Next Generation SCR-Dosing System Investigation

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The work was funded by the U.S. Department of Energy (DOE) Office of Vehicle Technologies.

June 11, 2015

Project Overview

Timeline

- Start – Oct 2014
- End – Sept 17

Budget

- Matched 80/20 by USCAR as per CRADA agreement
- DOE funding for FY15: $200K;

Barriers

- Discussed on next slide

Partners

- Pacific Northwest National Laboratory
- USCAR

Barriers - Relevance

Vehicle Technologies Office

- Selective Catalytic Removal of NO_x:

  $4\ NO + \mathbf{4\ NH_3} + O_2 \rightarrow 6\ N_2 + 6H_2O$
- SCR makes engines more efficient
- NOx reduction systems (SCR) will require **improved ammonia storage and delivery**.
- Needed for diesel and lean-burn engines
- Challenge: Safe and efficient ammonia storage and delivery

- Urea solution (DEFBlue or Adblue®) [Urea+ ~70% water] mitigates most issues

- New materials as needed to solve issues with aqueous urea
- Compact NH_3 storage coupled with long driving range will help minimize fuel consumption

Goals and Objectives

- Help fuel-efficient lean gasoline and diesel engines meet the current and future emission regulations with effective, inexpensive and reliable NOx emission control technologies
- 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
- Utilize PNNL's material research expertise and capabilities to evaluate and recommend ammonia transport materials

FEV solid SCR system: Ammonium carbamate

Liquid urea (DEF)

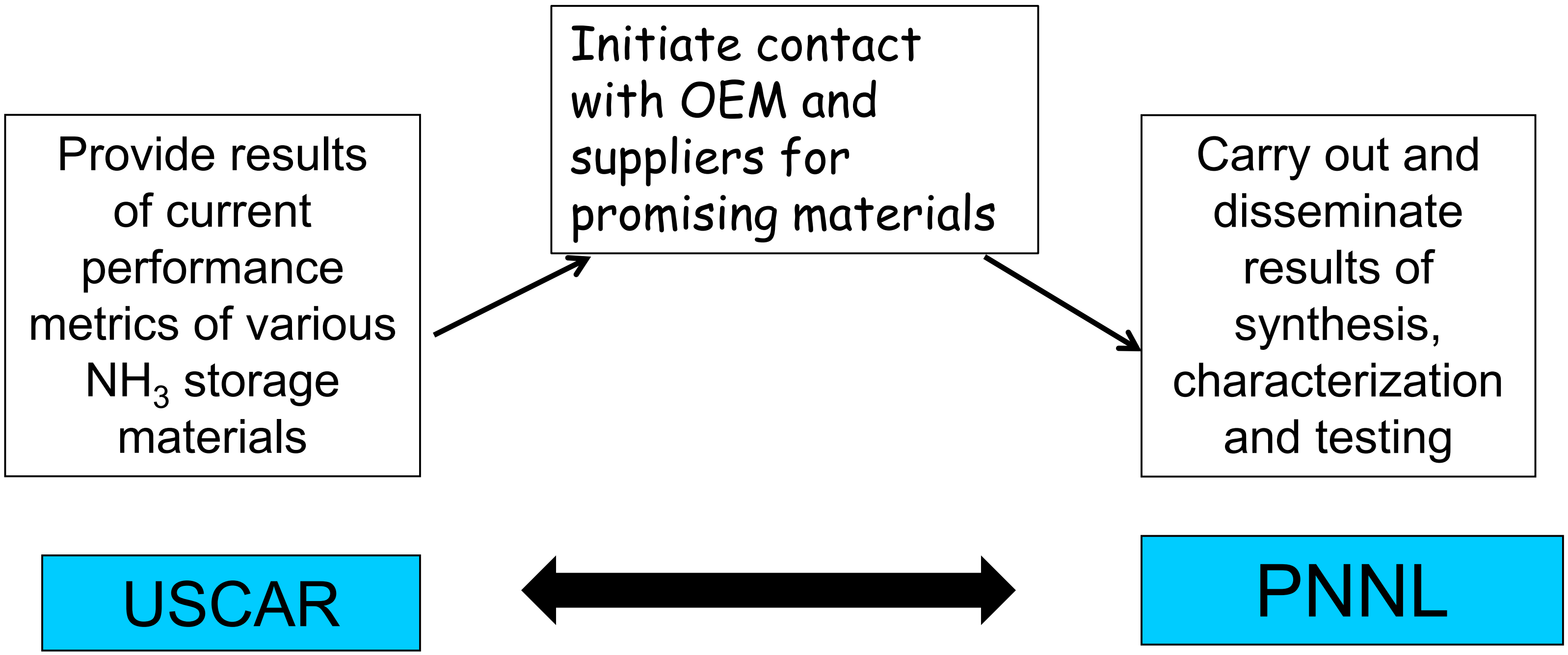
Approach

- Evaluate existing materials based on USCAR recommendations
- Synthesize new materials and composites to improve on existing materials

Develop testing protocol to:

- Determine ammonia storage capacity: wt.%/vol.%
- Determine ammonia release: temp, rate, energy requirement
- Solid material volume change during charge/discharge
- 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

Collaborations/Interactions



- Conference calls are held typically once every two or three months to discuss the results.
- The most recent annual face-to-face CRADA Review was held in Southfield, MI (March, 2015).

FY2015 Scope and Activities

Vehicle Technologies Office

1. Magnesium ammine chloride

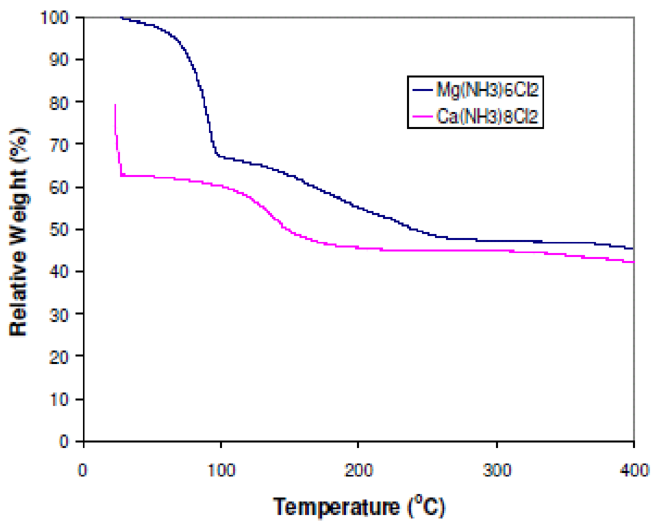
$$Mg(NH_3)_6Cl_2 \leftrightarrow Mg(NH_3)_2Cl_2 + 4NH_3$$
$$Mg(NH_3)_2Cl_2 \leftrightarrow Mg(NH_3)Cl_2 + NH_3$$
$$Mg(NH_3)Cl_2 \leftrightarrow MgCl_2 + NH_3$$

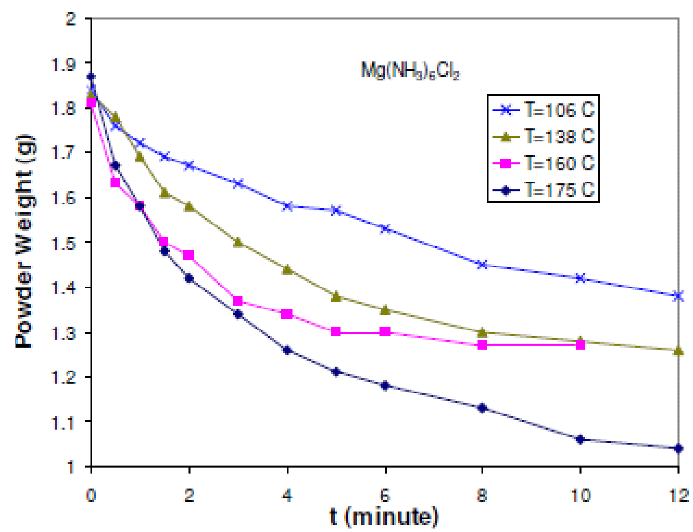
2. Calcium ammine chloride

$$Ca(NH_3)_8Cl_2 \leftrightarrow Ca(NH_3)_2Cl_2 + 6NH_3$$
$$Ca(NH_3)_2Cl_2 \leftrightarrow Ca(NH_3)Cl_2 + NH_3$$
$$Ca(NH_3)Cl_2 \leftrightarrow CaCl_2 + NH_3$$

3. Strontium ammine chloride

$$Sr(NH_3)_8Cl_2 \leftrightarrow Sr(NH_3)Cl_2 + 7NH_3$$
$$Sr(NH_3)Cl_2 \leftrightarrow SrCl_2 + NH_3$$





Develop testing protocol to:

