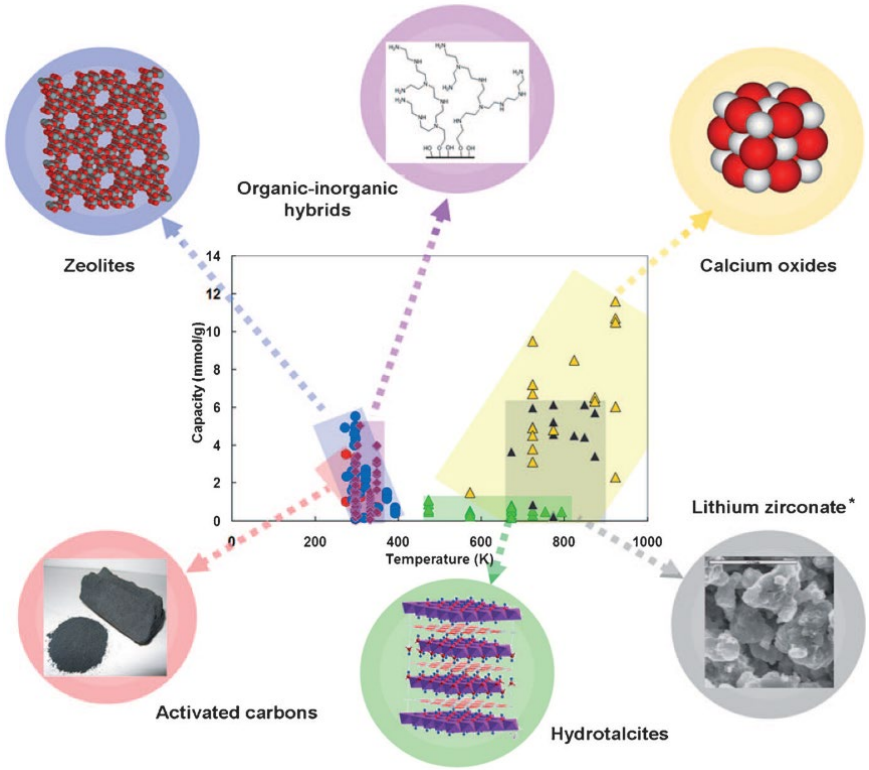
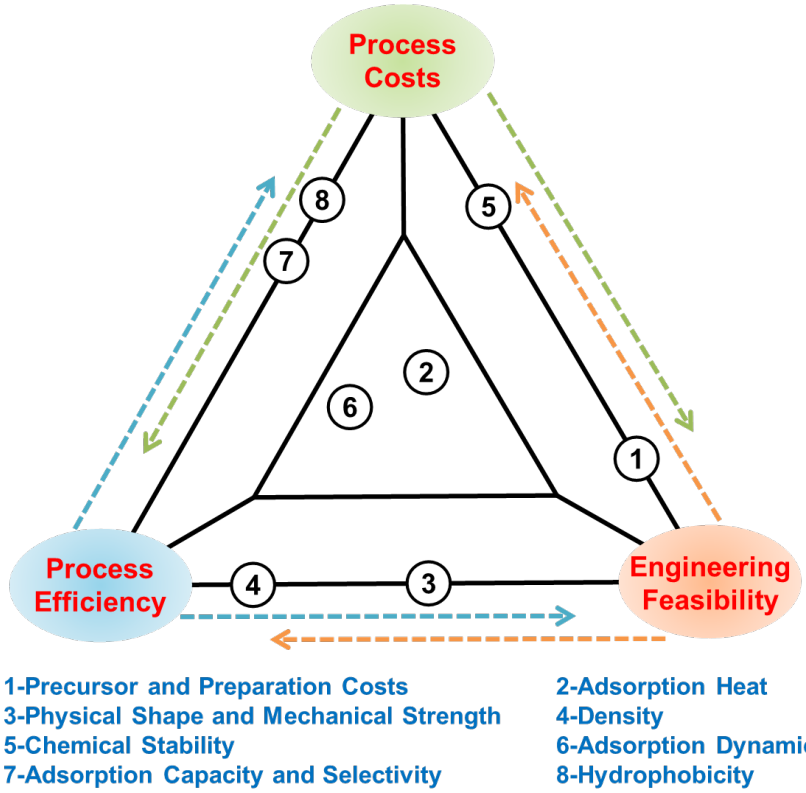
Background and Motivation – moving from lab. to pilot-scale with solid adsorbents

- Solid adsorbents are still at a relatively early stage of development for PCC and have not been investigated extensively at demonstration scale.





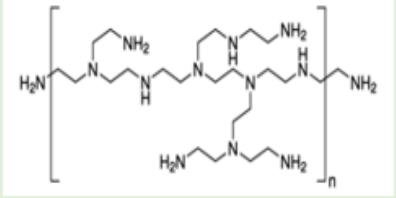
R. Xiong, et al., Chem. Eng. Sci., 58 (2003) 4377.

- ***Few of these has reached demonstration scale for post-combustion capture.***
- ***Many criteria need to be met regarding performance, stability and cost.***

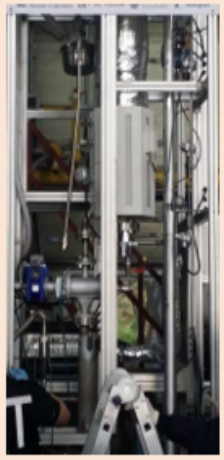
Schematic Representation of ABSALT

WP1 Silica Selection and Properties

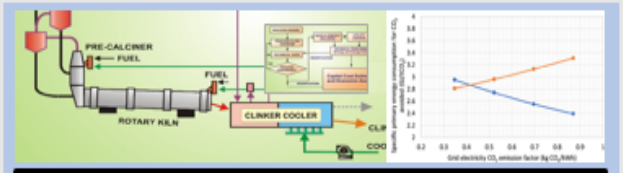
WP2 PEI Preparation and Properties



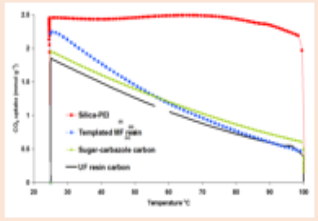
WP3 Additives, Silica-PEI Preparation and Screening



