SOUTH DAKOTA SCHOOL OF MINES & TECHNOLOGY

# Time Delays: The Path Toward Environmentally-Benign Formulations

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# The Common Delay Formulations

**Table 1.** Common U.S. Military Gasless Delay Compositions.

| Composition | Military Specification | Components | Available Burning Rates (mm/s) |
|---|---|---|---|
| tungsten delay | MIL-T-23132A | W, $BaCrO_4$, $KClO_4$, diatomaceous earth | 0.6 – 150 |
| manganese delay | MIL-M-21383A | Mn, $BaCrO_4$, $PbCrO_4$ | 1.8 – 13 |
| zirconium-nickel delay | MIL-C-13739A | Zr-Ni alloy, $BaCrO_4$, $KClO_4$ | 2.1 – 13 |
| T-10 delay | MIL-D-85306A | B (amorphous), $BaCrO_4$ | 7.3 – 70 |

***The issue is chromates, lead, potassium perchlorate.***

# A brief review of delay systems that have been explored

**Table 6.** Slowest-to-fastest burning rates ($u$) reported for selected delay compositions and thermites. The tube wall materials is also indicated.

| Fuel/Oxidant | Tube | $u$ (mm s$^{-1}$) | Ref. |
|---|---|---|---|
| $Si/Pb_3O_4$ | CM | 2.2–3.8 | [109] |
| $Si/Pb_3O_4 + CNT$[a] | CM | 4.4–5.85 | [109] |
| $Si/CaSO_4$ | Al | 6.9–12.5 | [19] |
| $Si/Sb_2O_3$ | Pb | 7–14 | [73c] |
| $Si/BaSO_4$ | Al | 8.4–16 | [18] |
| $Si/Cu(SbO_2)\cdot xZn(SbO_2)_2$ | Pb | 6–20 | [73c] |
| $Si/Sb_6O_{13}$ | Pb | 4.8–20.4 | [20] |
| $Si/CaSO_4$ | Al | 12.7–31.8[b] | [104a] |
| $Si/PbCrO_4$ | Pb | 10–30 | [73c] |
| $Si/Bi_2O_3$ | Pb | 15–155 | [20] |
| $Al/WO_3$ | – | 0.08–4.1 | [113] |
| $Al/MoO_3$ | – | 4–12 | [46] |
| Al/Viton B | – | 12.5–40 | [8] |
| $Al/MoO_3$ | Acrylic | 600–1000 | [86] |
| $Al + Si/CuO + Bi_2O_3$ | MS | 115–655 | [106] |
| $Mn/MnO_2$ | Al | 2.4–7.3 | [114] |
| $Mn/CuBi_2O_4$ | Al | 9.3 | [26] |
| $Mn/Sb_2O_3$ | Pb | 4.2–9.4 | [90] |
| $Mn/Cu_2O$ | Al | 5–10 | [26] |
| $Mn/V_2O_5$ | Al | 7.5–10 | [26] |
| $Mn/MnO_2$ | Al | 6–19 | [26] |
| $Mn/Bi_2O_3$ | Al | 11–22 | [26] |
| $W/Sb_2O_3$, $KIO_4$ | – | 1.38[c]–2.99 | [104b] |
| $W/MnO_2$ | Al, SS | 1.62–4.7 | [28] |
| MgSi/Viton B | — | 22–82 | [8] |
| $B_4C/NaIO_4 + PTFE$ | Al | 0.48–7.69 | [3] |
| $Ti/C + 3Ni/Al$ | Al | 2.1–38.1 | [27] |

[a]CNT = carbon nano tubes; [b]With aluminum as additive; [c]Calcium stearate additive; Al = Aluminum; CM = Cast metal; Pb = lead; SS = stainless steel. MS = mild steel.

# Our early work on SHS type systems

- Explored a binary reaction system where Ti/C and 3Ni/Al are paired together.

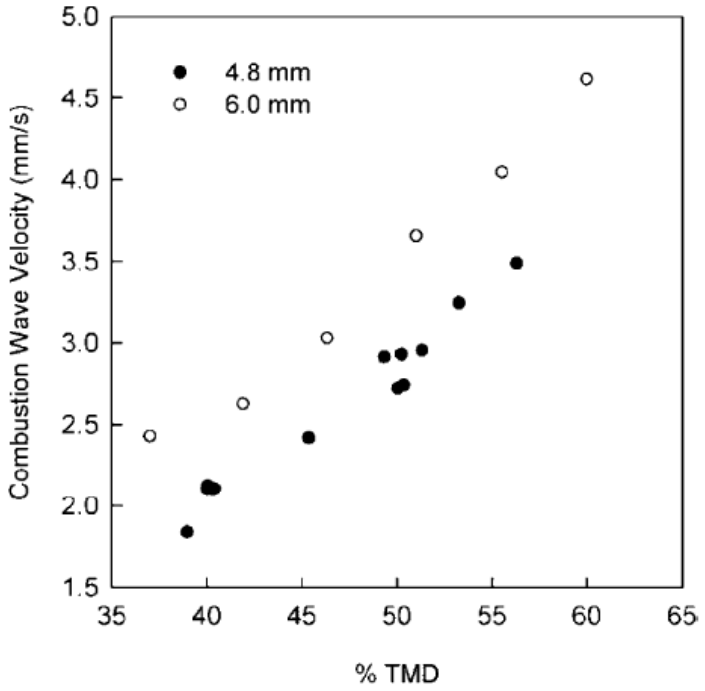


**Figure 2.** Combustion wave velocity of Ti/C-3Ni/Al(35/65 wt.-%) as a function of packing density in 4.8 and 6.0 mm inner diameter Al microchannels.

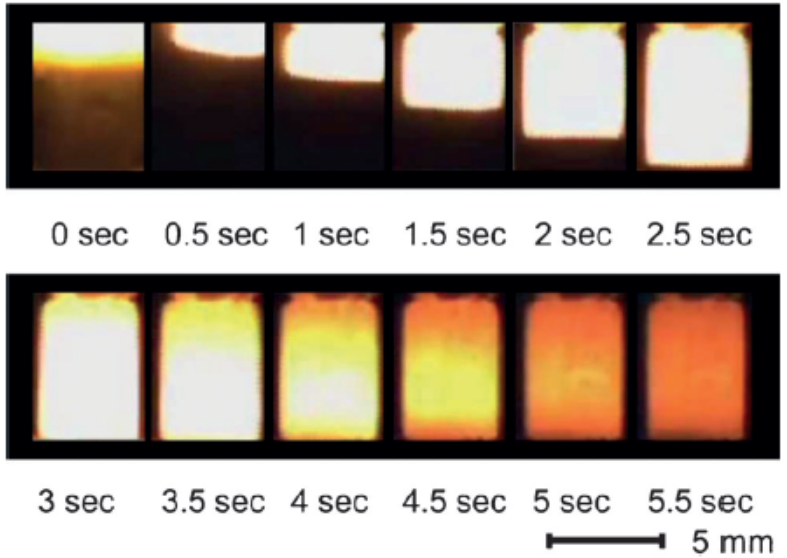


**Figure 6.** Images of the combustion front in a typical 4.8 mm diameter unconfined pellet experiment. (Composition #3 at 55% TMD).

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# The push for environmentally benign formulations – recently work funded by SERDP

- Advance the state of the art in pyrotechnic delays.
- Develop versatile environmentally benign gasless pyrotechnic delay compositions that will function in the M201A1 and M213/M228 fuzes.
  - Fuzes currently produced contain chromates and perchlorates.
- Study and understand the behavior of common component chemicals so that replacements can be developed intelligently.
- Implement continuous environmental safety occupational and health assessments (ESOH) and guidance from the US Army Public Health Command (PHC).

