CO_2 Capture from Flue Gas Using Solid Molecular Basket Sorbents

DOE NETL Award No. DE-FE0000458

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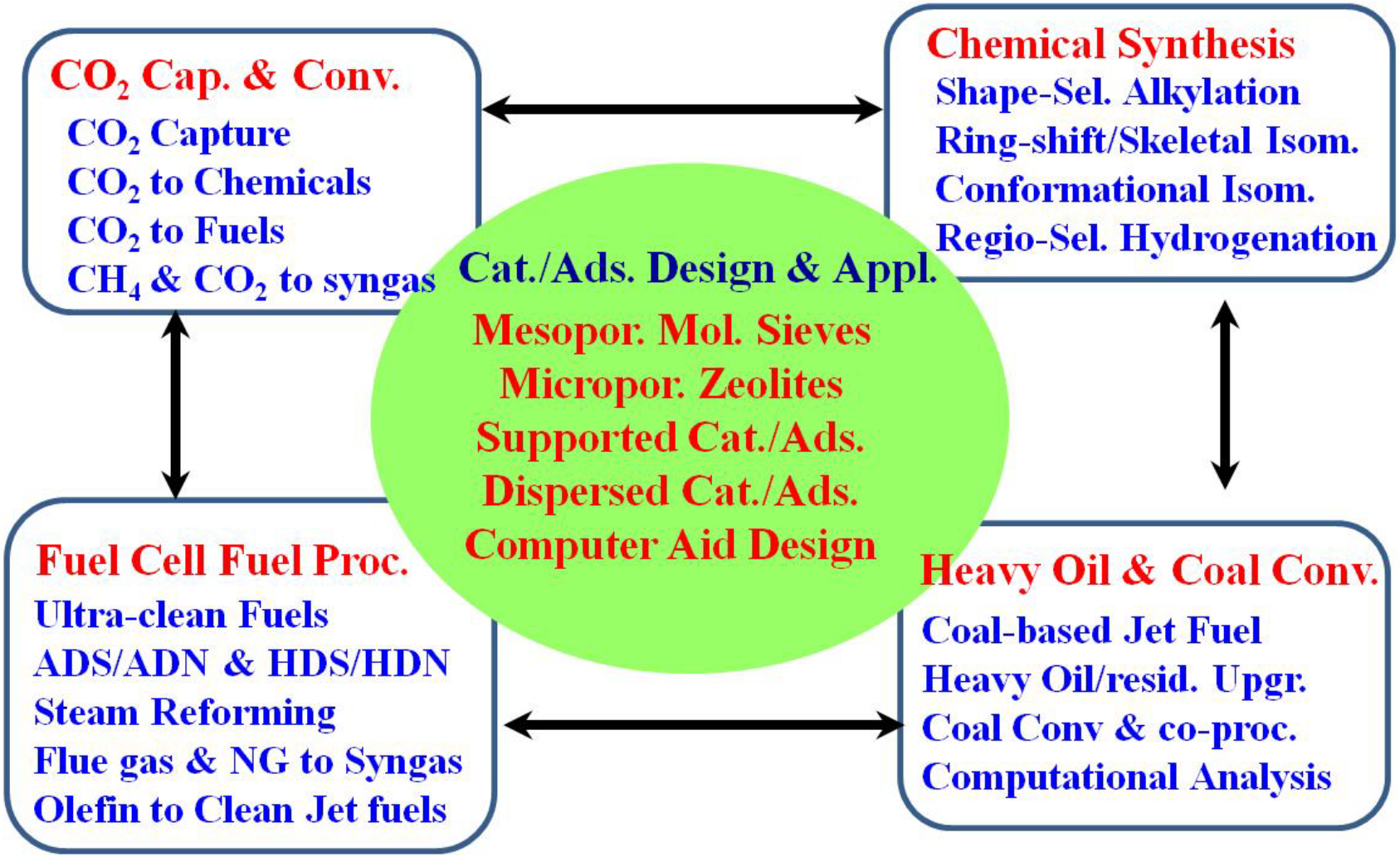
PENNSTATE

DOE NETL Project Manager: B. Andrew O'Palko

2010 NETL CO_2 Capture Technology Meeting
Sheration Station Square, Pittsburgh, Sept. 13-17, 2010

Clean Fuels and Catalysis Research at PSU



Team: 3 Faculty, 2 visiting scholars, 5 Post-doc, and 14 graduate Students

http://www.energy.psu.edu/personnel/CSong.html

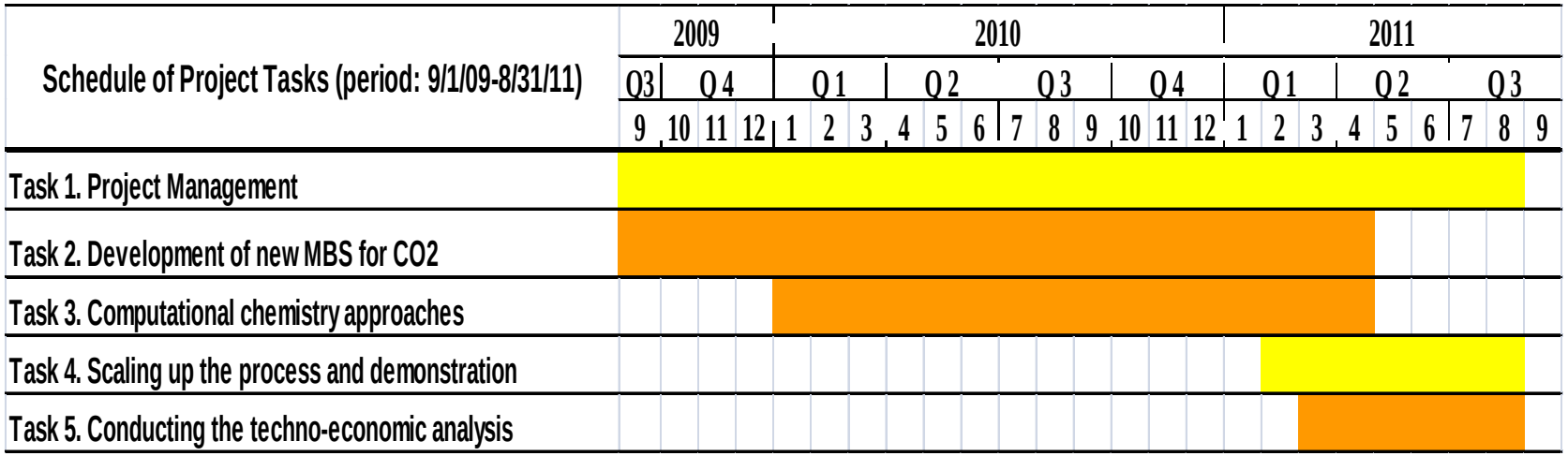
Project Overview

a) Funding (DOE and Cost Share)

Amount requested from DOE: $456,992; Non-federal Cost Share: $114,299

Total budget: $571,291

b) Overall Project Performance Dates: 9/1/2009-8/31/2011



c) Project Participants

Involving 3 research faculty, 1 post-doctor and 3 PhD students

Project Objective

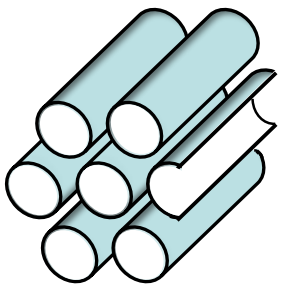
To develop a new generation of solid and regenerable polymeric "molecular basket" sorbent (MBS) for more efficient capture and separation of CO_2 from flue gas of coal-fired power plants.

