RDECOM

Experimental Deviations from Conventional Critical Temperature Models for Non-ideal Explosive Formulations

Dr. Brian D. Roos
U.S. Army Research Laboratory, Aberdeen Proving Grounds, MD

Phil Samuels, Kenneth Lee, Crane Robinson
U.S. Armament Research Development and Engineering Center, Picatinny Arsenal, NJ

Dr. Barry Fishburn (Janet's Consulting), Dr. Pai Lu (SAIC)
Picatinny Arsenal, NJ

Curtis Teague, Brian Alexander, Virgil Fung, Alberto Carrillo
BAE Systems, Holston Army Ammunition Plant, TN

2009 IMEMTS, Tucson, AZ
11-15 May 2009

Thermal Hazards – Why is it important?

- Prolonged exposure of energetic materials to elevated temperature
  - Produce some level of decomposition
  - Decomposition generates heat
  - Heat dissipates to surroundings

- Self-heating
  - Rate of heat generation exceeds losses to the environment
  - Non-catastrophic
    - ✓ **Simple non-violent decomposition**
    - ✓ **Reaction may be stopped if heat source removed**
    - ✓ **Over time may escalate into catastrophic reaction**
  - Catastrophic
    - ✓ **Thermal runaway or “point of no return”**
    - ✓ **May result in deflagration, explosion or detonation**

Critical Temperature

- Critical temperature, T_c
  - Defined the lowest constant surface temperature at which a given material of a specific shape and size will catastrophically self-heat
  - Utilized to assess the hazards associated with processing and loading of melt cast explosives
  - Parameter scales with charge size
    - ✓ Mass
    - ✓ Diameter
  - Other relationships for critical temperature
    1. Decreases as size increases
    2. Decreases as Surface/Volume decreases
    3. Determined by most rapid heat-producing reaction
    4. Can *usually* be predicted

Potential Problem

Novel Explosive Formulations

- Developed to meet Insensitive Munition (IM) requirements
- Non-ideal explosives
  - **Non-conventional ingredients (nitrate salts, NTO, DNAN)**
  - **Larger critical diameters**
- Responses to thermal stimuli
  - **Often very mild**
  - **Vary from critical temperature models (Observed with PAX-21)**

What is "catastrophic"

- Catastrophe:
  - an extremely large-scale disaster (wikipedia.com)
  - a sudden and widespread disaster (dictionary.com)
  - a sudden violent change (American Heritage dictionary)
- Can the mild "events" from some non-ideal explosives be described as "catastrophic?"

Objective

- Investigate the applicability of conventional thermal models and standard tests utilized for explosive qualification
- Demonstration for non-ideal explosives
  - Evaluate Non-ideal Insensitive Explosive Formulation (NIE)
    - ✓ **Melting point of 94.5°C**
    - ✓ **Likely be processed at 105 to 110°C**
  - Critical temperature
    - ✓ **F-K and Semenov Models are often too conservative**
    - ✓ **Conventional scaling factor does not apply**
  - Processing of NIE formulation is
    - ✓ **Safe to process and handle on large production scales**
    - ✓ **Despite the hazards incorrectly predicted using the traditional conservative models**

Technical Approach

- Conduct experiments at multiple scales
  - Obtain required parameters and variables
  - Conventional prediciton models
  - Milligram-scale (Henkin)
  - Gram-scale (thermal screening unit and small-scale cookoffs)
  - Kilogram-scale (1-L Cookoff)
  - Multikilogram-scale (12-Liter Cookoff)
- Combine and compare results
- Make assessment

Predictive Models

- **Frank-Kamenetsky (F-K) Model**
  - ❑ **Assumes conductive heat transfer**
  - ❑ **Worst-case predictive model under the limitations of pure conduction**
  - ❑ **Heat flow from reacting mass to establish temperature gradient**
  - ❑ **In essence, this scenario is the result of a viscous melt with failed stirring**