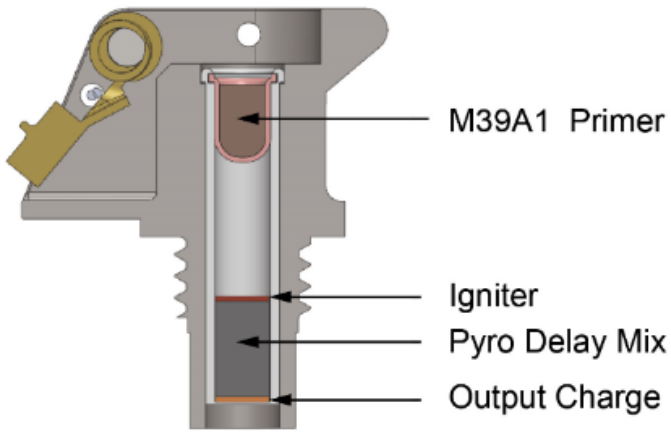


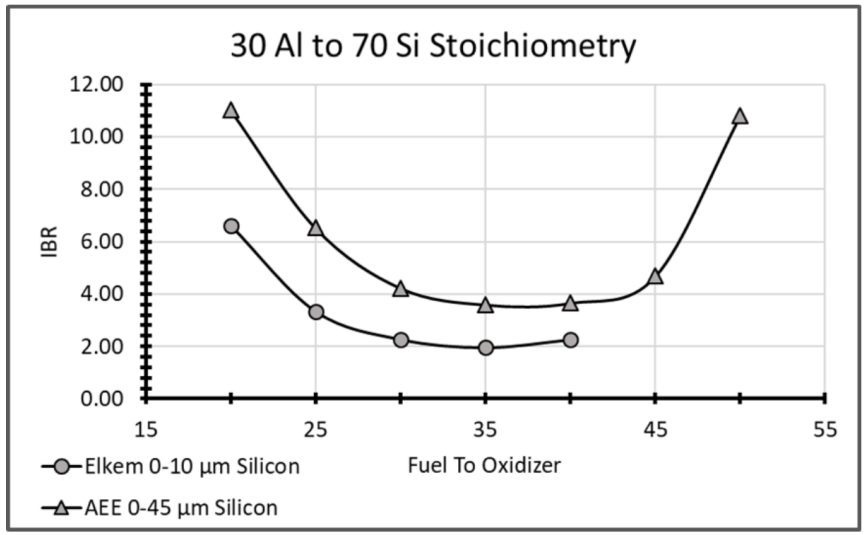

*Image courtesy of IMP*

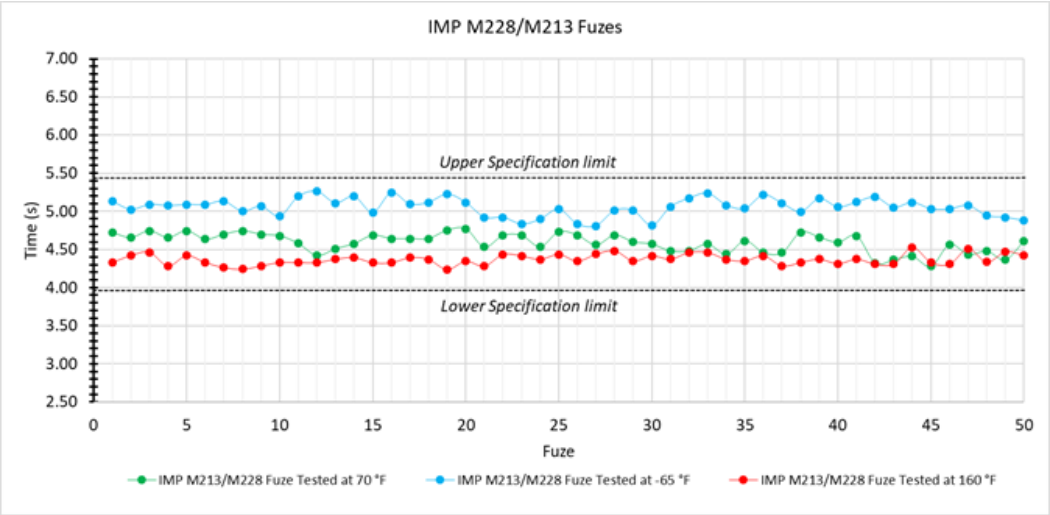
# The push for environmentally benign formulations

- New formulations (binary systems)
  - $Mn/MnO_2$
  - $W/MnO_2$
- Replacement of Barium Chromate in W-delay
  - Strontium Molybdate and Barium Molybdate
- Replacement of potassium perchlorate in W-delay
- IMP work
  - New formulation (Al/Si/Strontium molybdate)

# Highlights of those efforts

- IMP efforts produced a robust, tailorable formulation that has been extensively tested and shown to deliver excellent results.
- This formulation is a binary fuel mixture (Al/Si) with strontium molybdate serving as the oxidizer (primary)
  - Tailorable rates with Al/Si ratio and sizing of Aluminum fuel.




| IBR Stats | |
|---|---|
| Min | 4.76769 |
| Max | 5.33408 |
| Range | 0.56639 |
| Avg | 5.07877 |
| Std Dev | 0.113088 |
| CV% | 2.226676 |

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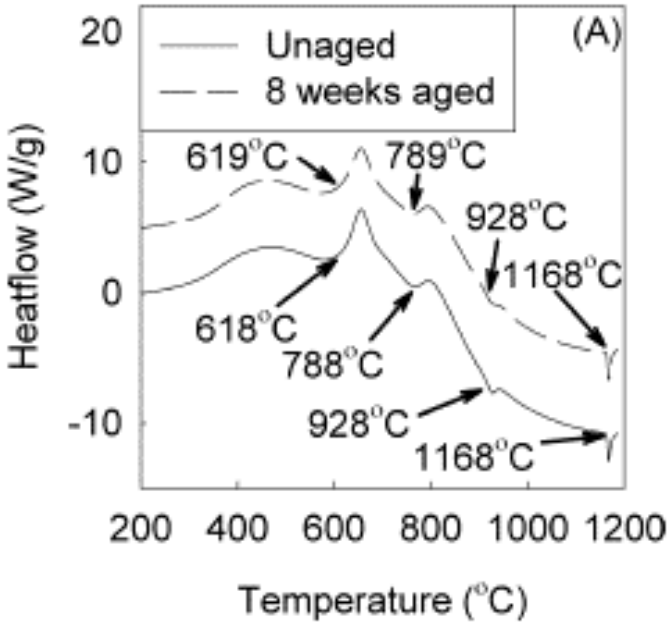
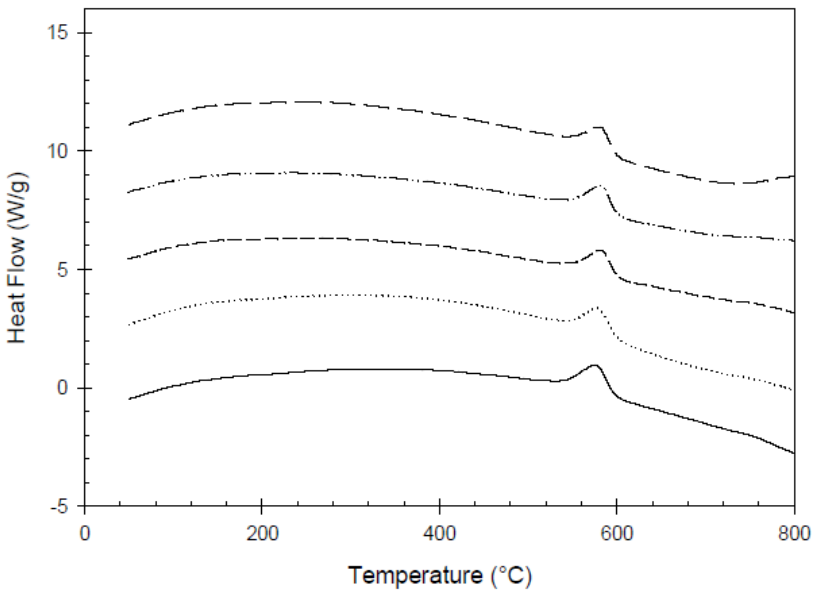
# CCDC/SD Mines efforts

- Binary systems to ease manufacturing and enhance reliability
  - $Mn/MnO_2$
  - $W/MnO_2$
- These simple systems have early onset reactions due to $MnO_2$ release of oxygen