The new generation of MBS should have:

- A regenerable working sorption capacity higher than 70 mg-CO_2/g-S
- A significantly lower cost for the sorbent preparation compared to the early generations of MBS

Concept of "Molecular Basket" Sorbent (MBS) – Nano-porous Inorganic Matrix-Polymer Composite

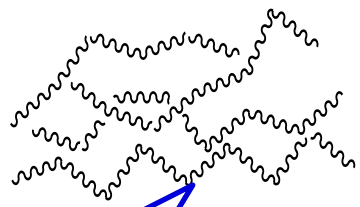
Nano-porous Material (MCM-41/SBA-15)

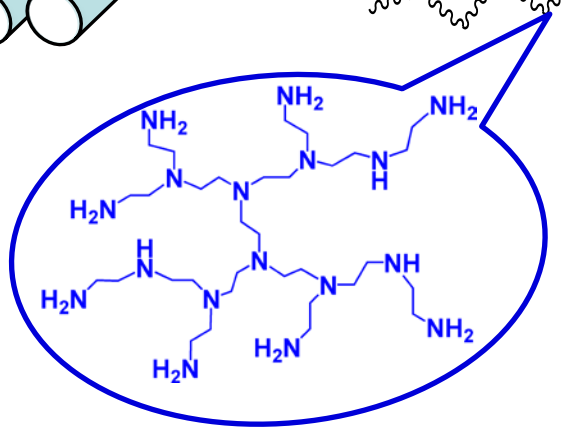


+

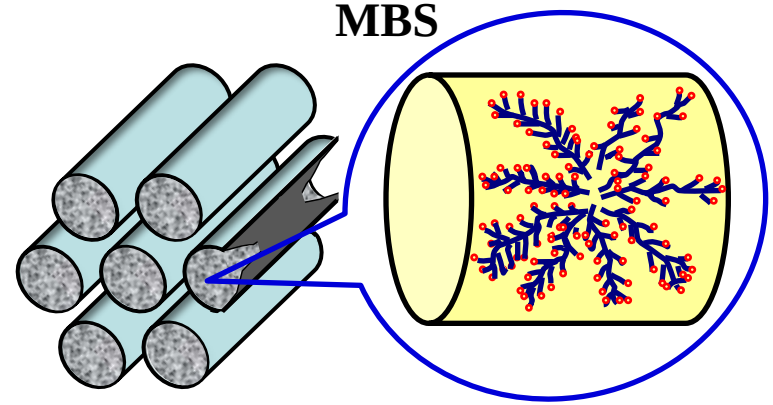
CO_2-philic Polymer (Polyethylenimine, PEI)

$H\text{-}\{CH_2\text{-}CH_2\text{-}NH\}_n\text{-}H$





Molecular Basket Sorbent MBS



$$CO_2 + 2RNH_2 \Leftrightarrow NH_4^+ + R_2NCOO^-$$

$$CO_2 + 2R_2NH \Leftrightarrow R_2NH_2^+ + R_2NCOO^-$$

$$CO_2 + 2R_3N \Leftrightarrow R_4N^+ + R_2NCOO^-$$

Immobilize CO_2-philic polymers into large pore volume nanoporous matrix

---- "Molecular Basket" Sorbent

Xu et al. ***Energy Fuels*** **2002,** ***16,*** **1463;** ***Microporous Mesoporous Mater.*** **2003,** ***62,*** **29;** ***Int. J. Environ. Technol. Manage.*** **2004,** ***4*** **(1-2), 32;** ***Ind. Eng. Chem. Res.*** **2005,** ***44,*** **8113-8119.**

Ma et al. ***J. Am. Chem. Soc.*** **2009,** ***131,*** **5777-5783.**

Advantages and Challenges of PSU-MBS

Advantages

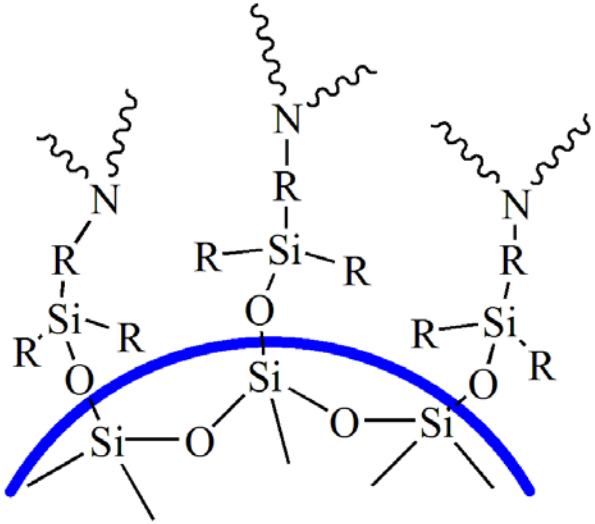
- High capacity: 3.2 mol-CO_2/kg (or 14%) at CO_2 conc. of 15%
- High selectivity: $CO_2/N_2 > 1000$
- No or less corrosion problem
- Suitable operation conditions
- High sorption/desorption rate
- Positive effect of moisture
- Regenerable at mild conditions

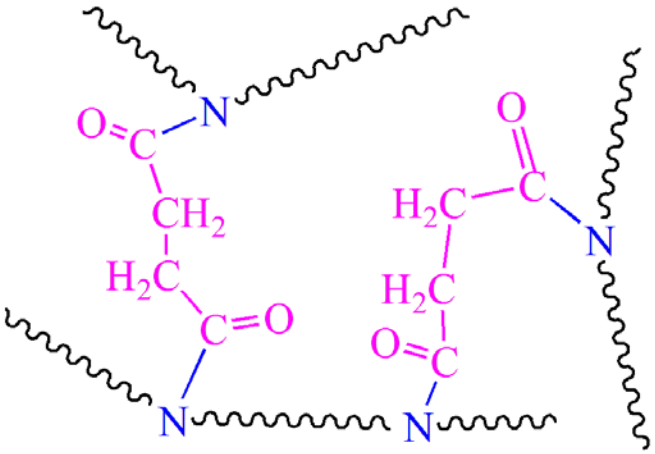
Challenges

- High Cost of SBA-15 & MCM-41
- Low Packing Density
- Thermal & regenerable stability needs further improved

Proposed Approaches

- Using cheaper nanoporous materials instead of SBA-15 and MCM-41 to reduce the cost for preparation of MBS
- Using structured mesoporous materials to improve further the sorption capacity and sorption/desorption rate
- Using crosslinkers to improve the thermal & regenerable stability of MBS via chemical bonding





Project Progress

a) **Nanoporous silica-gel (SG) as cheaper inorganic matrix for the preparation of MBS**

b) **Mesocellular silica foam (MCF) for the preparation of MBS to achieve higher sorption capacity**

c) **Improve the stability of PEI/SBA-15 (MBS-2) by crosslinking of PEI**

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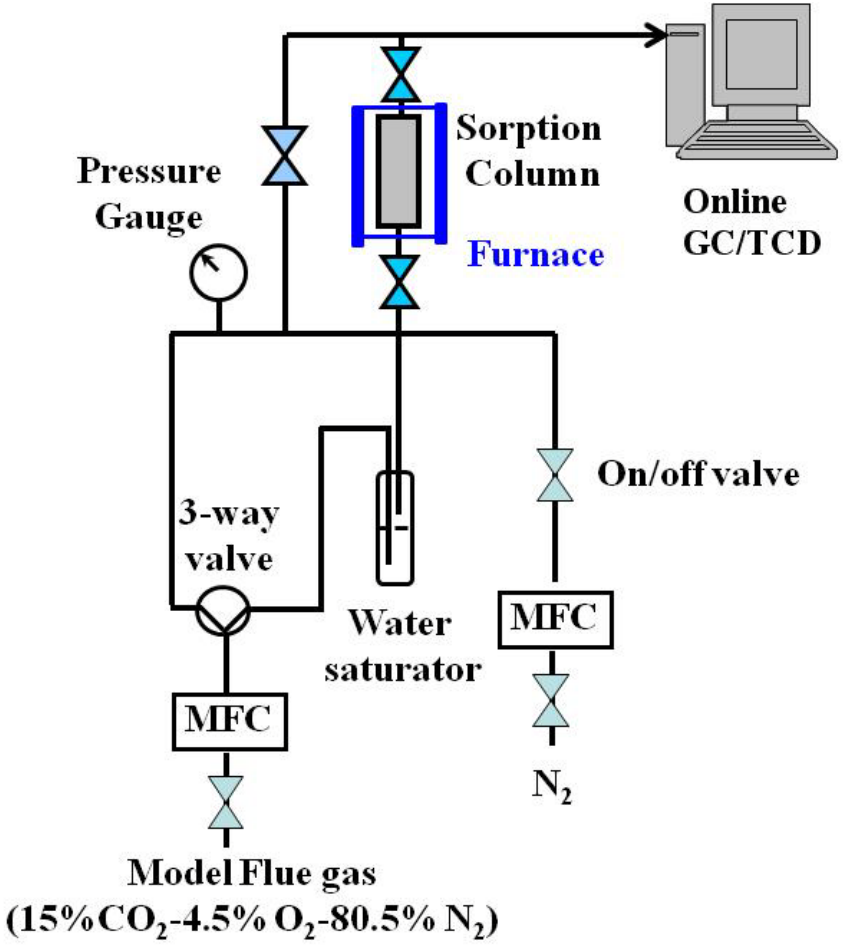
CO_2 Sorption Evaluation System



