Alternatives to Comp B Explosive

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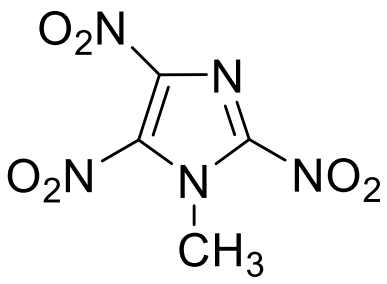
SERDP Project WP18-1203: MTNI-based Replacement for Comp B in a Printed M67 Grenade

TECHNICAL OBJECTIVE

- Develop an environmentally/toxicologically-acceptable, MTNI-based melt-pour explosive formulation and warhead system capable of replacing Comp B in a printed variant of the M67 hand grenade.



MTNI
(1-methyl-2,4,5-trinitro-1H-imidazole)

Cut-out view of M67 grenade

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Background: Explosive Formulations

- Main-fill secondary explosives typically incorporated into a formulation/mixture to improve processing and/or safe handling
  - Analogous (and often uses similar methods) to formulation of active drug ingredients in the pharmaceutical industry
- Various types of formulations are commonly used in the DoD depending on the type/configuration of the item to be loaded, examples include:
  - Pressed
  - Cast-cure
  - **Melt-pour (Melt-cast)**
- High-Blast (high overall energy output) vs. “Metal-Pushing” (rapid energy release) Explosives

Melt-pour explosive formulations

- Formulation which is stable in the molten form and can be poured directly into the end item
- Favored explosives production method in the Army; TNT-based is historically most common type
  - Used for loading grenades, mortars, artillery rounds, etc.
- **Advantages:**
  - Allows for a wide variety of item geometries
  - Relatively simple procedures and equipment
  - Generally requires minimal “diluting” of explosives with inert additives
- **Disadvantages:**
  - Restricted to compounds which can be safely melted between ~ 75 and 100 ^{o}C (steam heat)
  - Current formulations mostly TNT-based (toxicity, performance, and IM issues)
  - Cooling usually must be controlled

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Comp B History

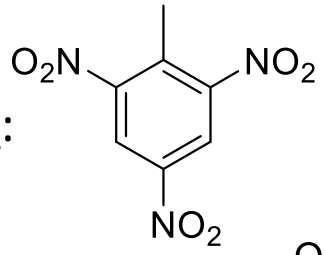
- Military use of 2,4,6-trinitrotoluene (TNT) began in early 20th century
- RDX took longer to adopt over concerns with its sensitivity
- "RDX Composition B" first fielded in 1943 by the Army Air Force as a bomb fill
- Post WWII it eventually became the primary explosive fill for Army projectile munitions

Comp B constituents:

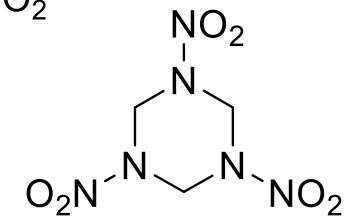
RDX: 60 wt. %

TNT: 40 wt. %

Wax: < 1 wt. %



TNT



RDX

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Environmental/Toxicological concerns

TNT (2,4,6-trinitrotoluene):

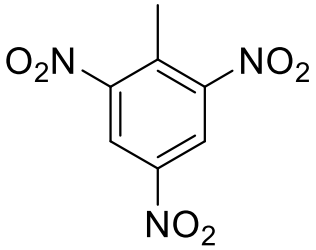
- Toxic occupational health hazard (EPA RfD = 5×10^{-4} mg/kg/day)
- Group C (possible human) carcinogen
- Hazardous Waste:
  - "**red water**": associated with purification step during production; alkaline mixture of nitroaromatics and inorganic salts
  - "**pink water**": TNT-saturated acidic wash water from post-purification rinsing and demilitarization

TNT/RDX-contaminated runoff at Blue Grass Army Depot washout facility (2010)

RDX (1,3,5-trinitro-1,3,5-triazacyclohexane):

- Mobile groundwater contaminant,
- Group C (possible human) carcinogen
- Toxicity to nervous system if inhaled or ingested in large amounts (EPA RfD = 3×10^{-3} mg/kg/day)

RDX



TNT

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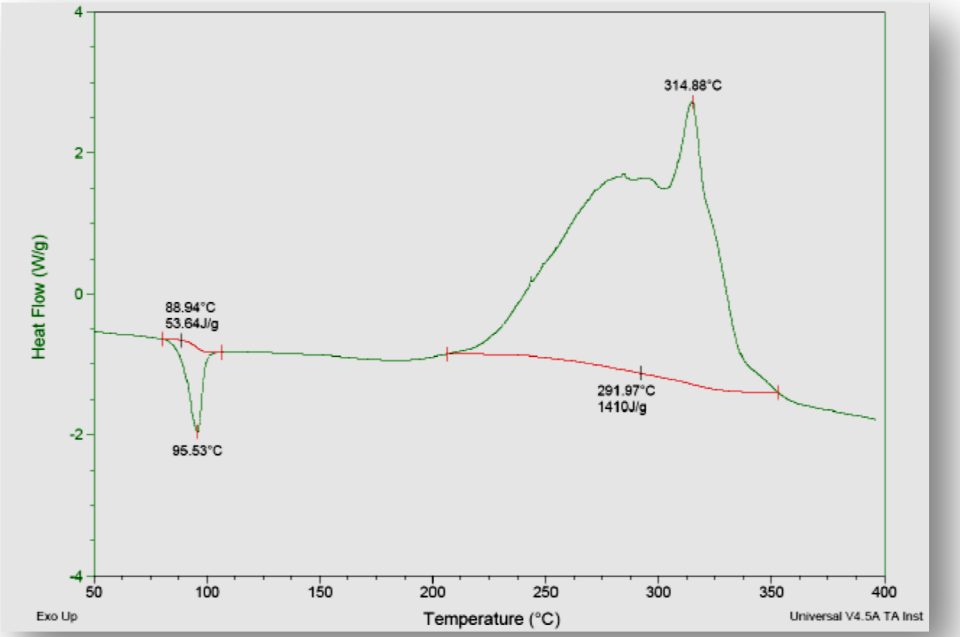
Melt-cast requirements

Ideal Melt-Cast Explosive:

- Melting pt. within 75 – 100°C
- Low vapor pressure
- High decomposition pt. (>200 °C)
- No shrinking/cracking or wall separation during cooling
- High density (>1.7 g/cm^3)
- Low toxicity
- Low-cost, “green” synthesis route

Example: DSC of MDNT



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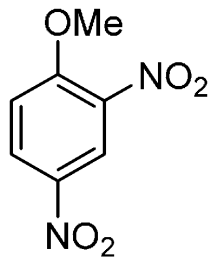
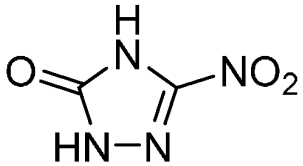
Existing TNT & Comp B Alternatives: IMX Melt-pour Formulations

