Degradation and Regeneration of Aminosilica Adsorbents in CO₂ Capture

**Keywords:** carbon capture, amine degradation, aminosilica adsorbents, adsorbent regeneration

**Hypotheses:** Aminosilica adsorbents used for post-combustion carbon capture can be partially regenerated through treatment with acid, transesterification, and a Hoffman rearrangement.

**Introduction:** The most readily available technology to reduce carbon emissions is carbon capture through amine scrubbing followed by geological sequestration. However, amine scrubbing has environmental risks: volatile amines escape into the atmosphere and carcinogenic nitrosamines form from NOₓ.¹

Other technologies exist to capture carbon, but most do not have the fundamental knowledge necessary for pilot testing. Amines covalently tethered to silica supports for adsorption (ASA) use similar chemistry as amine scrubbing to selectively bind CO₂ but avoid the environmental side effects because of a lack of volatility and by binding nitrosamines. The method for attaching amines to silica is common among industry,² so scaling up ASA production would be more feasible than other novel adsorbents. Similar to amine solvents, flue gas components, NOₓ and O₂, also reduce effectiveness of ASA. NOₓ preferentially bind to the amine group³ while pure O₂ oxidizes ASA to form imines, amides, and carboxylic acids, thus degrading the adsorbent.⁴

Since production of ASA has both environmental and economic costs, reusability is vital for any industrial application. A study by Hallenback and Kitchin explored using NaOH to regenerate adsorbent poisoned with SO₂,⁵ but there have been no studies to evaluate the regeneration capacity of amine adsorbents for carbon capture after exposure from NOₓ or O₂. I propose investigating the degradation of ASA from NOₓ and O₂ and developing regeneration methods to reduce the frequency of adsorbent replacement. More specifically I will

1) Synthesize and characterize the ASA from primary, secondary, and tertiary amines
2) Degrade the ASA using NOₓ and O₂ in a packed bed reactor
3) Regenerate NOₓ treated ASA using aqueous acetic acid and bromide
4) Regenerate O₂ treated ASA using the Hoffman rearrangement or transesterification

**1) Synthesis and Characterization:** ASA will be created through condensation of MCM-41 mesoporous silica with a chloroalkoxysilane followed by reaction with ammonia, ethylamine, and diethylamine to form primary, secondary, and tertiary ASA. Since the experimental procedures involve toxic chemicals, a risk assessment will be conducted to determine necessary safety precautions.

Between sections 1, 2, 3, and 4, ASA will be tested for surface area (using Brunauer-Emmett-Teller method⁶), pore size (Barrett-Joyner-Halenda method³), elemental analysis (sent for external testing), bonding structure (using C₁₃NMR and Fourier Transform Infrared Spectroscopy¹⁵), and CO₂ capacity and kinetics (in a packed bed reactor with live analysis of exiting gas composition⁵).

**2) Degradation:** The characterized ASA will be placed in packed bed reactors with a mixture of gas containing N₂, CO₂, H₂O, and either NOₓ or O₂. The NOₓ experiments will be conducted at 50°C, the standard adsorbing temperature, while the O₂ experiments will run at 150°C, the desorption temperature. The ASA will be considered degraded when the exiting concentration of pollutant approaches the inlet concentration. The degraded ASAs will then be characterized.

I expect that ASA will initially react with NOₓ and O₂ in a similar manner with amine solvents: NOₓ will form nitrosamines and nitramines, and O₂ will oxidize the α-carbon.
Furthermore, primary ASA should show a decrease in nitrogen content after exposure to NO\textsubscript{x} since primary nitrosamines degrade into N\textsubscript{2}. A mixture of alcohols, amides, imides, and acids should result from the O\textsubscript{2} exposure at elevate temperatures.\textsuperscript{4} These all decrease the capacity of the amine solvent.\textsuperscript{3–5}

3) Regeneration-NO\textsubscript{2}: To remove nitrosamine and nitramine functional groups, the denitrosation procedure for aliphatic nitrosamines described by Dix et al.\textsuperscript{6} will be followed. If more stringent conditions are necessary, testing an ASA embedded with 2-amino acetic acid would indicate whether oxidative degradation improves amine denitrosation.\textsuperscript{6} Regeneration from NO\textsubscript{x} may not work well for primary amines since they degrade into N\textsubscript{2}. Secondary and tertiary amines treated with NO\textsubscript{x} should increase in capacity as the original amines reform.

4) Regeneration-O\textsubscript{2}: For primary amines, a Hoffman rearrangement can produce an amine from the degraded amide using mild reagents.\textsuperscript{7} Secondary and tertiary amines would require too strong reducing agents and cause significant damage to the silica. For these, transesterification with ethanol amine will be employed to recover lost activity. Due to the variety of products formed, regeneration from O\textsubscript{2} exposure may be more difficult than denitrosation.

Further Analysis: The effluent from the regeneration steps will be tested for silica to determine the extent of support degradation. Assays requiring acidic treatments will use adsorbent with t-butyl groups near the organosilane bond to protect from hydrolysis. For the methods that show marginal improvement, conditions for regeneration will be altered to improve effectiveness. For these optimized methods, repeated degradation and regeneration cycles will assess durability.

Expected Results: These results will indicate the most suitable ASA given different capture conditions. For example, when NO\textsubscript{x} are removed before carbon capture, primary amines may be most beneficial since the Hoffman rearrangement can easily reform amines from O\textsubscript{2} oxidation. Furthermore, the findings may also correlate well with other solid amine adsorbents, so a general trend in regeneration can be seen regardless of the type of amine adsorbent.

Broader Impacts: Reducing CO\textsubscript{2} emissions will help stabilize our planet’s temperature to prevent negative effects of climate change like desertification and a rising sea level which would decrease food supply and increase land scarcity. ASA can isolate CO\textsubscript{2} to reduce emissions and slow climate change. The degradation studies in this project will further characterize ASA, and the regeneration methods developed will help make using ASA more economical. Since amine based adsorbents can capture CO\textsubscript{2} with reduced emissions of toxic amines and carcinogens, this work will also help reduce the negative environmental impact of carbon capture.

I will disseminate my results through conferences and publications so other researchers can improve upon and apply the findings towards further development and application. I will mentor undergraduate students and encourage them to develop their own projects so that they gain valuable research skills before graduate school. Since solving climate change requires international cooperation, I plan to collaborate with foreign institutions specializing in carbon capture like the Norwegian Technical University to accelerate the application of CO\textsubscript{2} capture.

(7) Patel, I.; Opieқnik, M.; Bohmdorfer, S.; Becker, M.; Rosenau, T. Holzforschung 2010, 64, 549–554.}