Flow system

TGA system

Silica-gel Used for Preparation of MBS

Physical properties of some typical silica gel samples

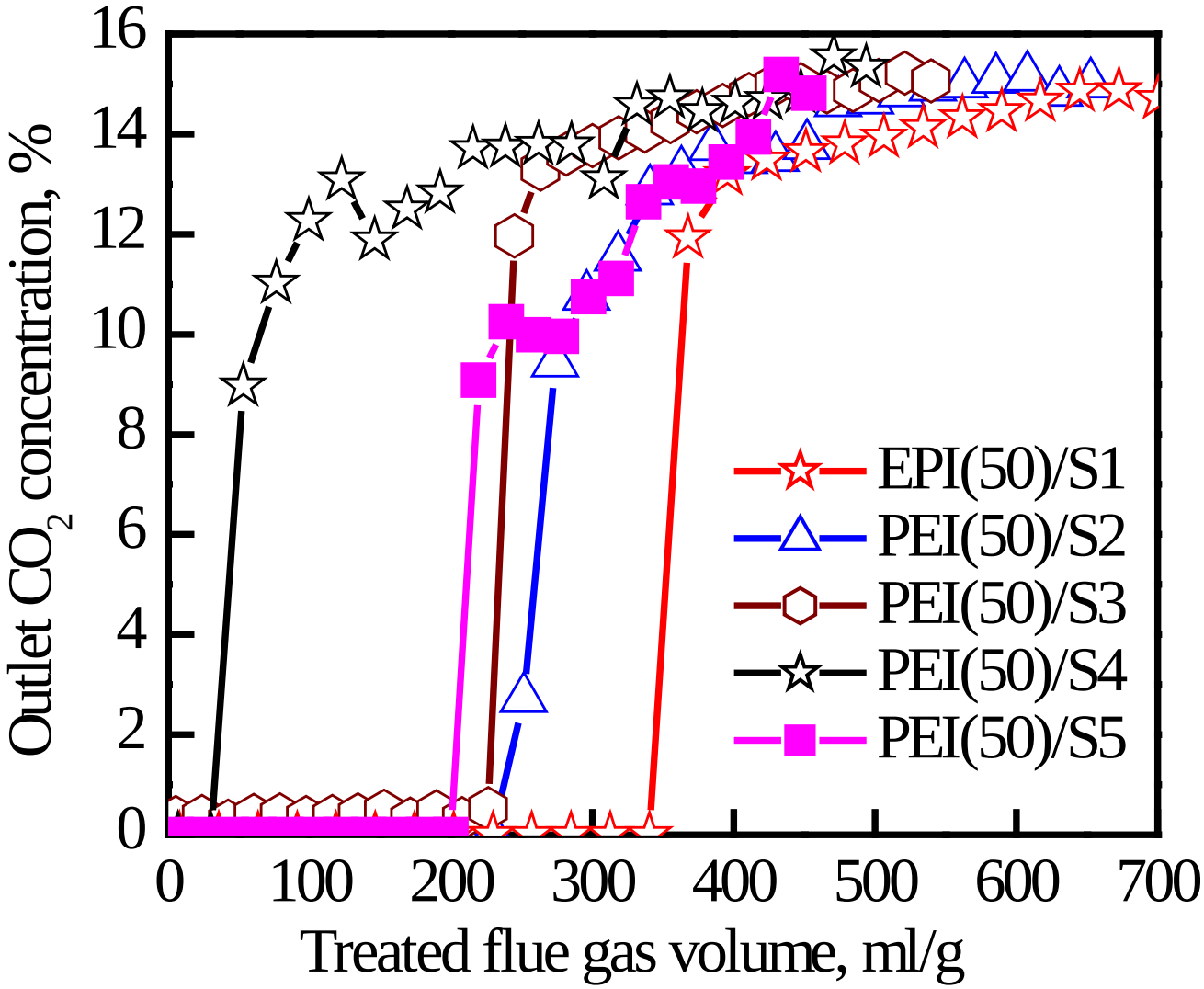
Sample	Particle size, μm	Mesh	Pore size nm	Pore volume ml/g	Surface area m^2/g
SG-1	60-74	200-425	15	1.15	300
SG-2	74-149	100-200	15	1.15	300
SG-3	250-500	35-60	15	1.15	300
SG-4	210-500	35-70	4	0.68	675
SG-5	74-149	100-200	6	0.75	480

PEI loaded Silica-gel MBS

Orthogonal Experiment Design and Results Obtained by TGA

N	Factor (3×3×3×3 =81)				Cap. mg/g
	Por. Dia. (nm)	Part. Size (mesh)	PEI Loading (%)	PEI Mw	
1	4	35~60	40	423	5.6
2	4	100~200	50	25000	12.0
3	4	200~425	60	50000	8.2
4	15	35~60	50	50000	22.5
5	15	100~200	60	423	76.0
6	15	200~425	40	25000	77.5
7	6	35~60	60	25000	7.8
8	6	100~200	40	50000	11.4
9	6	200~425	50	423	60.6
K1	8.6	12.0	31.5	**47.4**	**Best**
K2	**58.7**	33.1	**31.7**	32.4	**15 nm**
K3	26.6	**48.8**	30.6	14.0	**200~425**
R	50.1	36.8	1.1	33.4	**50%**
S	3863	2044	1.9	1676	**423**

CO_2 Sorption Breakthrough Curves



CO_2 Sorption Performance in Flow System

Sample	Weight-based capacity		Volume-based capacity	
	Cap(BT), mg/g	Cap(S) mg/g	Cap(BT), mg/ml	Cap(S), mg/ml
PEI(50)/SG-1	**102.2**	**113.8**	**51.7**	**57.5**
PEI(50)/SG-2	**68.9**	**88.2**	**43.2**	**55.4**
PEI(50)/SG-3	**68.0**	**73.2**	**51.7**	**55.7**
PEI(50)/SG-4	9.0	26.8	5.4	16.1
PEI(50)/SG-5	**60.1**	**77.8**	**43.2**	**56.0**
PEI(50)/SBA-15	**126.2**	**138.3**	**31.5**	**34.5**

Silica-gel based MBS showed higher volume-based sorption capacity except the one with 4 nm of pore diameter, although the weight-based capacity is lower than SBA-15-based MBS