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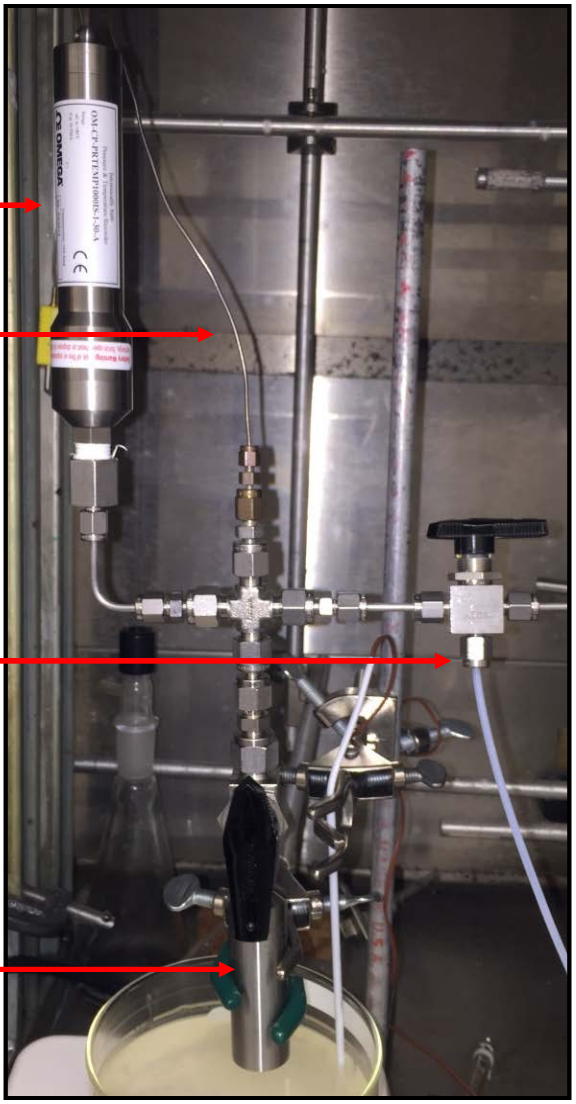
Task 1:Evaluation of Solid Existing Ammonia Storage Materials

Material name	Chemical Formula	Status
AdBlue®	(NH2)2CO+H2O (32.5wt%)	Lit
liquid ammonia	NH3	Lit
solid urea	(NH2)2CO	NH3 cap, ΔH
Ammonium carbamate	NH4COONH2	NH3 cap, ΔH
Ammonium carbamate	(NH4)2CO3	NH3 cap, ΔH
Ammonium formate	NH4CHO2	Not started
Magnesium ammine chloride	Mg(NH3)6Cl2	NH3 cap, ΔH
Calcium ammine chloride	Ca(NH3)8Cl2	NH3 cap, ΔH
Strontium ammine chloride	Sr(NH3)8Cl2	NH3 cap, ΔH
Lithium borate	LiBO2	
Boric acid	H3BO3	NH3 cap, ΔH
Solium borate	NaBO2	NH3 cap, ΔH
Lithium chloride	LiCl	NH3 cap, ΔH
Sodium chloride	NaCl	NH3 cap, ΔH
Other candidates	?	TBD

- Apparatus for vapor pressure measurements



Ammonia Transport Material	Molecular Formula	Molecular Weight g/mol	Density (g/cm^3)	Mols NH3 per Mol	Mols NH3 per Kg	Mols NH3 per Litre	Volume Factor (Norm to AdBlue®)	Decomp. Temp, C	NH3 release energy, KJ/mol NH3	NH3 Vapor pressure @ ~25 ℃ (bar)
Urea										
AdBlue®	(NH2)2CO+H2O	N/A	1.086	2	10.8	11.8	1.00			
Solid Urea	(NH2)2CO	60.07	1.33	2	33.3	44.3	0.27	140	106	

DEFBlue™ Vs. $MgCl_2.6NH_3$

DEFBlue™

- 30% Urea +70% Water
- 200 kg NH_3/m^3
- 17 wt% NH_3 (on composition basis)
- Convenient
- Freezing
- Solid deposits
- Lowering of exhaust temp due to water

$MgCl_2.6NH_3$

- ~ 600 kg NH_3/m^3
- 50 wt% NH_3 (on composition basis)
- Multi-step decomposition
- No complex chemistry
- Easily available $MgCl_2$ (10% of sea salt) and NH_3
- Freezing a non-issue

We will use DEF to benchmark our materials

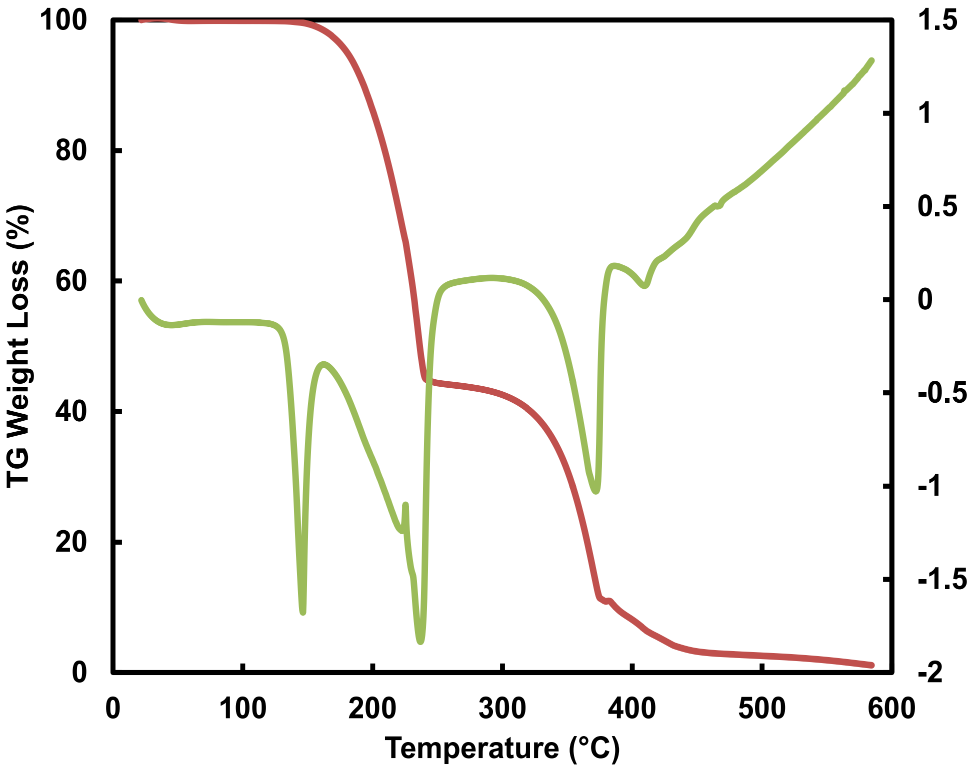
Technical Accomplishments – Initial screening

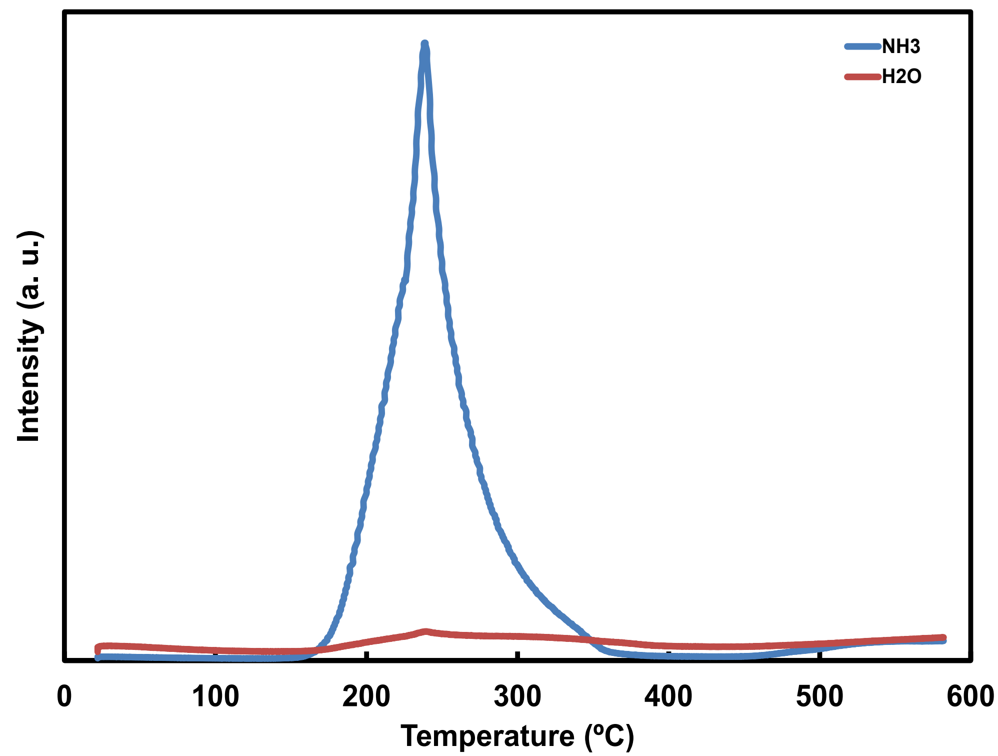
- Completed first set of evaluations on existing materials
- Identified and evaluated several new materials
- Identified 3 new materials and 3 additives for further screening
- Synthesized Double salt/Eutectics for further studies
- Identified issues and potential pathway to retain engineered form