$$T_m = \frac{E}{R \ln \dfrac{A^2 \rho QZE}{T_m^2 \lambda \delta R}}$$

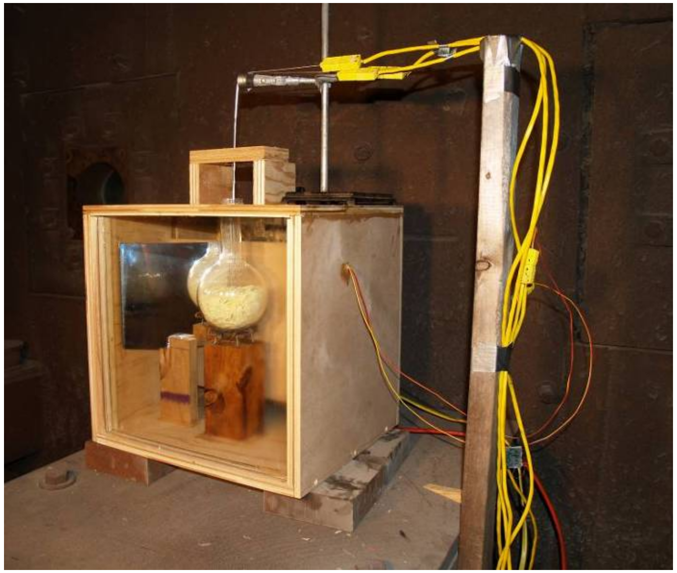
- **Semenov Model**
  - ❑ **Assumes perfect stirring**
  - ❑ **Convective heat flow**
  - ❑ **Uniform temperature in the reacting explosive**
  - ❑ **Heat lost to surroundings by Newtonian cooling with thermal gradient at vessel boundary**

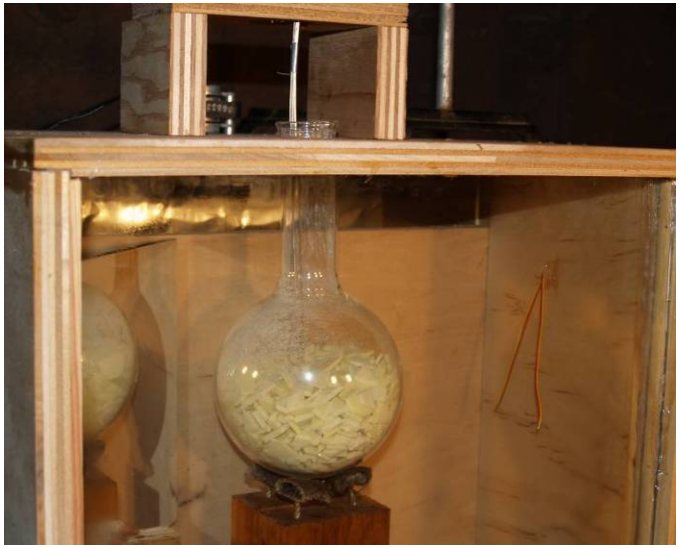
$$E/T_m = R \ln\left[\frac{V \rho QZE}{S \alpha R T_m^2}\right]$$

- ***R*** **is the gas constant**
- ***Q*** **is the heat of decomposition**
- ρ **is the density**
- ***E*** **is the activation energy**
- ***Z*** **is the frequency factor**
- λ **is the thermal conductivity**
- ***A*** **is the radius of the sphere, cylinder, or slab**
- δ **is the shape factor**
  - ❑ **0.88 for an infinite slab,**
  - ❑ **2.00 for a squat cylinder**
  - ❑ **3.32 for a sphere**
- ***V*** **is volume of the charge**
- ***S*** **is the surface area of the charge**
- α **is the heat flow coefficient at the boundary**
  - ❑ **Glass: 0.0105-0.0135 cal/(cm^2-s-°C)**
  - ❑ **Aluminum: 0.0085 cal/(cm^2-s-°C)**
  - ❑ **Steel: 0.0022 cal/(cm^2-s-°C)**

