Next Generation SCR-Dosing System Investigation

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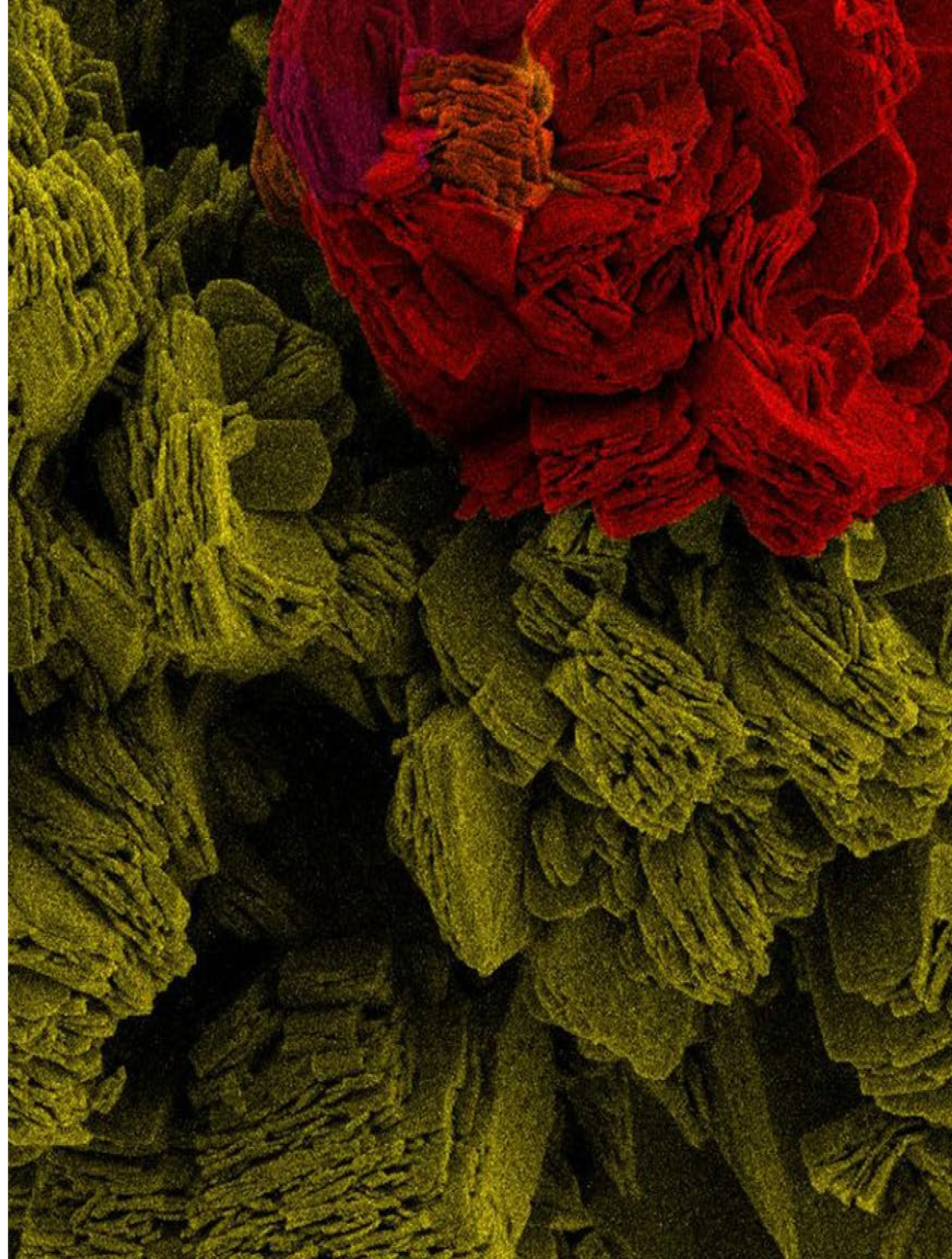


Project Overview

Timeline

- Start – Oct 2018
- End –Sept 2021

Budget

- Matched 80/20 by USCAR as per CRADA agreement
- DOE funding for FY19: $200K;