- Developed with a focus on insensitive munition properties (perform better in fast cook-off, slow cook-off, bullet impact, sympathetic detonation, etc.)
- Employ DNAN as the main melt-phase material in place of TNT
- **IMX-101**: alternative to TNT, contains NTO and other ingredients
- **IMX-104**: alternative to Comp B (contains RDX solid fill in addition to NTO and other ingredients)
- Both perform best in larger items (e.g. artillery shells)
- Possible environmental concerns with DNAN and NTO



DNAN
(2,4-dinitroanisole)



NTO
(nitrotriazolone)

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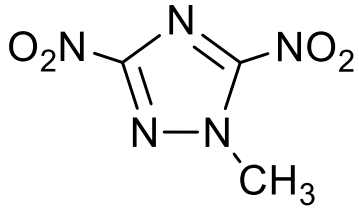
Other replacement investigations

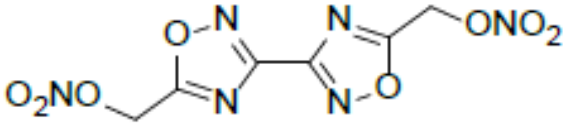
- MDNT investigated under previous SERDP program (WP201623: MDNT Manufacturing via Advanced Flow Reactor Technology)
- Comparable performance to Comp B
- Issues with dermal irritation & sensitization



MDNT
(3,4-dinitro-1-methyl-1,2,4-triazole)

Formula: $C_3H_3N_5O_4$
Density: 1.68 g/cm^3
Melting Point: 94 – 97 °C
Detonation Pressure: ~ Comp B
Detonation Velocity: ~ Comp B
Shock sensitivity: less than TNT

- BODN discovered by Sabatini et al (Army Research Lab)
- Developed as an energetic plasticizer, but also had potential as TNT/Comp B replacement due to favorable melt properties & explosive performance



BODN

T_{melt} = 82.0 °C
T_{dec} = 189.0 °C
Density = 1.834 g/cc
Heat of formation = -79.4 kJ/mol
P_{cj} = 29.4 GPa
V_{det} = 8200 m/s

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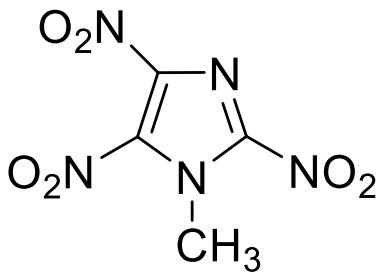
New Candidate: MTNI (1-methyl-2,4,5-trinitroimidazole)

- Current focus of SERDP Project WP18-1203
- First reported in 1970's by Russian chemists and later re-investigated by both South Korea and US Army CCDC AC
- Explosive Performance: MTNI outperforms Comp B in many key explosive performance parameters and is comparable in sensitivity
- Toxicological: only data previously collected was TOPKAT computer modeling
- Predicted low acute toxicity for oral, inhalation, and dermal exposure
- May pose moderate occupational hazard: skin sensitization and ocular irritation

Material	Melt Pt.(°C)	DSC (°C)	Density (g/cm^3)	Detonation Velocity (km/s)	Detonation Pressure (kbar)	Gurney (km/s)	Impact (cm)	Frict. (N)
MTNI	86	280	1.77	8.17	321*	2.96*	32.7	232
Comp B	80	202	1.71	7.8-8.0	275-280	2.65-2.76	38.3	324
TNT	80	300	1.65	6.7-6.9	188	2.42	108	240



MTNI

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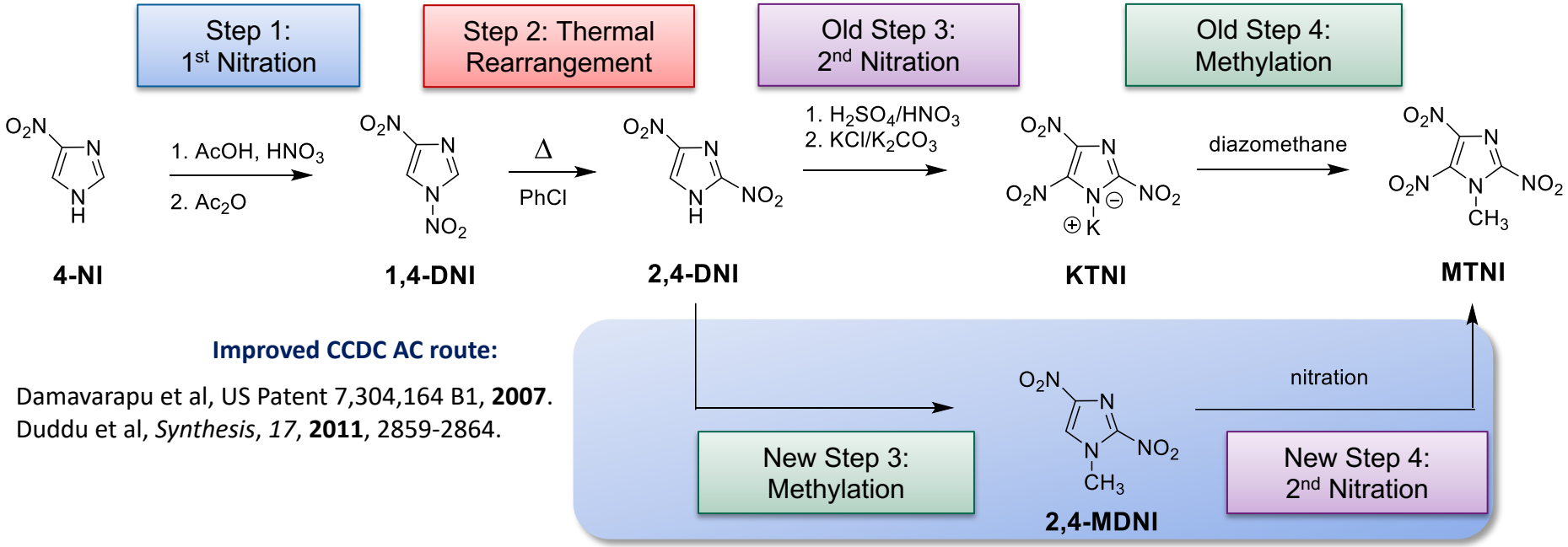
MTNI Synthesis overview

Original synthesis (Cho et al, *J. Heterocycl. Chem.* **2002,** *39* (1), 141-147)**:**



Improved CCDC AC route:

Damavarapu et al, US Patent 7,304,164 B1, **2007**.
Duddu et al, *Synthesis*, *17*, **2011**, 2859-2864.