1-L Slow Cookoff Test

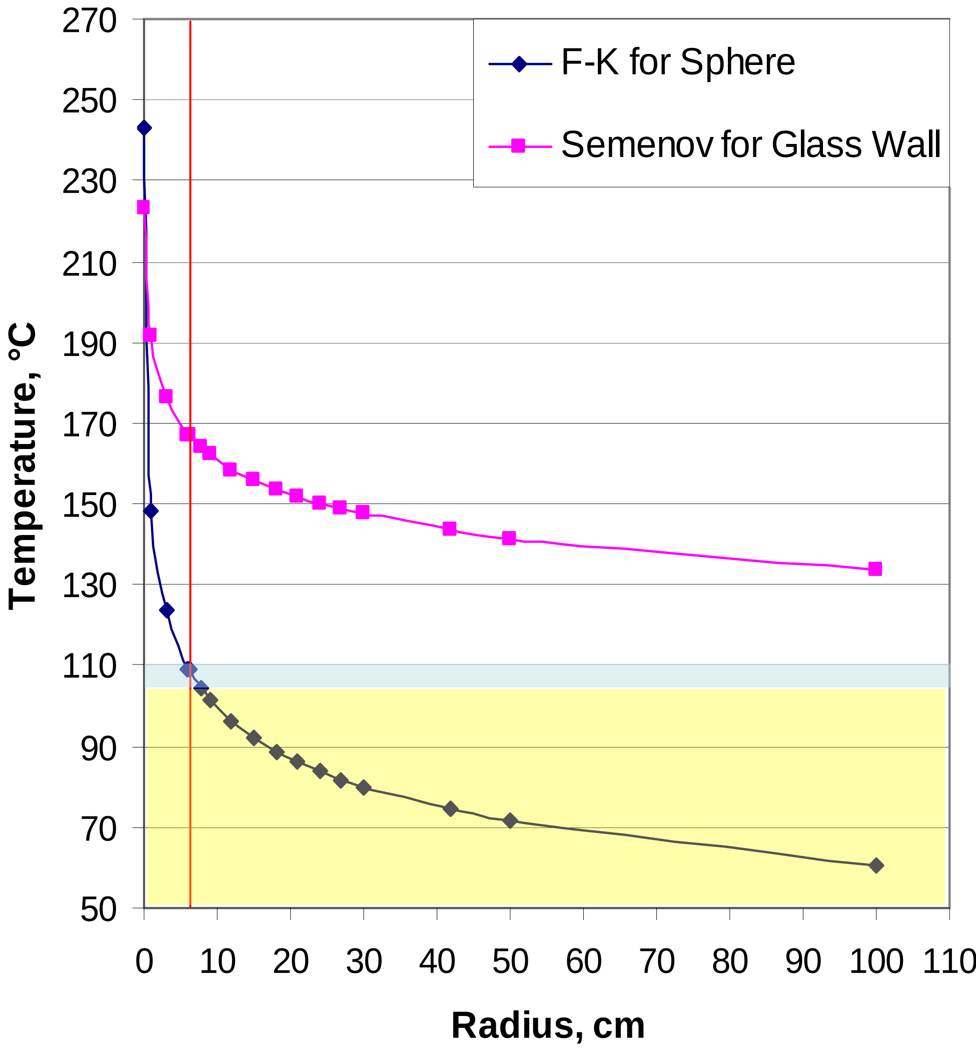
- Dual Purpose
  - **Validate accuracy of self-heating predictions for larger geometries**
  - **Provides measure of reaction severity**
- Preparation
  - **1-L Pyrex round-bottom flask containing sample and thermocouple bundle**
  - **Disposable plywood oven**
    - ✓ **Resistive heater and circulating fan**
    - ✓ **Tempered oven glass window for video observation**
- Test
  - **Sample preconditioned at ~10°C > melt point**
  - **Heat oven at 3.3°C/hr**
  - **Thermocouple data recorded**
  - **Procedure continues until decomposition, explosion, or cracking of the flask**