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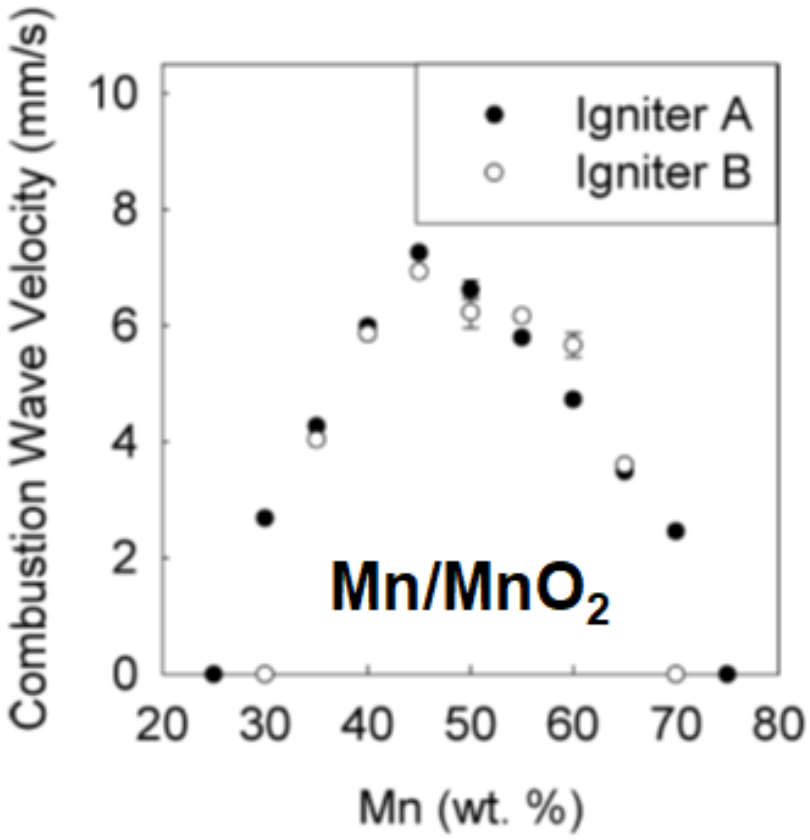
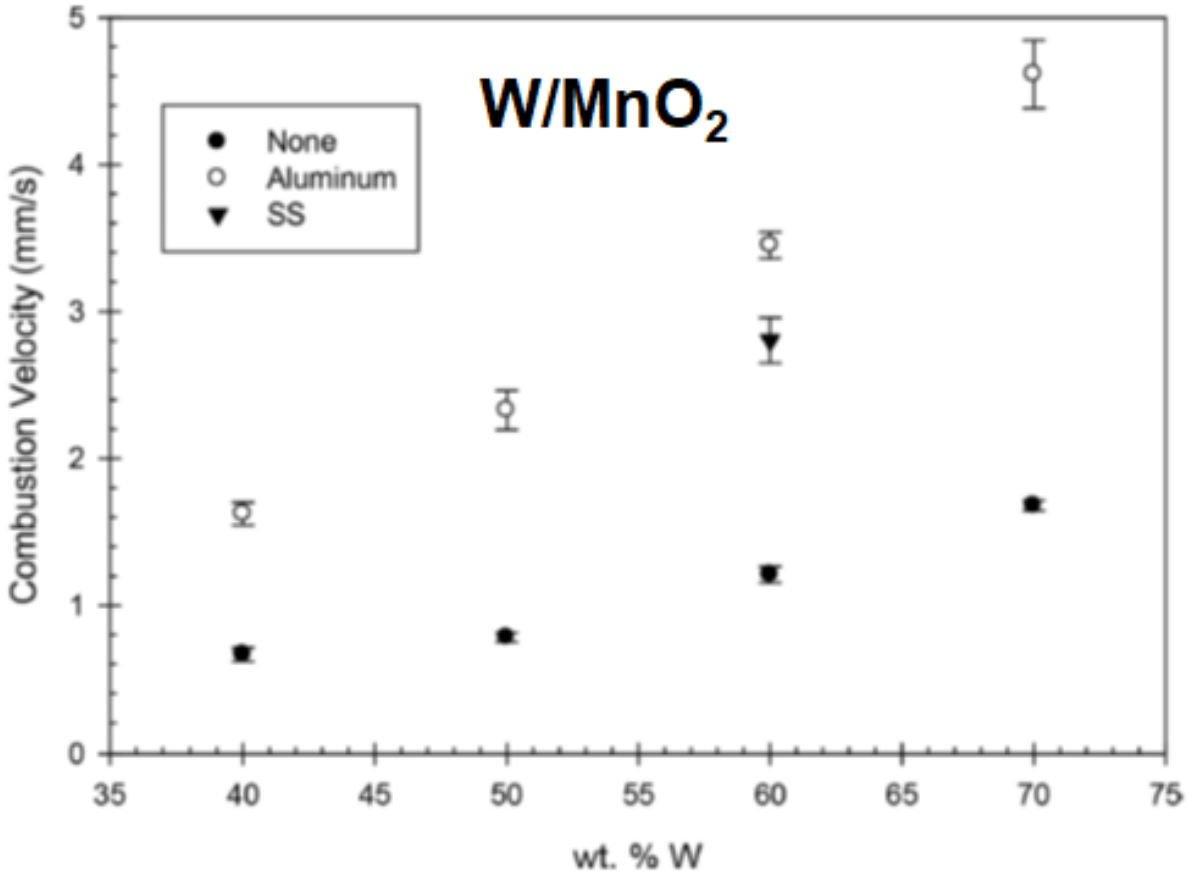
# Binary Systems



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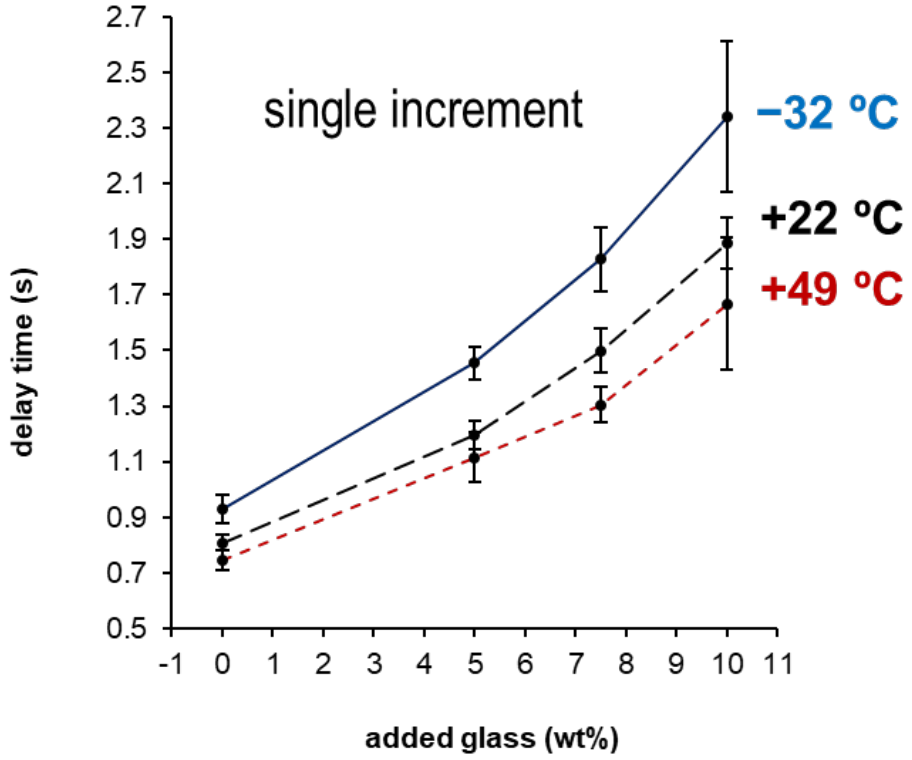
# CCDC-AC testing in fuze configuration




**50 W/50 $MnO_2$ for M213**

| Temperature (ºC) | Average time (s) | Standard Deviation (s) |
|---|---|---|
| -51 | 6.139 | 0.136 |
| 18-22 | 5.179 | 0.173 |
| 63 | 4.822 | 0.149 |

