

Fourth Annual Conference on Carbon Capture & Sequestration

*Developing Potential Paths Forward Based on the
Knowledge, Science and Experience to Date*

Capture and Sequestration – Sorbent 1

Temperature Effect on the Capture of Carbon Dioxide by Immobilized Amine Sorbents

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Abstract and Authors

Temperature Effect on the Capture of Carbon Dioxide by Immobilized Amine Sorbents

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ABSTRACT

Michael addition reaction products of **ethylenediamine** (ED) and **tetraethylenepentamine** (TEPA) were immobilized within the pores of high-surface-area poly (methyl methacrylate) PMMA solid beads. The primary amine sites present in the ED and TEPA were converted to secondary amine sites by reacting them with acrylonitrile (AN). The performance of the new immobilized modified solid amine sorbents (IMSA) were evaluated to determine their carbon dioxide (CO₂) capture capacities in a temperature swing system using a 10 % CO₂/2 % H₂O/He gas stream. Over the studied temperature range of 20-65 °C, it was determined that the CO₂ capture capacities significantly improved at temperatures between 45-65 °C. The average CO₂ capture capacities for the IMSA sorbents over 4 adsorption/desorption cycles ranged from 3.4 -6.6 moles of CO₂/kg sorbent. The thermal stability of the IMSA sorbents was also investigated over a ten cycle study. These results suggest that there are potential applications of these of IMSA sorbents in the capture of CO₂ from flue gas streams produce by the combustion of coal for the generation of electricity.

Presentation Outline

- Overview and Background
- Preliminary System Analysis
- Experimental Conditions and Results
- Conclusion

Overview

General Background

Overview

- **Objective**

- To develop low-cost solid sorbents to be used in an efficient process for the capture of CO₂ from flue gas streams

- **Technical Challenges**

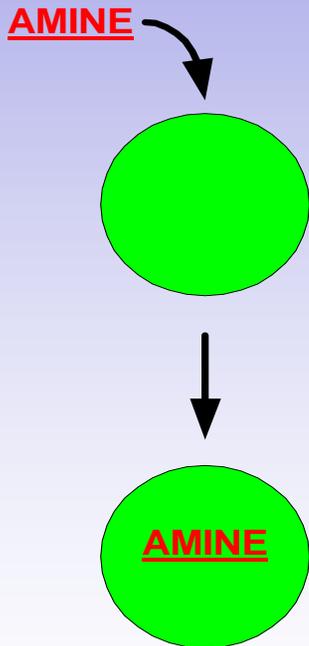
- To reduce the energy intensity of current capture processes (e.g.. MEA process)
- To improve the capture capacity of sorbents
- To produce affordable solid sorbents for the capture of CO₂
- To improve the mass and heat transfer parameters
- To increase the available contact surface
- To eliminate the corrosion problems associated with liquid amine systems

Overview - Potential Applications

- Fossil-fuel power generation plants contribute about 1/3 of anthropogenic CO₂ emissions
- Power generation point sources
 - Pulverized coal combustion plants
 - Advanced power system
- Capture step
 - **Post-combustion- SCR & FGD cleanup systems resulting in 40-70 ppm SO₂ and 20-40 NO at 50-70 °C before CO₂ capture**
- Storage step in carbon sequestration requires concentrated CO₂
- Natural gas cleanup and life support systems

Overview-Capture Technology

IMMOBILIZATION



Birbara US 6,364,938

25 °C Life Support Systems

Sorbent Criteria

- Basicity
- Vapor Pressure
- Viscosity
- Substrate
- Capture Capacity
- Temperature Stability
- Regenerable
- Flue Gas Stream

Overview – Amine Modifications

Ethylenediamine



50 °C

2.3



Ethylenediamineacrylonitrile (EAN)

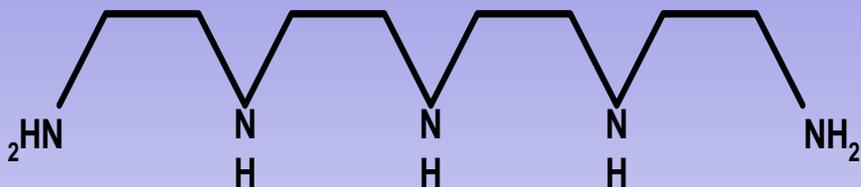
De Filippis

Int. Eng. Chem. Res.

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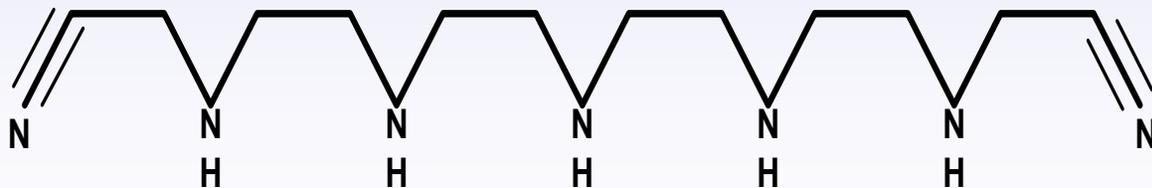
Overview – Amine Modifications

Tetraethylenepentamine **TEPA**

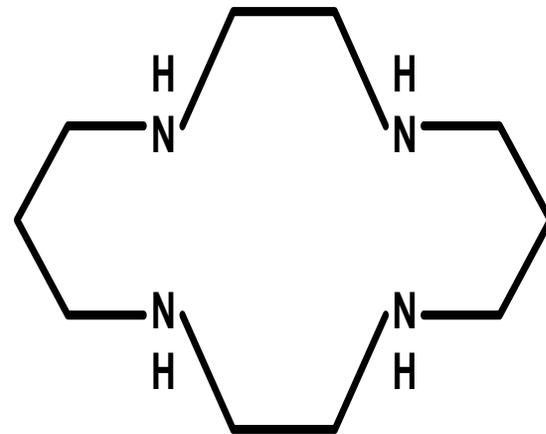


50 °C

2.3 $\text{H}_2\text{C}=\text{CHCN}$



Tetraethylenepentamineacrylonitrile (**TEPAN**)