Mettler Toledo EasyMax Workstation & in situ IR probe

Grams

Kilograms

20 L reactor

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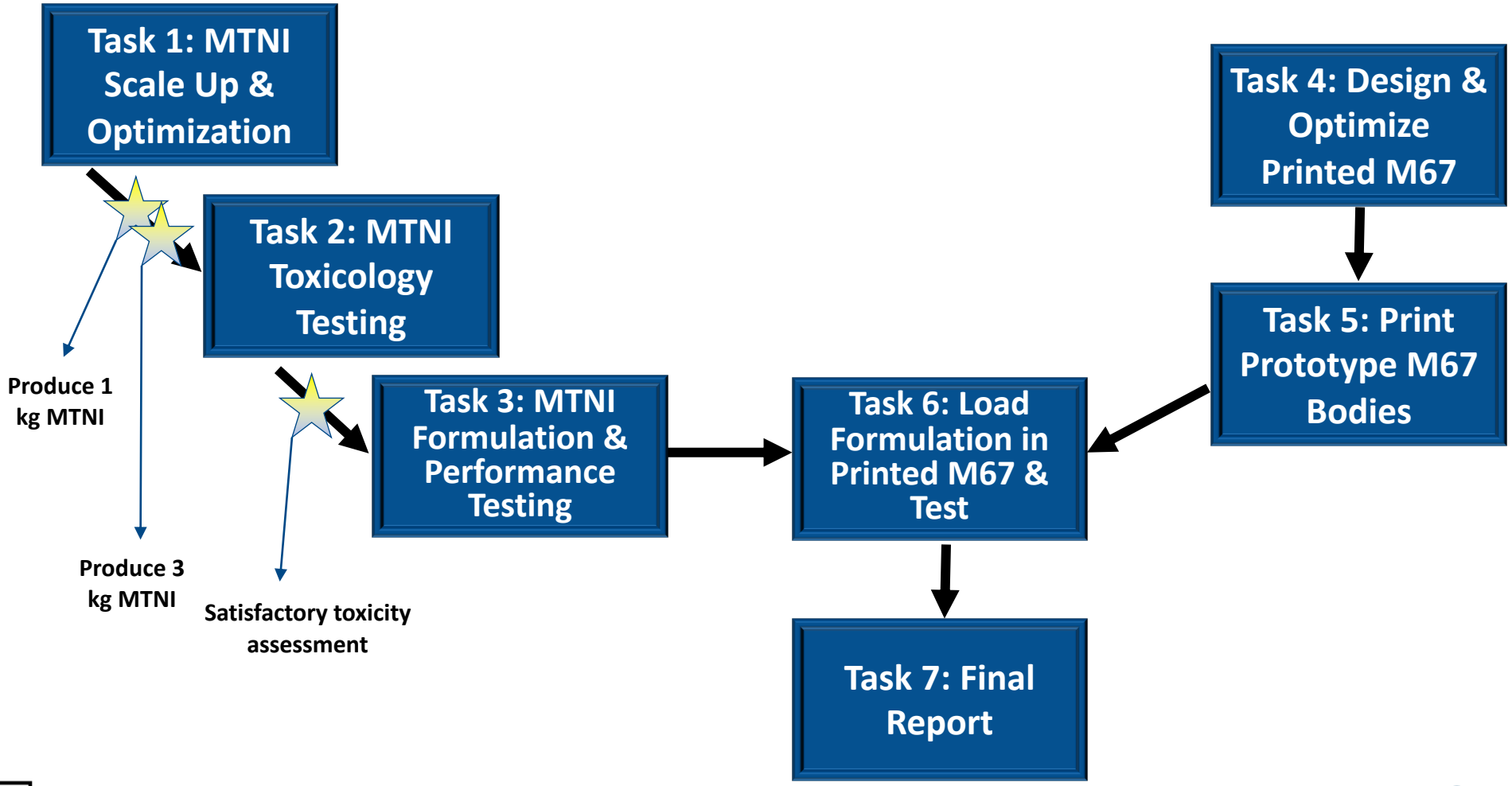
Technical Approach



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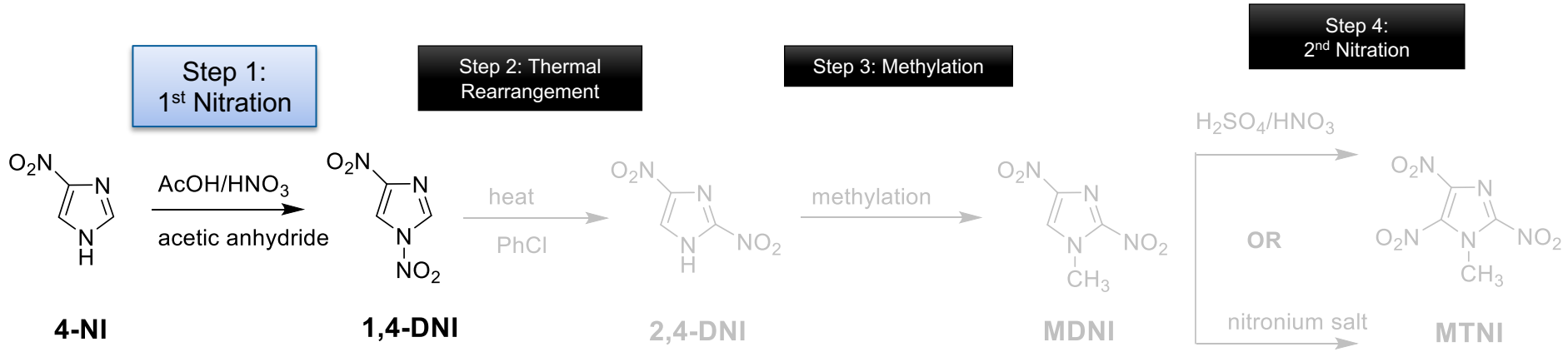
Results: MTNI Scale-up Optimization (Step 1)



STEP 1 OPTIMIZATION:

- Evaluated at 10, 35, 100, and 200 gram scale before increasing to large-scale batch
- Successfully scaled up to kg batches with high yield
- Optimized reagent order of addition, addition rate, and quenching conditions

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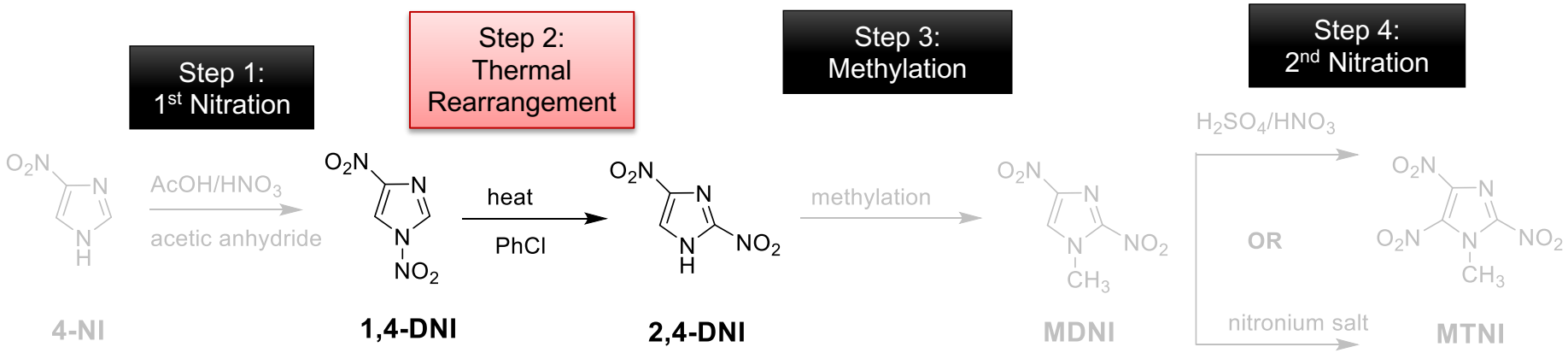
Results: MTNI Scale-up Optimization (Step 2)