Brief highlights of recent results

Solid Urea

$$NH_2CONH_2 \rightarrow NH_3 + HCNO$$



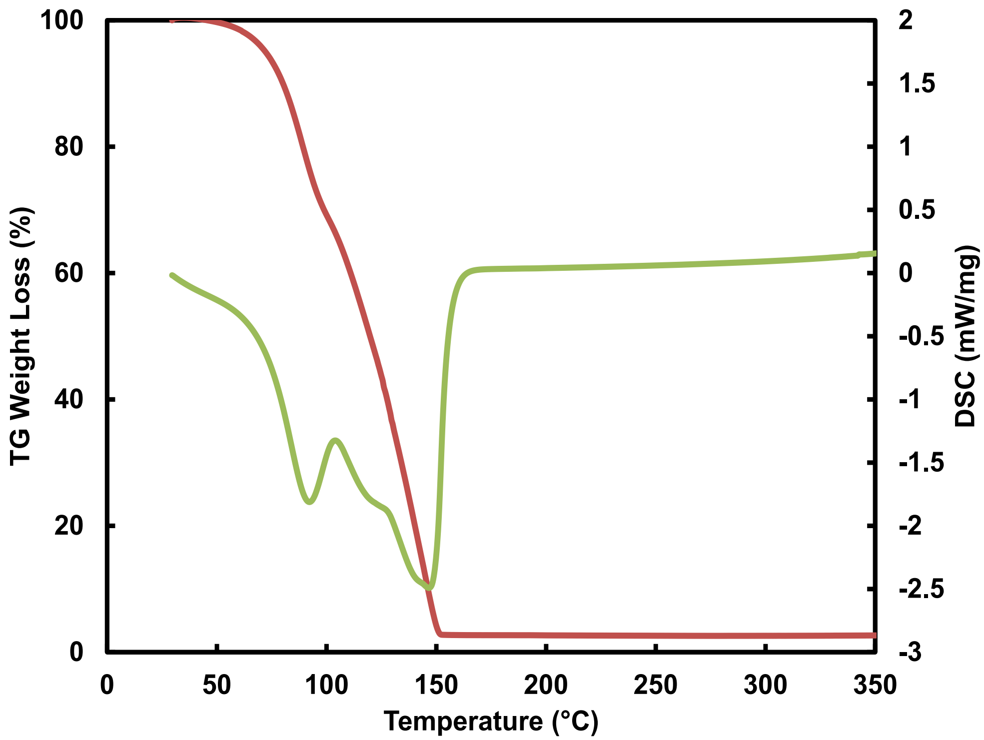


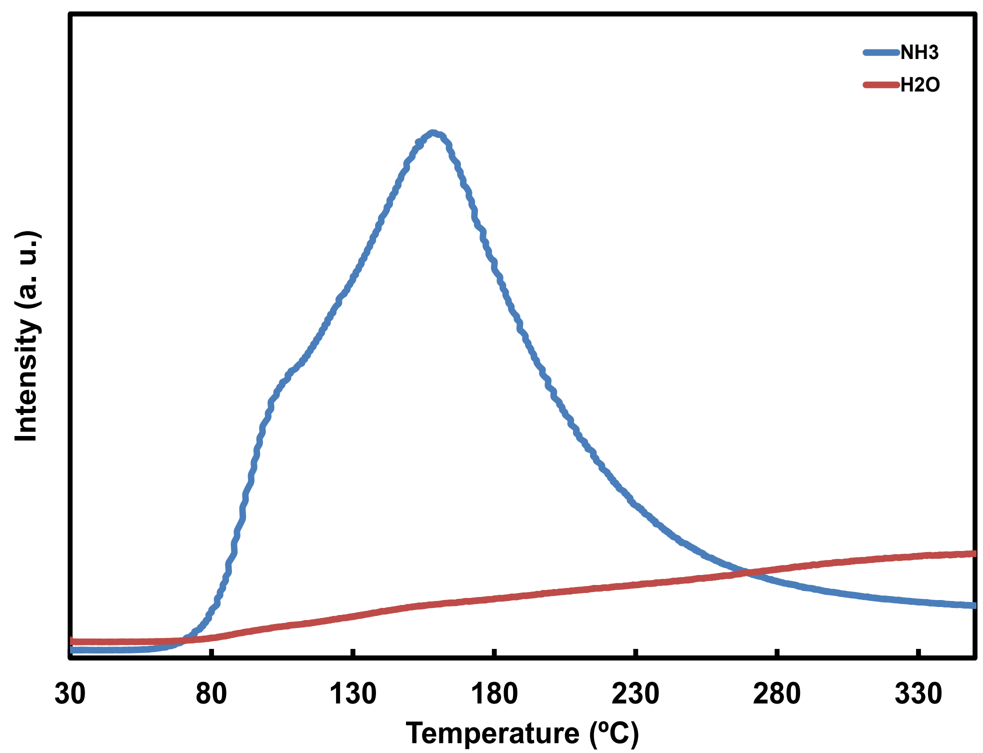
- Undesirable side product HCNO ✕
- Low gravimetric capacity ✕
- High temp ✕

Unlikely to meet targets (discontinue)

Ammonium Carbonate

- $(NH_4)_2CO_3 \rightarrow 2NH_3 + H_2O + CO_2$



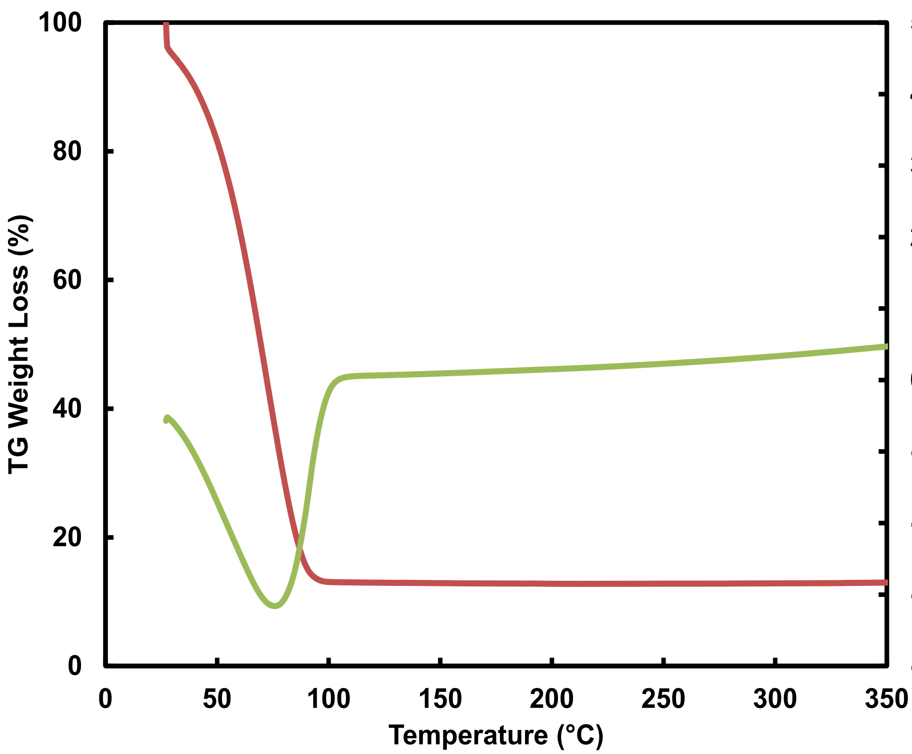


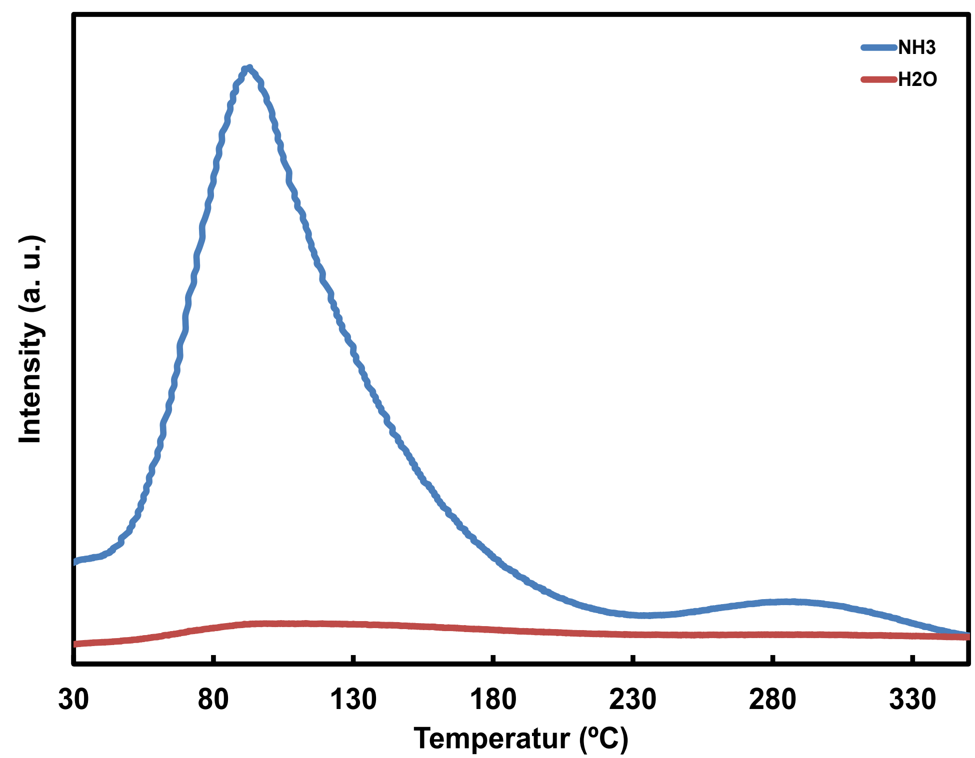
- Produces H_2O and CO_2 ✗
- 35 wt% gravimetric capacity ✓

Likely to meet targets (continue)