Project Progress

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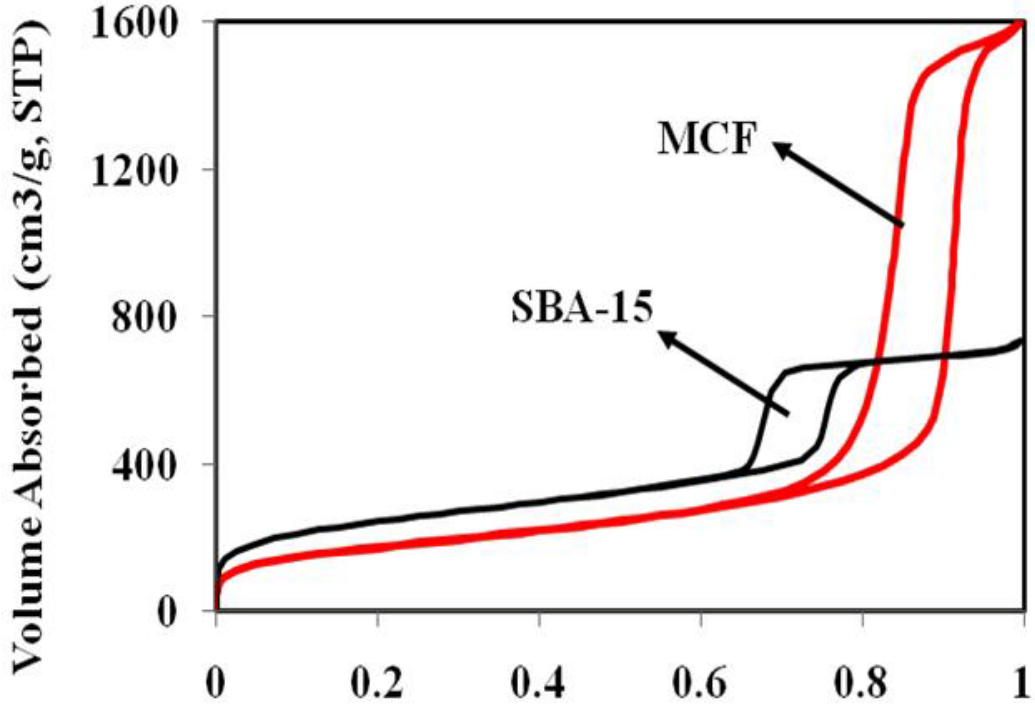
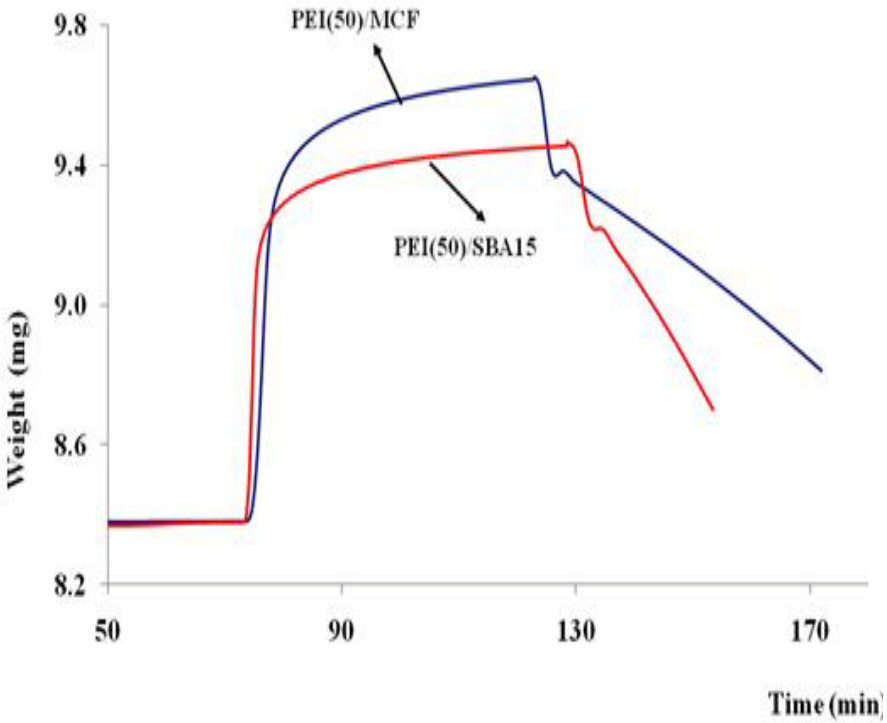
MCF-based MBS

N_2 sorption/desorption isotherm of MCF and SBA-15



Sample	S_{BET} (m^2/g)	V_{total} (ml/g)	V_{micro} (ml/g)	V_{meso} (ml/g)	Average pore (cell) size (nm)	Window size (nm)
MCF	950	2.40	-	2.40	18	13
SBA-15	950	1.31	-	1.31	6.6	-
MCM-41	1229	1.15	-	1.15	2.7	-

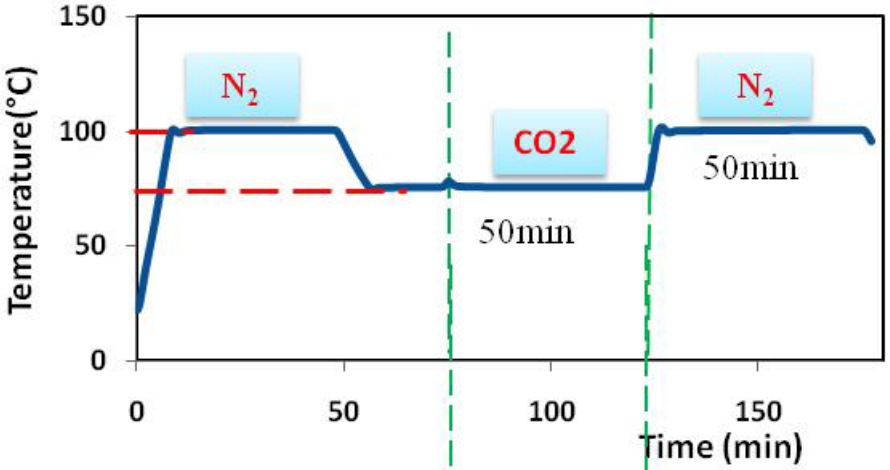
Typical TGA profiles for CO_2 sorption/desorption over SBA-15 and MCF-based MBSs



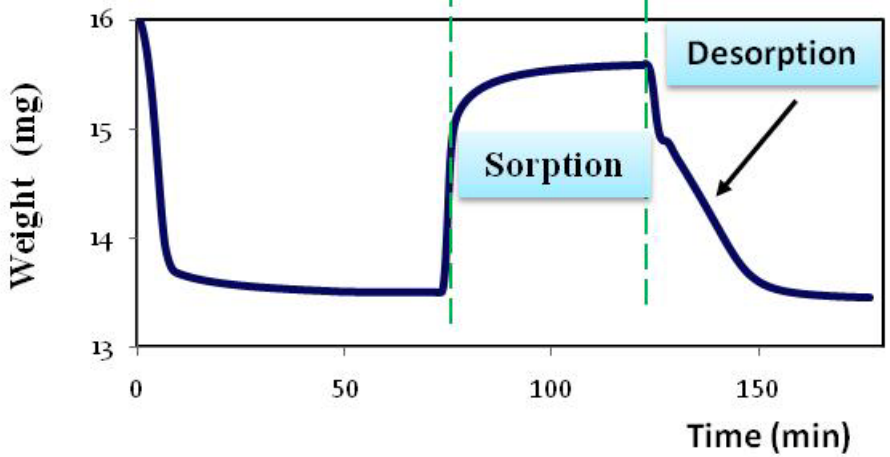
PEI(50)/MCF, 151 mg/g

PEI(50)/SBA-15, 136 mg/g

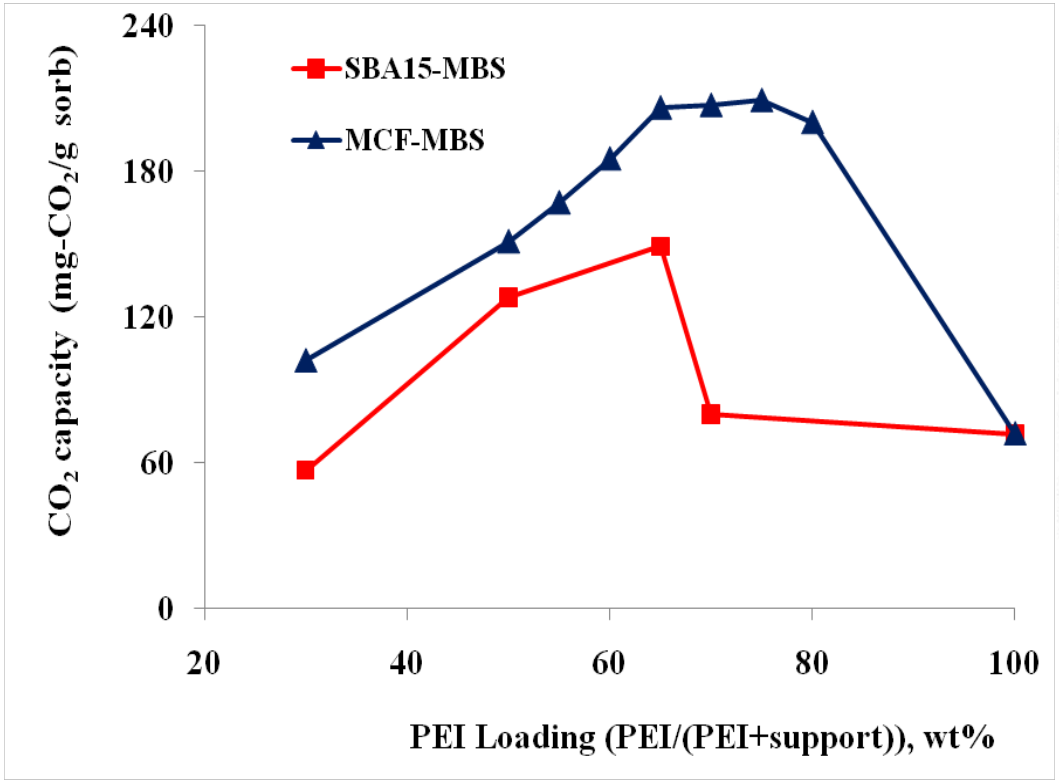
- **Standard conditions for evaluation**