WP4 Pilot-scale Testing



WP6 Techno-economics and High-level Demonstration Plant Design



WP5 Regeneration Strategies for PEI

WP7 Environmental Assessment via Life Cycle Analysis (LCA) and Project Risk Assessment

Silica Selection

Optimal silica selected based on 11 samples screened

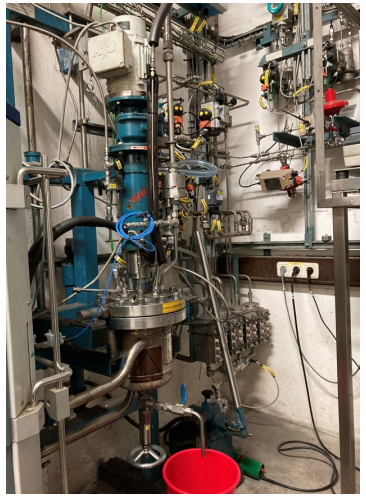
- Silicas prepared from sodium silicate offering an order of magnitude cost advantage over siliceous mesocellular foams requiring organic precursors

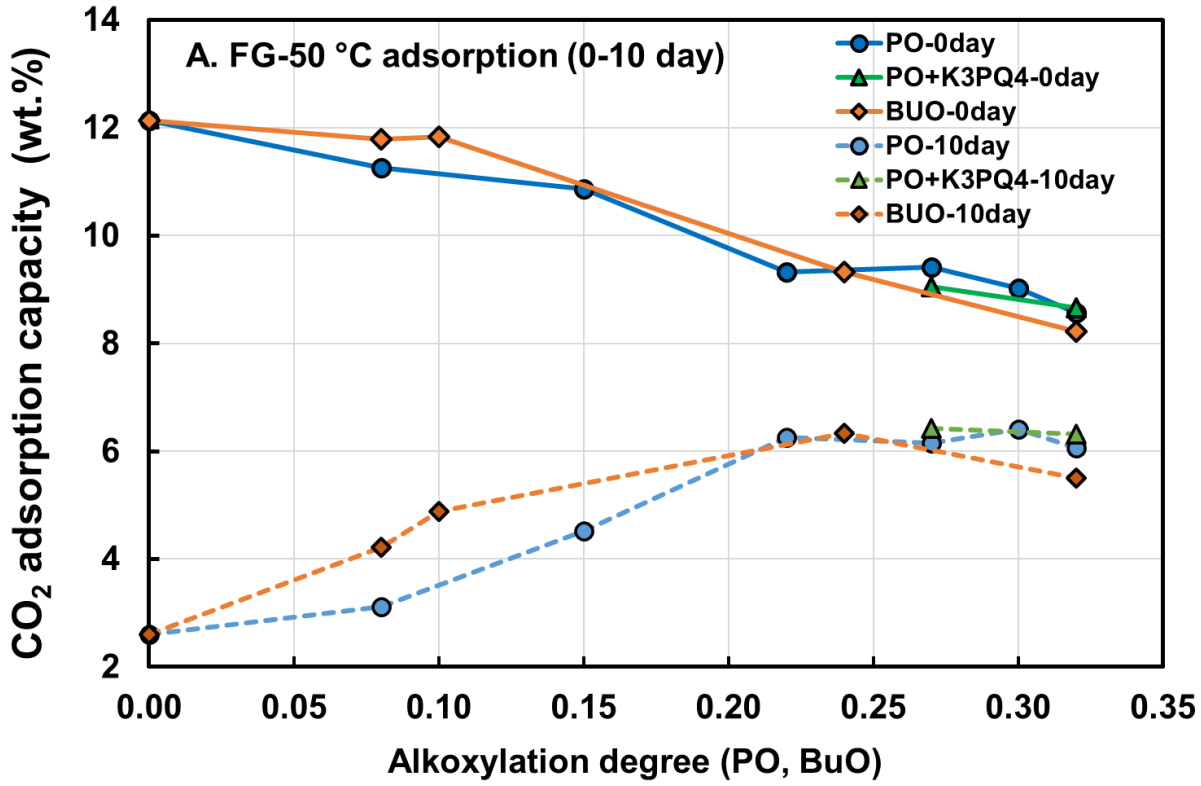
Sample	BET SA (m^2/g)	Vmicro (ml/g)	Vmeso (ml/g)	Vtot (ml/g)	D (nm)	Particle Size (µm)		
						D(10)	D(50)	D(90)
PQ1	289	0.11	1.69	1.81	25.00	25	151	370
PQ2	413	0.15	2.53	2.77	26.86	10	55	104
PQ3	306	0.11	1.60	1.72	22.47	155	249	404
PQ4	284	0.11	1.63	1.75	24.67	64	116	191
PQ5	323	0.12	0.96	1.08	13.37	20	177	396
PQ6	344	0.12	0.88	1.01	11.76	215	340	484
PQ7	191	0.08	0.45	0.90	18.80	73	251	438
PQ8	209	0.08	0.39	0.56	10.63	78	259	444
PQ9	422	0.15	1.64	1.80	17.05	43	173	379
PQ10	422	0.16	1.66	1.83	17.37	195	303	452
PQ11	246	0.09	0.16	0.25	4.11	61	183	391

- Based on the desired particle size range for fluidized-bed operation, PQ3 was selected having a relatively large mesopore volume with 50% of particles less than 249 µm for scale-up - 5 and 100 kg batches.
- Larger particle sizes are desirable for fixed and moving-bed operation.