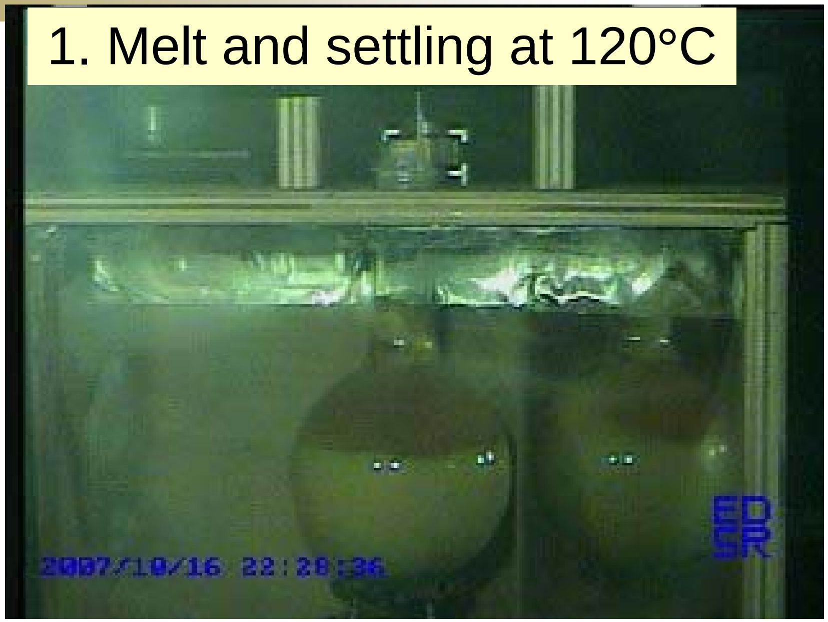


Predictions for 1-L Cookoff Scenario

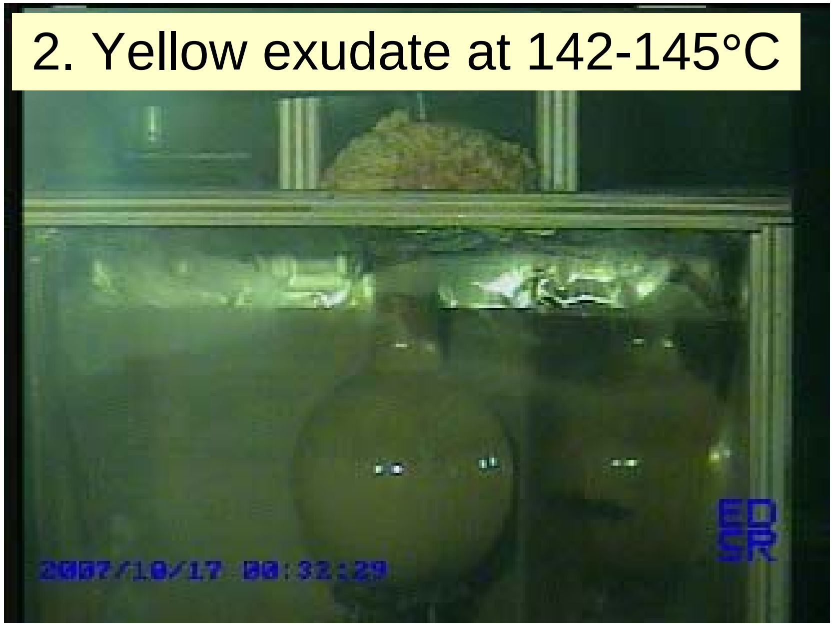
- Henkin time-to-explosion
  - Sealed, confined sample
  - T_c of 220°C
- F-K
  - For 1-L (r=6.1cm), predicts 108°C
  - Extrapolates to T_c below melt point of formulation at large diameters
- Semenov
  - For 1-L, predicts 166°C
  - Extrapolates to t_c of 134 at large diameters
- Large scale production meets 30°C safety margin ***if*** NIE follows Semenov closely
- F-K predicts T_c well below melt point!