Target is 4-5.5 sec

Target is 1-2.3 sec



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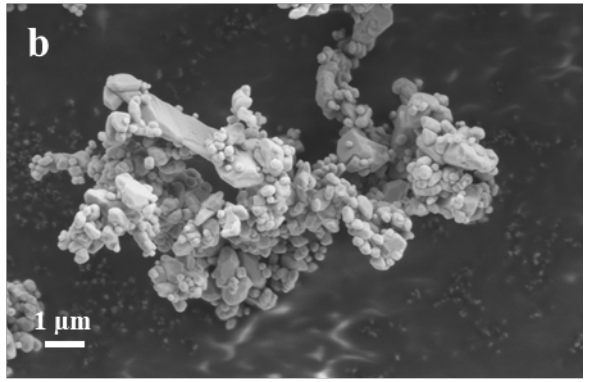
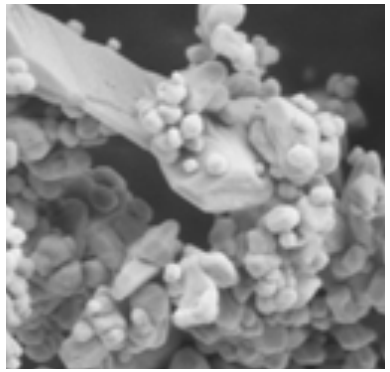
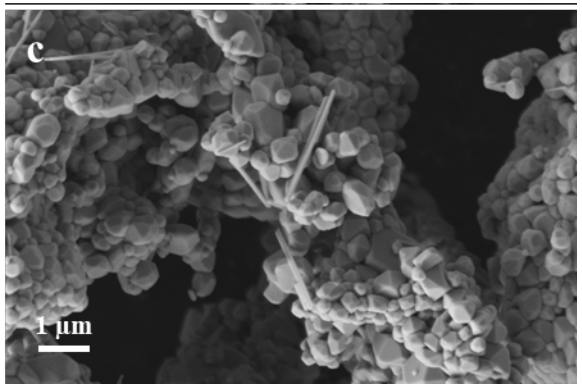
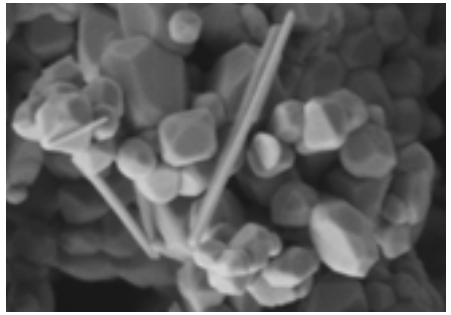
# Mechanistic studies

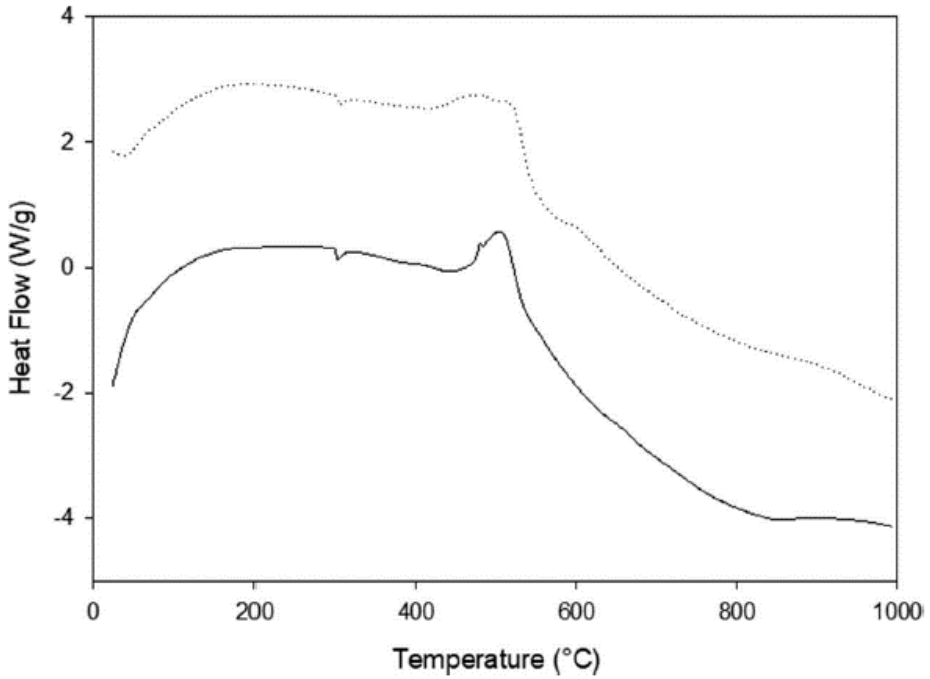
- Swap the primary oxidizer (Barium Chromate) with Strontium Molybdate
  - Similar particle size/structure
  - Initial screening via DSC indicated similar reaction behavior







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# Range of combustion velocities