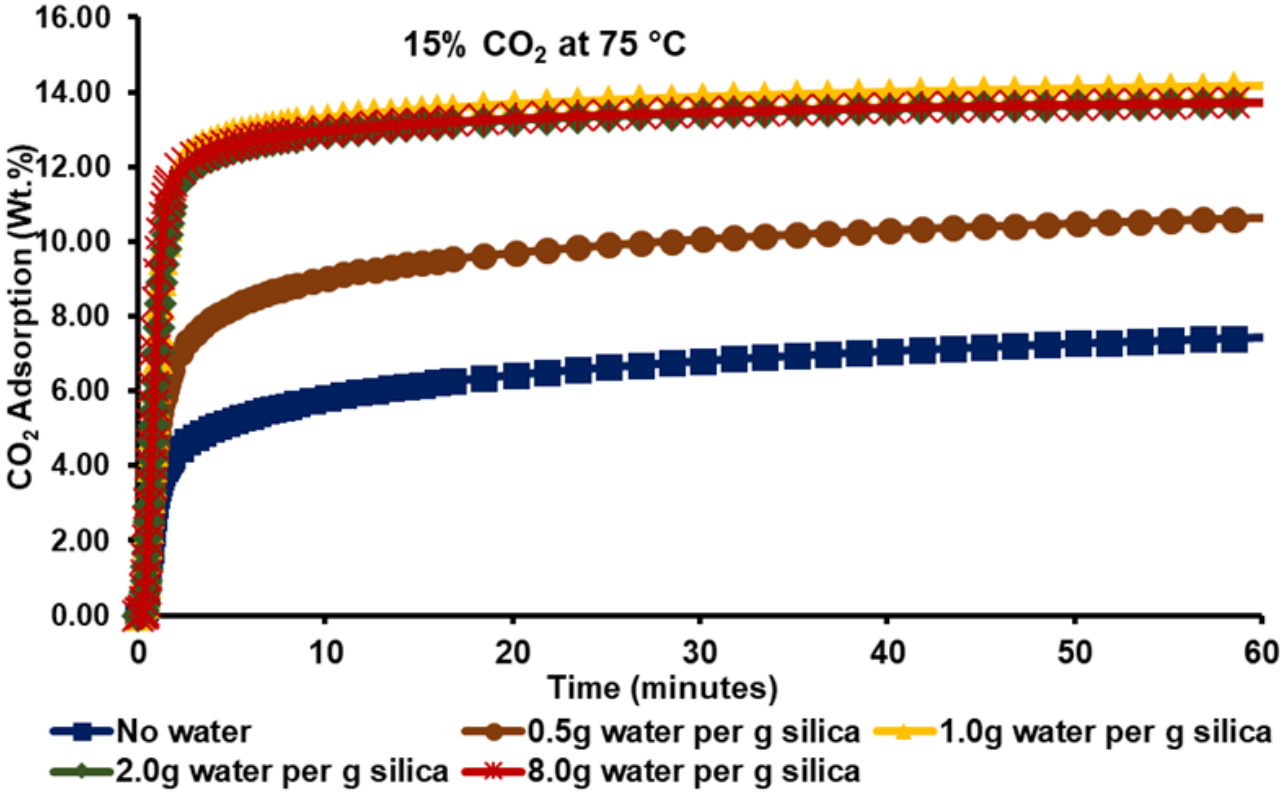
Screening of alkoxylated PEIs and scale-up

- **No solvents other than water.**
- The viscosity is low enough for the alkoxylation reaction to proceed without water for FG (Mn 800).
- Four pilot samples (100 kg) prepared.
- Trade-off between CO_2 adsorption capacity and oxidative stability (after 10 days at 80°C), ca. 0.32 close to optimum.





Minimising the quantity of water required for silica PEI mixing.



- No loss in CO_2 adsorption capacity until the amount of water drops below 1.0 g per g of silica.
- No significant differences in performance between water and organic solvents.
- In many earlier studies, up to 10 g of solvent (typically methanol) used per g of silica.

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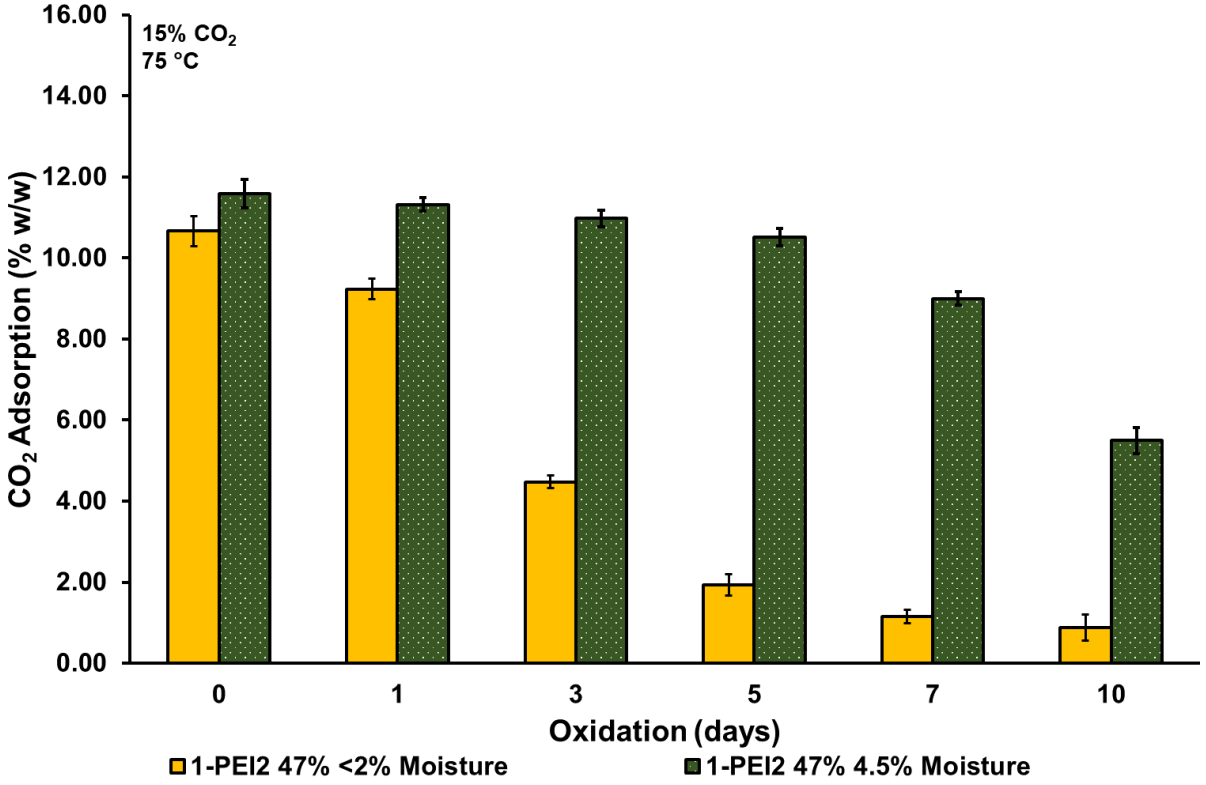
Identifying the water content after large-scale drying needed to prevent oxidative degradation.