Ammonium Carbamate

• $NH_2CO_2NH_4 \rightarrow 2NH_3 + CO_2$





- Produces CO_2 ✗
- 43 wt% gravimetric capacity ✓
- Low decomposition temp ✓ ✗
- Undesirable side reactions ✗

Likely to meet targets (continue)

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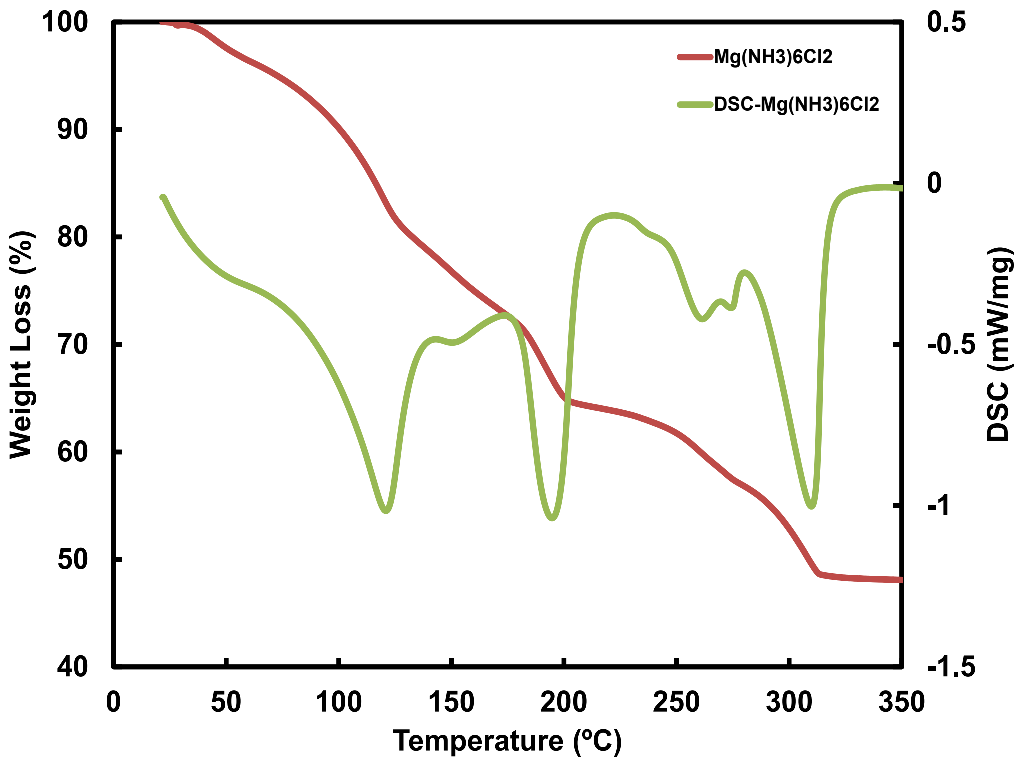
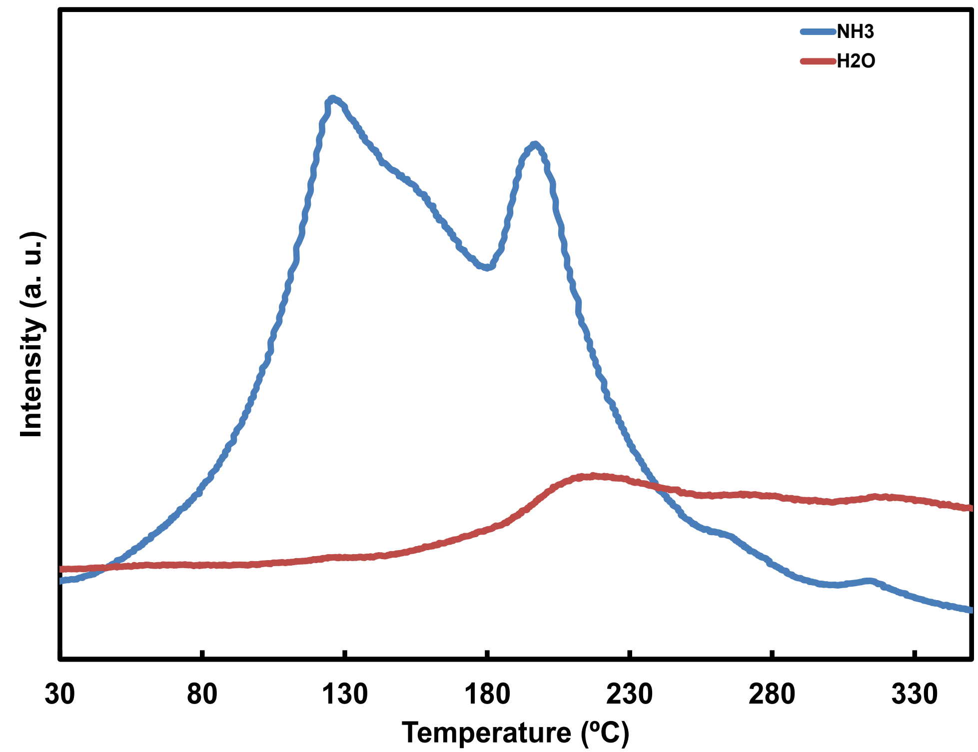
Magnesium Chloride ($MgCl_2.6NH_3$)

$$MgCl_2.6NH_3 \rightarrow MgCl_2 + 6NH_3$$





- Multi-step process ✗
- Only NH3 released ✓
- 51 wt% gravimetric capacity ✓
- Reversible ✓

Likely to meet targets (continue)

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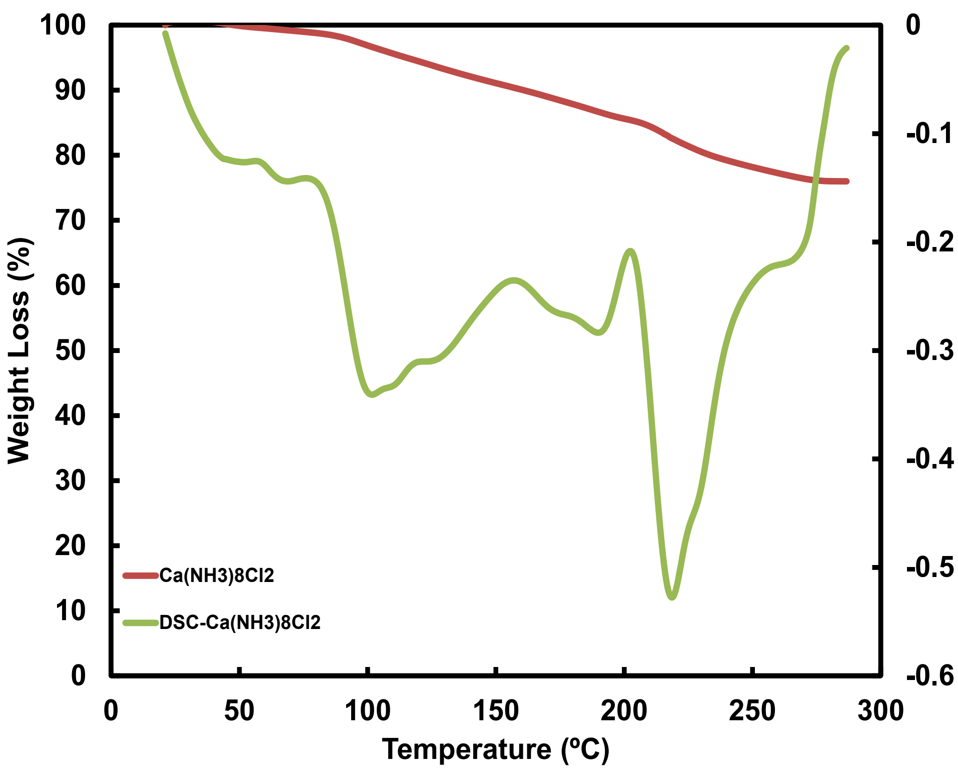
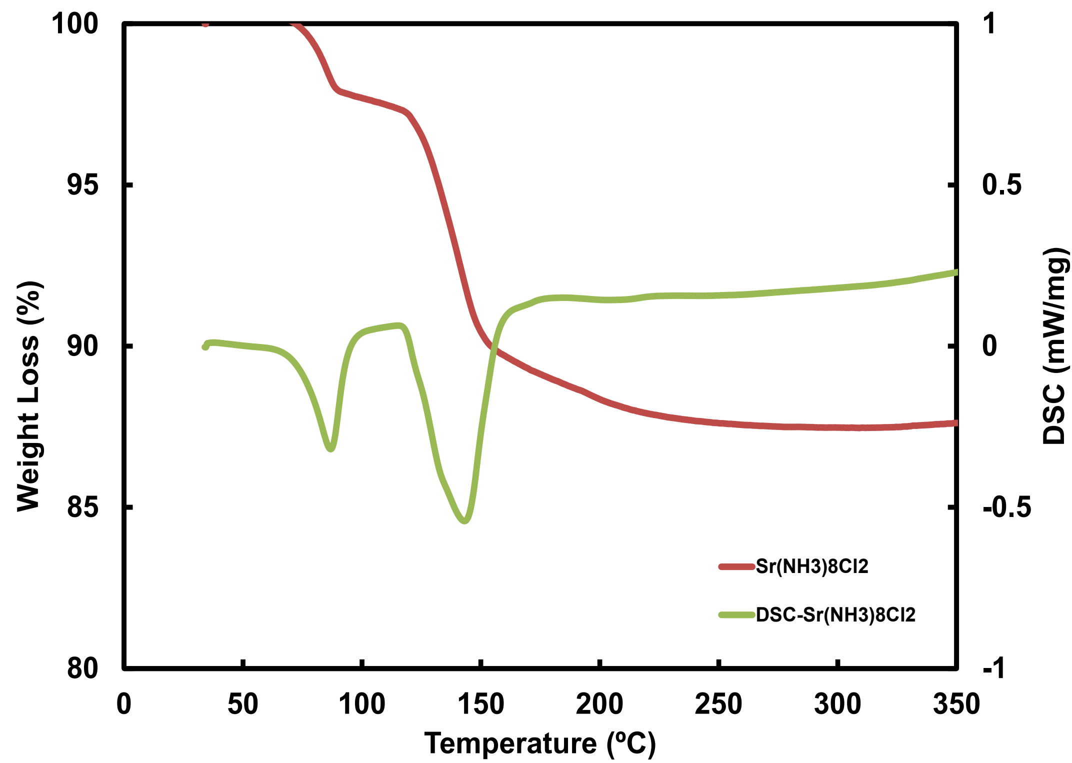
$CaCl_2$ and $SrCl_2$