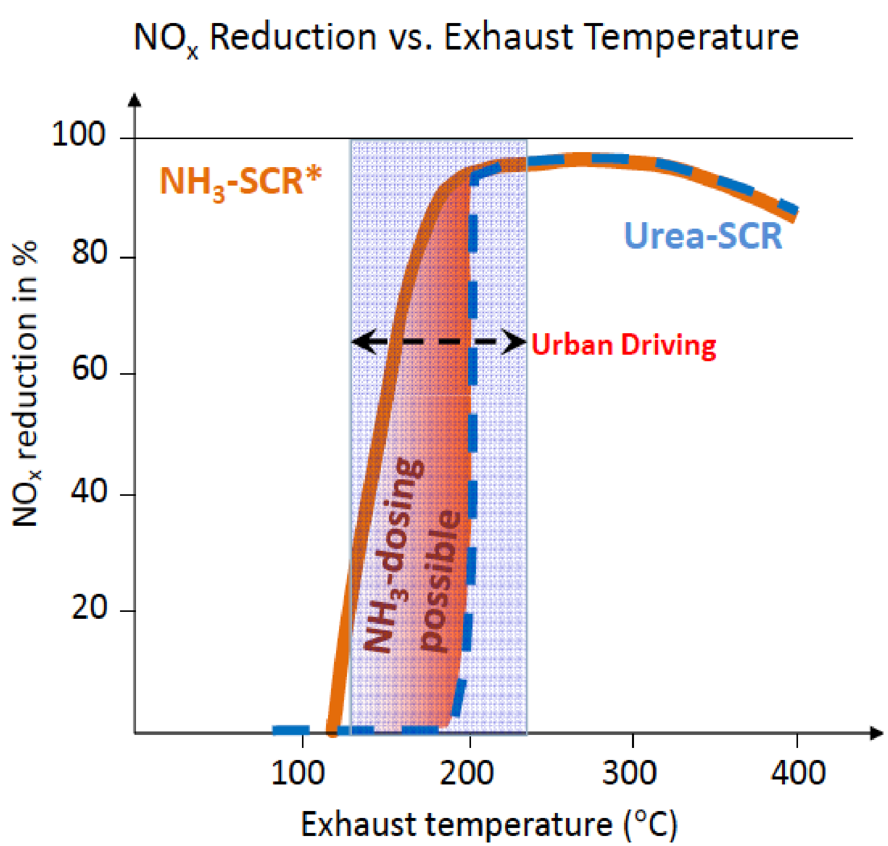
Barriers

- NOx reduction systems (SCR) will require **improved ammonia storage and low temperature delivery**
- Reduction of fuel consumption
- Use of non-aqueous urea reductants
- Use of non-chlorine containing materials

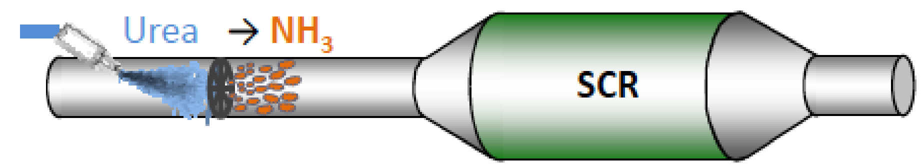
Partners

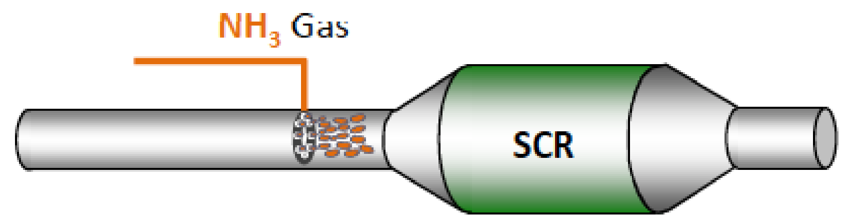
- Pacific Northwest National Laboratory
- USCAR

Relevance: Direct NH_3 dosing



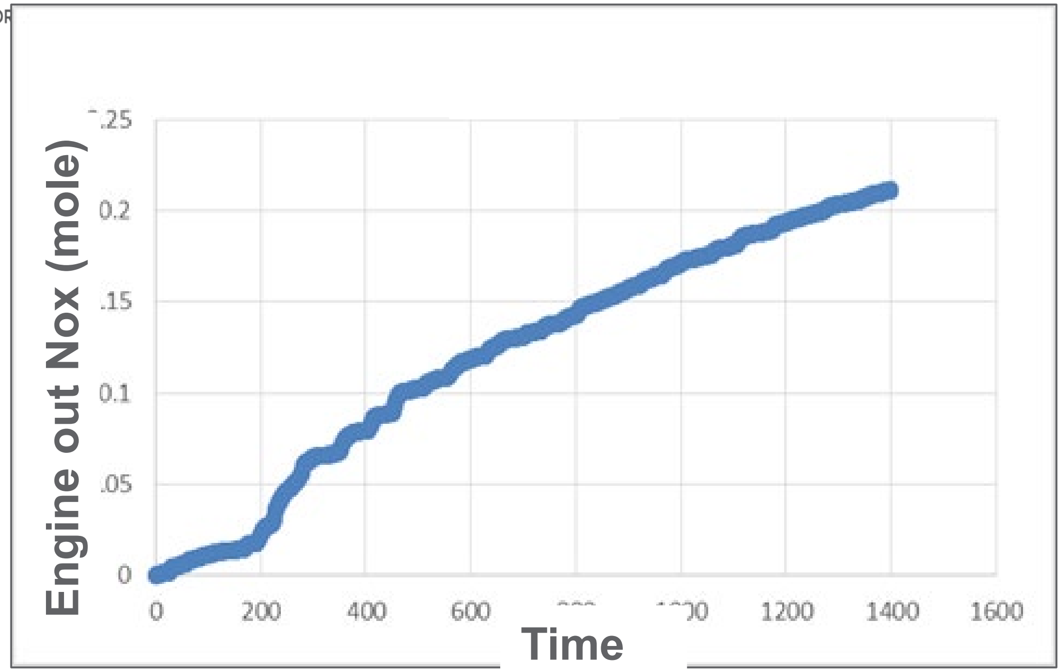
* NH_3-SCR efficiency: W. Tang et al. BASF, DOE-DEER conference, October 4th 2011, p.3





Direct NH_3-dosing enables good SCR performance during urban driving without deposit risk.

NOx tail-pipe emission and USCAR FTP cycle



	USCAR FTP cycle
Total NH3	4.8 g
Avg. mass flow	3.1 mg/s
Peal flow	22.6 mg/s
Cycle length	1399 sec

Opportunity: Explore fuel economy improvement enabled by low-temperature dosing of ammonia gas.