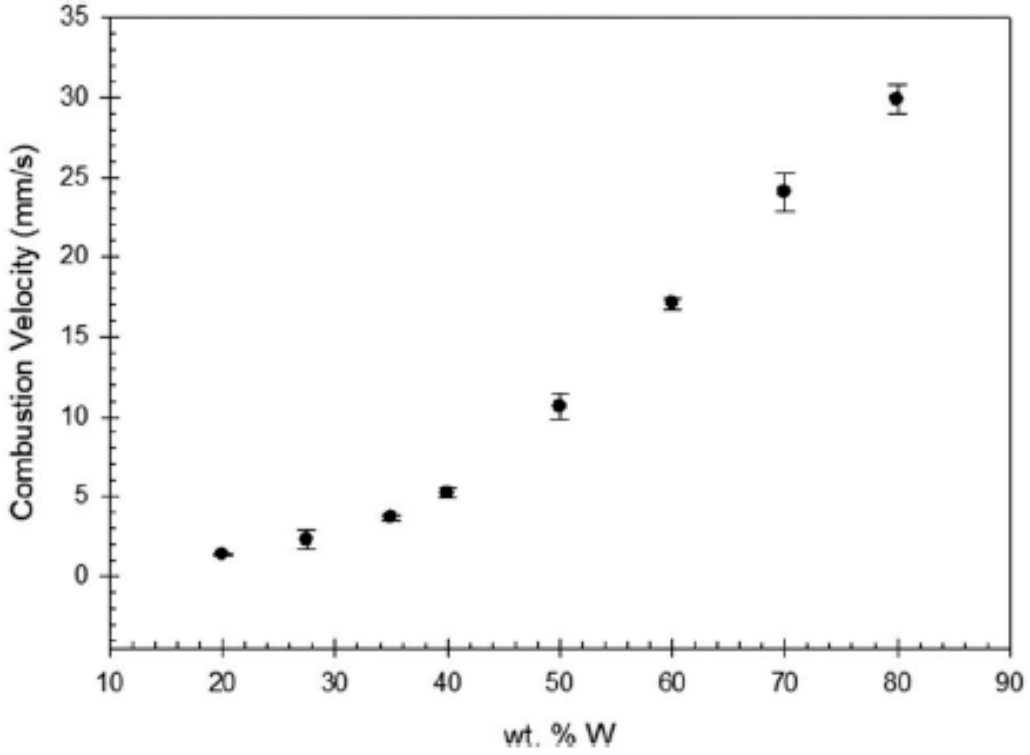


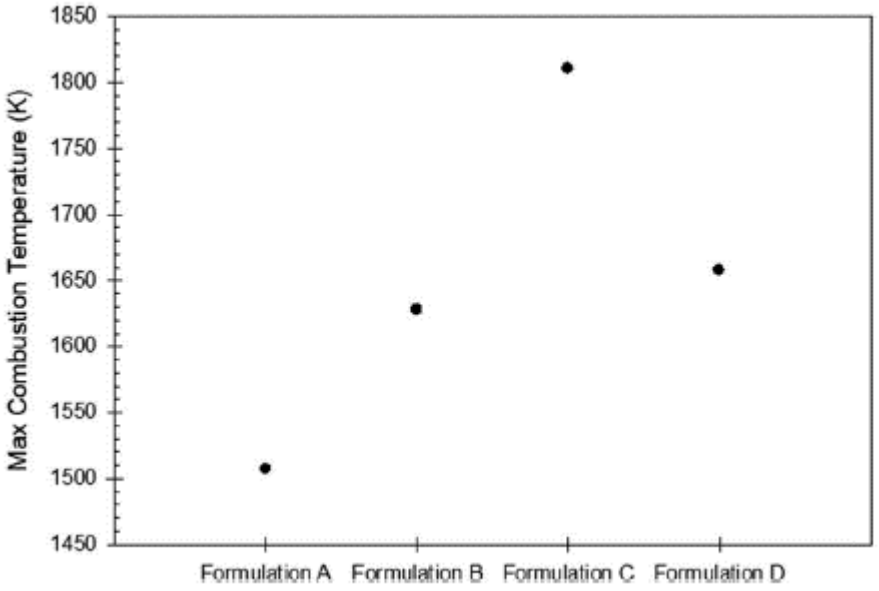

Figure 6. Combustion velocities of the W/$SrMoO_4$/10$KClO_4$/5DE system with a pellet diameter of 4.7 mm for formulations pressed into 4.7 mm ID Al housings.

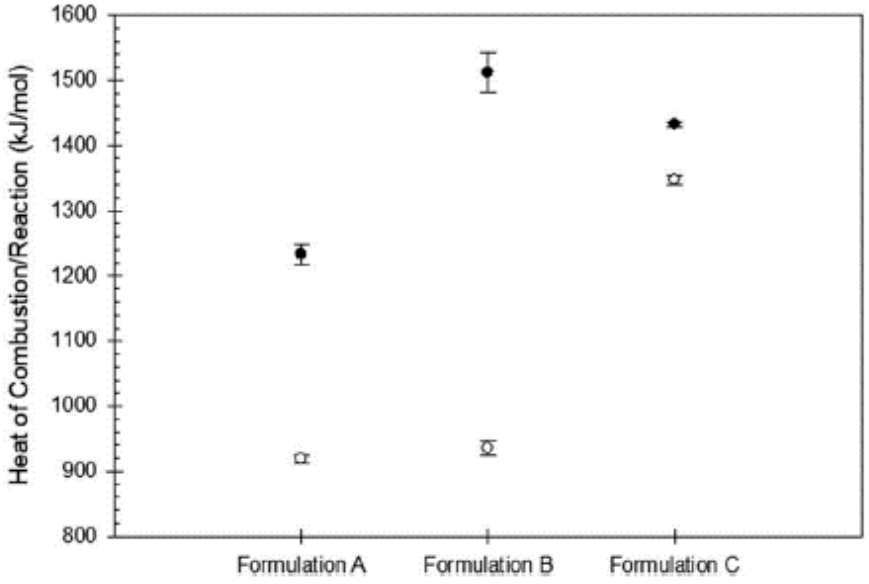
# Combustion temperatures/activation energies/etc.

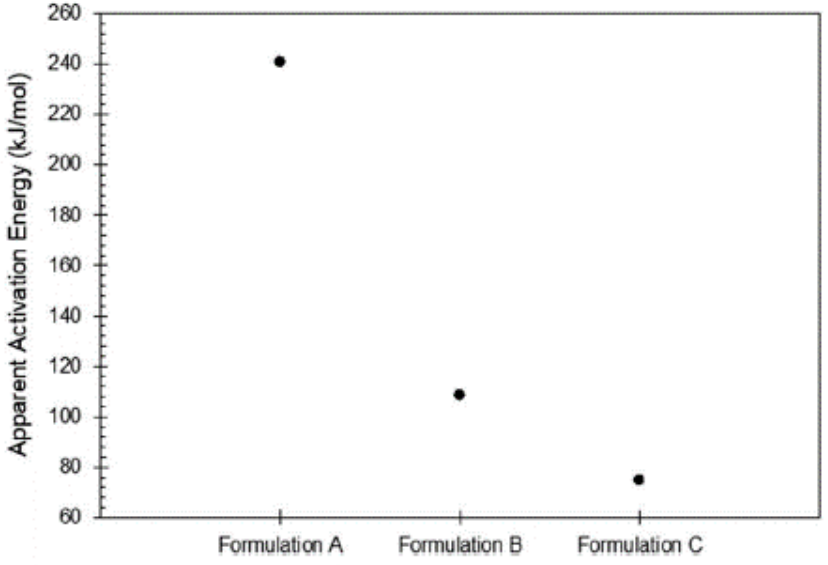
Table 2. Formulation list.

| Formulation | Composition [a)] |
|---|---|
| A | 27.5W/57.5$SrMoO_4$/10$KClO_4$/5DE |
| B | 42.5W/42.5$SrMoO_4$/10$KClO_4$/5DE |
| C | 35W/50$BaCrO_4$/10$KClO_4$/5DE |
| D | 60W/25$SrMoO_4$/10$KClO_4$/5DE |

a) In this notation, the numbers refer to percentages by mass (wt-%).