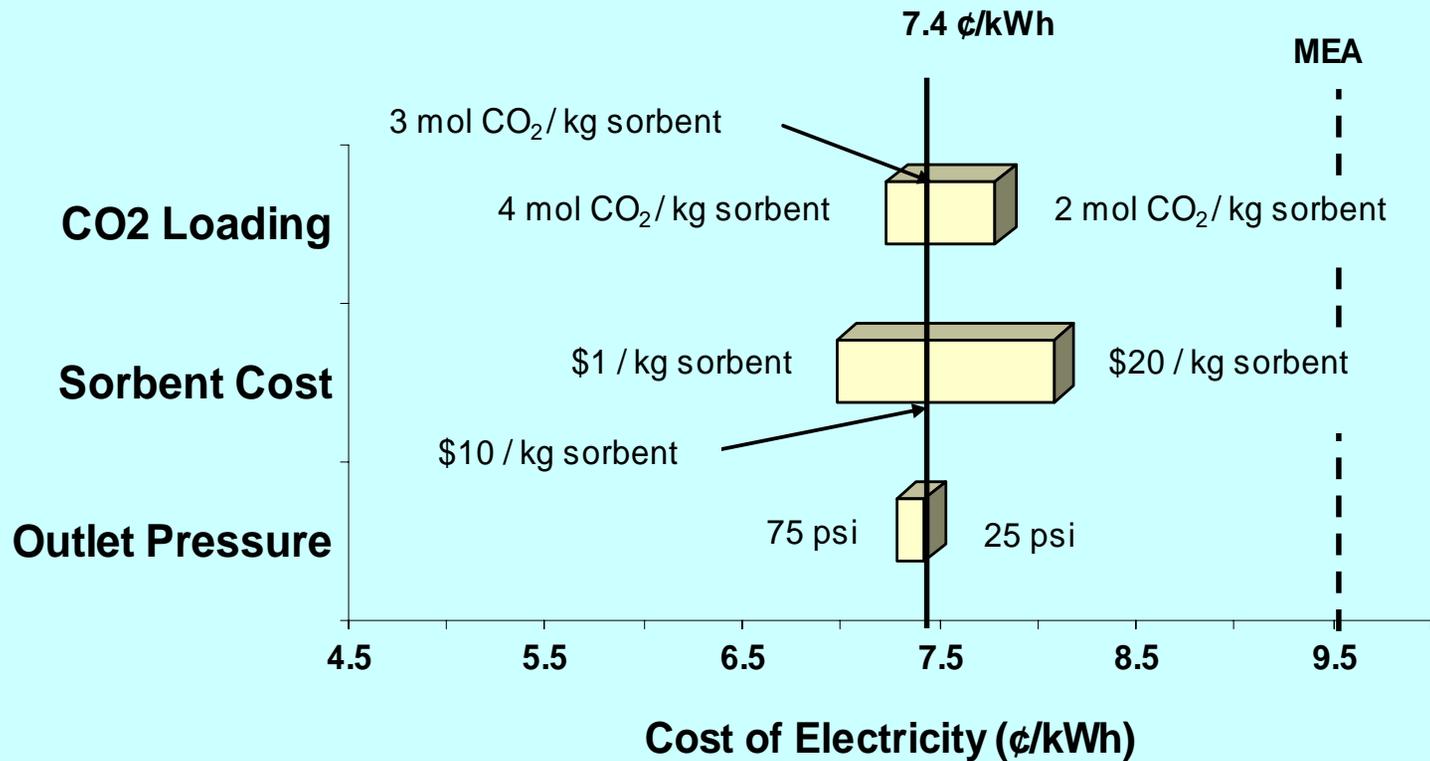
1,4,8,11-Tetraazacyclotetradecane **Cyclam**

System Analysis

Preliminary System Analysis

Preliminary System Analysis

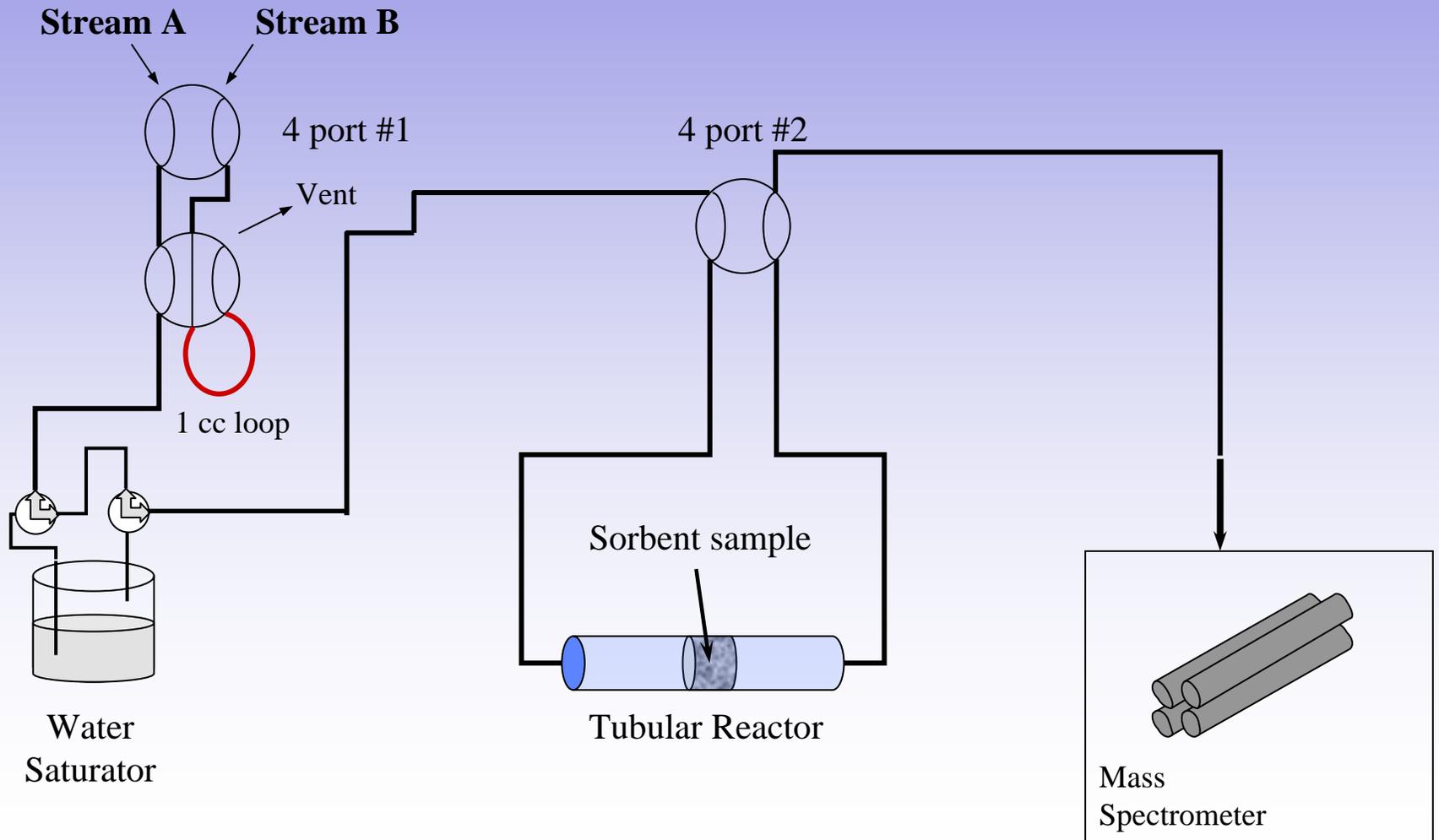
Amine Enriched Sorbent Sensitivity Analysis