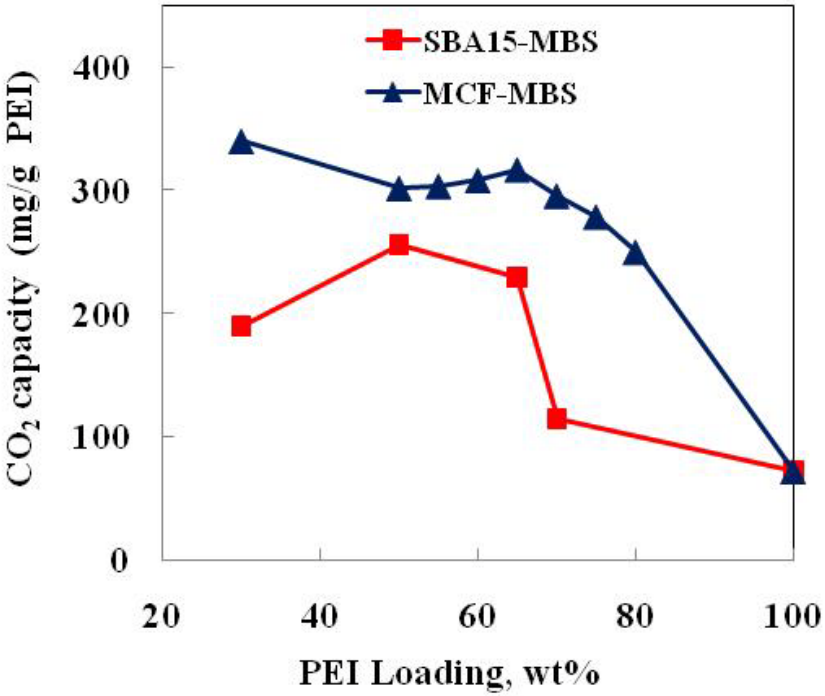


- **Sorption and desorption profile of TGA**



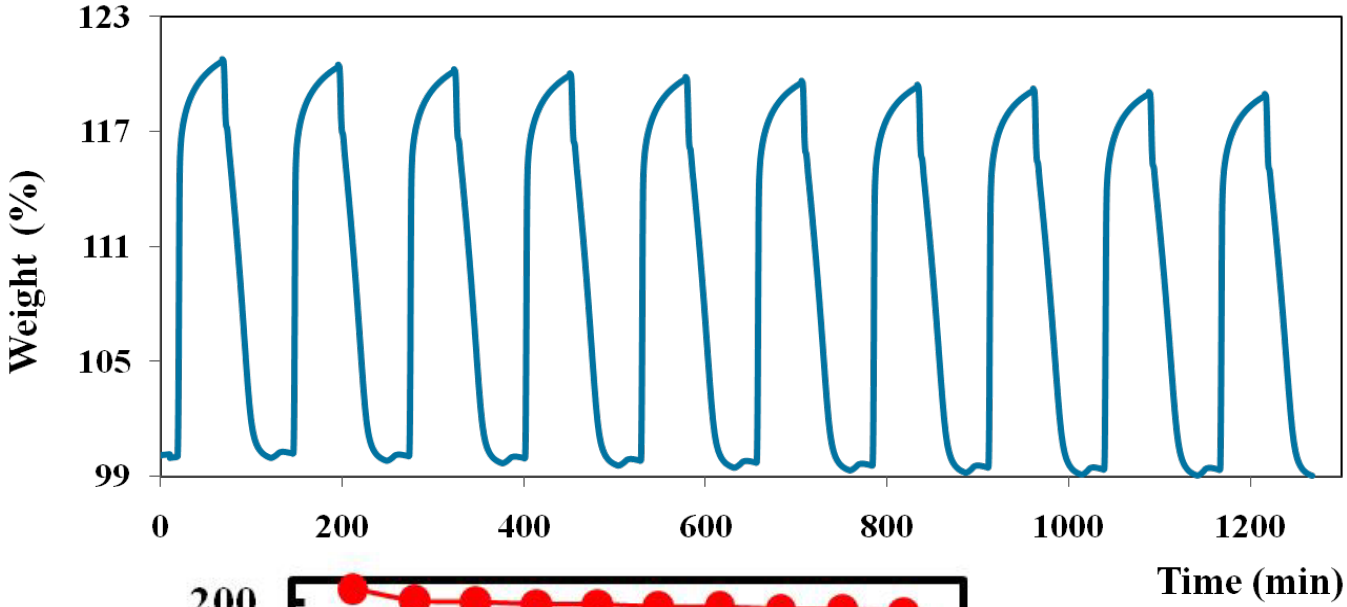
Effect of PEI Loading on Different Support

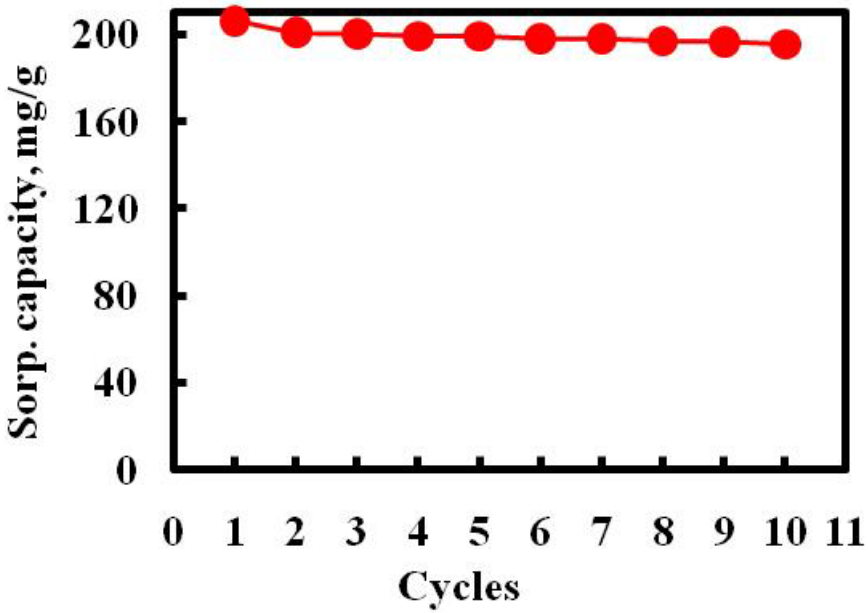




Sample	PEI/MCF			PEI/SBA-15	
PEI loading, wt%	30-70	80	90	30-65	70
Form	powder	powder with bit sticky	like paste	powder	like paste

Regenerability and Stability of PEI(65)/MCF





After 10 cycles, the sorption capacity decreased by ~ 5%.

Project Progress

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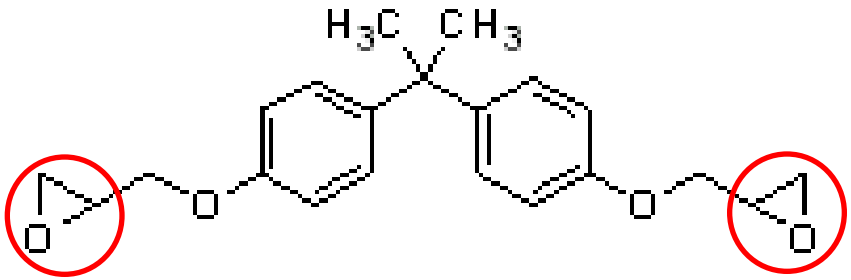
c) Improve the stability of PEI/SBA-15 (MBS-2) by crosslinking of PEI

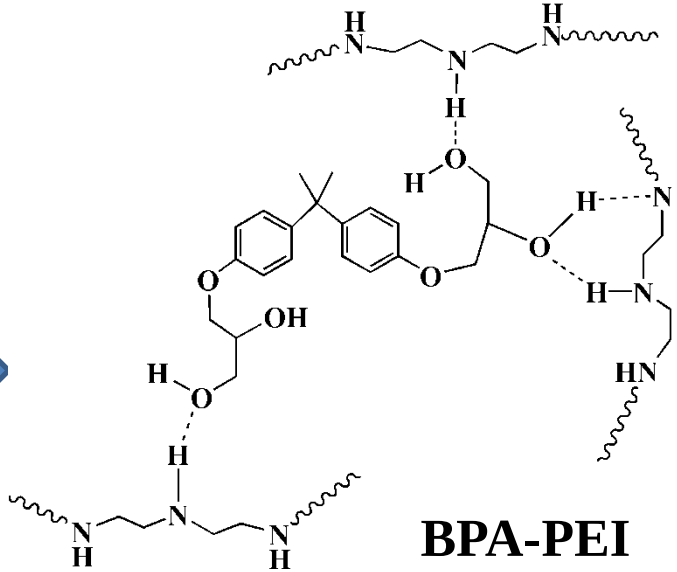
PEI-crosslinking

PEI-crosslinking agent:

Bisphenol A Diglycidyl Ether (BPA)

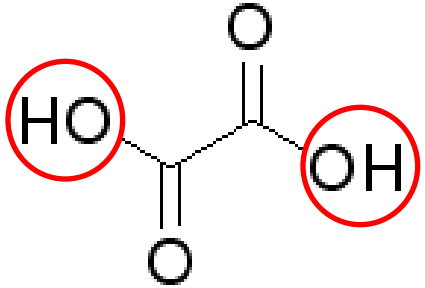


PEI →

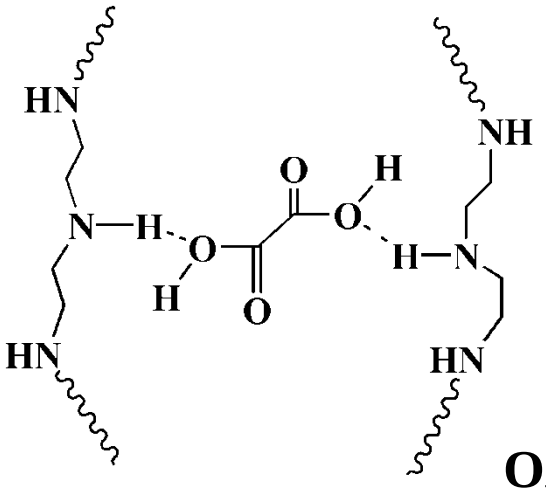


BPA-PEI

Oxalic acid (OA)