Item	Unit	20 °C	-7 °C	-15 °C
Start time	sec	<90	<123	<152
Total energy requirement	kJ	64	98	107
Peak power requirement	kW	0.2/0.3	0.2/0.3	0.2/0.3

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Collaborations/Interactions

OEM
Development Teams and Suppliers

Project Management
PNNL

USCAR

Provide results of current performance metrics of various NH_3 storage materials and feedback on material performance

PNNL

Carry out and disseminate results of synthesis, characterization, testing and provide recommendations to USCAR

- Monthly updates and teleconference with USCAR PI
- Quarterly teleconference with USCAR SCR team
- Bi-annual F2F meeting with USCAR SCR team

Goals and Objectives

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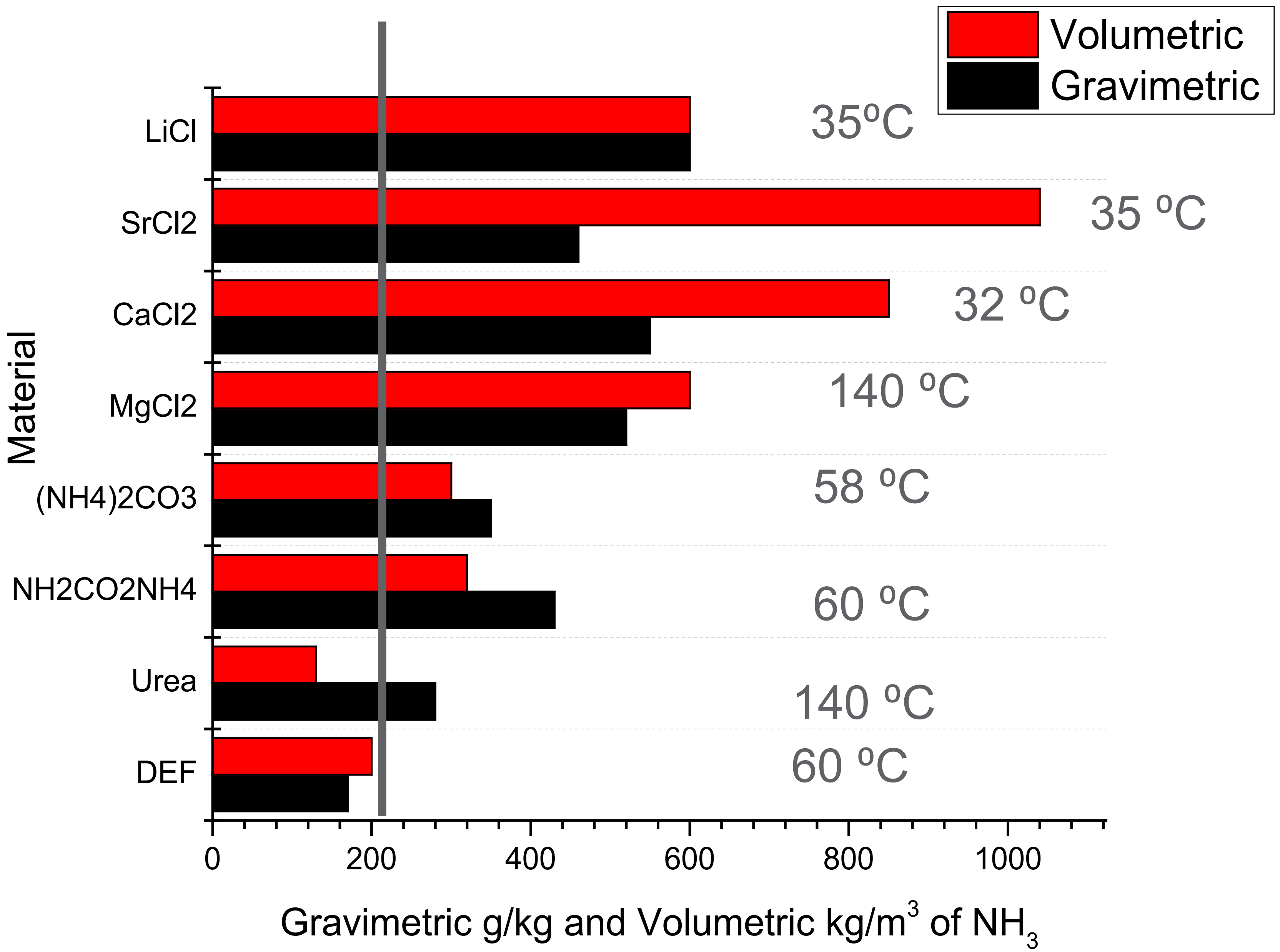
- Develop alternative ammonia carrier materials for low temperature NH_3 dosing system
- 32.5 wt% aqueous Urea contains 17wt% NH_3 (gravimetric) and 200 kg/m^3 (volumetric): Any proposed materials should exceed these targets.
- Help develop the next generation SCR dosing system for improved low-temperature performance
- Convenient handling and distribution of ammonia carriers, and reduced overall system volume, weight, and cost

FEV solid SCR system:
Ammonium carbamate

Liquid urea (DEF)