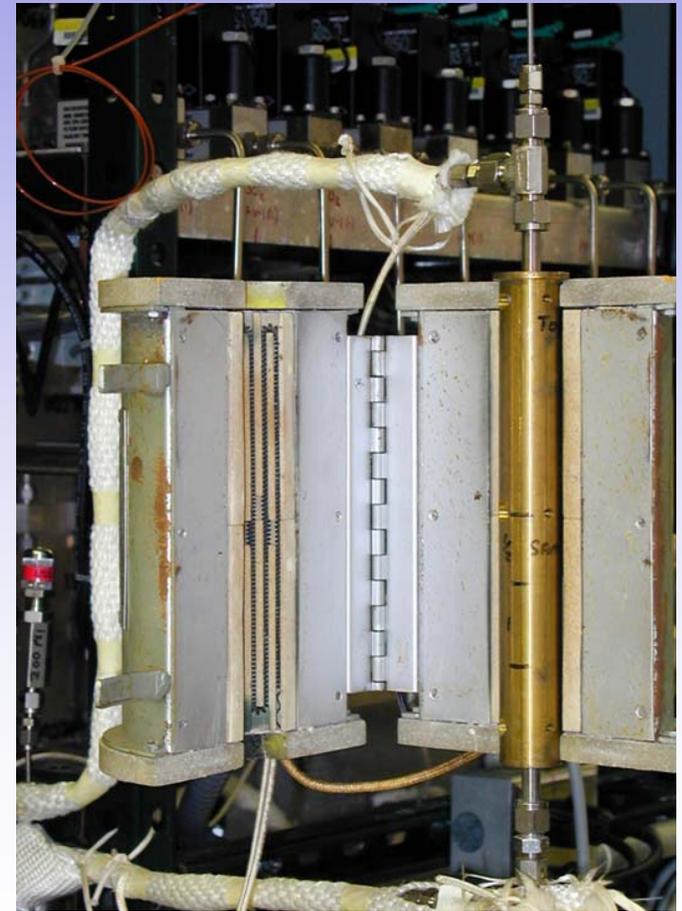
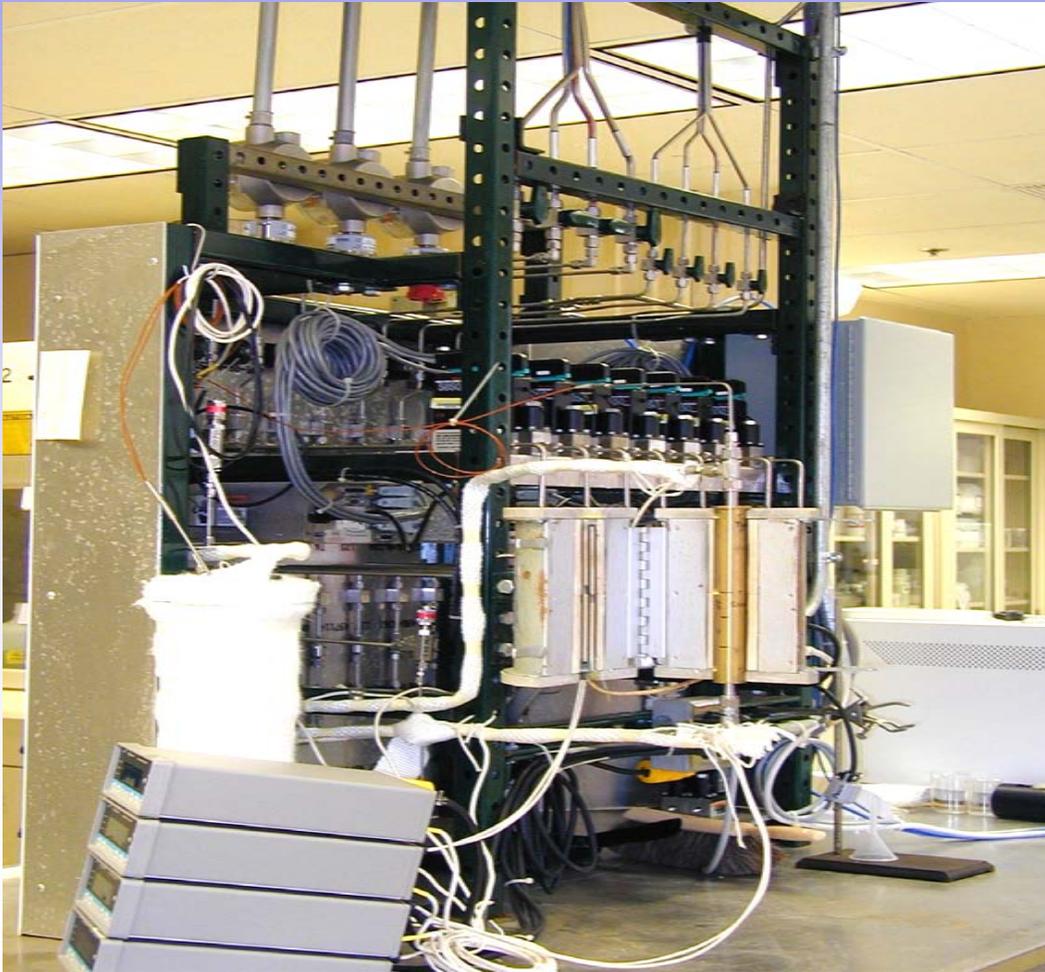
Experimental