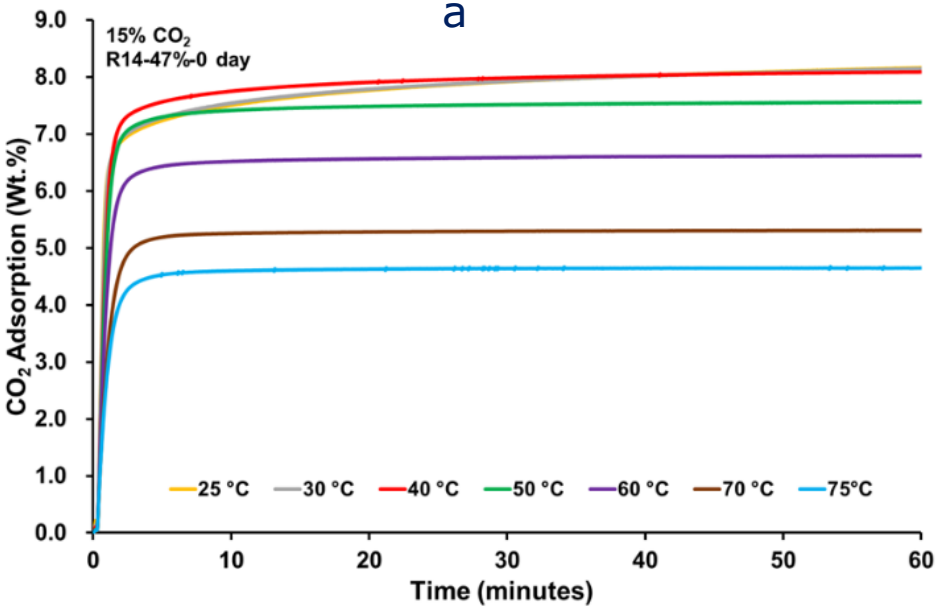
- double cone vacuum dryer



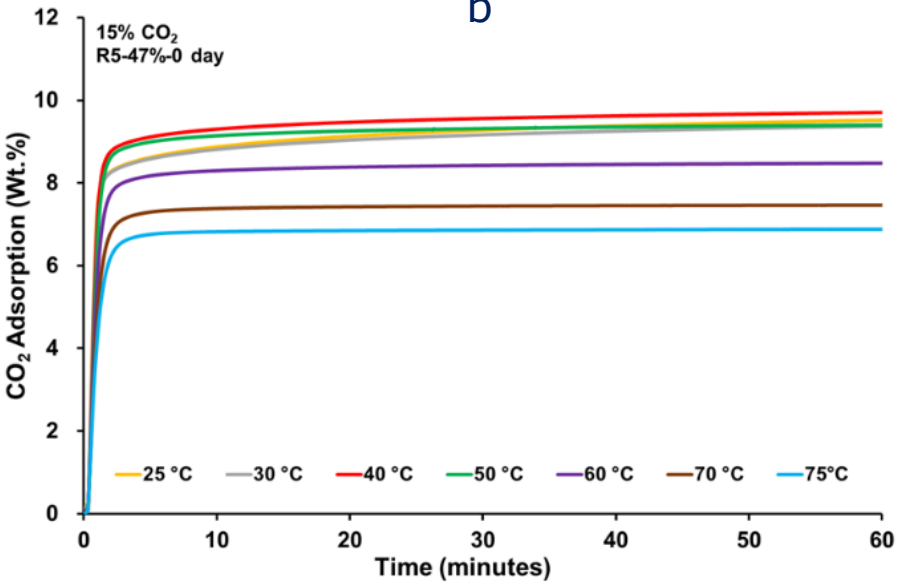
- The silica-PEI sample containing 4.5% wt. moisture gave significantly improved oxidative stability in the accelerated degradation test compared to the sample dried to less than 2%.