- Investigated heat flow and performed in situ reaction studies (ReactIR)
- Exothermic nature made scale up challenging
- Successfully produced kg scale batches in 20 L reactor
- Explored high boiling point, non-halogenated solvents as alternatives to chlorobenzene
- Also studied effect of water content on yield

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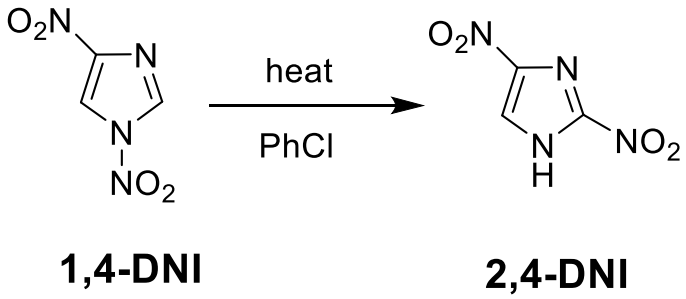
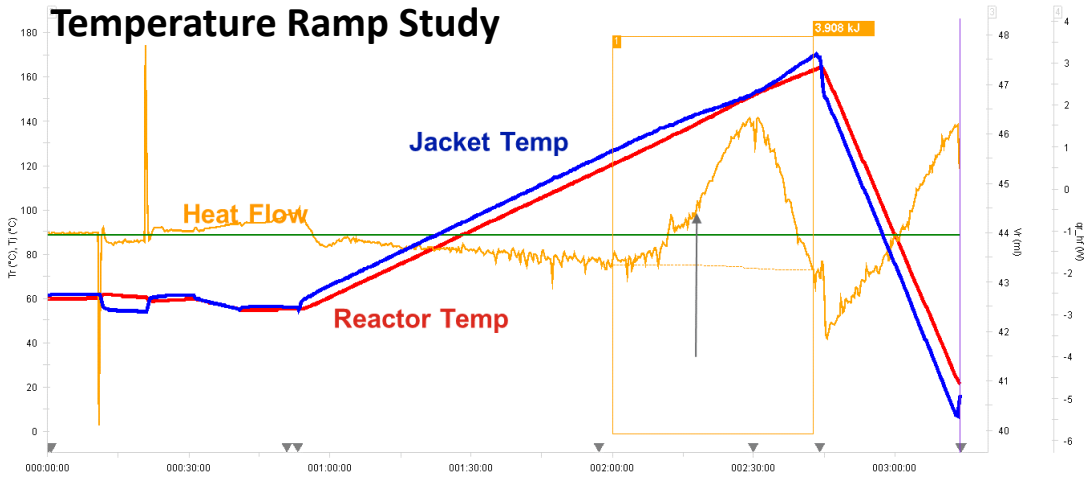
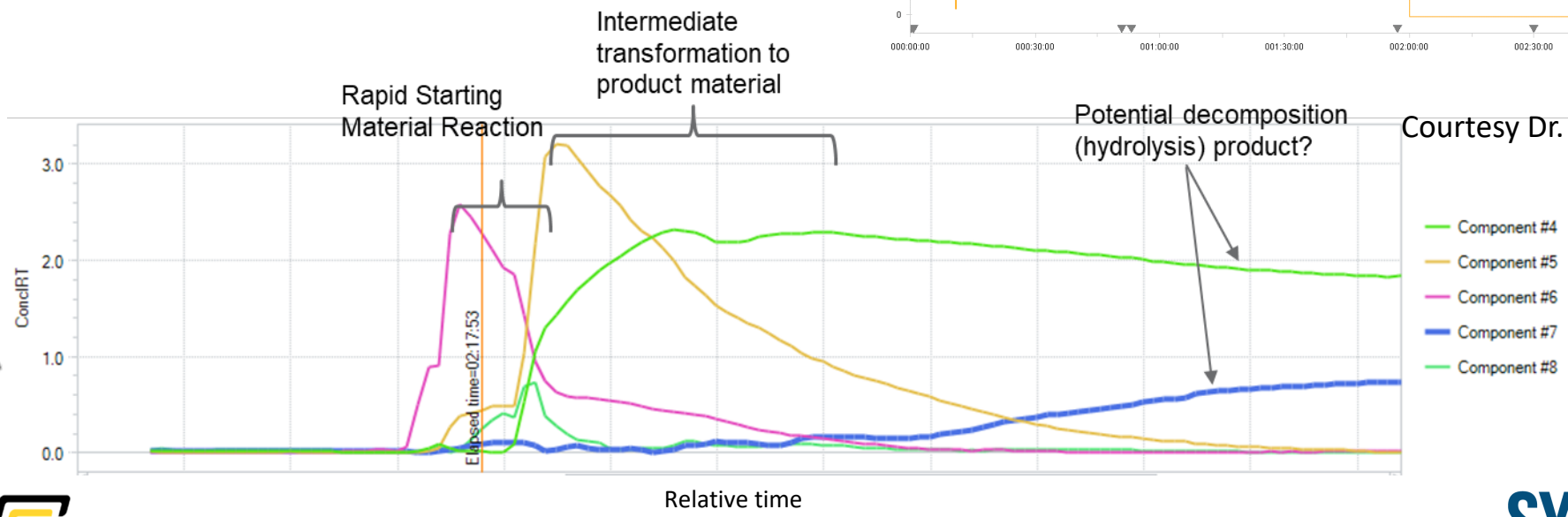
1,4-DNI → 2,4-DNI: EasyMax Data