Conditions and Results

Experimental Schematic Diagram



Experimental CO₂ Capture Reactor



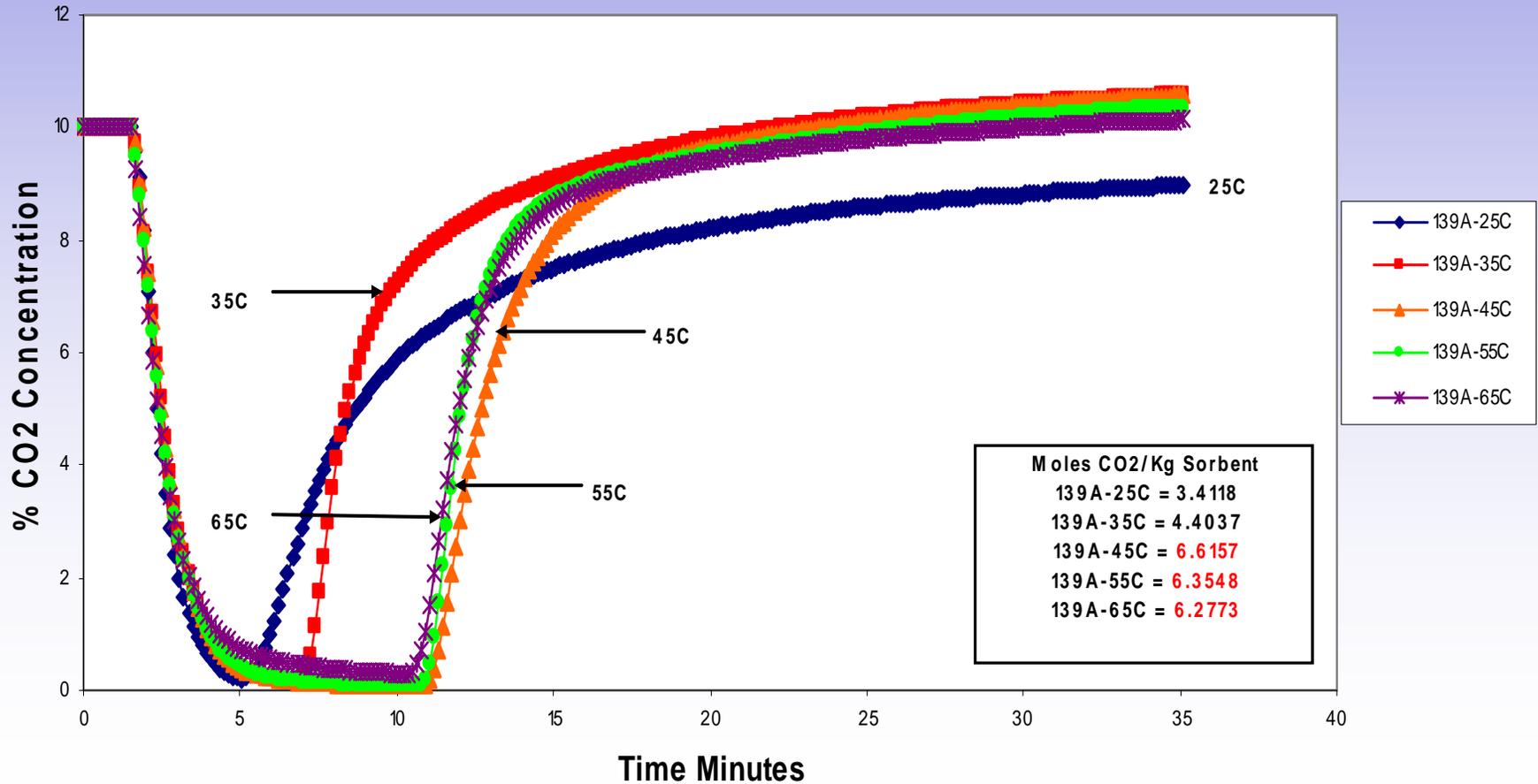
Experimental Conditions

- **1.0 Gram sample (Immobilized Secondary Amine Sorbents)**
- **He/2% H₂O Pretreatment at 25 °C (180-200 ml/min)**
- **10% CO₂/2 % H₂O/He at 25-65 °C (160-170 ml/min) Adsorption**
- **He/2% H₂O at 90 °C (180-200 ml/min) Desorption**
- **Pfeiffer Vacuum OminiStar 300 Mass Spectrometer**