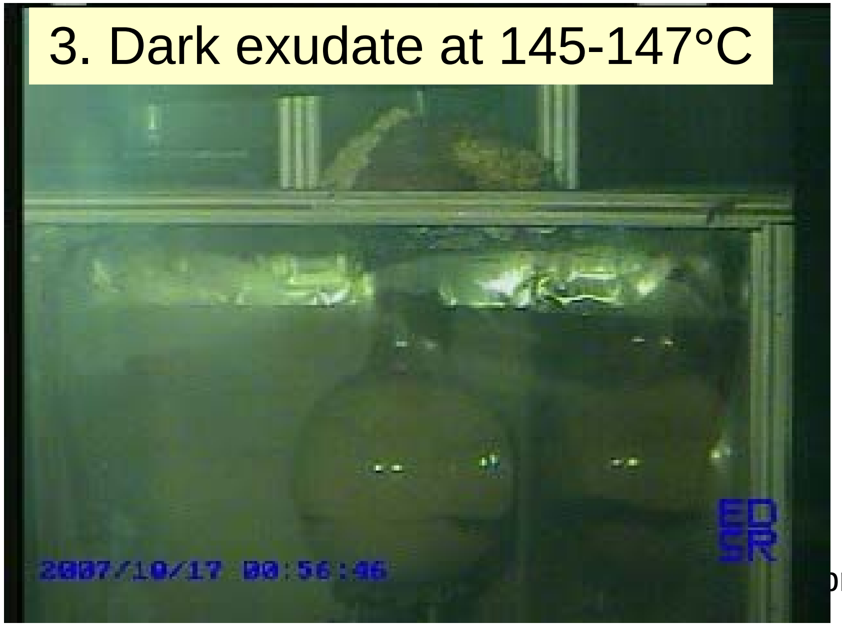
Video Stills from 1-L Cookoff



1. Melt and settling at 120°C



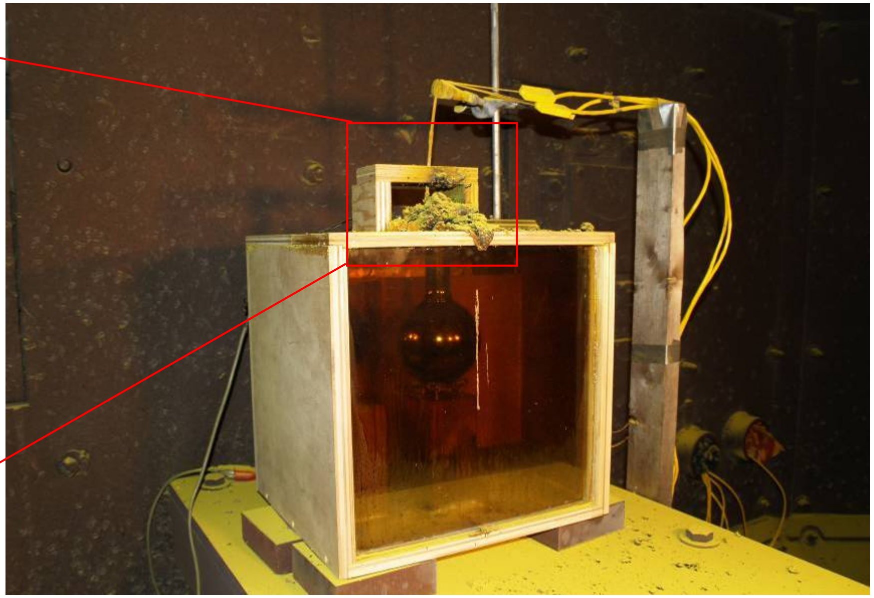
2. Yellow exudate at 142-145°C



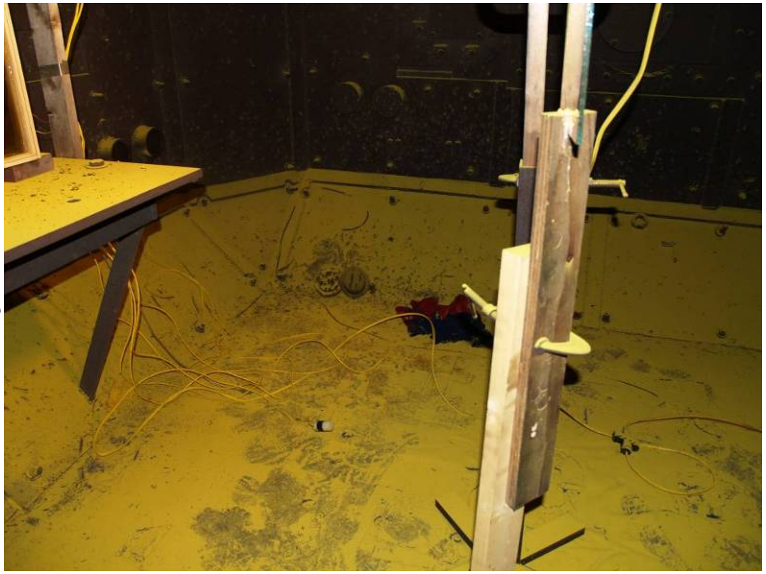
3. Dark exudate at 145-147°C

4. Fuming at 147-149°C