$CaCl_2 . 8NH_3 \rightarrow CaCl_2 + 8\ NH_3$



$SrCl_2 . 8NH_3 \rightarrow SrCl_2 + 8\ NH_3$

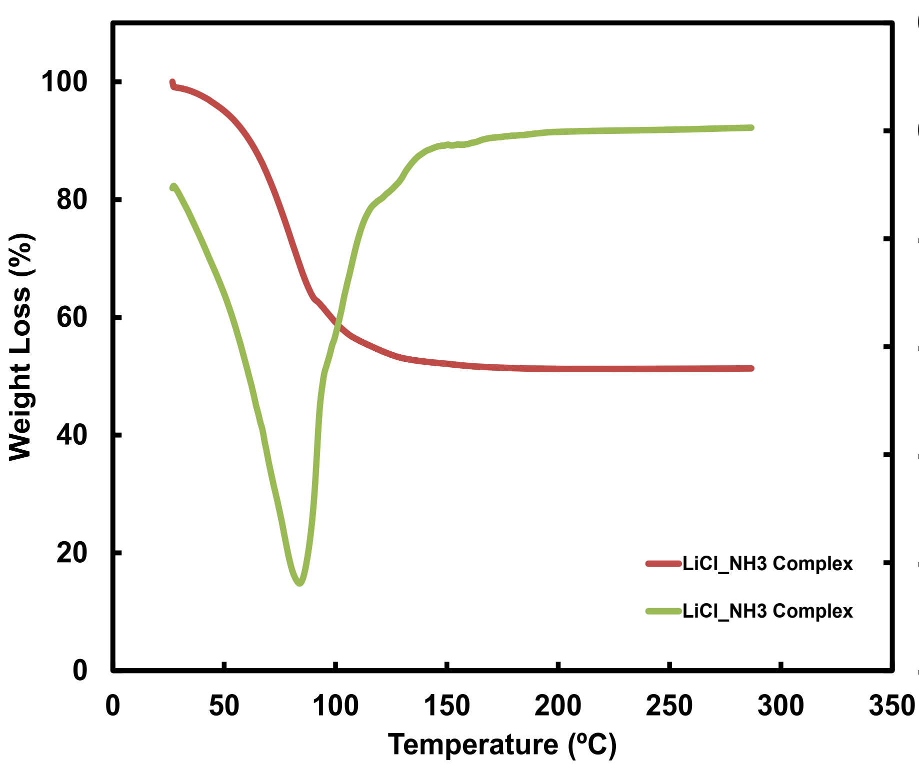


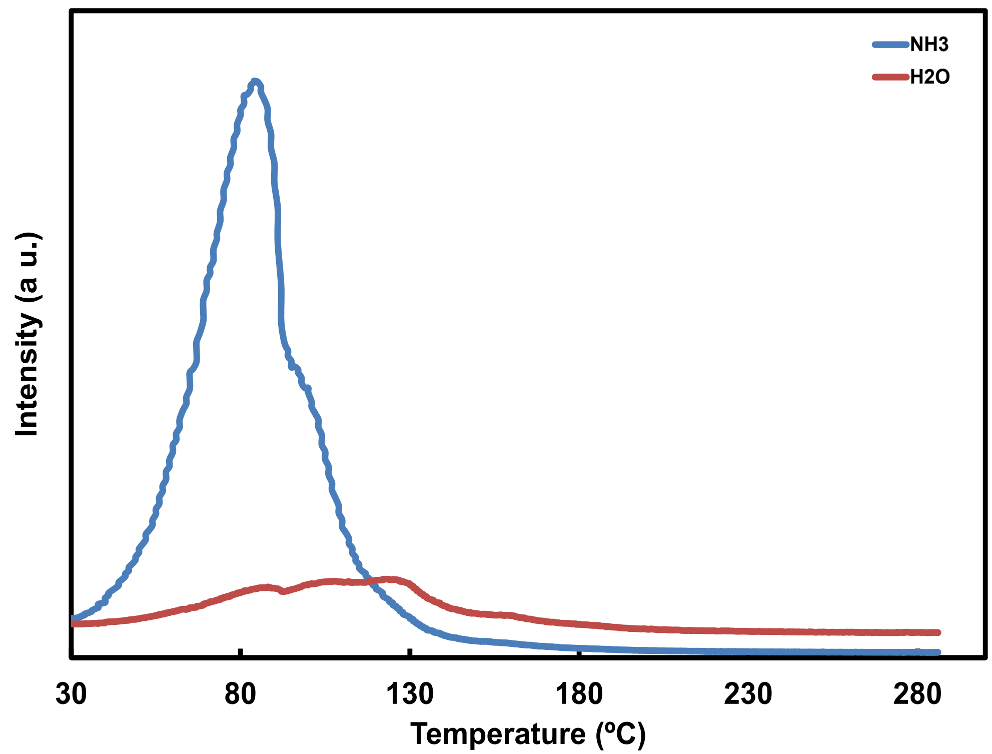
- Multi-step process ✗
- Only NH3 released ✓
- High gravimetric capacity ✓ (if 8 eq. released)
- Reversible ✓

Unlikely to meet targets as pure salts (discontinue);
Continue double salt approach (discussed later)

Lithium Chloride ($LiCl.xNH_3$)

$LiCl.xNH_3 \rightarrow LiCl + x\ NH_3$





- Low NH_3 release temperature ✗ ✓
- Only NH_3 released ✓
- > 50 wt% gravimetric capacity ✓
- Reversible ✓

Likely to meet targets (continue)

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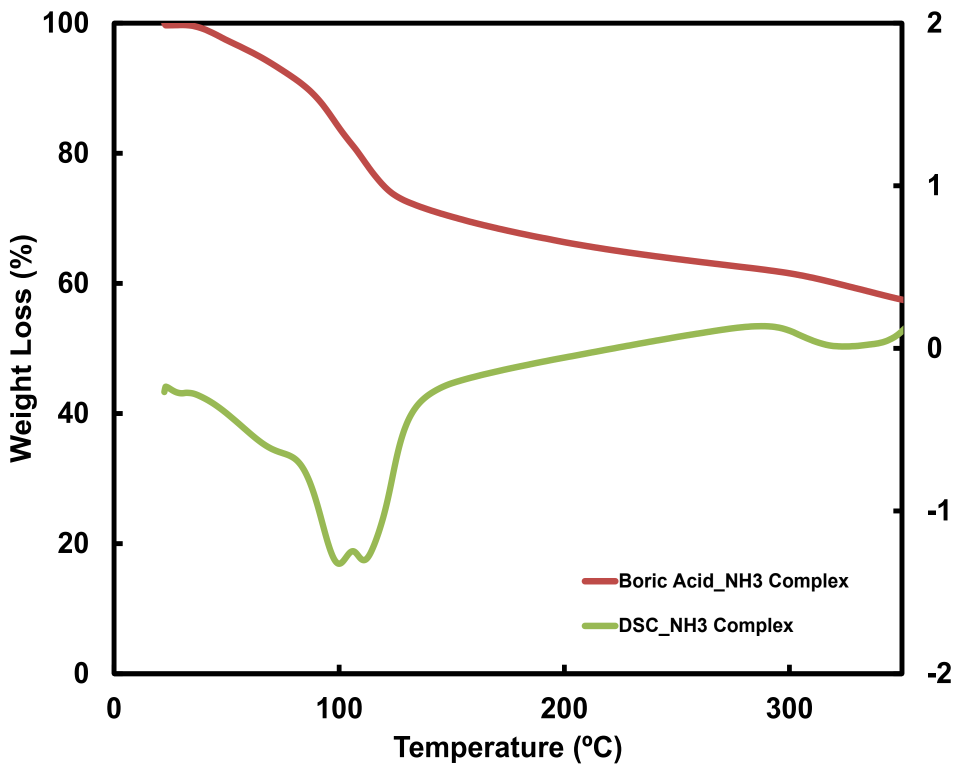
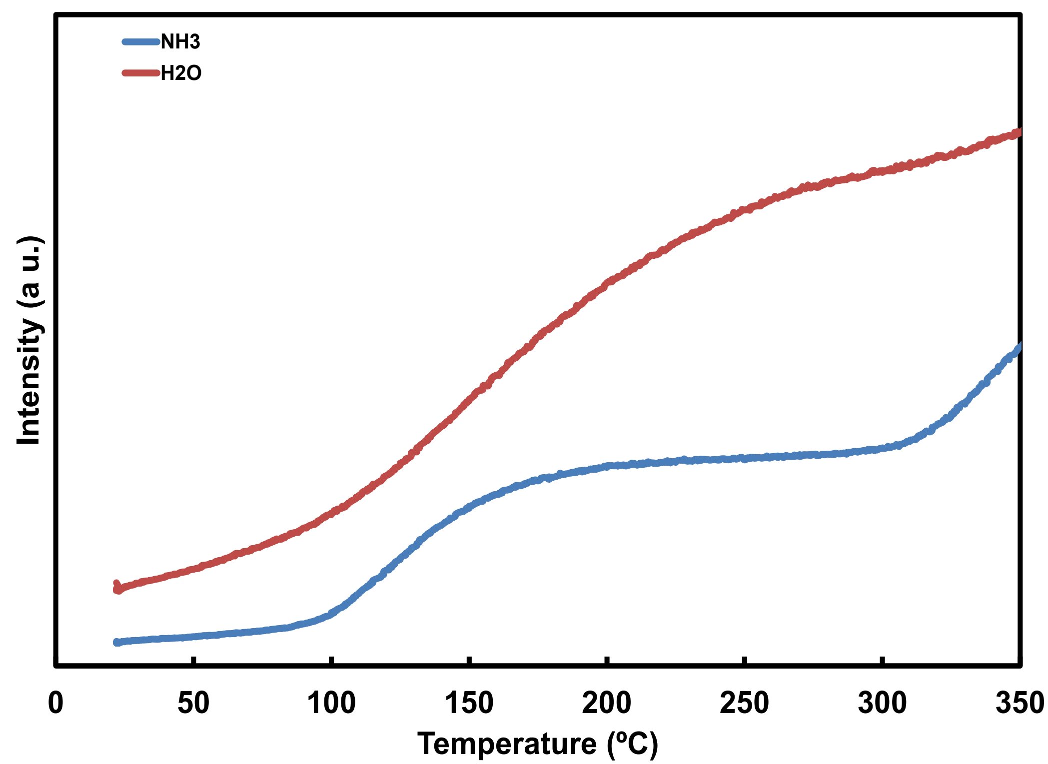
Boric Acid ($H_3BO_3.xNH_3$)