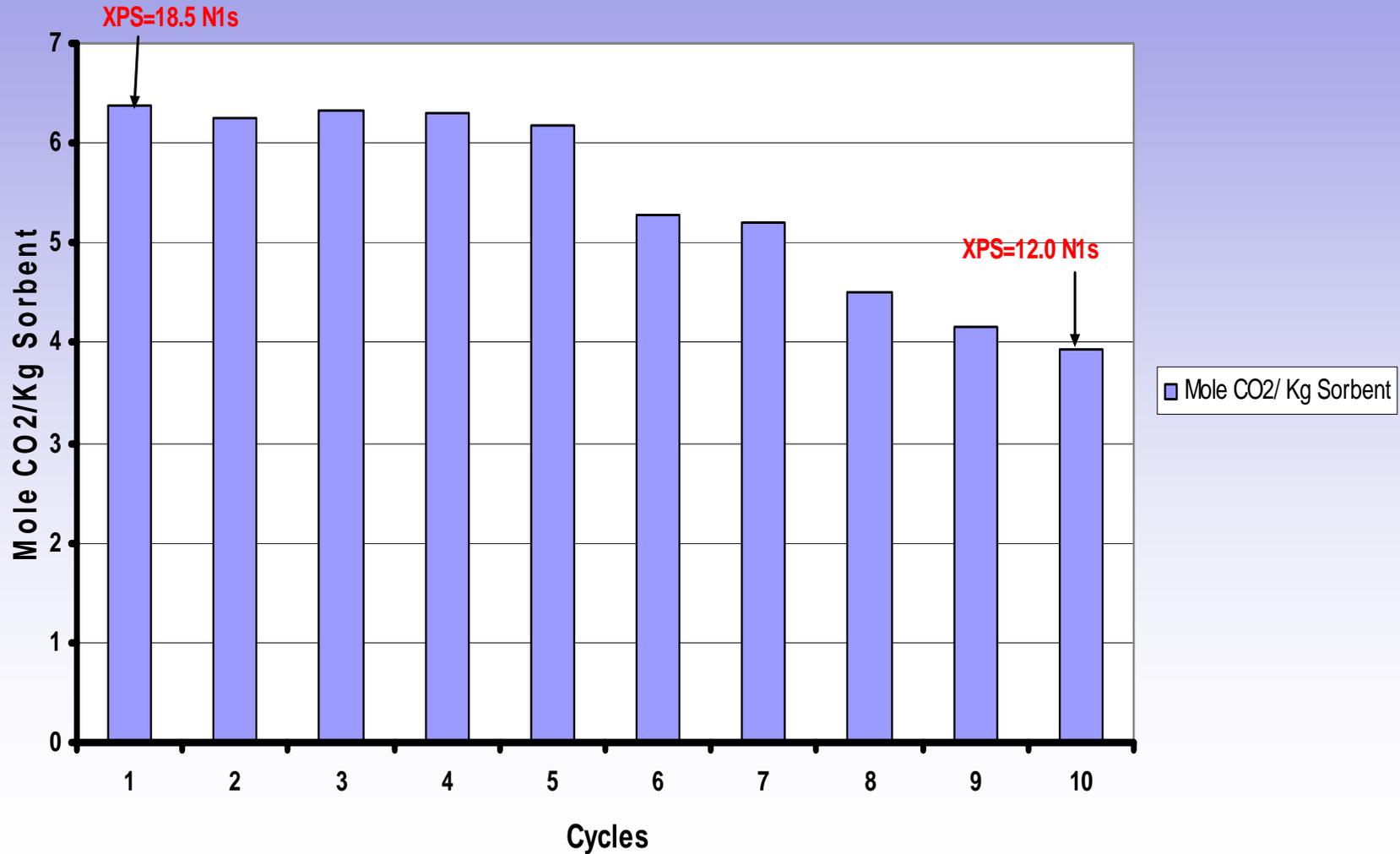
Experimental – Sorbent Preparation

- 1:1 Weight ratio of amine/PMMA substrate with methanol
- 100% EAN or TEPAN/10% CYCLAM
- Rotary vacuum at 90 °C over 300-10 mmHg
- Stored sorbents under refrigeration
- XPS used for qualitative analysis

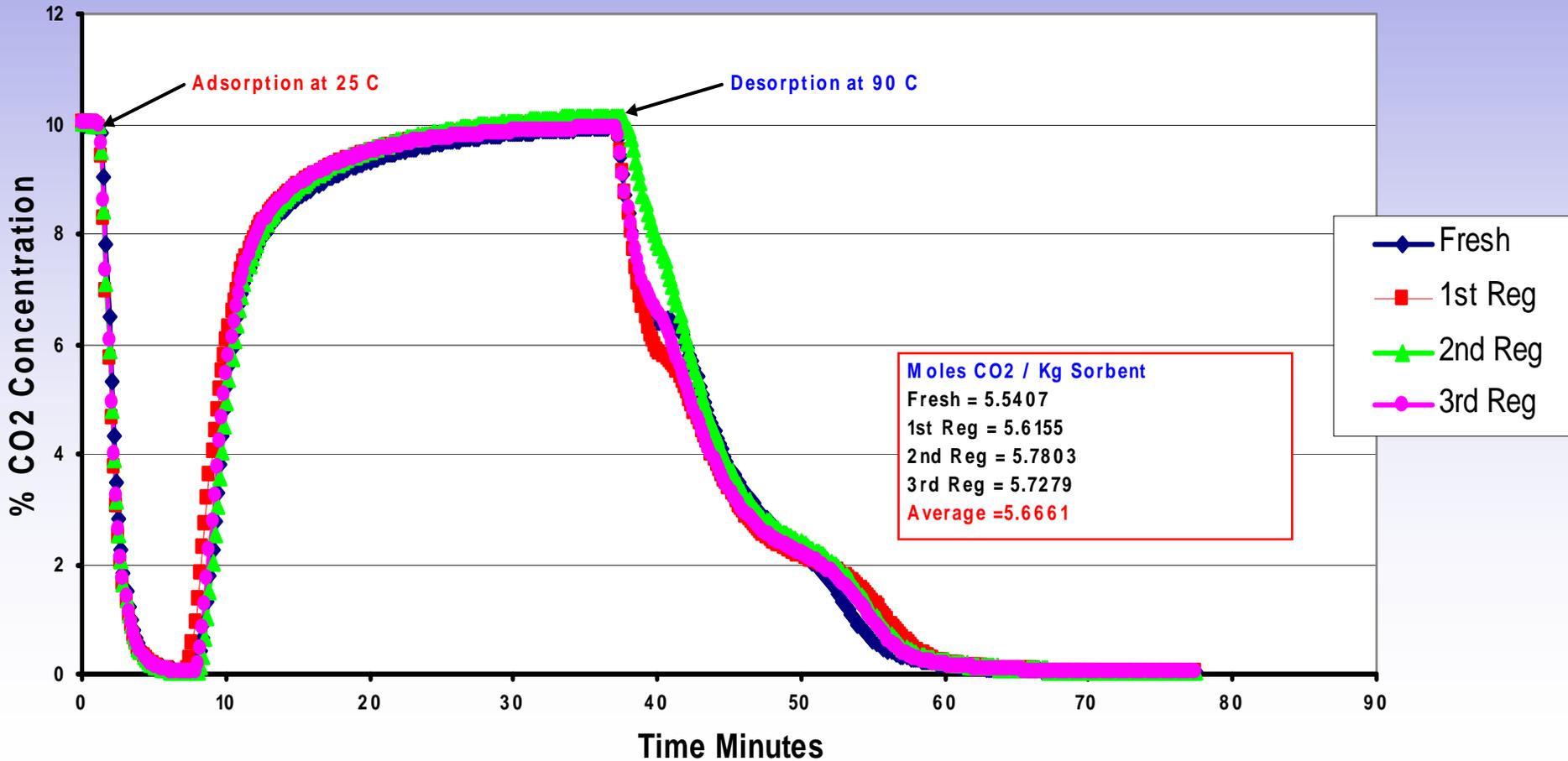
Adsorption Breakthrough Curves for 139A EAN Sorbent at Various Temperatures in 10%CO₂/2%H₂O/He at 160-170 ml/min