Optimising silica-PEIs for capture at different temperatures

a

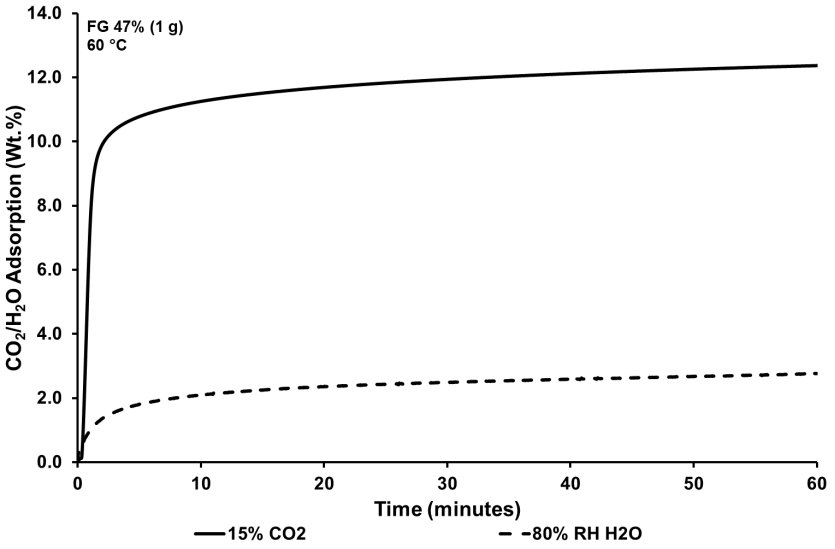


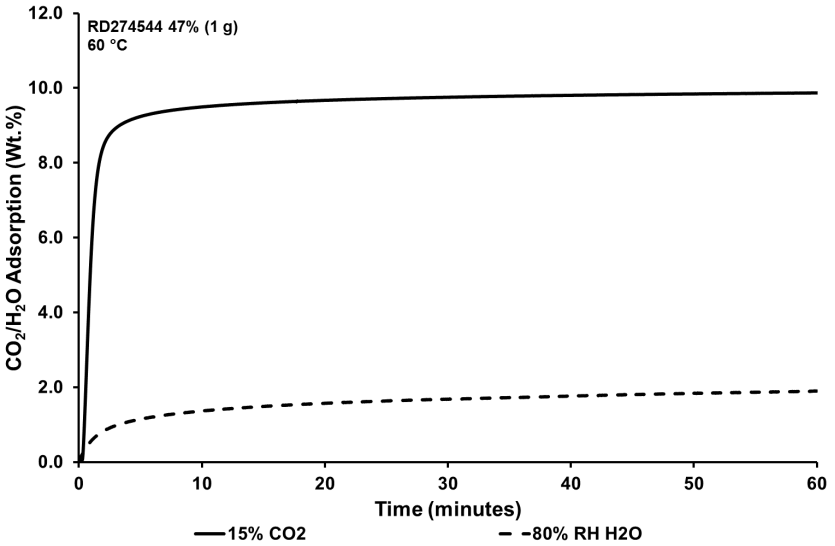
b



- Alkoxylation has the advantage of shifting the maximum CO_2 uptake to lower temperatures which also reduces the desorption temperatures, fast kinetics.
- Two samples optimised to maximum CO_2 uptake over the temperature range of 25-60^{o}C to apply SALT to direct air capture at 25^{o}C (sample a) and cement other industrial processes at 50-60^{o}C (sample b).

Alkoxylation reduces moisture co-adsorption (1 g AND 5 Kg scales)



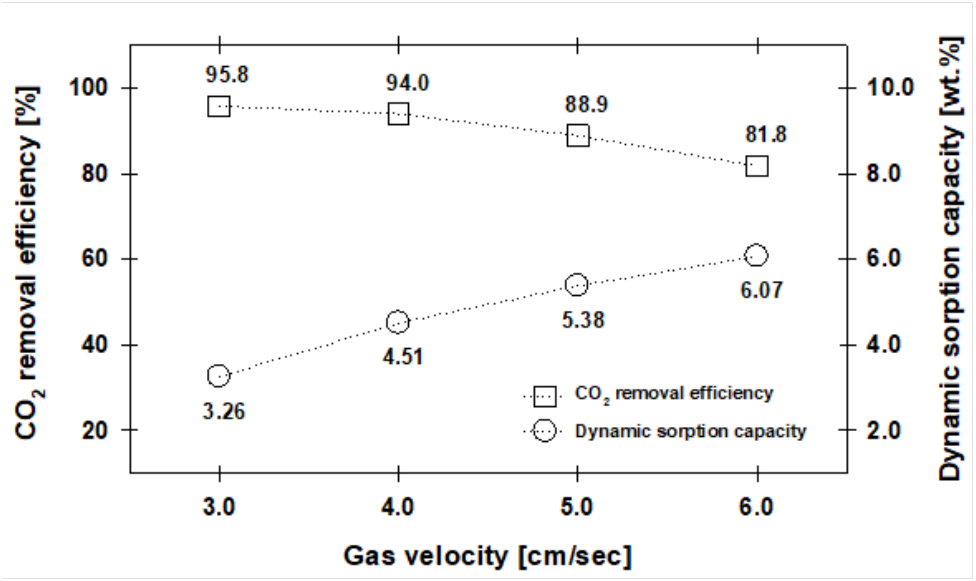


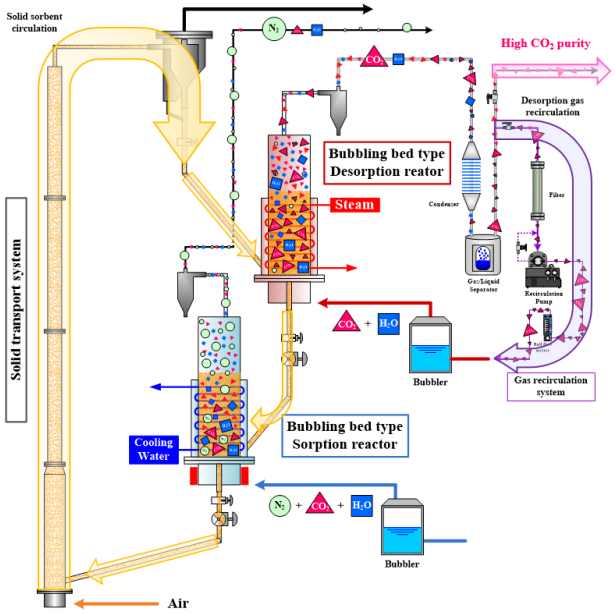
Temperature (ºC)	Uptake[a] (Wt.%)	Uptake[b] (Wt.%)	Uptake[c] (Wt.%)
60 (1g/CO_2)	9.91	11.69	12.37
60 (1g/H_2O)	1.36	2.35	2.78
60 (5Kg/CO_2)	9.16	11.22	11.94
60 (5Kg/H_2O)	1.22	2.56	3.11

	Uptake[a] (Wt.%)	Uptake[b] (Wt.%)	Uptake[c] (Wt.%)
60 (1g/CO_2)	8.45	9.67	9.87
60 (1g/H_2O)	0.83	1.58	1.91
60 (5Kg/CO_2)	8.78	10.24	10.42
60 (5Kg/H_2O)	0.83	1.62	1.98

a = CO_2/H_2O adsorption at 2 mins. b = CO_2/H_2O adsorption at 20 mins. c = equilibrium CO_2/H_2O adsorption.).