$$H_3BO_3 + 3NH_3 \rightarrow (NH_4)_3BO_3 \rightarrow H_3BO_3 + 3NH_3$$



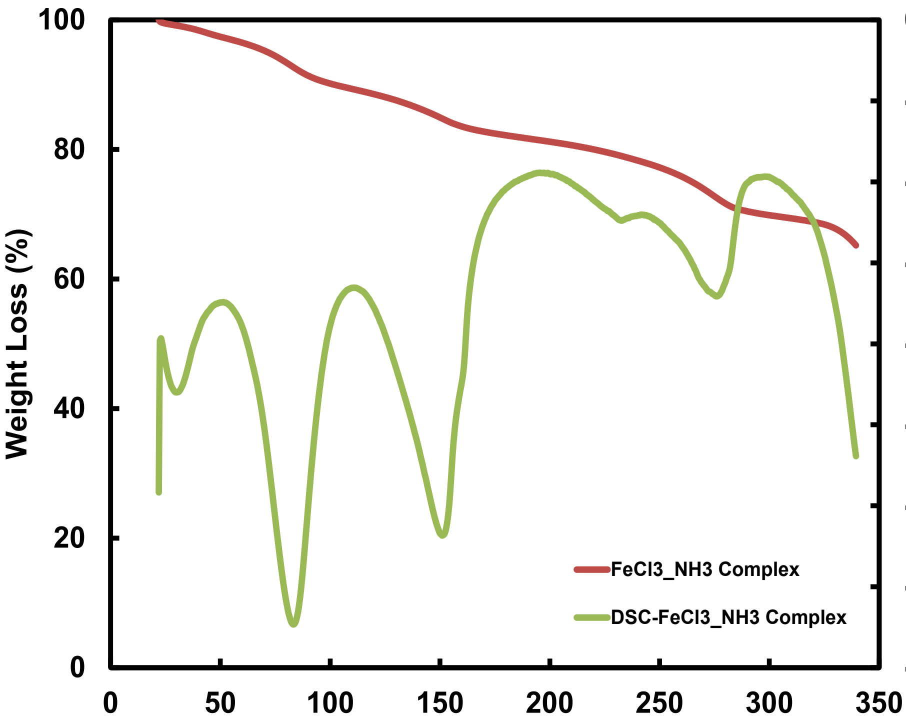


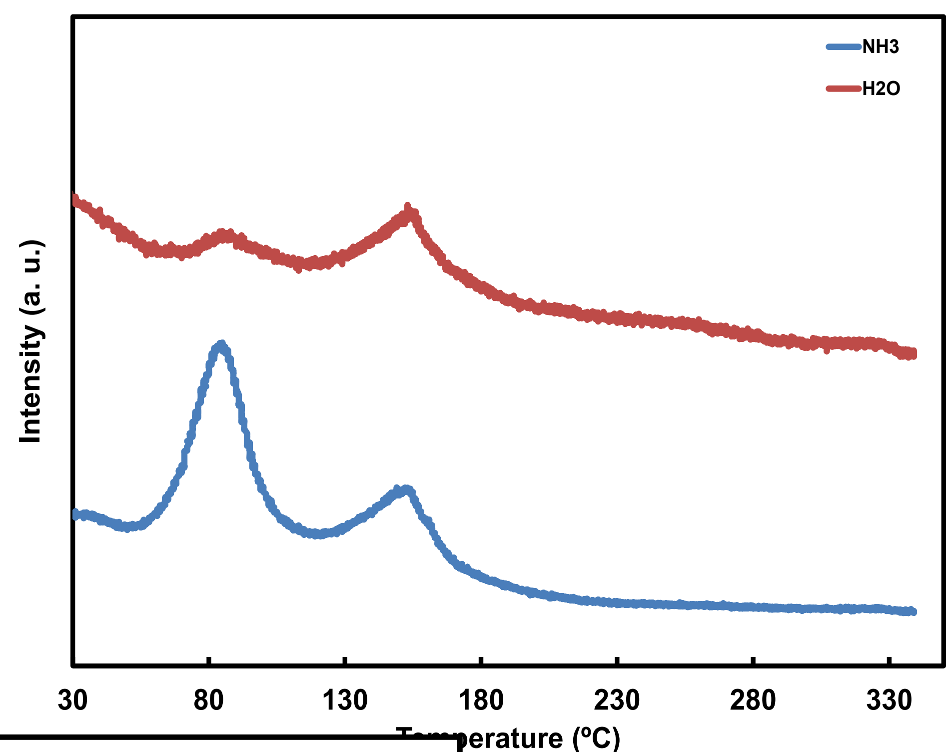
- Complex chemistry ✗
- Only NH3 released ✓
- High potential gravimetric capacity ✓ (Expt. not achieved) ✗

Unlikely to meet targets (discontinue)

$FeCl_3 . 6NH_3$

$$FeCl_3.6NH_3 \rightarrow FeCl_3 + 6NH_3$$





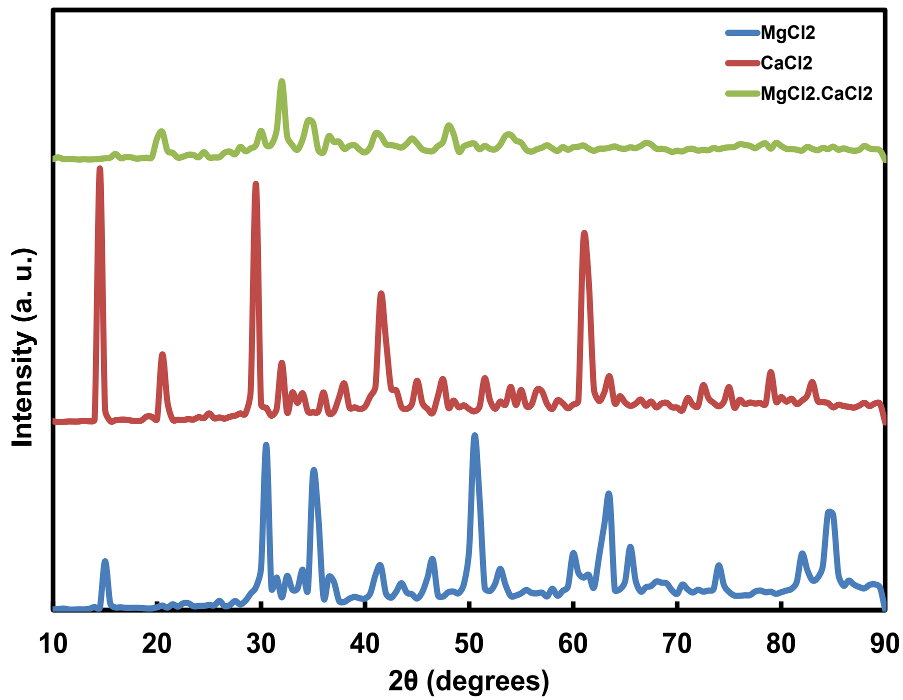
- Multi-step process ✗
- High theoretical gravimetric capacity ✓ (Expt. challenging) ✗
- Cheap ✓