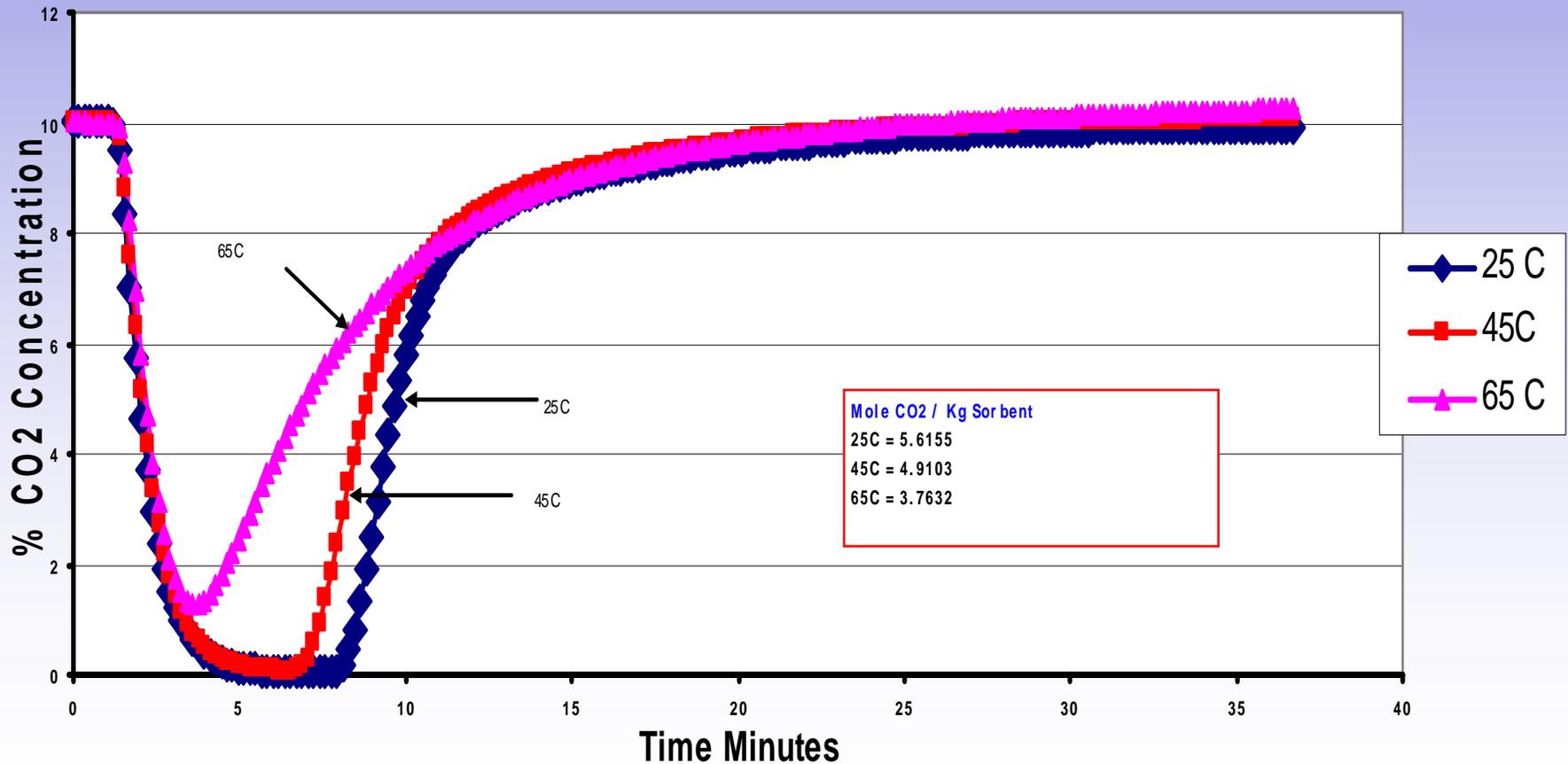
Regeneration of 139A EAN Over Ten Cycles at 90 °C in 10%CO₂/2%H₂O/He at 160-170 ml/min