Courtesy Dr. Eric Gauthier, CCDC AC

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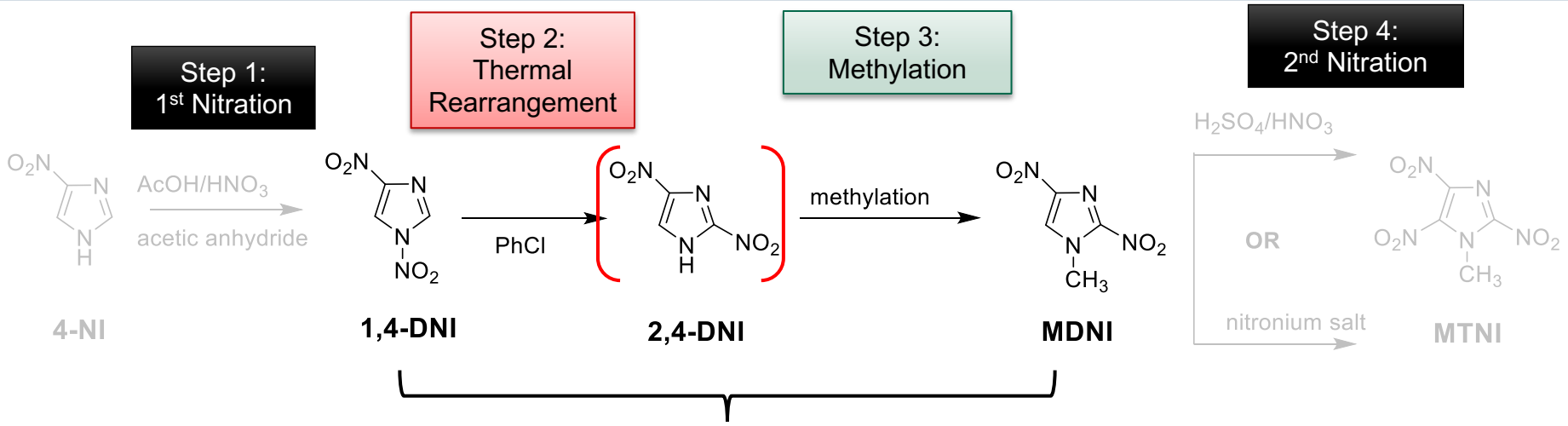
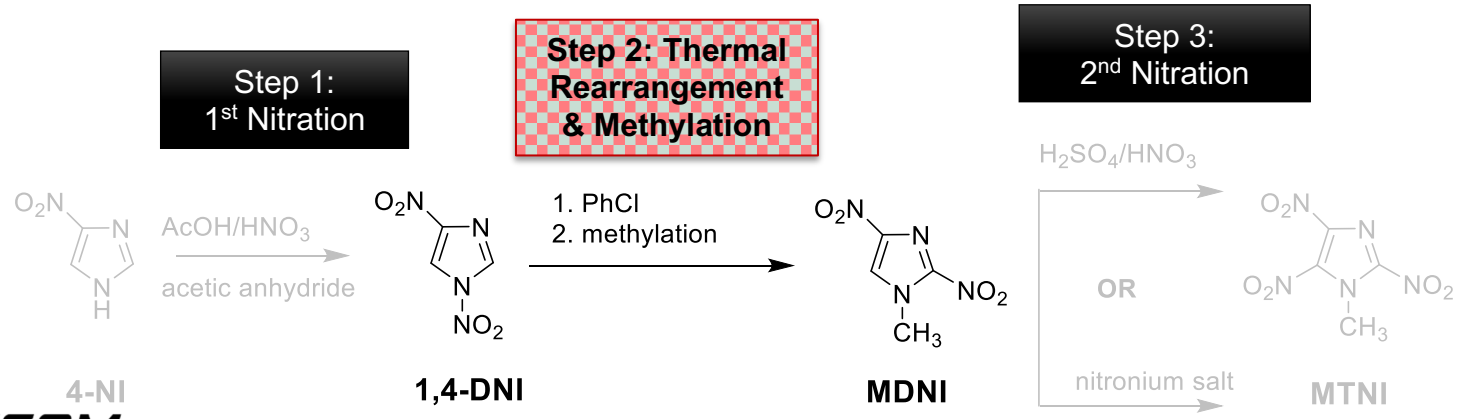
Results: MTNI Scale-Up Optimization (Step 3)





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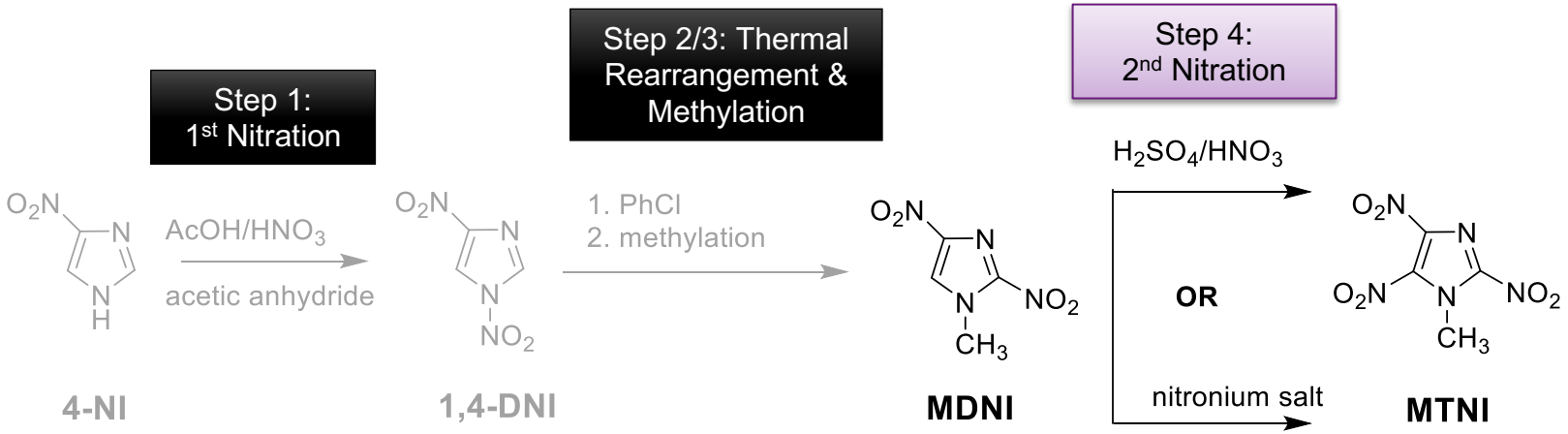
Results: MTNI Scale-up Optimization (Step 4)



- Currently the most difficult step to scale up
- Investigating traditional mixed acid, as well as nitronium-based molten salts (NO_2X)
  - Pros: commercially available, milder reaction conditions, reduced waste, good regioselectivity
  - Cons: expensive, can be labor-intensive, limited number of substrates