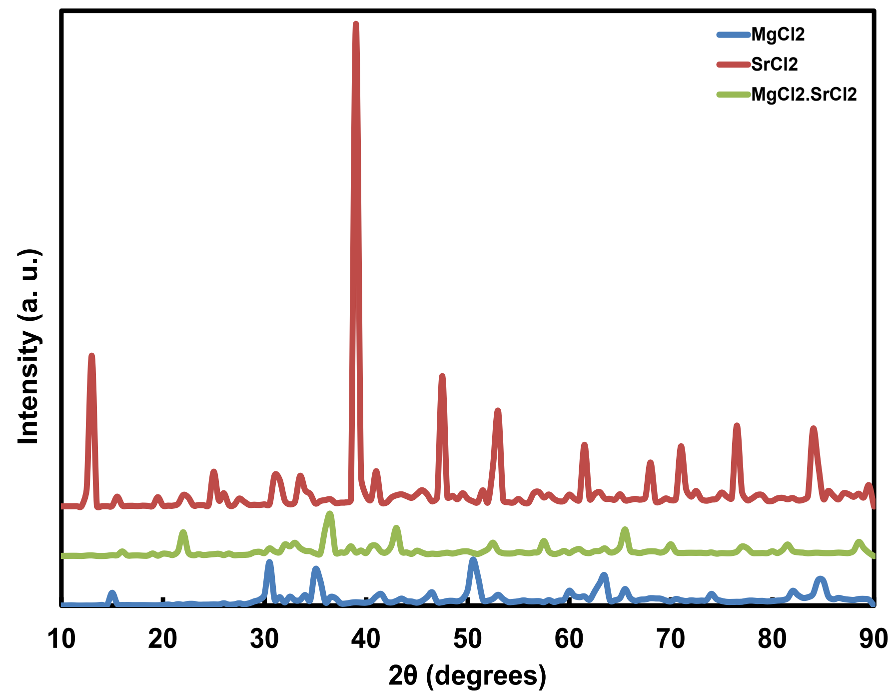
Potential additive or catalyst ✓

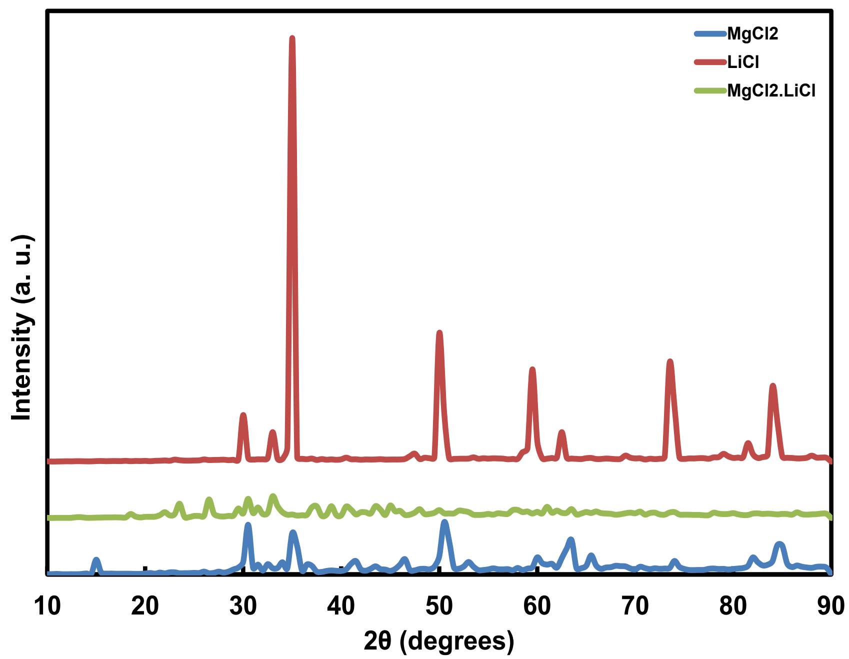
Need for new materials

- Existing materials have limitations
- New materials and composites are needed to address these limitations
- Synthesis of Eutectics and double salts
- Ammonia Absorption into Alkaline Earth Metal Halide Mixtures as an Ammonia Storage Material *Chun Yi Liu and Ken-ichi Aika Ind. Eng. Chem. Res. 2004, 43, 7484-7491*
- Development of new additives to enhance kinetics, thermodynamics and stability
- Ammonia Adsorption on Ion Exchanged Y-zeolites as Ammonia Storage Material *Chun Yi Liu and Ken-ichi Aika Journal of the Japan Petroleum Institute, 46, (5), 301-307 (2003*
- Theory can help identify potential systems
- *Designing mixed metal halide ammines for ammonia storage using density functional theory and genetic algorithms Peter Bjerre Jensen,Steen Lysgaard,Ulrich J. Quaade and Tejs Vegge, Phys.Chem.Chem.Phys.,2014,16, 19732—19740*