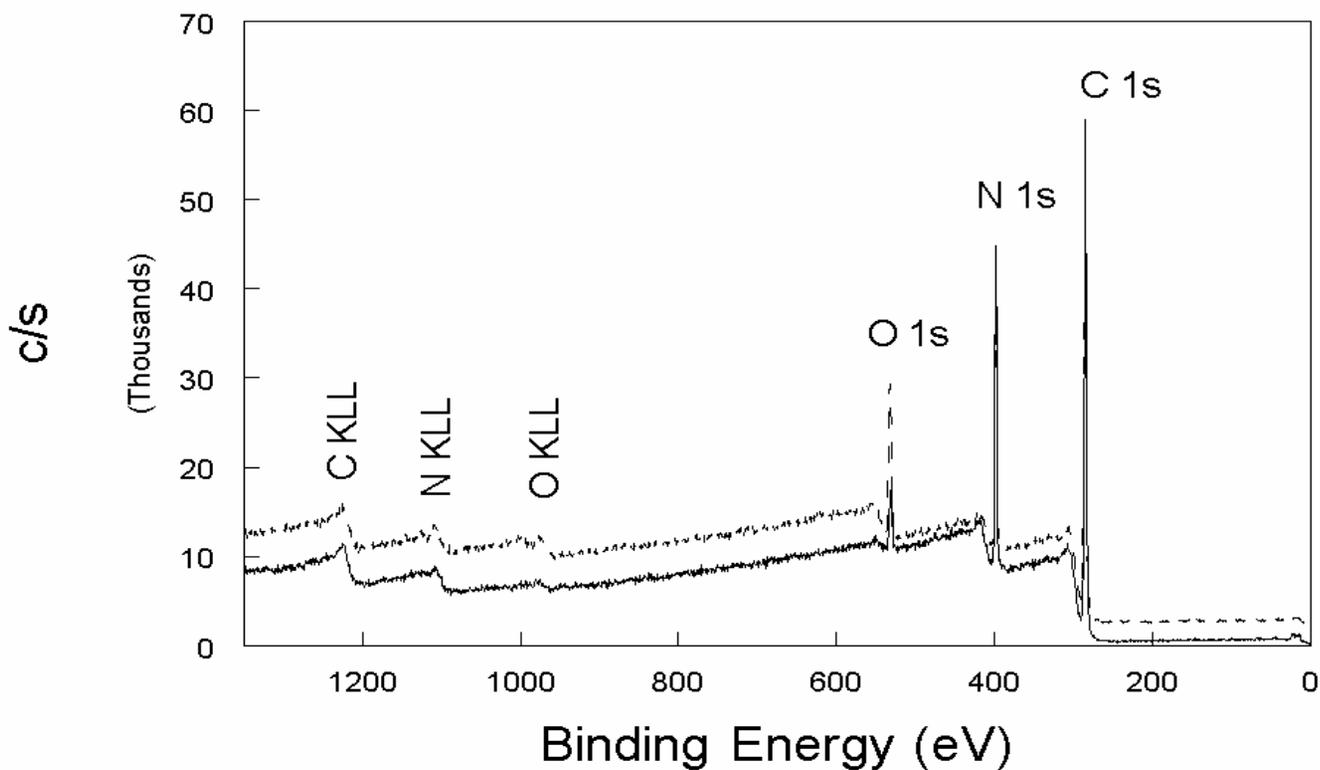
Adsorption / Desorption Breakthrough Curves for 167A TEPAN/10%CYCLAM at 25 °C in 10%CO₂/2%H₂O/He at 160-170 ml/min



Adsorption Breakthrough Curves for TEPAN/10%CYCLAM at Various Temperatures in 10%CO₂/2%H₂O/He at 160-170 ml/min



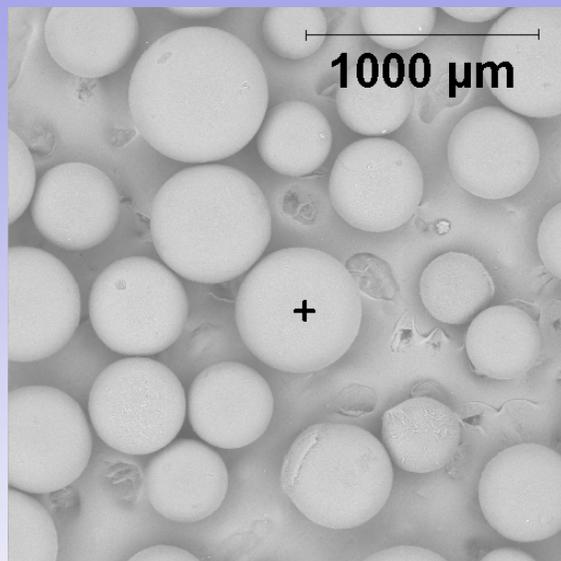
XPS Analysis of 167A TEPAN/10%CYCLAM Over 25 – 65 °C in 10%CO₂/2%H₂O/He at 160-170 ml/min