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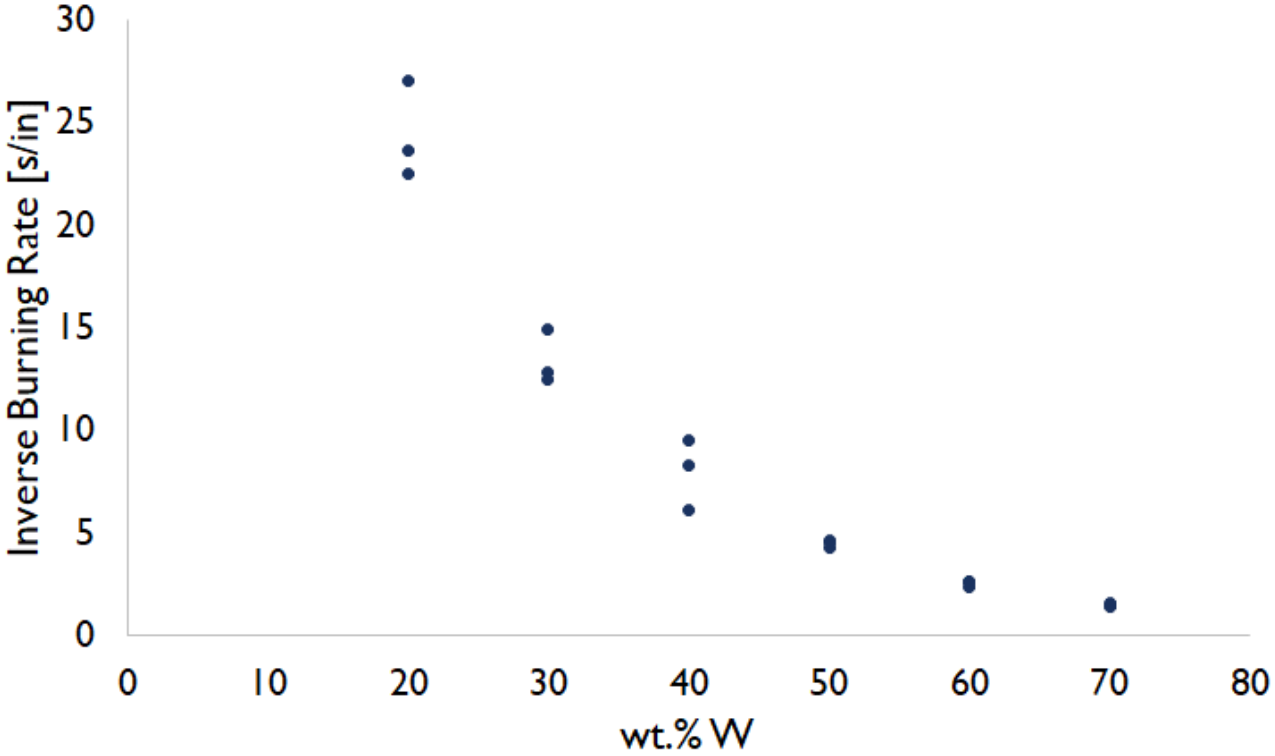
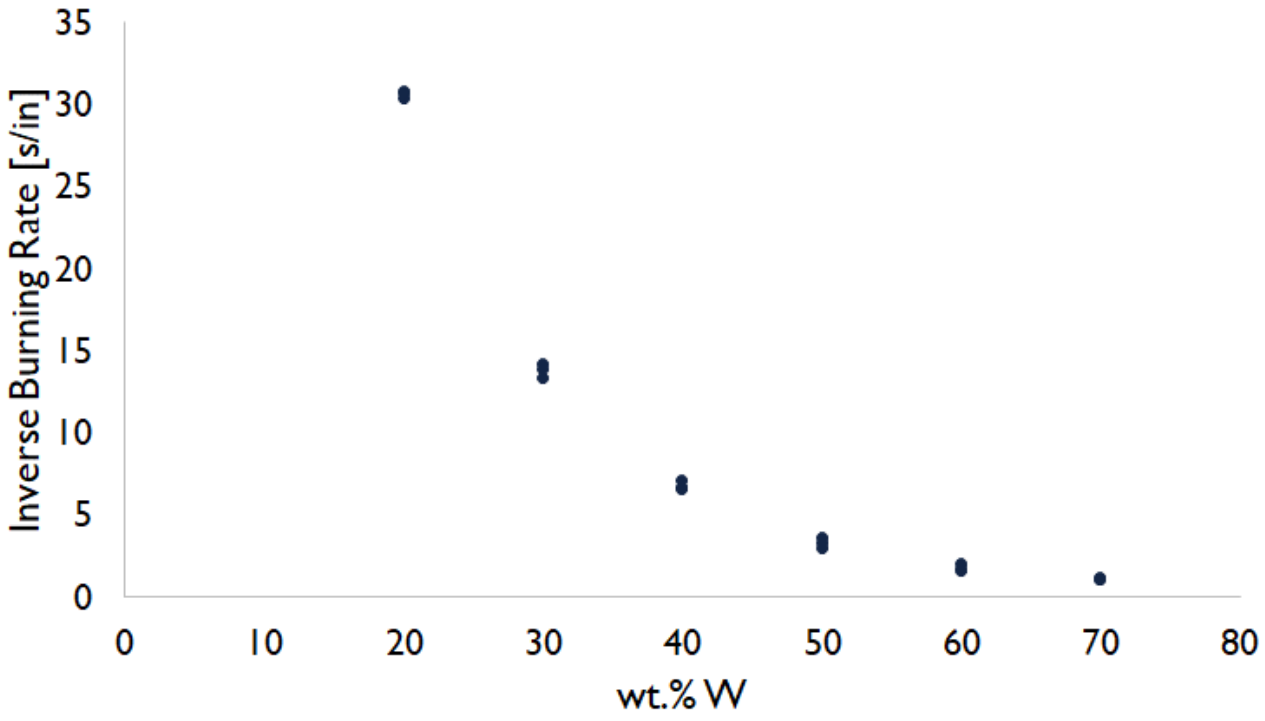
# What about just removing the chromate and keeping Barium (Barium Molybdate work)



# What about just removing the chromate and keeping Barium (Barium Molybdate work)

- Study the role of $BaCrO_4$ in the original W-delay
  - $W/BaCrO_4/KClO_4/DE$ (DE = diatomaceous earth)



# Burning Rate Comparisons

- We still don't have anything that compares to the versatility of the W-delay.

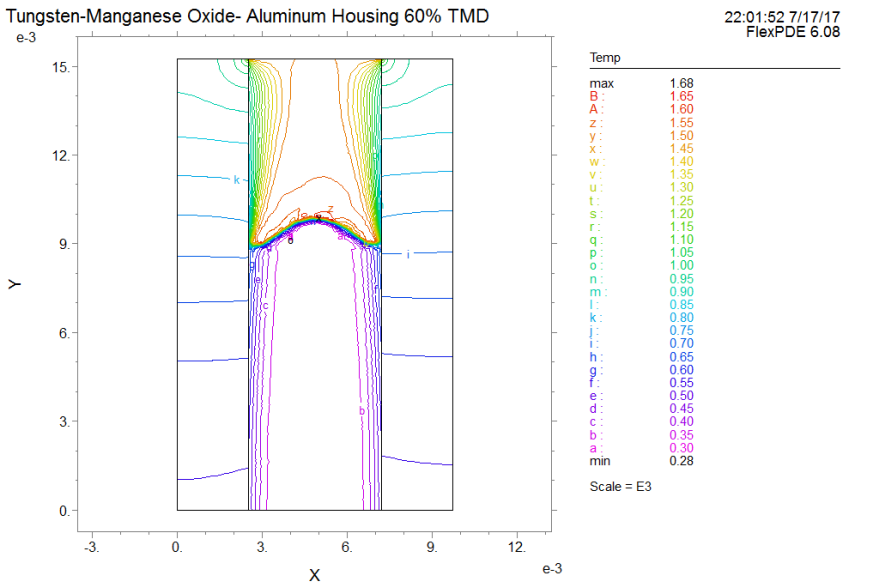
| Delay | Inverse burning rate |
|---|---|
| $W/MnO_2$ [14] | 5.5 -15.7 s/in (1.6-4.6 mm/s) |
| Traditional [1, 2] | 0.15 - 38 s/in (0.7-169.3 mm/s) |
| Strontium Molybdate [15] | 0.85 - 18.7 s/in (1.4-29.9 mm/s) |
| Barium Molybdate | 1.13 - 30.9 s/in (0.65-11.0 mm/s) |
| Al/Si/Strontium Molybdate (IMP's) | 1.3-11 s/in |

# Outcomes

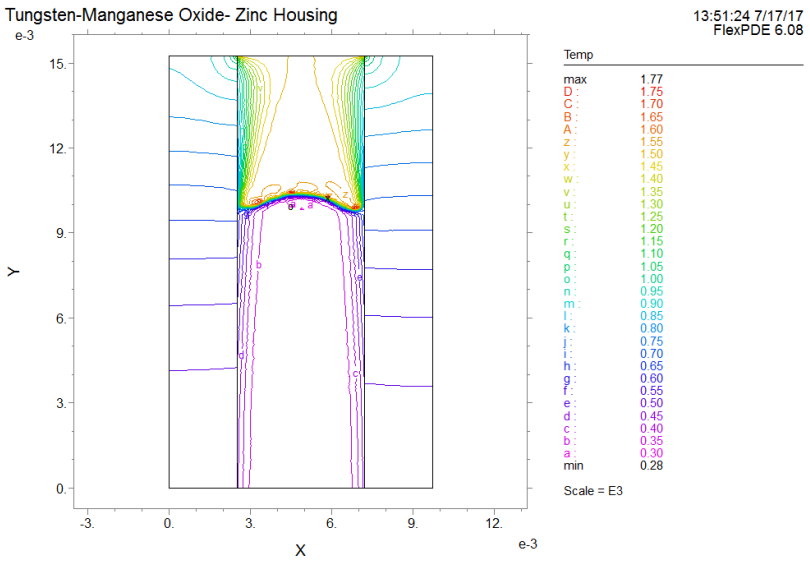
- Developed environmentally benign delay formulations for both the M201A1 and M213/M228 fuzes
  - Compounds are readily available from domestic sources
  - Compositions tested in fuze hardware at cold, ambient, and hot temperatures
  - Measured delay times meet military specifications
- A new ignition/output charge was developed to replace the currently used A1A igniter *and* Ti/$KClO_4$ output charge
  - A ternary mixture of Ti/$MnO_2$/polytetrafluoroethylene used in BOTH the input and output charges
  - This single system replaced *both* A1A and T/$KClO_4$
  - This igniter system was used in both the input and output for ALL of our M201A1 and M213/M228 fuze testing