Summary of material properties



Impurity Quantification and Mitigation: HCl Measurements

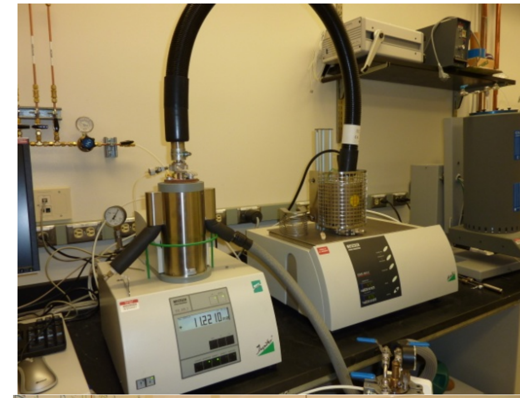
Material (Quantity, g)	Time (hr)	Temperature* (°C)	Amount of HCl (ppm)
$MgCl_2$	3	400	~550
$MgCl_2$	24	400	>600
$MgCl_2$	24	400	>600
$MgCl_2$	100	400	>600
$MgCl_2$	24	400	~580
$Mg(NH_3)_6Cl_2$	24	250	20
$MgCl_2$:AC (2:1)	24	600	>600
$Mg(NH_3)_6Cl_2$:AC (1:1)	24	400	No HCl
$Mg(NH_3)_6Cl_2$:AC (1:1)	24	400	No HCl
$Mg(NH_3)_6Cl_2$:AC (2:1)	24	250	No HCl
$Mg(NH_3)_6Cl_2$:KBB (3:1)	24	250	No HCl

KITAGAWA Gas Detection Tubes

Successful mitigation of HCl by development of composites

Approach

- ➢Synthesize new materials and composites to improve on existing materials
- ➢Use theory as a screening tool for guiding experiment
- ➢Use PNNL's Combi-Cat as a high throughput screening tool
- ➢Develop testing protocol to:
- ➢Determine ammonia storage capacity: wt.%/vol.%
- ➢Determine ammonia release: temp, rate, energy requirement
- ➢Stability and Safety: volatility under storage & handling conditions extended temp.
- ➢Utilize expertise and state-of-the-art characterization and testing facilities at PNNL to address structure/function and performance
  - ➢ XRD, NMR, NH_3 TPD, DSC-TGA with MS
  - ➢ Time resolved FTIR studies for kinetics
  - ➢ Calorimetric studies for thermodynamics
  - ➢ Volumetric gas analyzer for vapor pressure studies



NH_3 adsorption on porous media

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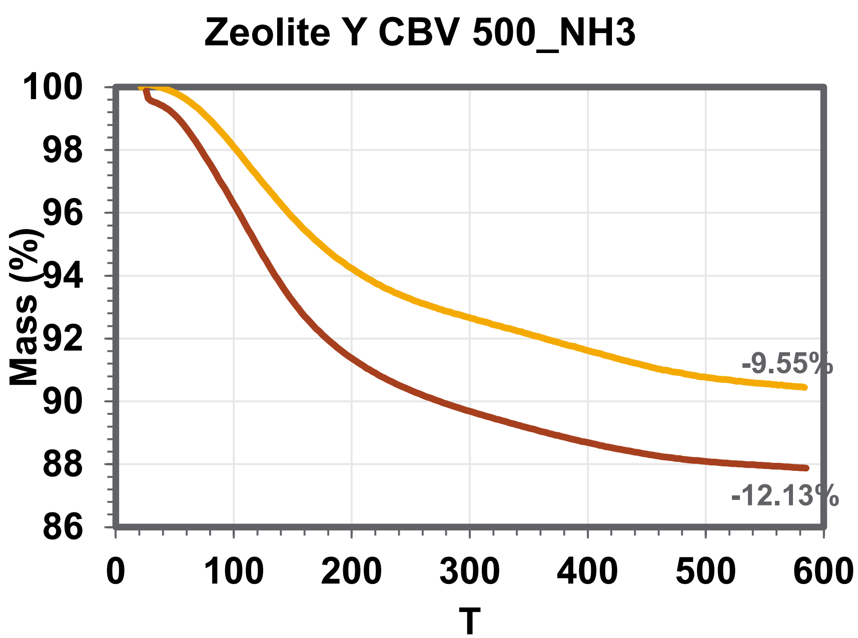
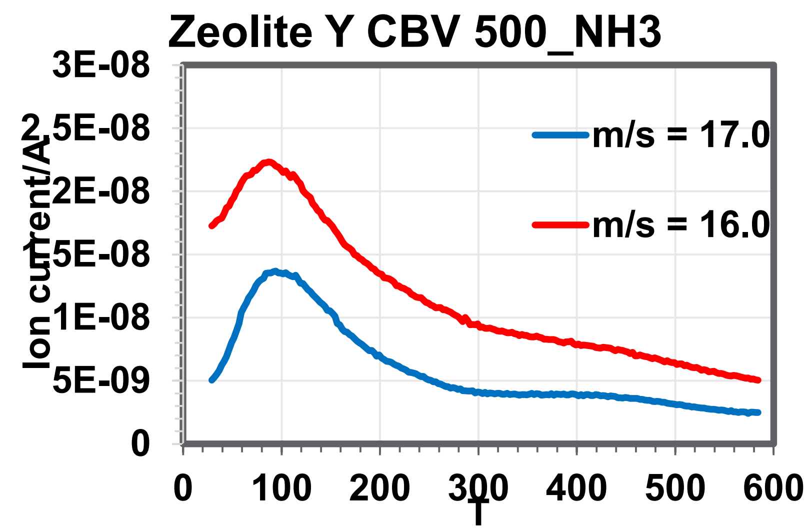
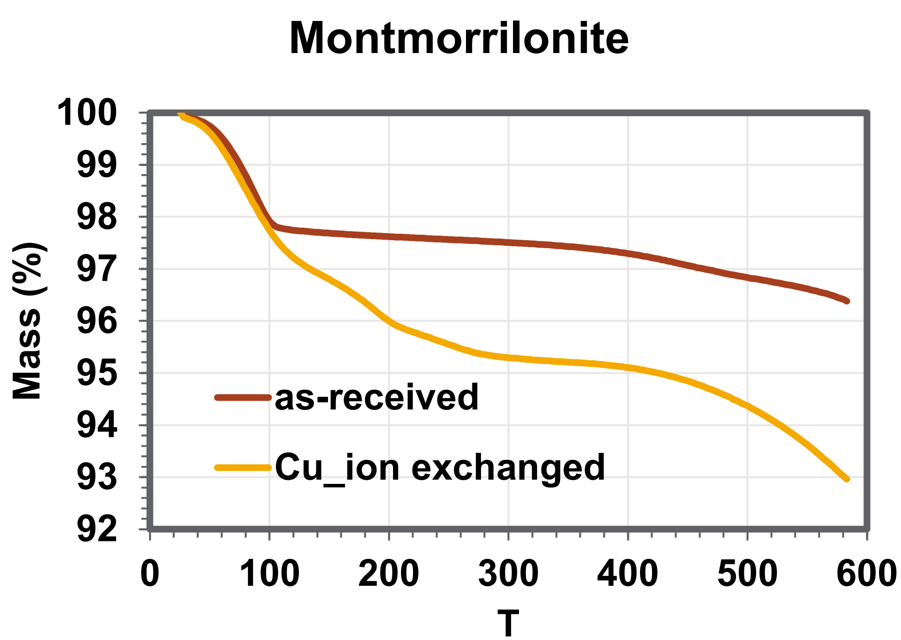
- Screen wide range of porous metal oxide materials for NH_3 uptake:
  - ZSM 5, Zeolite Y, MCM-41, Al-MCM 41, Al_2O_3, and clays
  - Aluminum-doped porous materials (i.e. zeolite) takes ammonia through the dative bonding of NH_3