Post-test Analysis for 1-L Cookoff

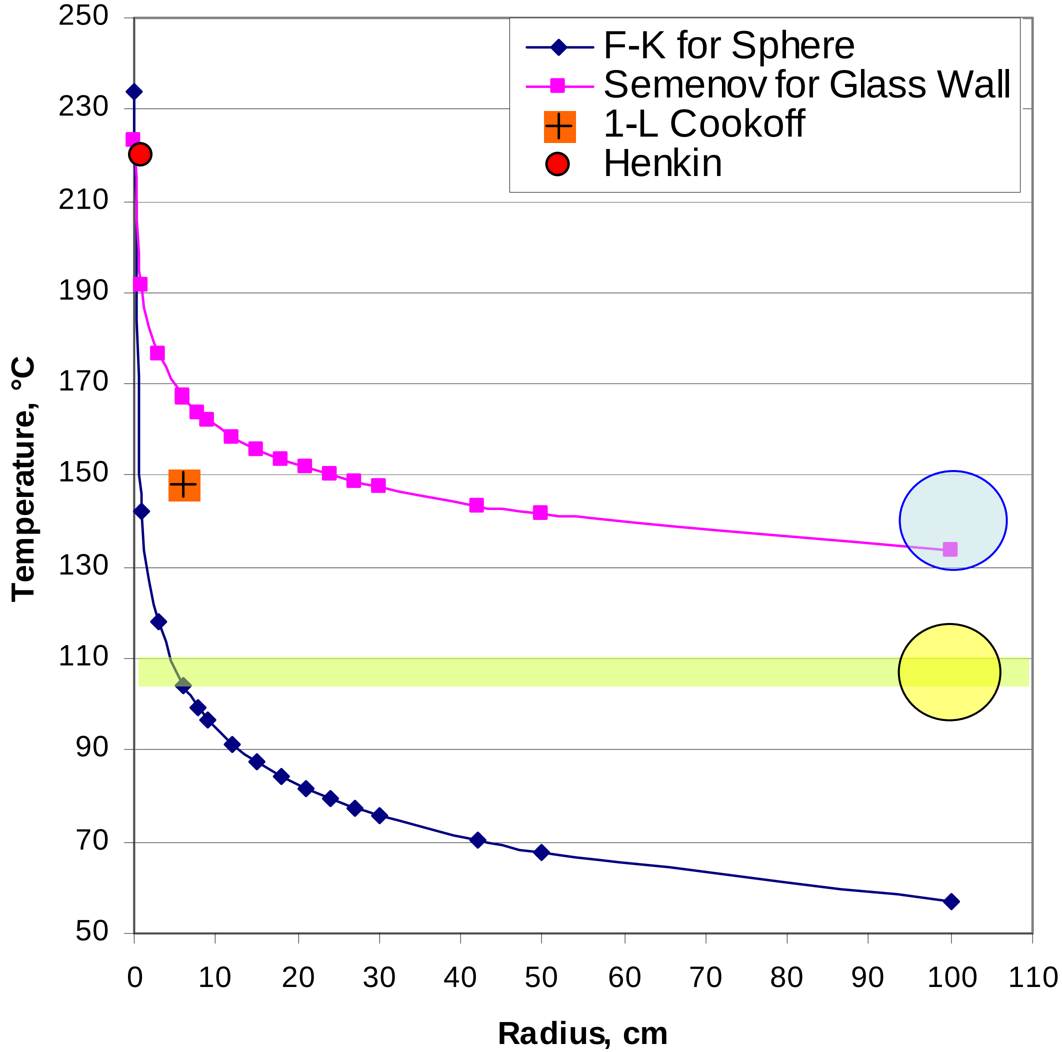


- Exudate on top of oven around flask opening
- Oven intact
- Flask discolored, but undamaged
- Fine yellow coating on all horizontal surfaces
  - **DNAN**
  - **Confirmed by DSC**