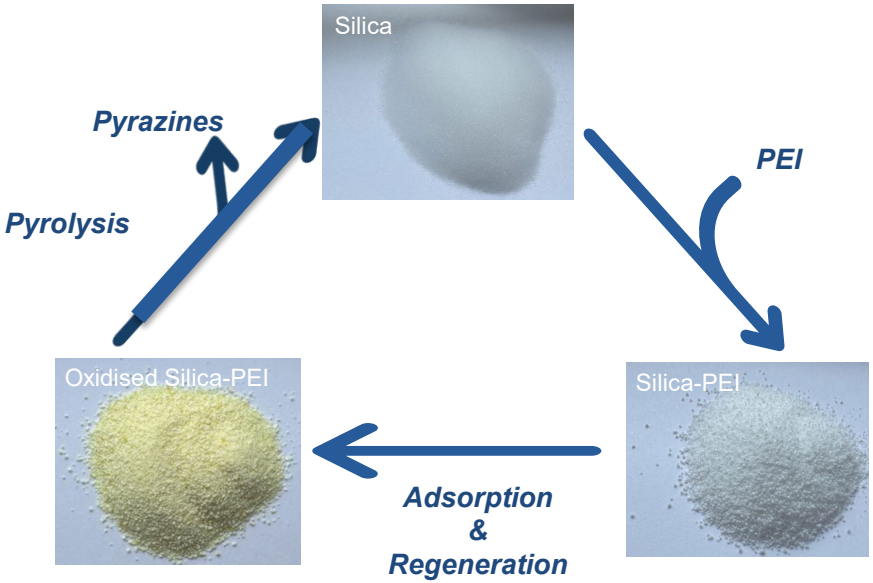
Successful pilot-scale test on 100 kg of silica-APEI at KIER





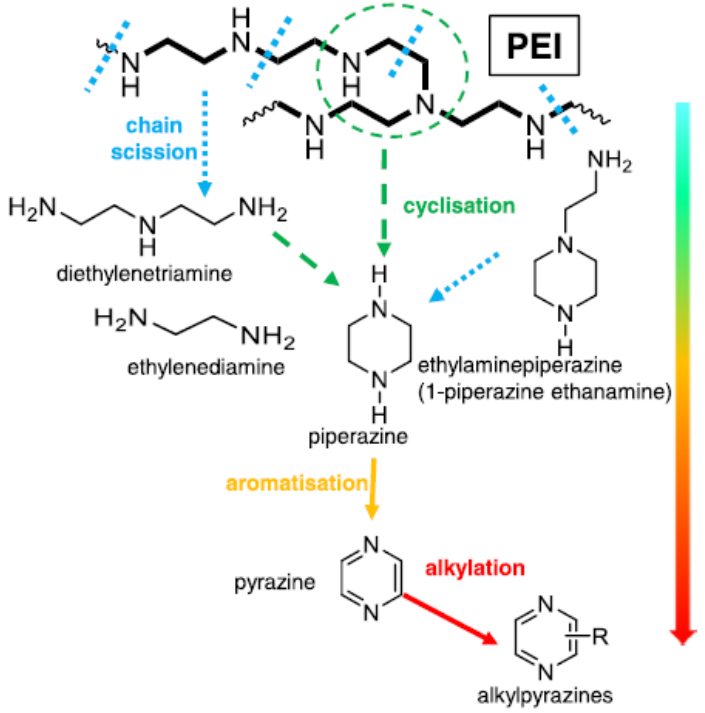
- Test conducted over 10 days at KIER with bubbling fluidised-beds.
- Capture efficiencies over 90% with dynamic working capacities of *ca*. 5% which can increase by raising the regeneration temperature.
- Adsorbent lost no activity over the test period.
- Supporting tests on a 5 kg scale demonstrated that the adsorbent is stable over 2 months at 50°C, dependent on moisture partial pressure.

Re-use of Silica and recovery of chemicals from Spent Silica-PEI



- Spent silica-APEI adsorbent (2 months oxidised in air at 60°C) was subjected to pyrolysis treatments.
- The recovered silica was then treated with fresh PEI for reuse.

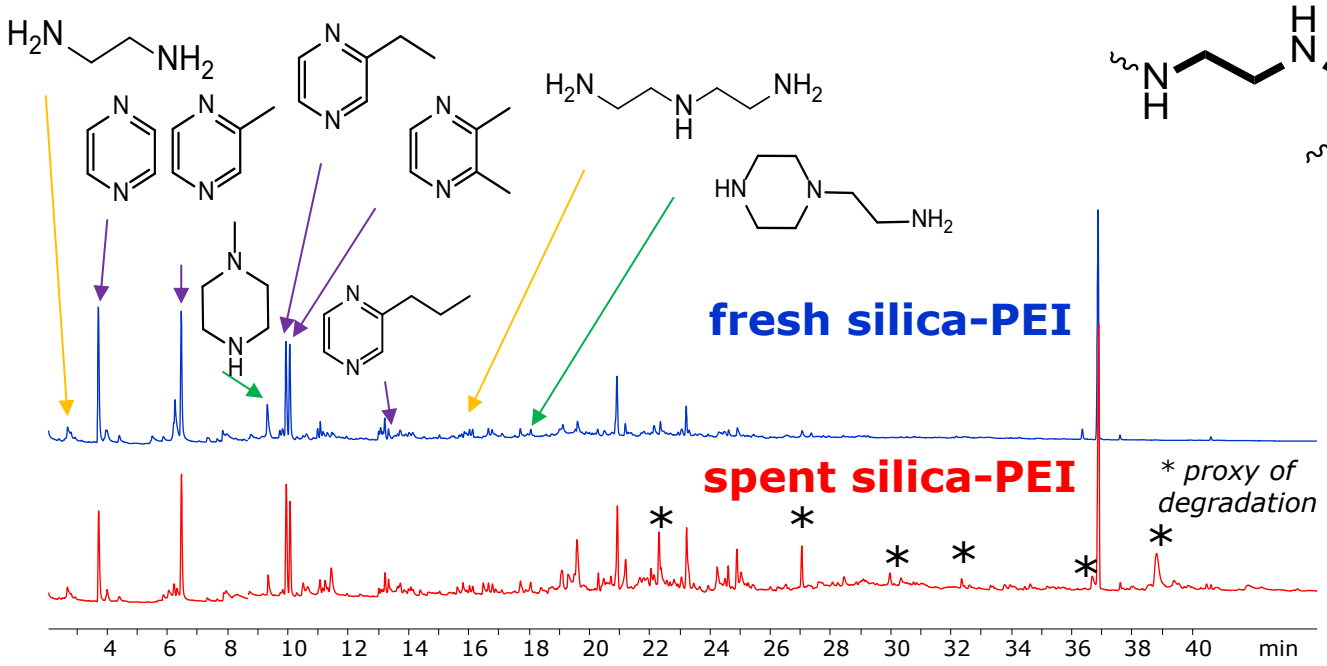
- **Pyrolysis:**
- Recover valuable components from PEI and regenerate the silica to enhance sustainability.