# Modeling Efforts

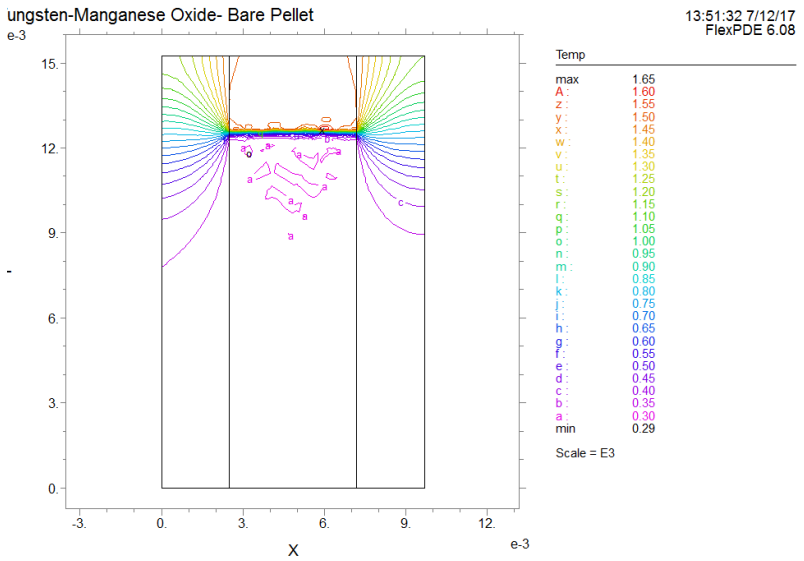
- Both IMP and SD Mines have modeled these reactions in various housings
  - Allows predictive capability to assess propagation rates as a function of porosity and housing material




aluminum housing_tungsten_manganese oxide 60% TMD: Cycle=19676 Time= 2.0000 dt= 9.8456e-5 P2 Nodes=3515 Cell
Integral= 0.107629




zinc housing_tungsten manganese oxide 60% TMD: Cycle=16251 Time= 1.7500 dt= 1.7513e-4 P2 Nodes=3258 Cells=159
Integral= 0.097964




·D geometry full cross-section_bare pellet_tungsten_manganese oxide: Cycle=7574 Time= 0.7999 dt= 1.1174e-4 P2 Nod
tegral= 0.074877

# Additive Manufacturing Routes for Configurability

- Very recently both SD Mines and IMP demonstrated AM as a potential route for these more environmentally benign formulations.
- Allows configurability of path/redundancy/reduced operator handling.

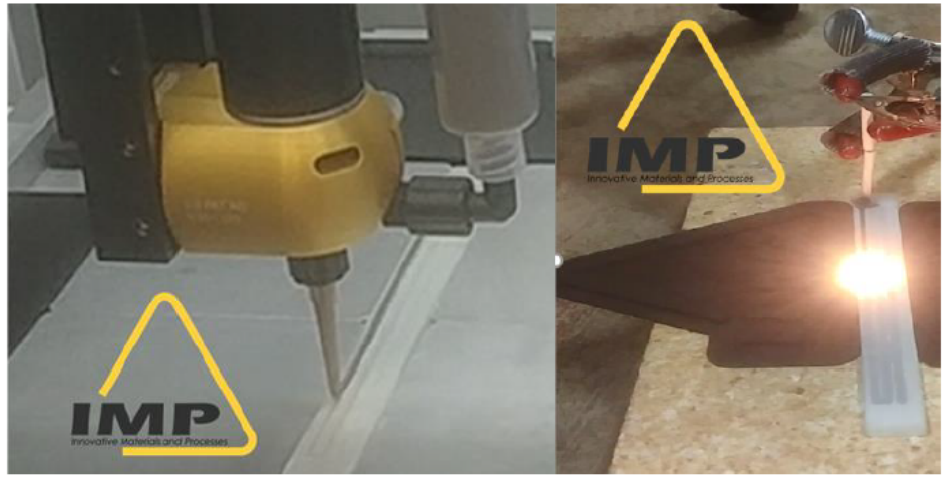
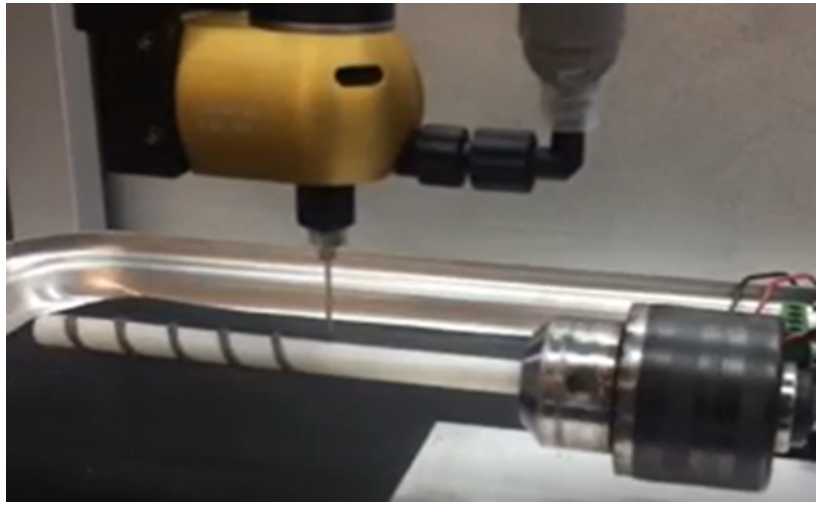
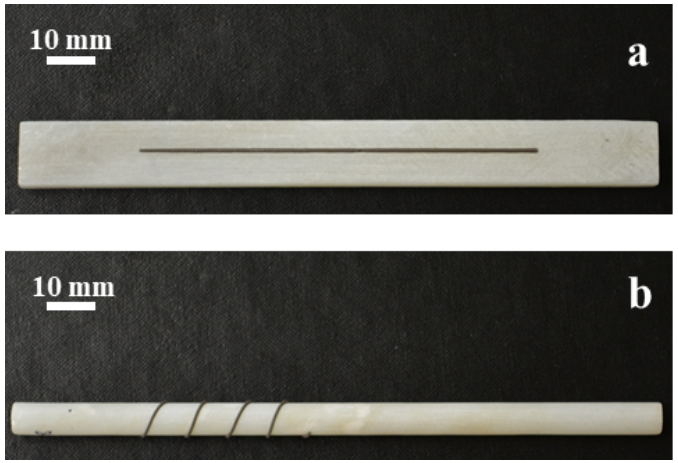
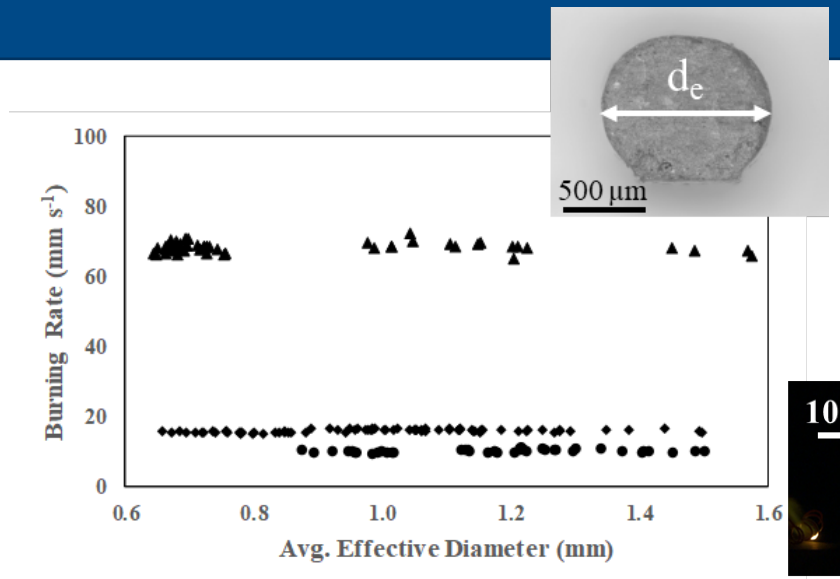