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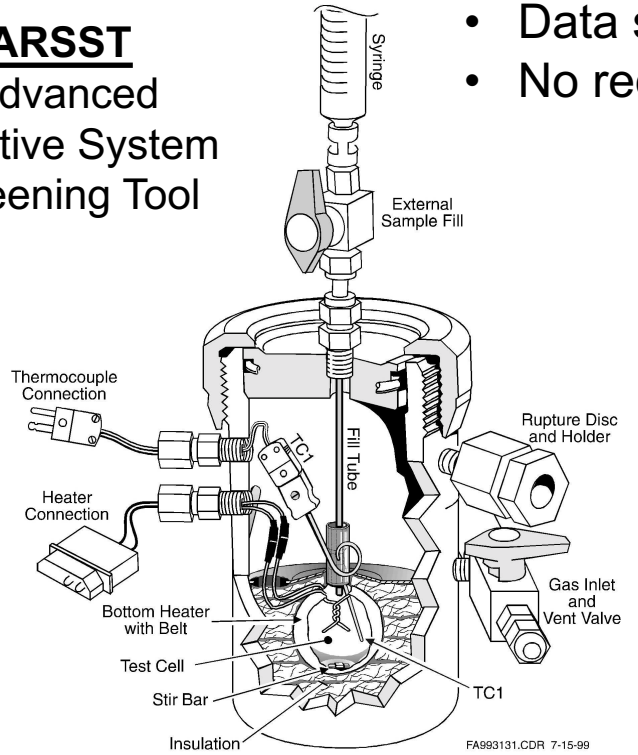
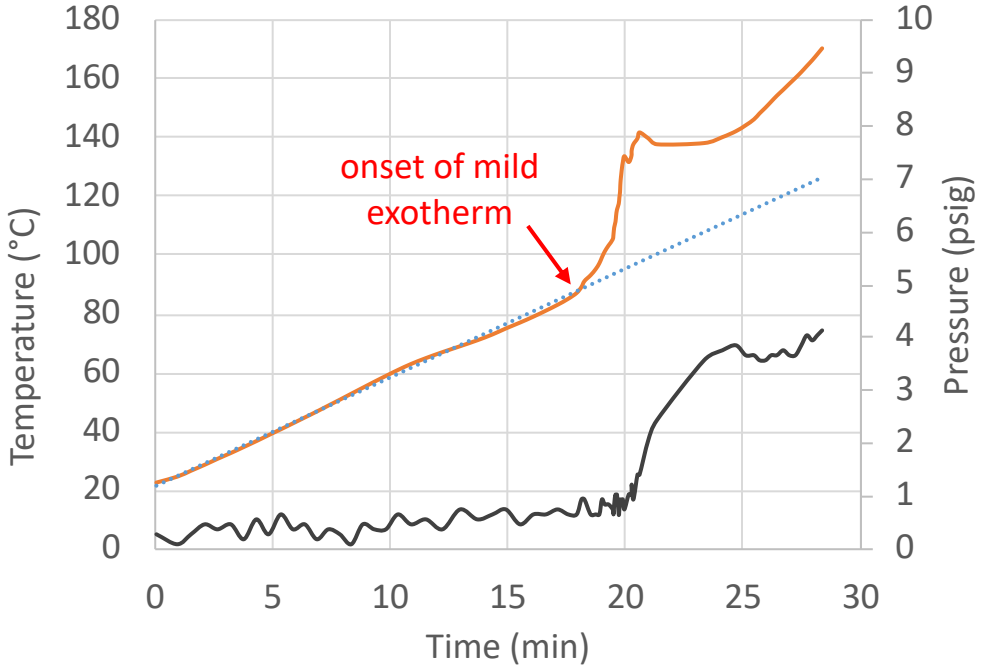
MDNI to MTNI initial Safety Evaluation

- Performed safety assessment prior to larger scale attempts
- Data shows only mild exotherm and no abnormal pressure build-up through 180°C
- No red flags for continued reaction scale-up with nitronium salt

ARSST
Advanced
Reactive System
Screening Tool



Burelbach, N. 28th Annual Conference of the N. American Thermal Analysis Society, Oct 4-6, 2000.



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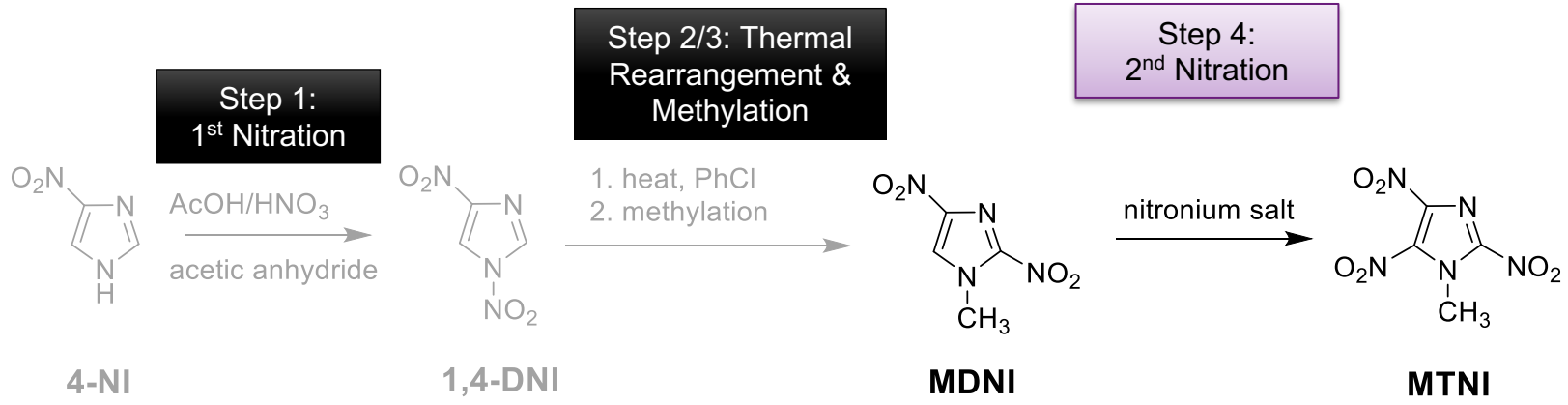
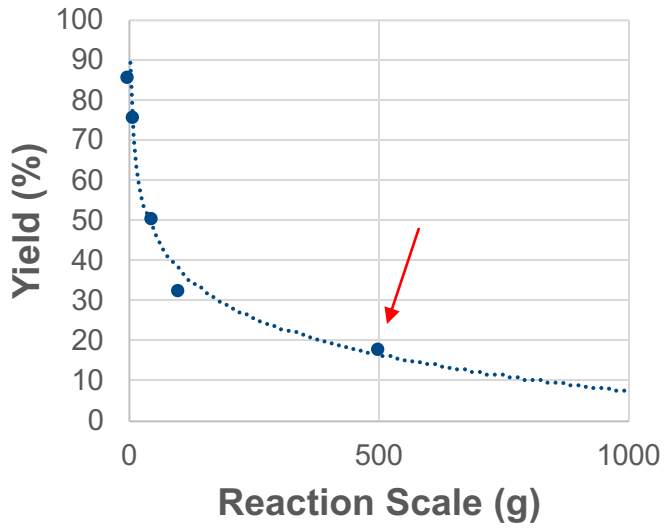
Scale-up of MDNI to MTNI