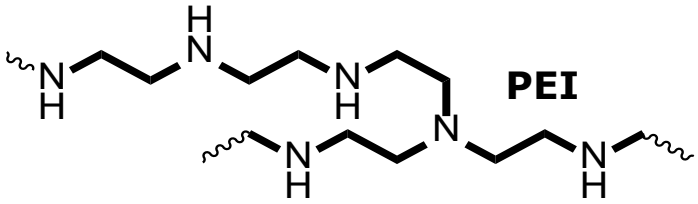


Coralli, I., et al (2023): University of Bologna

PEI Pyrolysis

Mechanisms identified leading to high yields of pyrazines

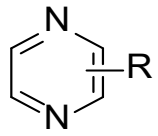




cyclisation

aromatisation

alkylation



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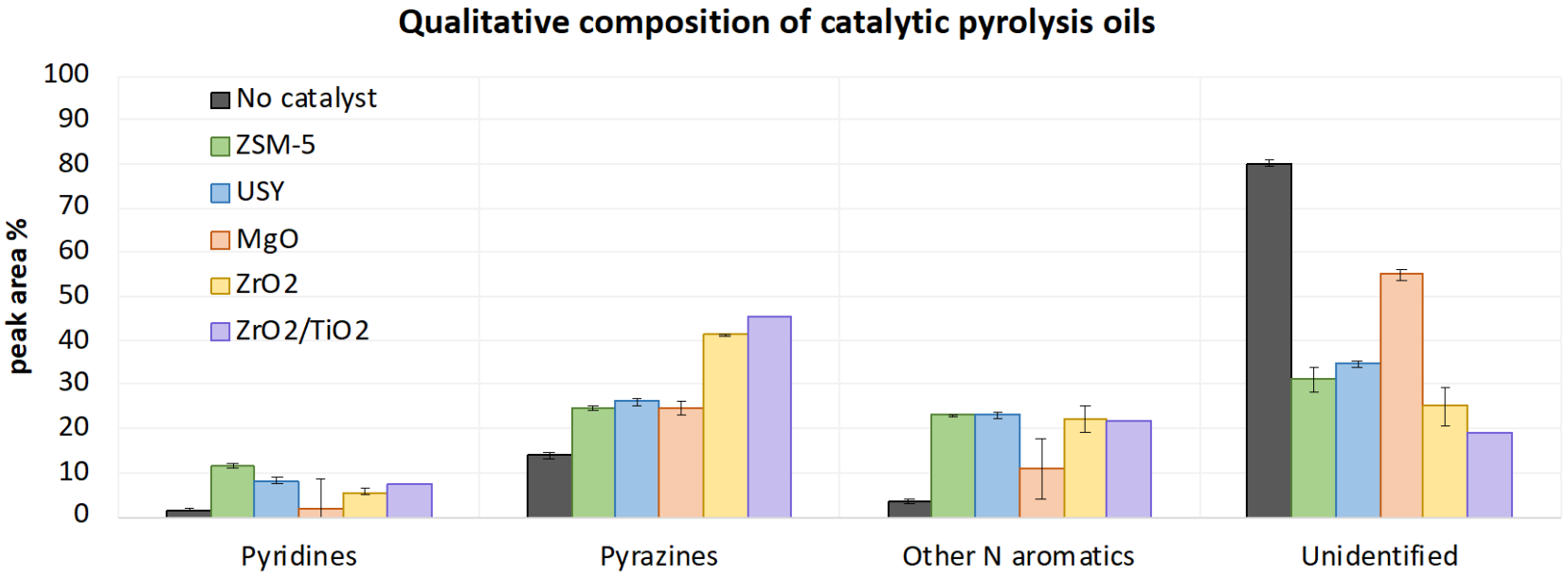
SILICA

- Py-GC-MS of model PEI, fresh and spent Si-PEI evidenced main chemical families of pyrolysis products.
- Pyrograms of Si-PEI were dominated by pyrazines; spent Si-PEIs exhibited additional pyrolysis products useful proxy of degradation.
- Mechanisms of formation of pyrolysis products and effect of silica to favour pyrazines postulated.

Catalytic upgrading of the spent Si-PEI pyrolysis vapours to increase the concentration of pyrazines and other heteroaromatics



- The catalytic upgrading of the vapours coming from the pyrolysis of spent Si-PIE (ex-situ pyrolysis) significantly increases the pyrazines and other heteroaromatics in the pyrolysis oils.
- The presence of a catalyst reduces the unidentified compounds in the pyrolysis oil by converting them to useful chemicals.
- Several active catalysts were tested most promising are: ZrO_2/TiO_2 > ZrO_2 > ZSM-5 ≈ USY > MgO.