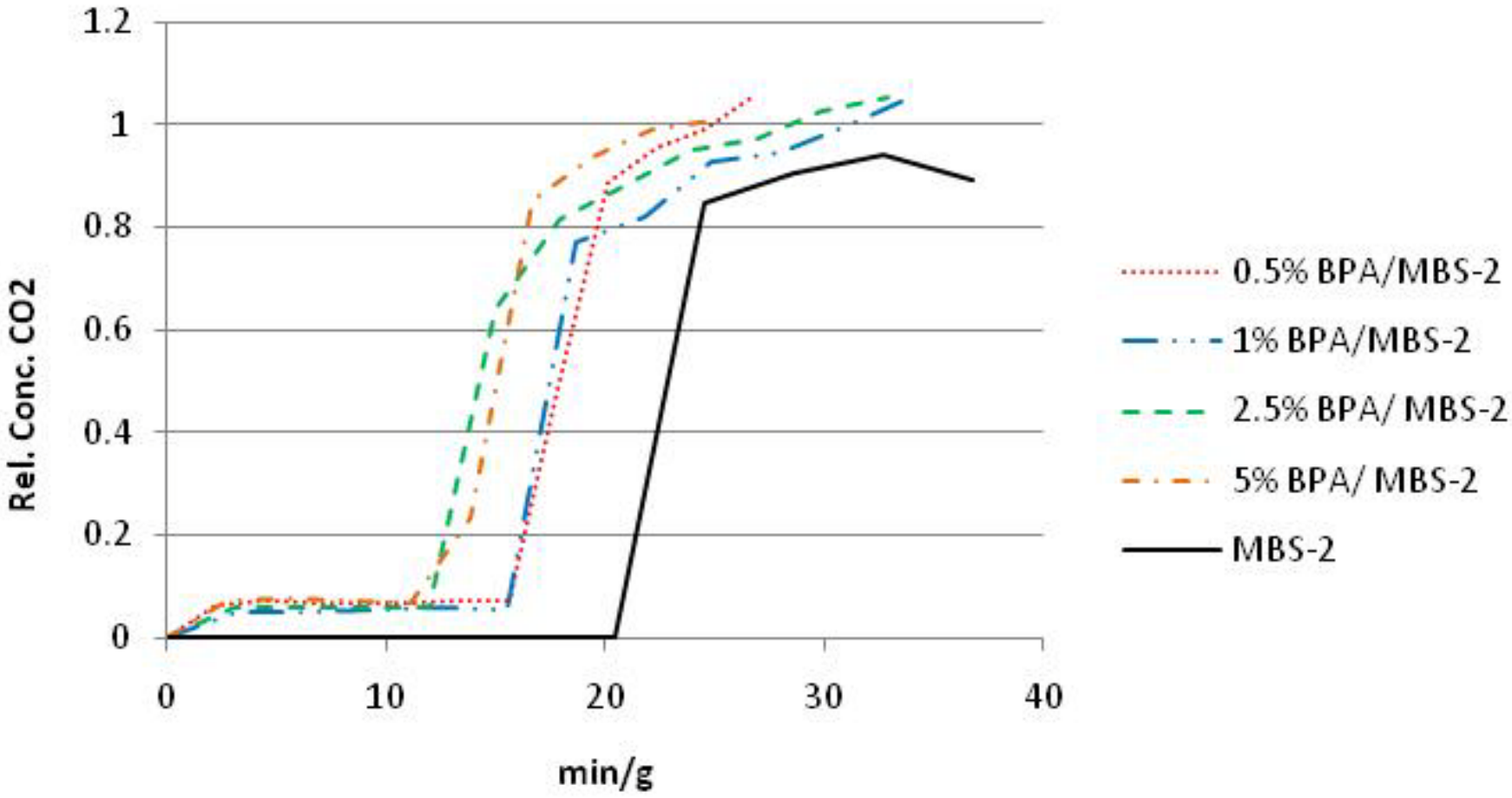


PEI →

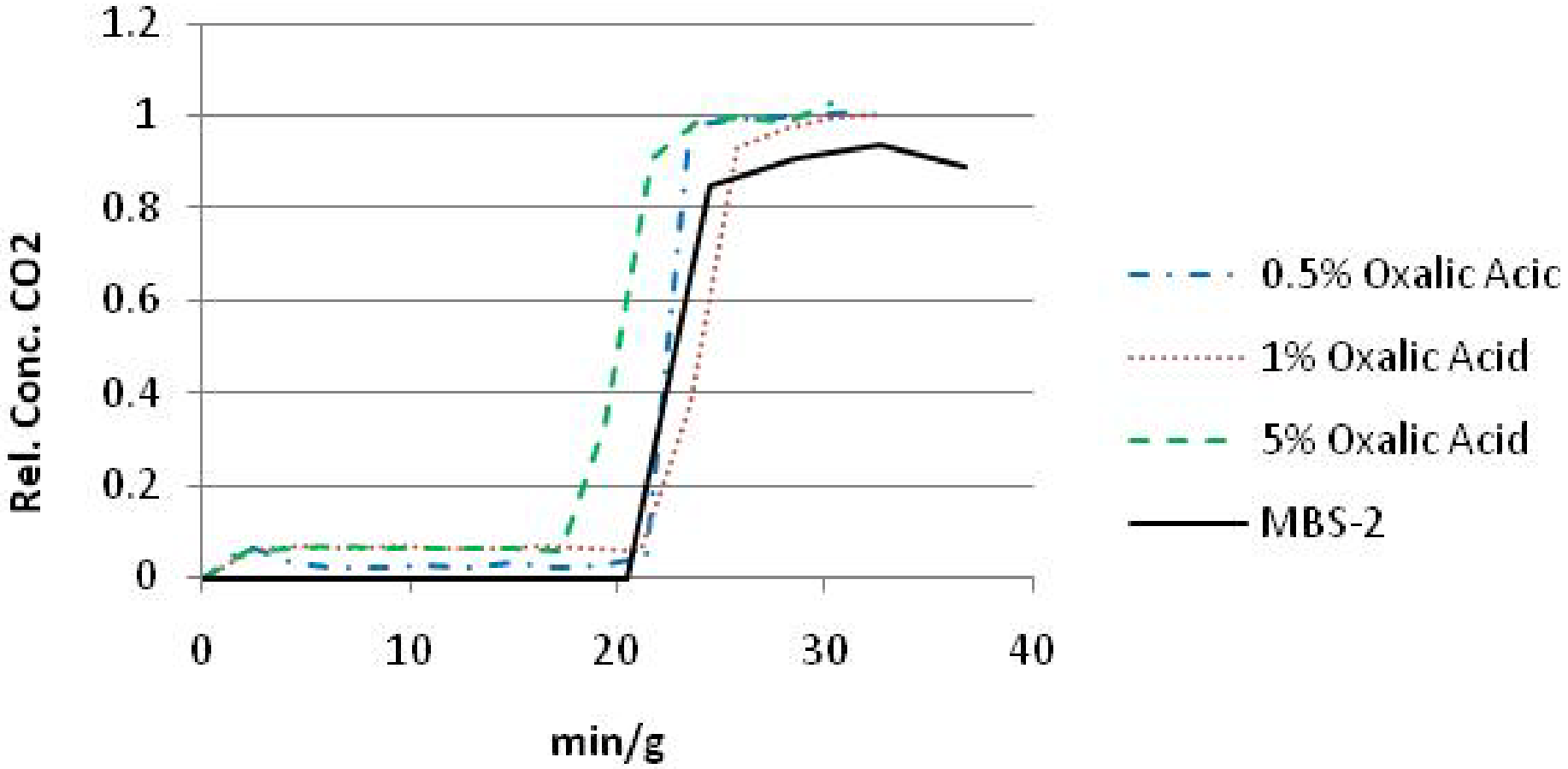


OA-PEI

CO_2 Sorption Breakthrough Curves over BPA-PEI(50)/SBA-15



CO_2 Sorption Breakthrough Curves over OA-PEI(50)/SBA-15

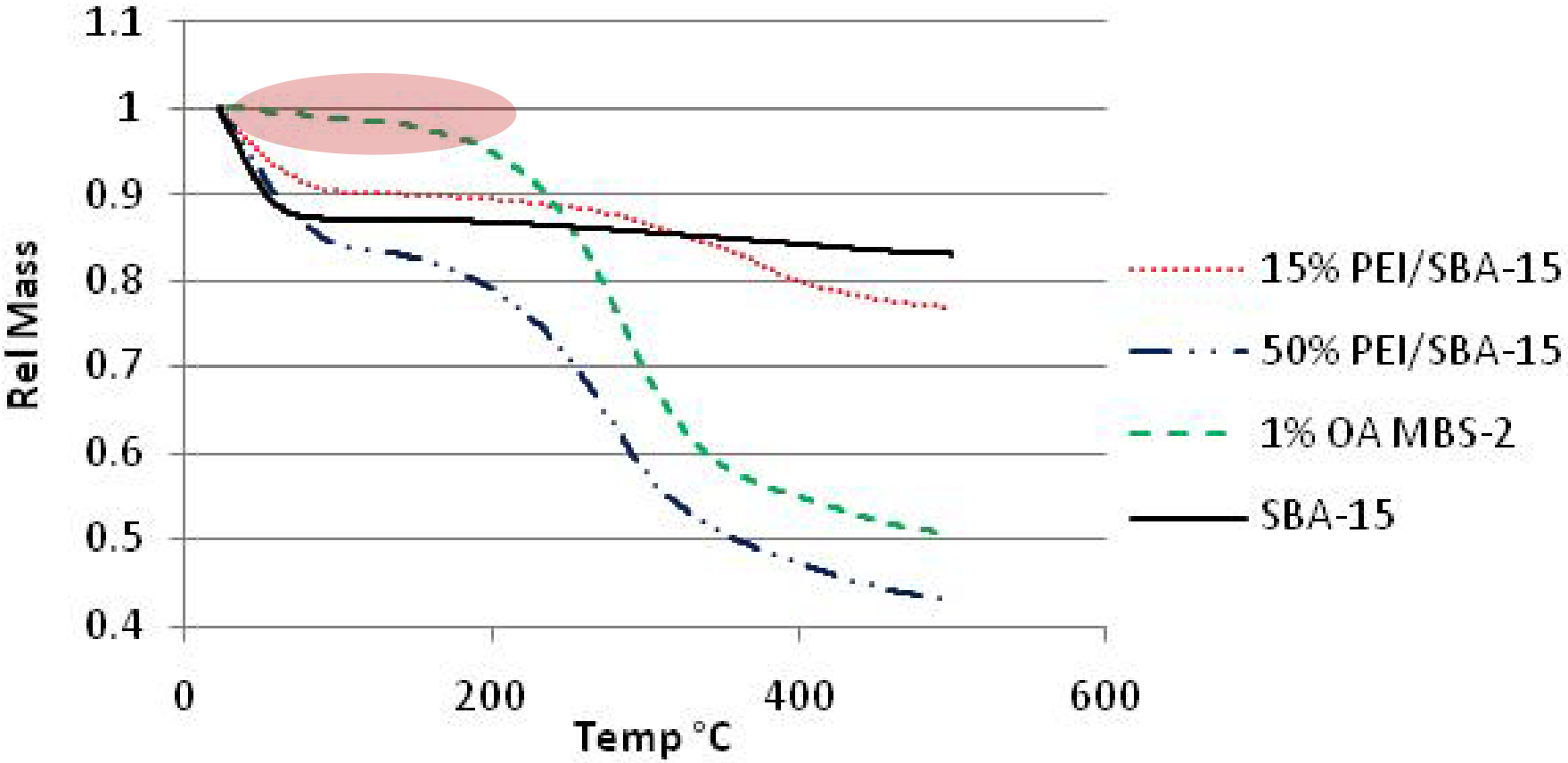


CO_2 sorption performance of crosslinked MBS obtained by flow system

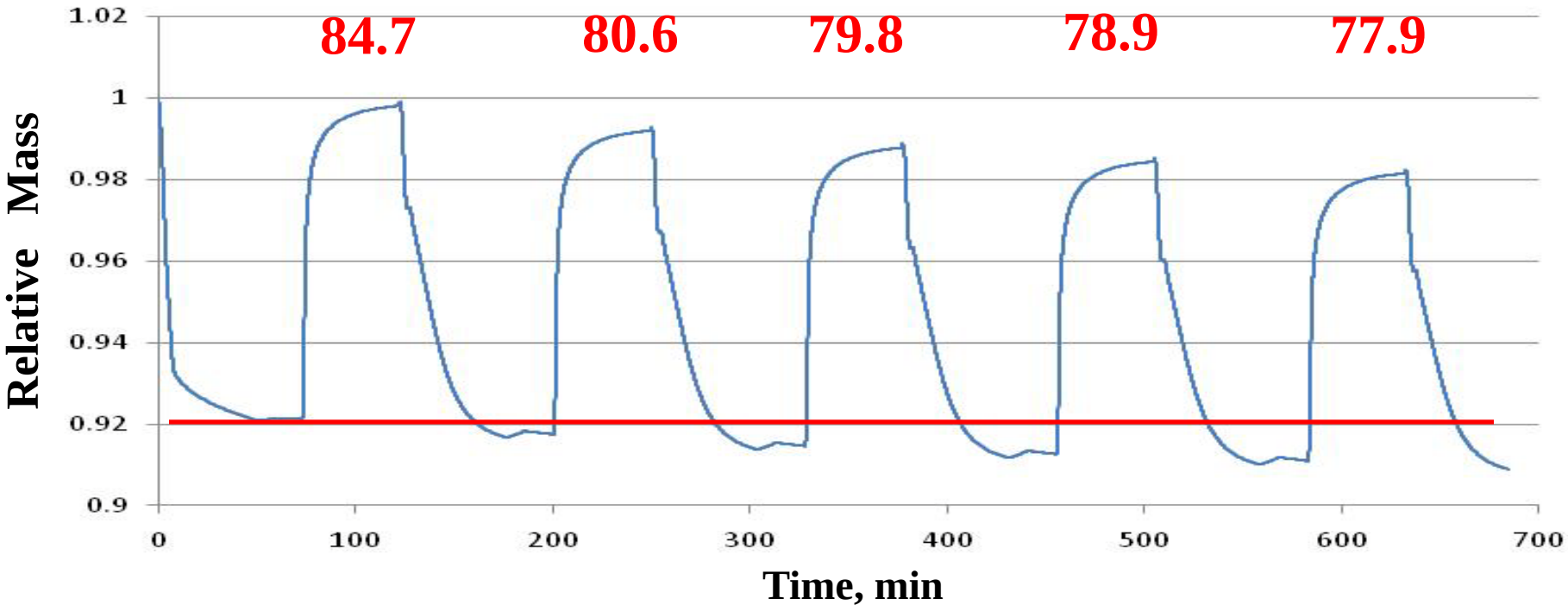
Sample	Ads. Cap. (mg/g)	Amine Efficiency (%)
0.5% BPA-PEI(50)/SBA-15	92.8	18.9
1% BPA-PEI(50)/SBA-15	96.7	19.7
2.5% BPA-PEI(50)/SBA-15	80.1	16.3
5% BPA-PEI(50)/SBA-15	77.9	15.9
0.5% OA-PEI(50)/SBA-15	119	24.2
1% OA-PEI(50)/SBA-15	131.1	25.1
5% OA-PEI(50)/SBA-15	105	20.9
PEI(50)/SBA-15	140.5	28.7