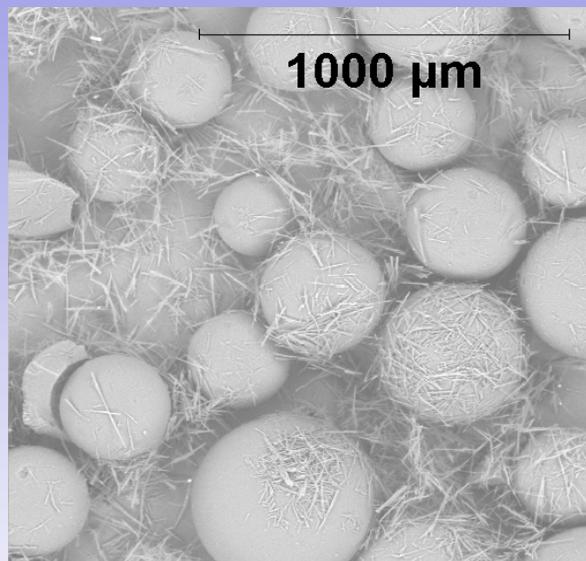
XPS Before
24.76 N1s

XPS After
19.52 N1s

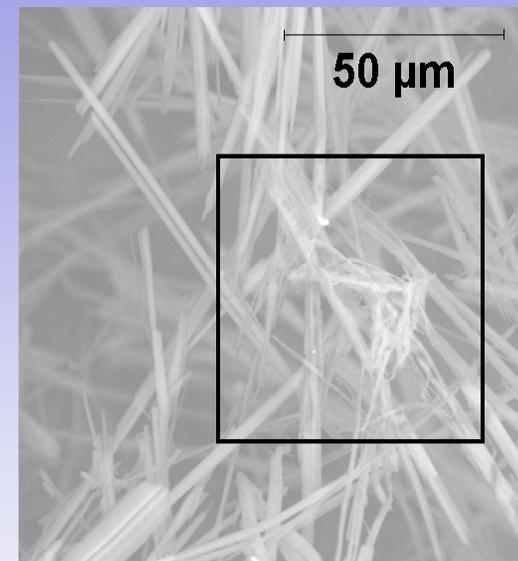
SEM-EDS Analysis TEPAN/10%CYCLAM 167A Over 6 Cycles at 25-90 °C in 10%CO₂/2%H₂O/He at 160-170 ml/min



Before



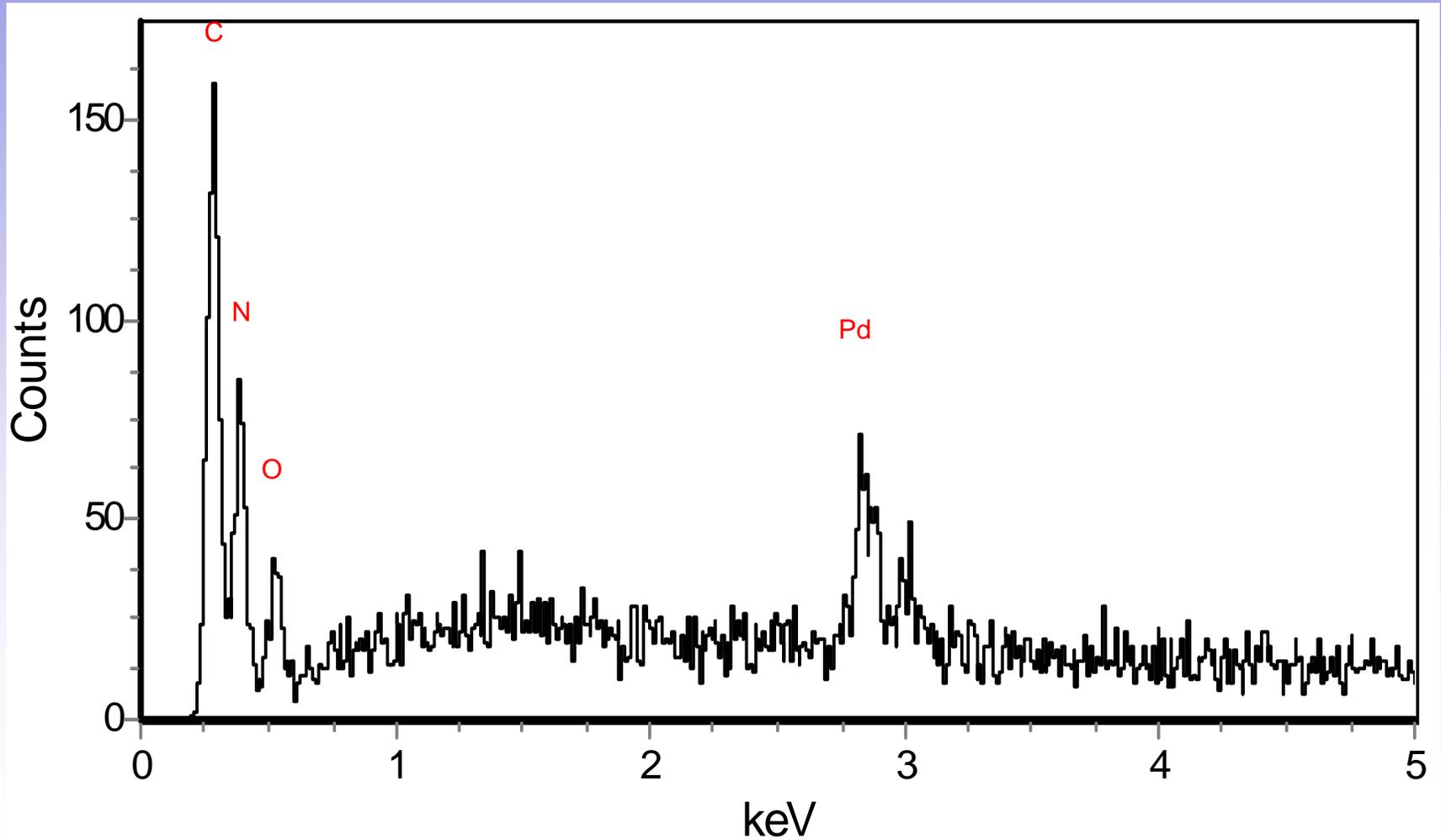
After 6 cycles



Crystal Formation

SEM-EDS analysis of 167A
(Samples mounted on carbon tape and Pd coated)

SEM-EDS SPECTRA of TEPAN/10% CYCLAM 167A



Conclusions

Immobilized Solid Amine Sorbent Performance in 10%CO₂/2%H₂O/He at 160-170 ml/min over 25-90 °C

- Thermal stability issue for sorbents needs to be improved
- Performance
 - *3.4-6.6 mole CO₂/Kg Sorbents – Patent application filed 1/12/05*
 - *CO₂ capacities for EAN increased and TEPAN/10%CYCLAM Decreased in relationship to higher temperatures > 25 °C*
- Future Plans
 - *Immobilized sorbents performance under coal contaminant conditions are underway and will be reported at the 2005 Pittsburgh Coal in September*
 - *TGA study to identify more thermally stable amine and/or chemical blends*
- Synthetic and Polymeric Solid Amine Sorbents
 - *Research work is now underway to improve the performance of these solid amine sorbents*

Acknowledgements

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