- Currently exploring optimization methods at larger scales
- Other synthetic strategies may be needed for future scale up



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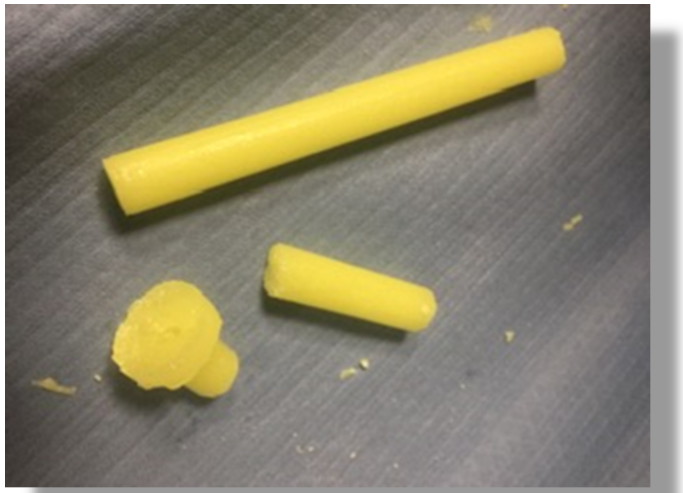
Developing & Assessing formulations

Task	Purpose
Thermochemical calculations (Jaguar, Cheetah)	Provides starting point to begin formulation work
Pouring/casting studies	Determine pourability and mechanical strength of cooled material on lab-scale (no cracking, pulling away from container walls, etc.)
Sensitivity Tests (impact/friction/ESD)	Verify safe handling of formulation
Critical Diameter Test	Assess performance potential in small items
IHE Gap Test	Assess shock sensitivity of formulation (key IM/safety test)
Henkin Test	Assess stability at extreme temperatures (common test for melt-cast)
Slow Cook-off Test	Assess stability under prolonged high temperatures (IM test)
Detonation Velocity & Pressure Testing	Common measurement of explosive performance
Cylinder Expansion (Cylex) Testing	Assesses “metal pushing” ability of formulation (ability to shatter metal casing into lethal fragments)
6 and 12 month Aging Studies	Assess long term stability of formulation

Initial MTNI Formulation efforts

Lab-scale melt-pour setup

Melted MTNI



MTNI Rate Sticks Cast

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MTNI Formulation: Binder studies

- Waxes & other additives typically added to melt-pour formulations to improve processability, mechanical properties, and/or aging behavior
- Investigating a family of wax candidate materials, including biologically-derived
- “Wax A” downselected based on favorable vacuum thermal stability and initial lab evaluation
- Sensitivity testing pending, followed by performance evaluations

MTNI Eco-Toxicology Screening

- Complete battery of toxicity testing being carried out by the Army Public Health Center (APHC) at Aberdeen Proving Ground, MD
- Go/No-Go decision for MTNI development will be based on APHC's final toxicity assessment
- Initial in vitro testing shows potential for strong aquatic toxicity; follow-on in vivo testing is planned

APHC
ARMY PUBLIC HEALTH CENTER

Toxicological Test	OECD Guideline #	Screens for:
Bacterial Reverse Mutation Test (Ames Test)	471	Genotoxicity/Mutagenicity
Microtox® Aquatic Toxicity Test	--	Acute Aquatic Toxicity
Human Cell Line Activation Test (h-CLAT)	442E	Dermal Sensitization
Eukaryotic Cytotoxicity Prediction (EuC)		Acute Cytotoxicity (calculation derived from h-CLAT data)

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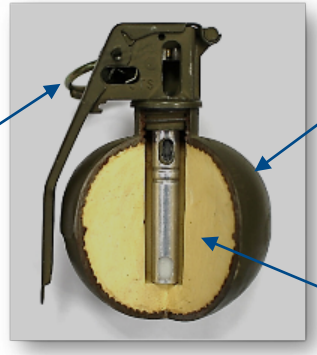
M67 Fragmentation Hand Grenade

- First fielded by the U.S. in 1968
- Intended use: supplement small arms fire in close-combat situations
  - Lethality primarily due to high velocity projection of fragments in a uniform distribution pattern
- Grenade body is a 2.5” diameter steel sphere containing ~180 grams of Comp B
- Reasons for investigating under this effort:
  - Very common explosive item
  - Small size
    - Can detonate full item using local test facilities
    - Can do more testing with less explosive material



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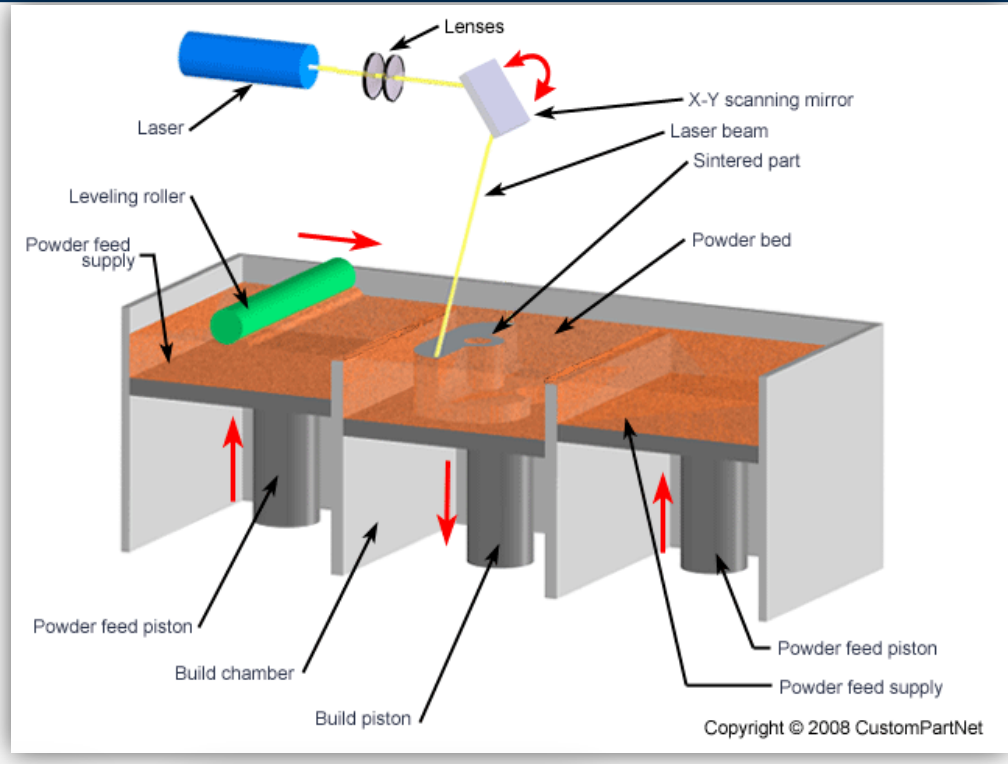
Direct Metal Laser Sintering (DMLS)

- Additive Manufacturing technique that uses iterative sintering of metal powder by high intensity laser
- Also known as: Selective Laser Sintering (**SLS**) or Laser Powder Bed Fusion (**LPBF**)
- Wide variety of shapes are possible
- Environmentally friendly process: waste is minimal and un-sintered metal powder can be recycled

<u>Typical Build Process</u>

1. Steel Base placed in build chamber
2. Base coated with initial layer of metal powder
3. Laser-based heat source sinters layer of powder, bonding it to base plate
4. Fresh layer of metal powder coated onto build
5. Go to step 3, repeat until part is completed.