XRD of Eutectic Complex







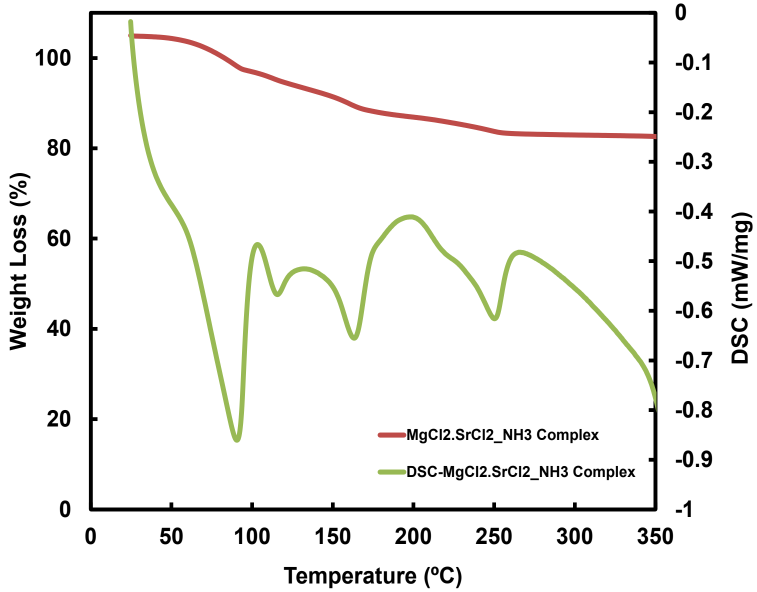
Need further characterization

New mixed metal salts

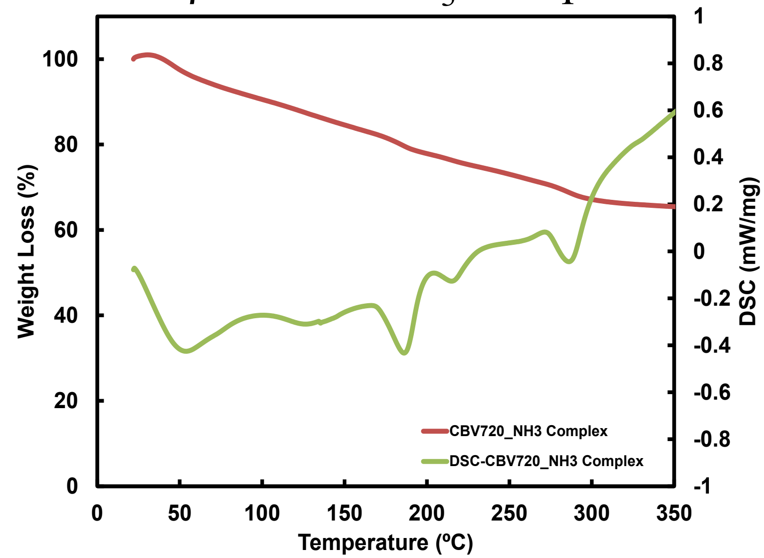
Preliminary screening

Vehicle Technologies Office

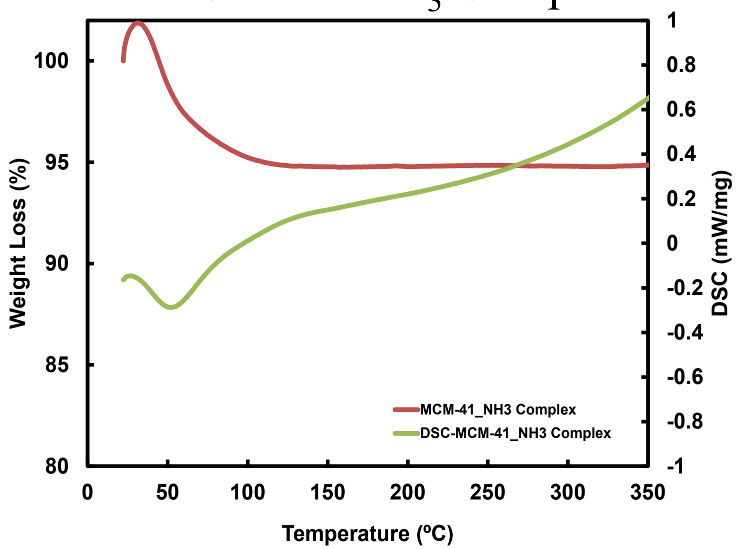
$MgCl_2.SrCl_2$ $(NH_3)x$



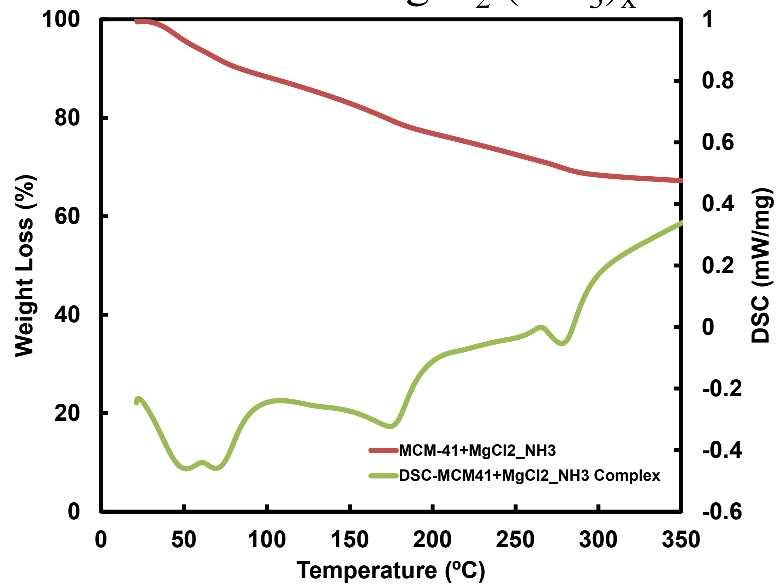
β Zeolite NH_3 Complex



MCM-41. NH_3 Complex

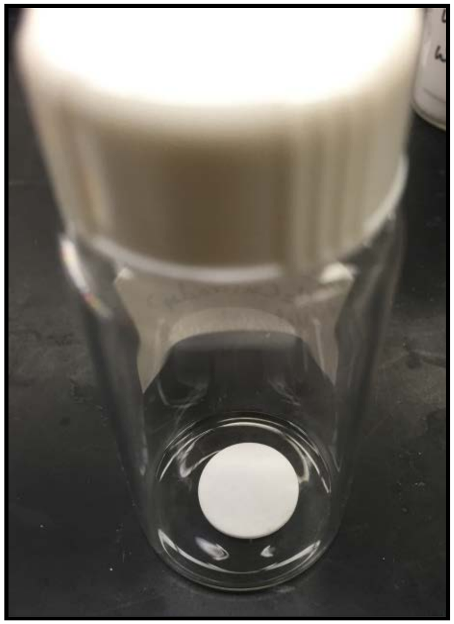


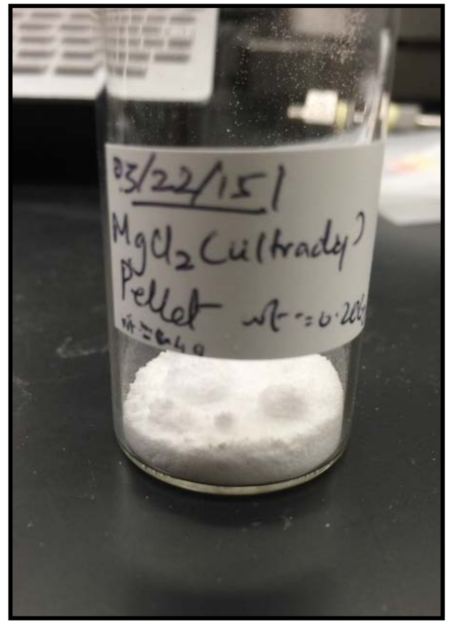
MCM-41+$MgCl_2.(NH_3)_x$



New compositions and additives have potential

Effect of NH_3 on pellets





•Pellet-$MgCl_2$
•Before NH_3 adsorption
•Wt.=0.205 g
•Dia.= 9 mm
•Height = 0.05 mm

•Pellet-$MgCl_2$
•After NH_3 adsorption
•Wt.=0.4 g

- Loses engineered form ✗
- Only NH_3 released ✓
- > 50 wt% gravimetric capacity ✓
- Reversible ✓

New additives are needed to retain engineered form

Planned Future Work

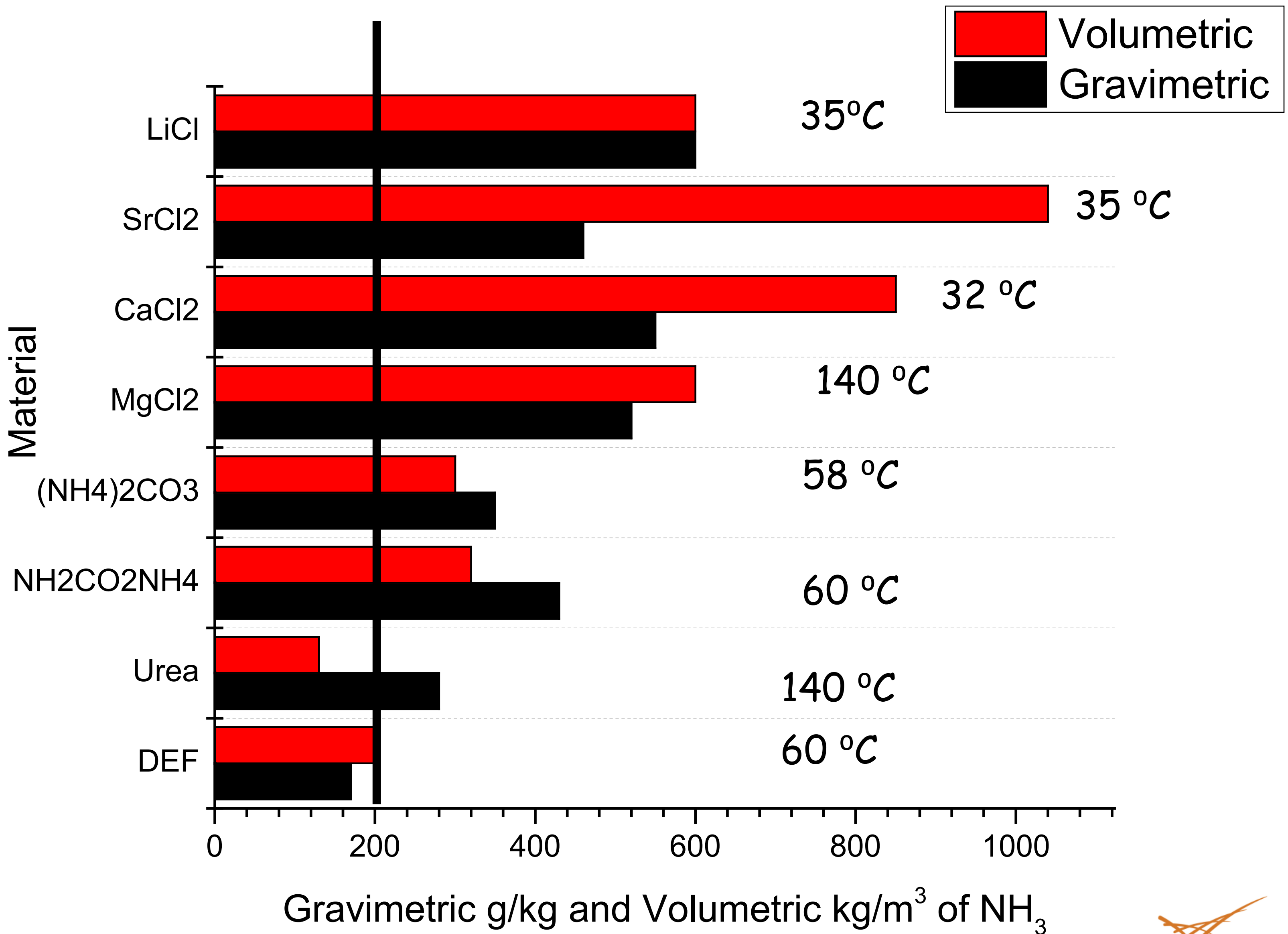
1. **NH_3 Adsorption Materials:**
    - Finish stability testing of existing materials
    - Vapor pressure and ARC studies
    - Down-select promising materials
    - Heat capacity measurements
2. **Double Salts and Eutectics:**
    - Detailed characterization
    - Studies will be especially focused on mechanisms/limitations for low temperature performance. Some specific questions:
        - How will additives alter capacity?
        - Can control of additive acidity or surface area alter thermodynamics and kinetics?
        - Can additives help retain engineered form?

Future Studies

- **High capacity NH_3 storage materials prepared by PNNL**
  - Studies of the effects of additives and various supports on the NH_3 storage capacity,
  - Detailed thermodynamic and kinetic studies of the ammonia release mechanisms in these eutectics and composites. These studies involve heat capacity, vapor pressure, and extensive characterization.
- **Engineered form of NH_3 storage materials**
  - Optimum preparation of double salts and eutectics.
  - Characterization and reactivity as a function of composition and structure
  - Role of support acidity on ammonia binding strength
  - Initiate discussion of cost analysis target systems

•Cat litter (Clay or zeolite)

Summary of material properties



Summary

- A critical need for future NH_3 storage: **improved capacity and higher performance** and stability.

- PNNL and USCAR are carrying out collaborative research aimed at addressing these critical performance issues in solid state ammonia storage. This CRADA is also focused on stability and safety of ammonia storage materials

- Primary focus of future work for this next year will be on development of new materials with high ammonia gravimetric and volumetric ammonia storage capacities

- Continue optimization of $MgCl_2$, LiCl and double salts with additives