- Select best NH_3 storage materials and modify with alkaline earth metal ions (Ca^{2+} or Mg^{2+}) and transitions metal ions (Cu, Co, Ni, Mn) by ion-exchange process or incipient wetness procedure .
  - These metals ions are potential NH_3 adsorbents by ammonium ion formation or amine complex formation
  - If 1.0 g zeolite Y CBV 500 (SiO_2/Al_2O_3 molar ratio= 5.2, surface area = 750m^2/g) contains 9.5 mmol of Al sites and take 4.75 mmol of metal ions: theoretically, ≥ 30 wt% of NH_3 can be stored if all Al sites are accessible

NH_3 adsorption on porous media





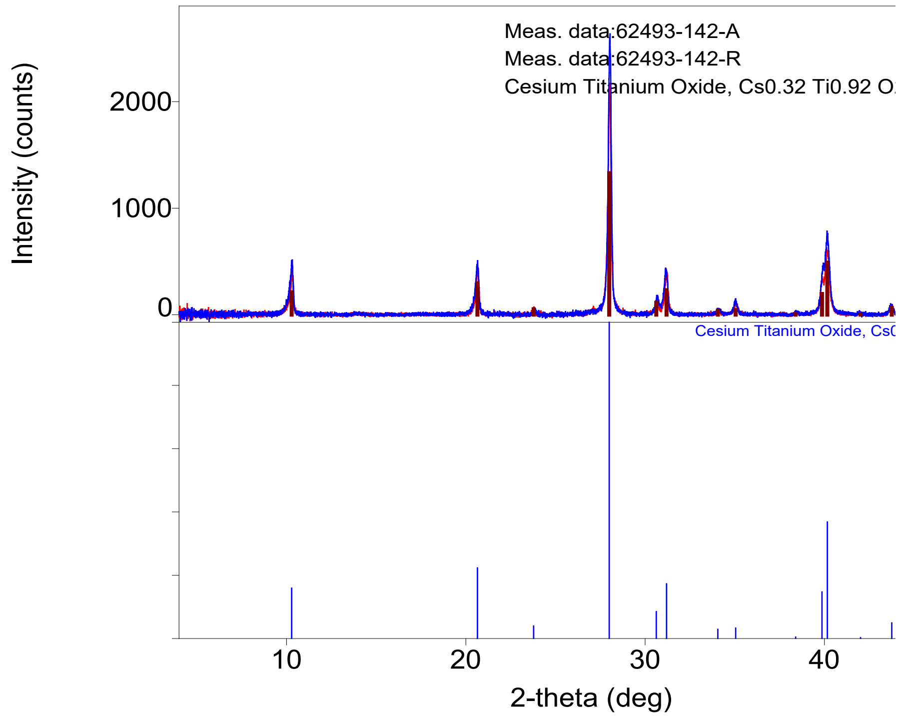


materials	NH3 capacity (Wt%)	Impregnation method
MCM-41	4.55	
Al-MCM-41	5.55	Incipient wetness
Zeolite Y CBV500	9.55	
2%Cu_zeolite Y CBV500	12.13	Incipient wetness
Ca_zeolite Y CBV 500	16.68	Ion-exchange
Montmorillonite_AR	3.62	
Cu_montmorillonite	7.10	Ion-exchange