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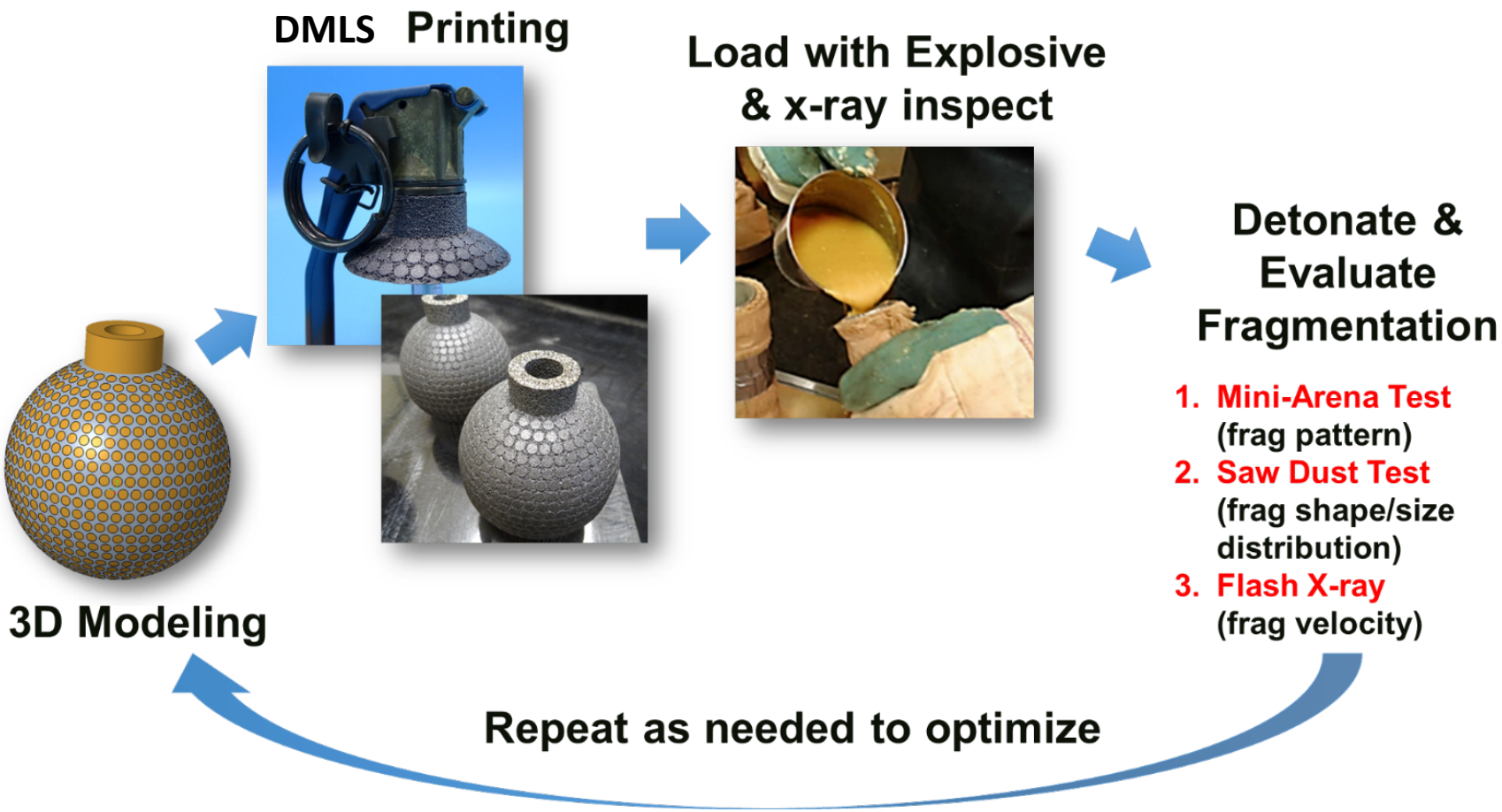
Grenade Evaluation



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Summary

- For environmental/toxicological and performance reasons, effective alternatives are needed for Comp B explosives
- MTNI is under investigation as one candidate
- Scale-up of MTNI successfully produced kilogram quantities of material for formulation & performance studies
- Formulation work has down-selected promising formulation for further development
- In vivo aquatic toxicity testing is planned

Acknowledgements

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- Phil Samuels

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- Dr. Emily Reinke
- Dr. Bill Eck

Leidos

- Dr. Raja Duddu
- Dr. John Hoare

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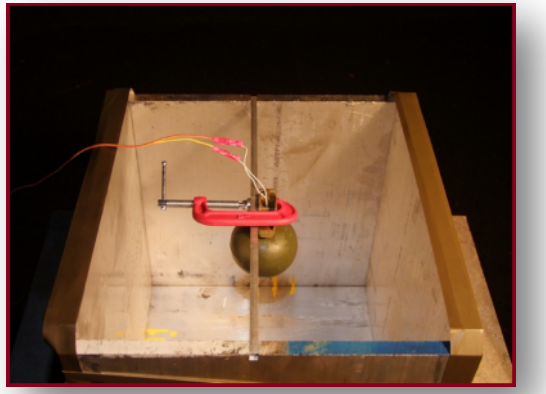
- Dr. Robin Nissan
- Braxton Lewis
- Dr. Niru Trivedi

BACK-UP SLIDES

Task 6: Load MTNI Formulation in Printed M67 & Test

- GOAL: Perform screening test to assess performance of MTNI in M67 grenades (both conventional and printed)
- Up to Four Total Evaluations (Similar to Task 4):
  - Mini-Arena Test: Analyzes fragment impact pattern on witness plates
  - Saw Dust Test: Collects individual fragments for size/shape analysis
  - Flash X-ray Analysis: Measures fragment velocity
  - Lethality Analysis: Computational analysis of the first 3 tests
- 3 test series (at least 3 grenades tested for each):
  - Comp B-filled printed M67 grenade
  - MTNI-filled conventional M67 grenade
  - MTNI-filled printed M67 grenade
- Analysis:
  - Compare performance of MTNI-filled to Comp B-filled conventional M67
  - Compare performance of MTNI-filled to Comp B-filled printed M67
  - Confirm performance of printed M67 grenade meets or exceeds conventional M67



Mini-Arena Test Setup