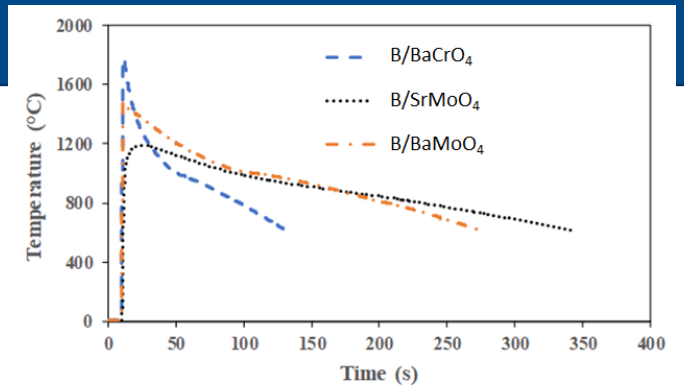

***Figure 7.*** *Photograph of automated system used by IMP for AM deposition of energetic slurries (left) and photograph of IMPs AM deposited delay propagation deposited on soapstone substrate (right).*

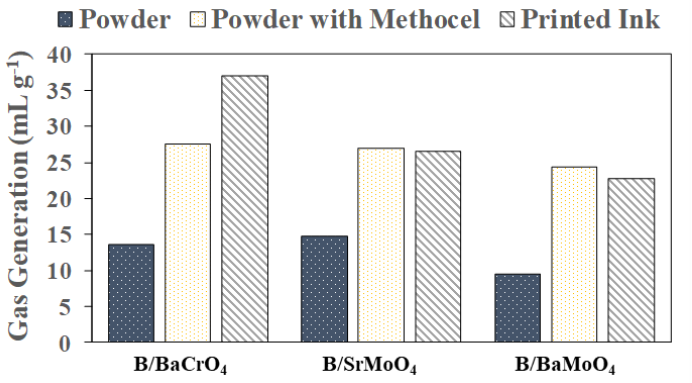


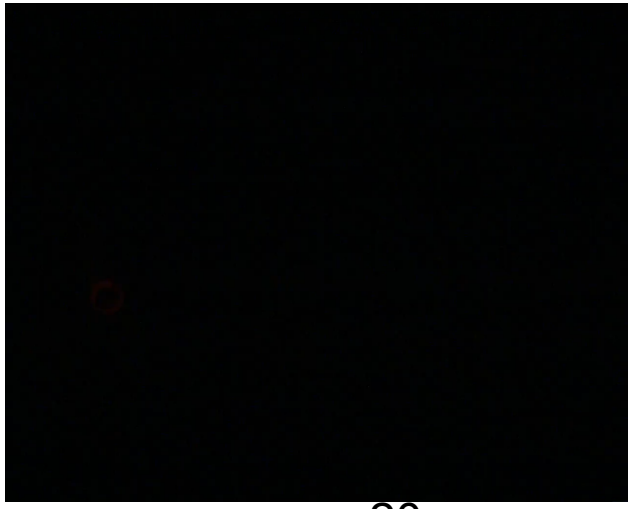
# Boron based formulations

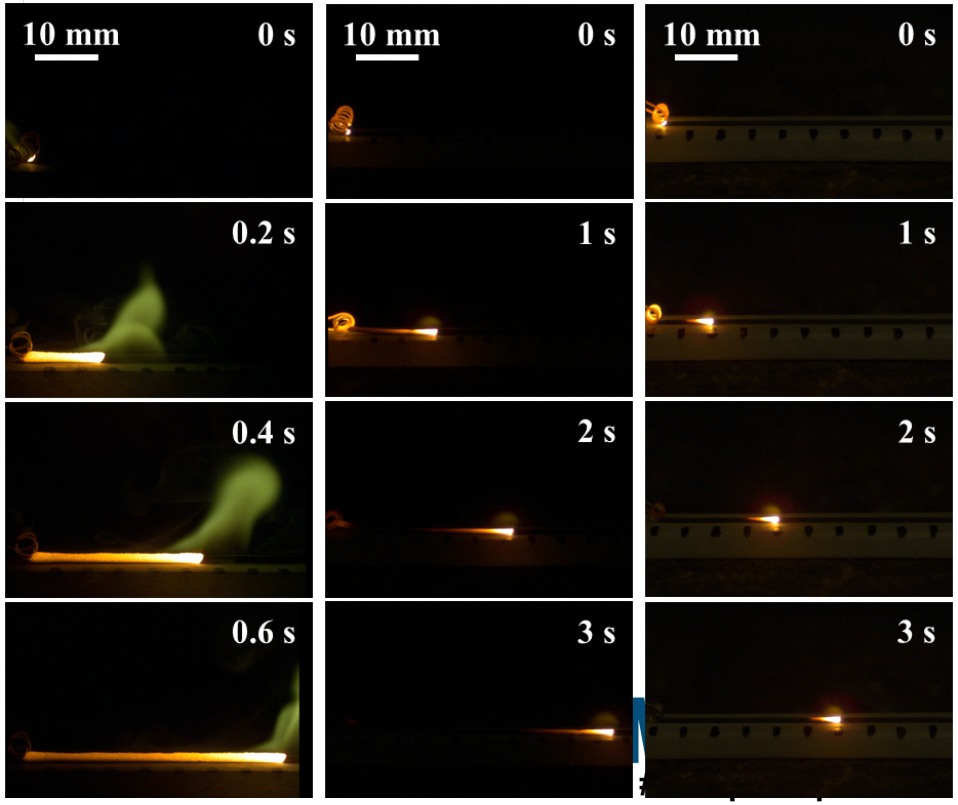


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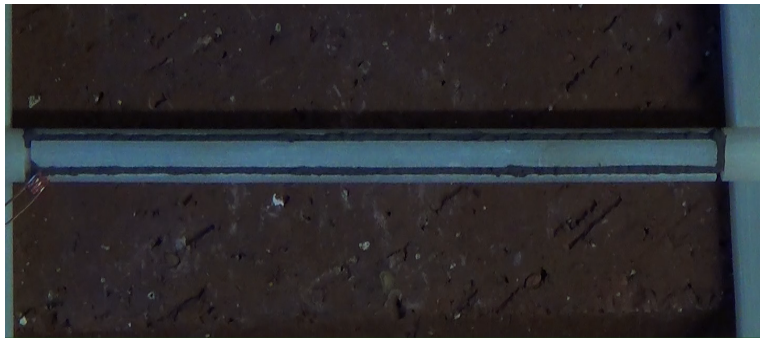
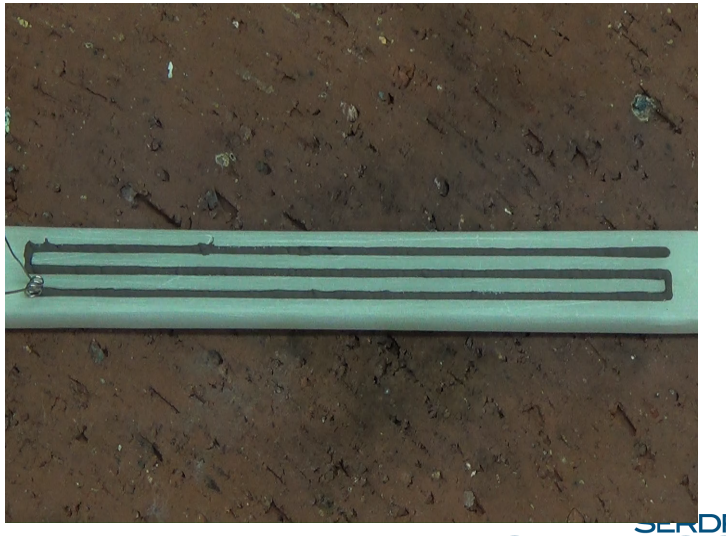
# Turning capability on circular and flat geometries

B/Barium Chromate

B/Barium Molybdate





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# Current Trends and Moving Forward

- There is still the need for robust formulations that can meet the time requirements and be reliably manufactured
- New environmentally benign oxidizer that can serve the role of potassium perchlorate should be studied with the molybdates to expand the range of burning rates
- Boron based systems or Zr based systems this jump start is not necessary as the molybdates readily oxidize them
- ***Current formulations can move forward for implementation which is a huge success***

# Acknowledgements


- Funding for this work was provided by the Strategic Environmental Research and Development Program (SERDP), Project WP-2518, "Environmentally Sustainable Gasless Delay Compositions for Fuzes"