- Utilize feedback from theory and perform high throughput screening

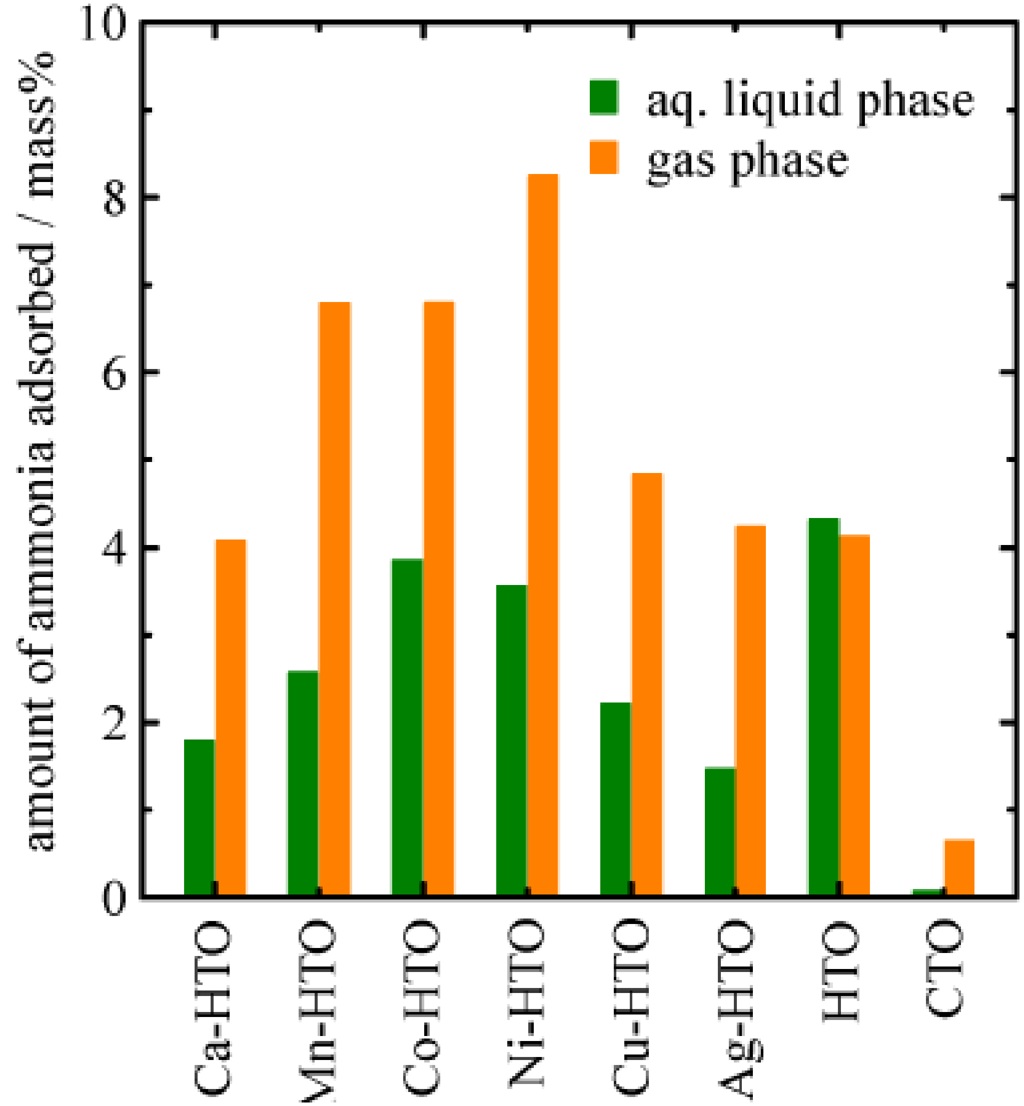
Synthesis of Layered Titanate: Lepidocrete

XRD results



Layer structure confirmed

NH_3 capacity

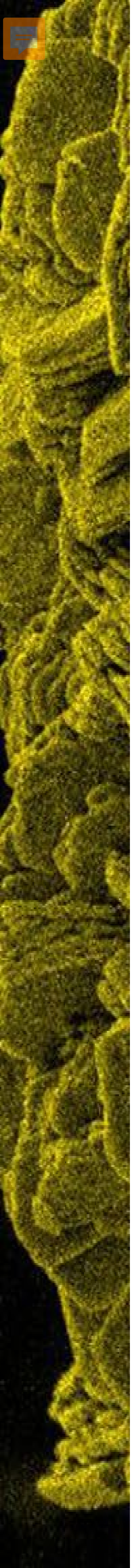


- Increasing surface area and ion-exchange will increase NH_3 capacity

Ref: K.Yokosawa; T.Takei, S.Yanagida, N.Kumada, K.Katsumata,"Ion exchange of layered titanate with transition metal and application to ammonia storage", *Journal of Ceramic Society Japan*, 126 [10], 808-813, 2018