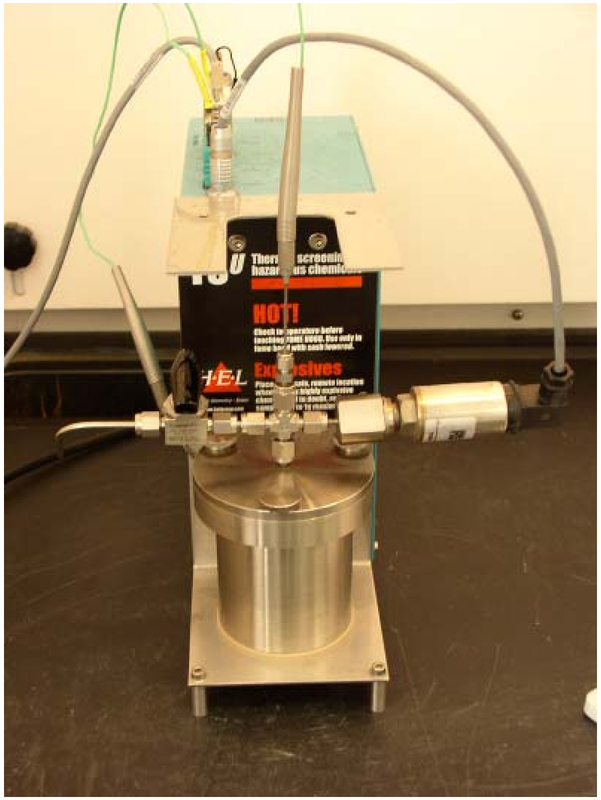
Concerns over Predictive Models

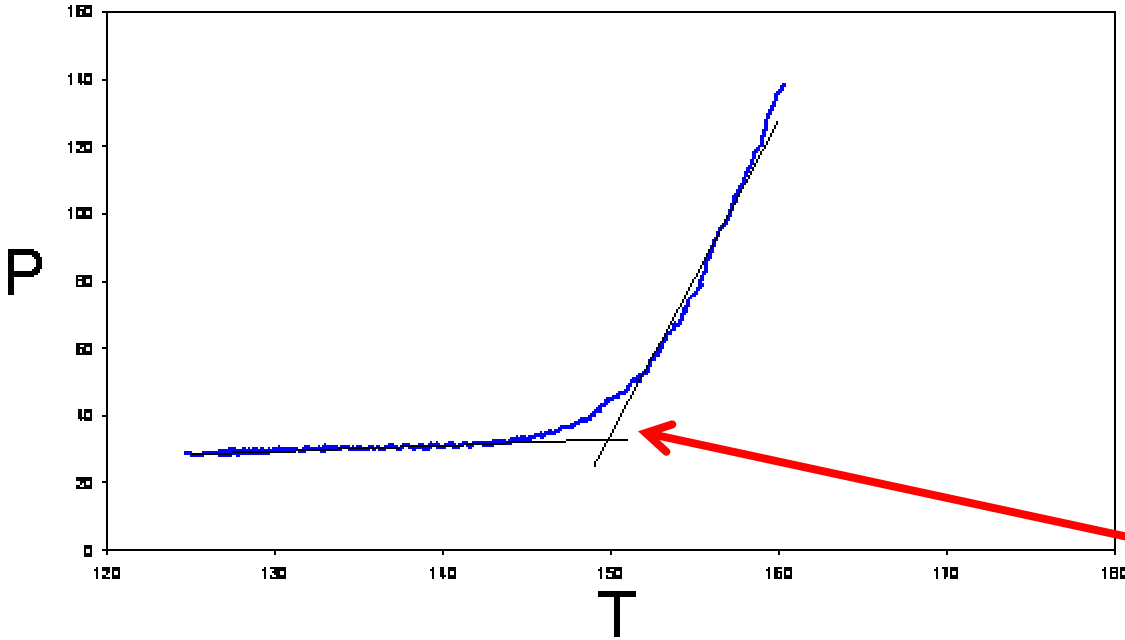
- Processing at 100-105°C
- If a curve is drawn based upon deviation from F-K and Semenov
    - Yellow circle
    - T_c between 95 and 115°C
- Preferred margin
    - Blue Circle
    - T_c in range of 130-150°C
- Further Testing Required



Thermal Screening Unit

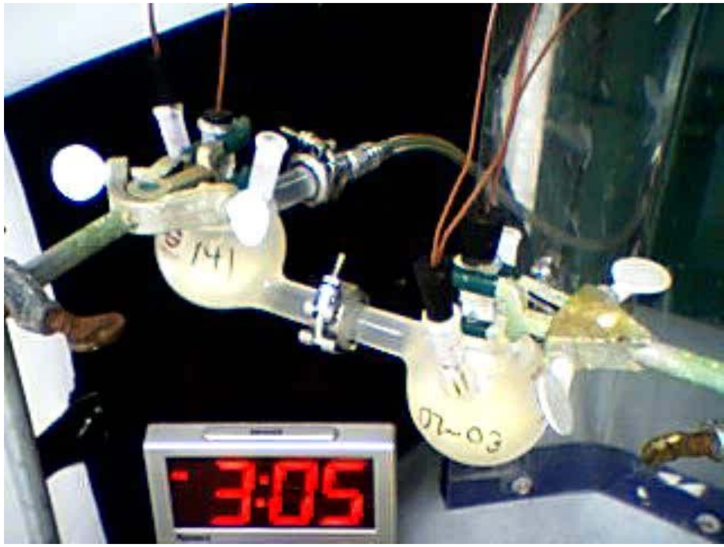
- Computer controlled temperature ramp (3.3°C/hr)
- Records several parameters (temperature pressure, time) during experiment
- Uses Hastelloy Bombs (ARC type) with Type K thermocouples, pressure transducer