OA is better than BPA to maintain a high capacity of PEI(50)/SBA-15

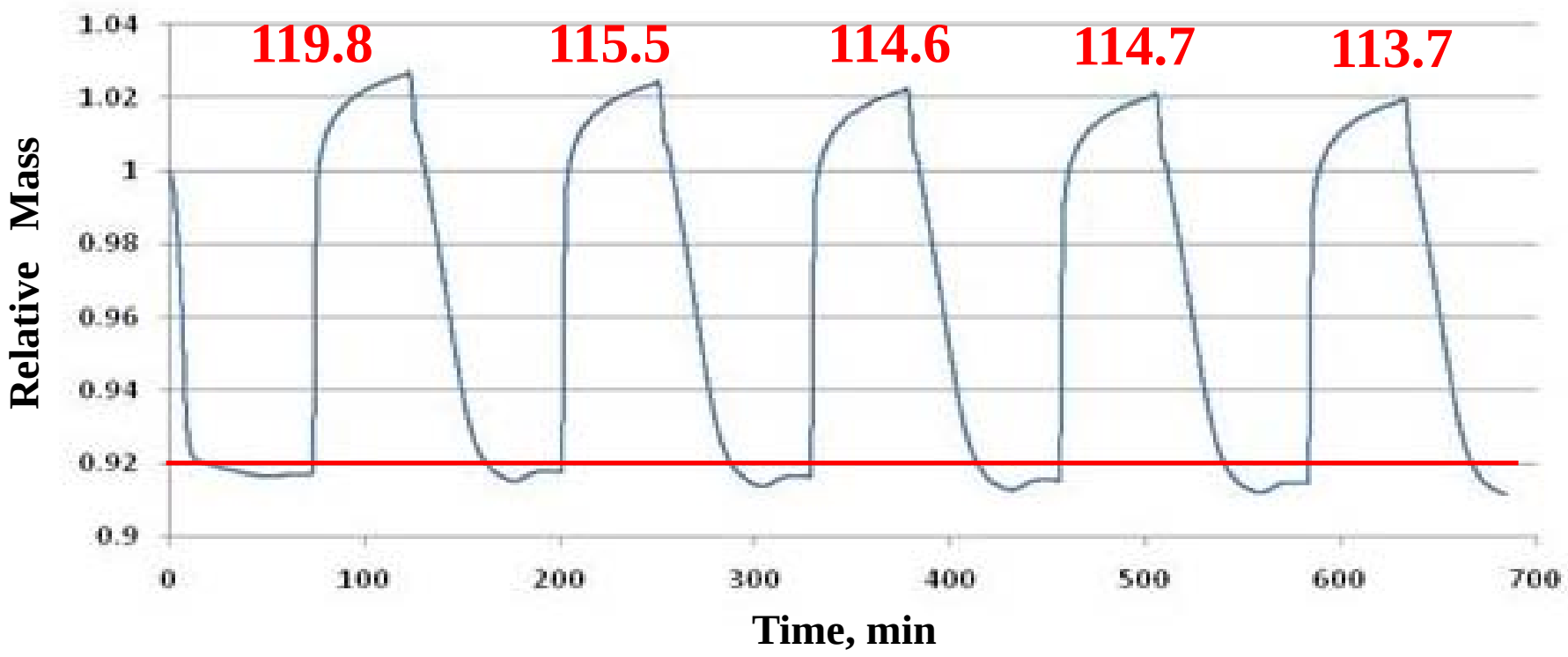
Thermal Stability of Crosslinked MBS Examined by TGA



Regenerability and Stability of 5% BPA-PEI(50)/SBA-15



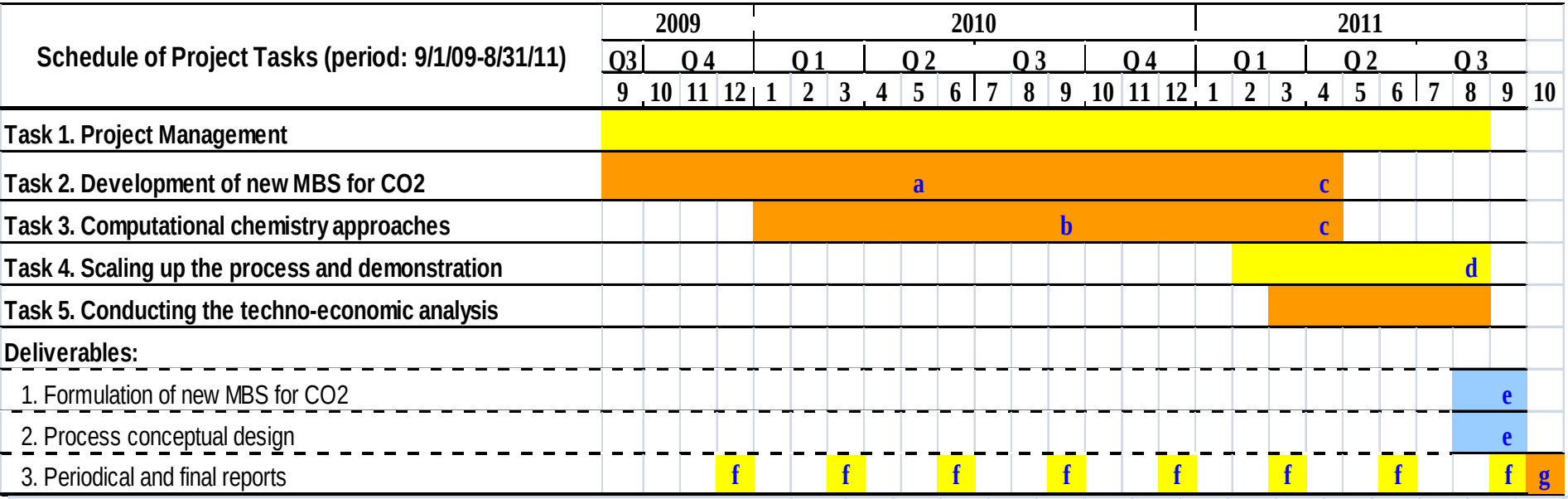
Regenerability and Stability of 5% OA-PEI(50)/SBA-15



Summary

- **Silica-gel is a promising support for preparing MBS, which showed slightly lower weight-based capacity, but much higher volume-based capacity than SBA-15-based MBS**
- **Using Mesocellular silica Foam (MCF), much higher sorption capacity can be achieved (ca. 200 mg/g). The best PEI loading is about 65 wt%. The MCF-MBS also exhibited good regenerability and stability**
- **Bisphenol A Digyldidyl ether (BPA) and oxalic acid (OA) were used as crosslinking agents for PEI to improve the stability of MBS. From the point view of both sorption capacity and stability, OA is an better option than BPA.**

Current Status of Project



Milestones

a: Provide primary results in development of MBS for CO2 capture — **Complete**

b: Provide primary results in computational calculations

c: Complete the computation calculation and the development of MBS for CO2 capture with working capacity of > 70 mg-CO2/g-S

d: Complete the scale-up CO2 sorption process using MBS

e: Provide the formulation of MBS and concept process for CO2 capture from flue gas

f: Provide the quarterly technical & budgetary reports

g: Provide the final technical report including scale-up and economic analysis data

On schedule

Future Plans

- MCF-based MBS will be further examined over fixed-bed flow system using model flue gas
- Other agents like succinic acid, malonic acid, DL-malic acid and citric acid will be tested for PEI-crosslinking. To produce an amide bonding will be another option
- Computational calculation and simulation will be performed for fundamental understanding of CO_2 sorption over the developed MBS and for guiding the development of MBS
- The best regeneration conditions and method (TAS and/or PSA) will be determined
- Based on the developed MBS, scale-up of CO_2 sorption process using MBS will be carried out (about 200 ml sorber in the lab)
- Based on the selected materials and sorption performacne, a primary analysis on the techno-economy of MBS technology will be conducted

Acknowledgment

- **Financial support from DOE through National Energy Technology Laboratory (Award DE-FE0000458).**
- **DOE Project Manager, B. Andrew O'Palko for his time, management and valuable discussions and suggestions on this project.**

Thank you for your attention

Question?