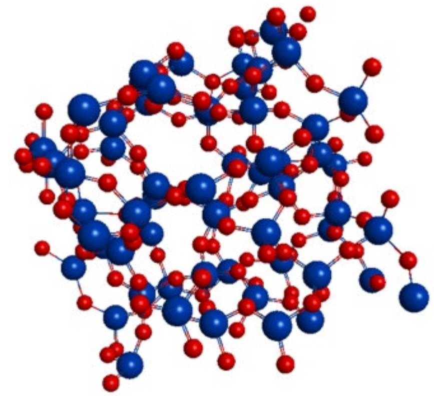
Computational modeling for materials screening

- Use of atomistic simulations to screen suitable materials for efficient NH_3 storage
  - The ideal material should bind NH_3 strongly enough to safely store, and release with minimal energy expense
  - Computational screening is an ideal way of tackling such problems, that can potentially save time and money for unsuccessful experimental investigations
- We will employ a combination of computational methods that allow us to not only calculate reliable binding energies but also:
  - Determine optimal materials, doping elements and sites
  - Built reduced order models to accelerate screening process
    - Decomposition analysis of binding will allow us to better understand the binding/release process, eg electrostatic vs dispersive forces



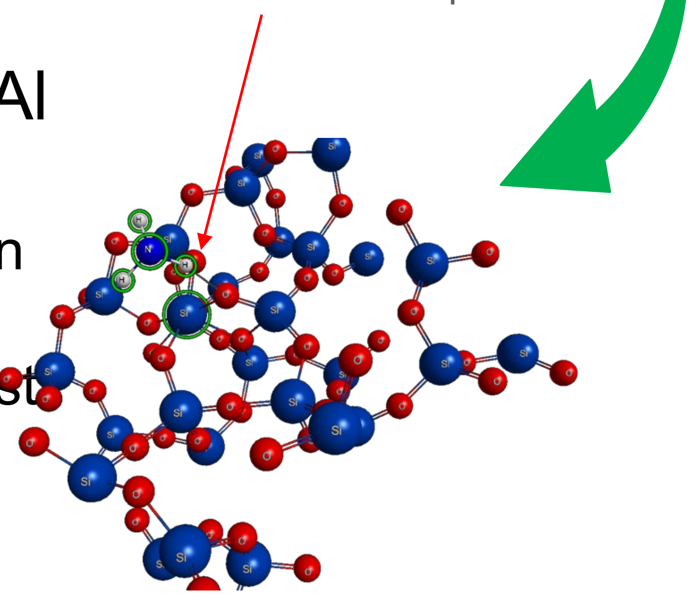
Computational modeling for materials screening

- We have identified the following materials initial screening:
  - Amorphous and doped silica (Al, Ti dopants
  - Layered minerals, such as Montmorillonite
  - Quarz-type minerals, such as ion exchanged lepidocrocite



Global optimization and annealing to obtain optimal doping and adsorption sites

- Initial simulations on plain and doped silica (Al and Ti):
  - Determined force-field parameters to simulate plain and doped material
  - Performed global optimization to determine the best doping and binding sites
  - Additional materials will be screened in the next cycle, including MD simulations to assess temperature effects



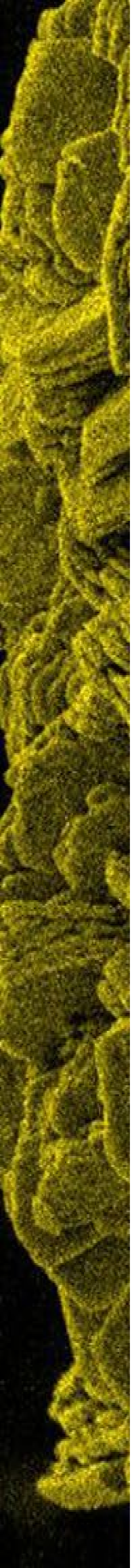
E (kJ/mol)	Silica	Ti-doped	Al-doped
DFT(B3LYP)	-6.0	-8.0	-28.0
SAPT0	2.0	2.0	-23.0
Electrostatics	-57.0	-57.0	-77.0

Preliminary results from computational studies

Interaction energies	Pure Si surface	Ti-doped Si surface	Al-doped Si surface
B3LYP	-5.97	-7.96	-27.50
B3LYP (BSSE corrected)	11.64	12.70	-8.15
B3LYP, average1	2.84	2.37	-17.83
SAPT0 Total interaction energy	2.07	1.92	-23.45
Electrostatics	-57.14	-56.99	-76.82
Induction	-15.65	-16.33	-21.64
Dispersion	-17.28	-19.20	-17.58
Exchange-repulsion	92.15	94.44	92.59
HF total interaction energy2	19.36	21.11	-5.87

Based on preliminary screening: Pure silicates bind very weakly
Need to incorporate more metal dopants in screening

1 Average of BSSE corrected and uncorrected energies is known to yield better interaction energies than purely uncorrected/corrected energies.
2 HF interaction energies to be taken with a pinch of salt - just to check if the trend changes tremendously with added correlation corrections, which is not the case here.