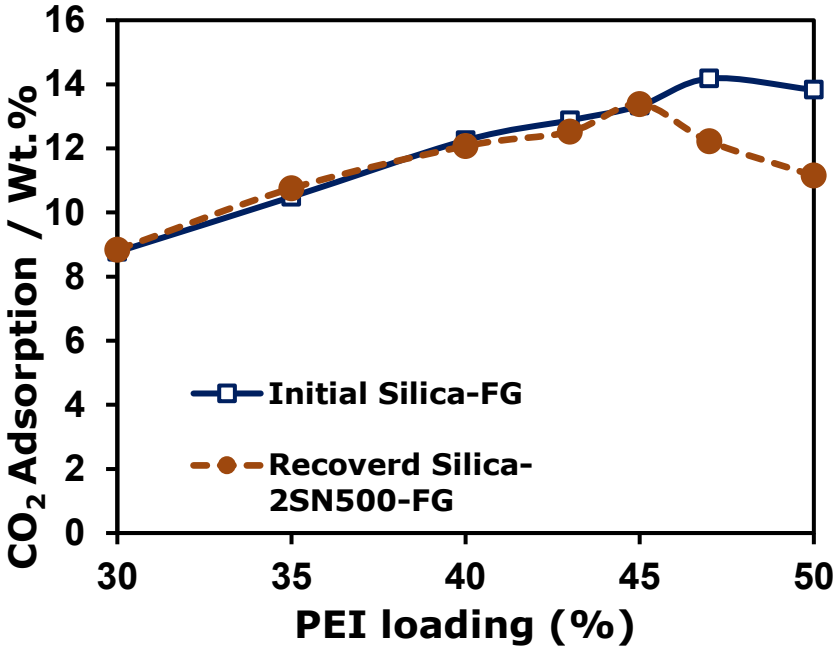
Characteristics of initial and pyrolysed silicas

Sample	BET SA (m^2 /g)	Vmicro (cm^3/g)	Vmeso (cm^3/g)	Vtot (cm^3/g)
Initial silica	306	0.114	1.60	1.72
Silica-500	310	0.115	1.62	1.74
Silica-600	311	0.115	1.62	1.74
RS-500	330	0.121	1.42	1.55
RS-600	326	0.117	1.36	1.49
RS-2S	316	0.114	1.39	1.51
RS-2SN	321	0.115	1.38	1.50

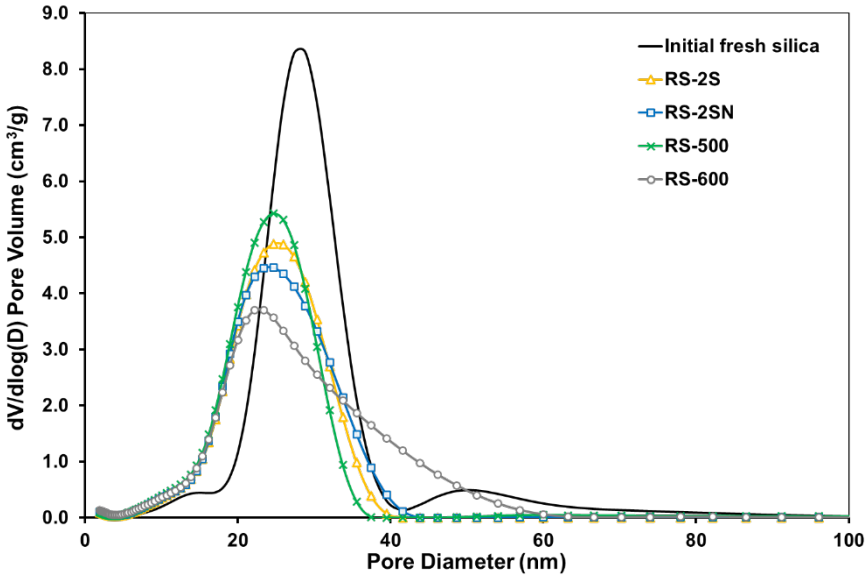
- Silica-500 and 600 are controls showing no change in surface area and pore volume for the initial silica at 500 and 600°C.
- 4 different pyrolysis conditions investigated, showing increase in surface area and up to 15% reduction in mesopore and total pore volume.

Re-use of Silica from Spent Silica-PEI

CO_2 adsorption capacities for initial and recovered silica–PEI-FG with loadings of 30 to 50 wt.% at 75 °C in 15% CO_2.



Pore size distribution of initial and recovered silicas.



- Initial silica-optimal PEI loading: 47 wt.%; Recovered silica-optimal PEI loading: 45 wt.%
- The properties of the recovered silica showed minimal variation between procedures, a slight mesopore volume reduction (~13%), resulting in less than small loss in CO_2 adsorption capacity.
- Three or more regeneration cycles may be feasible before total capacity loss exceeds ~30%.

Conclusions

- The total porosity and mesopore volume of the recovered silicas exhibited only a slight decrease compared to the initial silica.
- The initial silica had an optimal PEI loading of 47 wt.%, while the recovered silicas all maintained a slightly lower optimal loading of 45 wt.%, with the CO_2 adsorption capacities of the selected PEIs decreasing by less than 10% of their initial capacities for the two PEIs investigated.
- The relatively small loss in adsorption performance suggests that the silica could be subjected to more than one, possibly three, regeneration cycle before being discarded.
- Although capital and operating costs for large-scale thermal regeneration remain to be determined, these are estimated to be *ca*. 10 times lower than the cost of silica.
- Reducing the quantity of silica required lowers both material costs and associated emissions.

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ABSALT Publications and Patents

EP22207176.3 Process for preparing compositions containing alkoxylated polyalkyleneimines, said compositions and their uses. Filed 14 November 2022. Proceeded to secondary filing, application no. PCT/EP2023/08671. International filing date 19 October 2023. publication date, 23 May 2024, publication number WO2024/104700 A1

EP22215665.5 Sorbents for carbon dioxide capture. Filed 21 December 2022. Proceeded to secondary filing, application no. PCT/EP 2023/086718. International filing date 19 December 2023. publication date, 27 June 2024, publication number WO2024/ 133317 A1

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2. I. Coralli, D Giuri, L Spada, J Ortolani, L Mazzocchetti, C.Tomasini, L.A Stevens, C.E Snape and D.Fabbri, Valorization Strategies in CO_2 Capture: A new life for exhausted silica-polyethylenimine, International J. of Molecular Sciences, 2023, **24**, 14115.

3. I. Coralli and D Fabbri, Pyrolysis acetylation: a novel on-line Py-GC-MS derivatisation for the characterisation of nitrogen-containing polymers J. of Analytical and Applied Pyrolysis, **2023**, 175, 106178.

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