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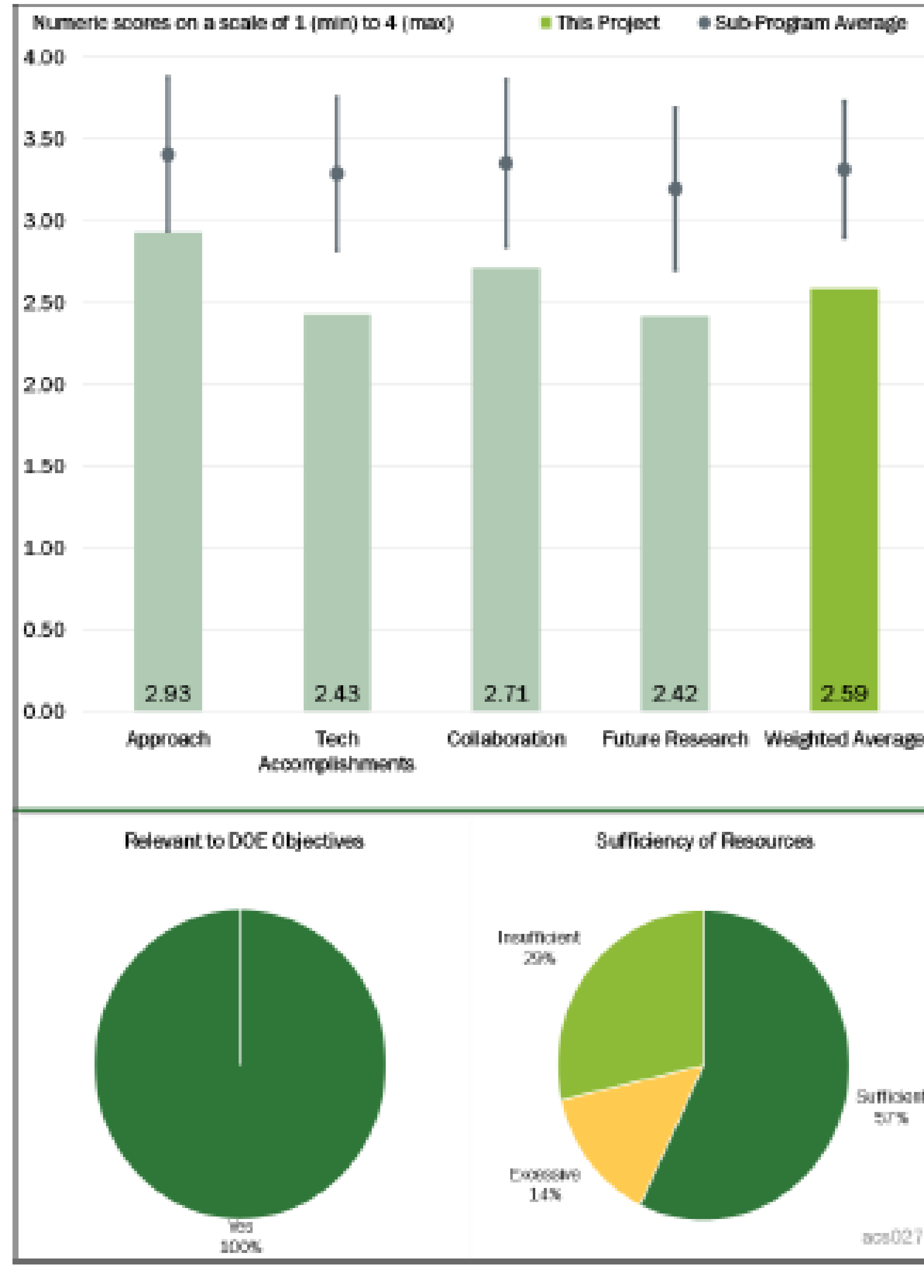
Reviewer Comments

- Approach is good but rapid screening needs to be undertaken
- Project may benefit from molecular computational methods
- USCAR team is appropriate wider set of contacts should be added
- Team should consider non chlorine materials
- Progress is incremental rather than revolutionary



Response to Reviewer Comments

- We have added a new team member to focus molecular computational methods for rapid screening
- We have completely switched efforts to light weight metal oxides
- We are in the process of implementing high throughput studies to screen materials
- We are exploring additional industrial partners

Milestones and Go-No Gos

	Title	Description	End Date
Milestone	Next generation ammonia storage materials	Synthesis and evaluation of at least 5 oxide based ammonia storage materials	Sept 2019
Go/no-go	Selection of next generation ammonia storage materials	Down selection of ammonia storage materials for high throughput screening	Sept. 2019
Milestone	High throughput screening	Complete first round of high throughput screening	Dec 2019
Milestone	Properties of ammonia storage materials	Determine thermodynamic and kinetic parameters	March 2020
Go/no-go	Selection of next generation of ammonia storage materials	Down select based on high throughput screening and thermodynamic/kinetic studies for optimization	Sept. 2020

Recent Accomplishments

- Initiated molecular computational modeling to screen materials
- Down-selected class of oxide based materials based on literature and theoretical screening
- Evaluated ammonia storage capacity of oxide based materials
- Synthesized and developed new oxide based compositions for screening NH_3 uptake and release
- Developing experimental protocol for high throughput experimental screening

Future plan

- Complete water removal: thermal treatment of samples under mild conditions
- NH_3 is physisorbed in the presence of water molecules: released at low temperature (< 100^{o}C)
- Focusing on ion-exchange samples to keep more accessible metal ions on the surface to NH_3 gas
- Rapid screening of material composition and binding energy wrt NH_3
- Reversible and irreversible NH_3 will be calculated
- Adsorption isotherms as function of temperature and pressure will be investigated
- NH_3 TPD and FT-IR to understand adsorption desorption cycles
- Utilize Design of Experiments and Combi-Cat to high through put screening