- Pressure spike and small exotherm at 150°C
- Inflection point at 150°C

Reduced Scale Cookoff Experiments

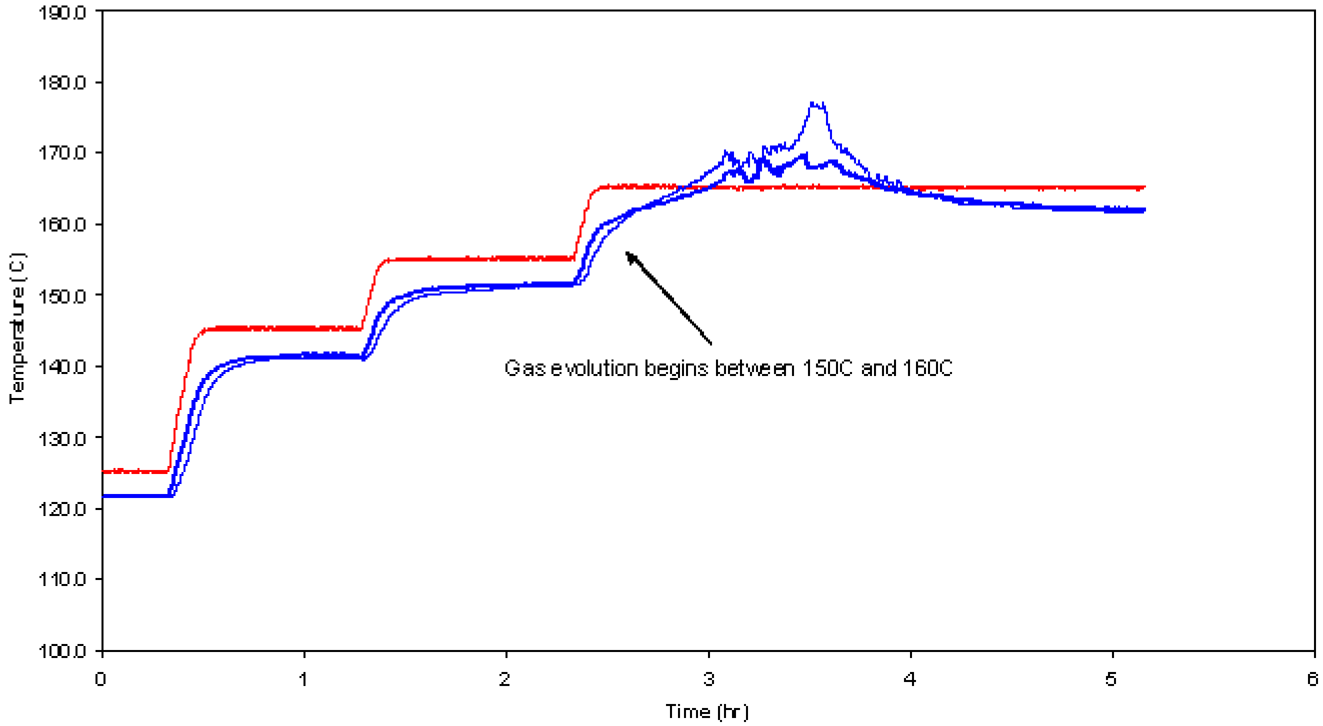


- Test Setup
  - Silicone oil bath (Recirculation)
  - Three Neck Jacketed Round Bottom Flask
  - Thermocouple Data Recorder (K Type)
  - 2 Thermocouples per sample (Center,Side)
  - 2 Samples run simultaneously per experiment
- Test Method
  - Limitation: Non programmable bath
  - Heated at 120°C and held for 2 hours
  - Ramped in increments of 10°C and held for 1 hr
  - Cool down was not initialized until sample returned to bath temperature

- BAE used 3 varied mass/volume ratios: 15g/50ml, 30g/100ml, 30g/50ml
- ARDEC conducted similar test using 20g in 25ml flask, but at ramp of 3°C/hr

Reduced Scale Cookoff Test Data

- BAE Small Scale Cook Off Tests
  - **Thermal event observed between 150 and 160°C (at all 3 scales)**
  - **Very mild exotherm “event”; gentle rising and cooling back into thermal equilibrium with the bath temperature**



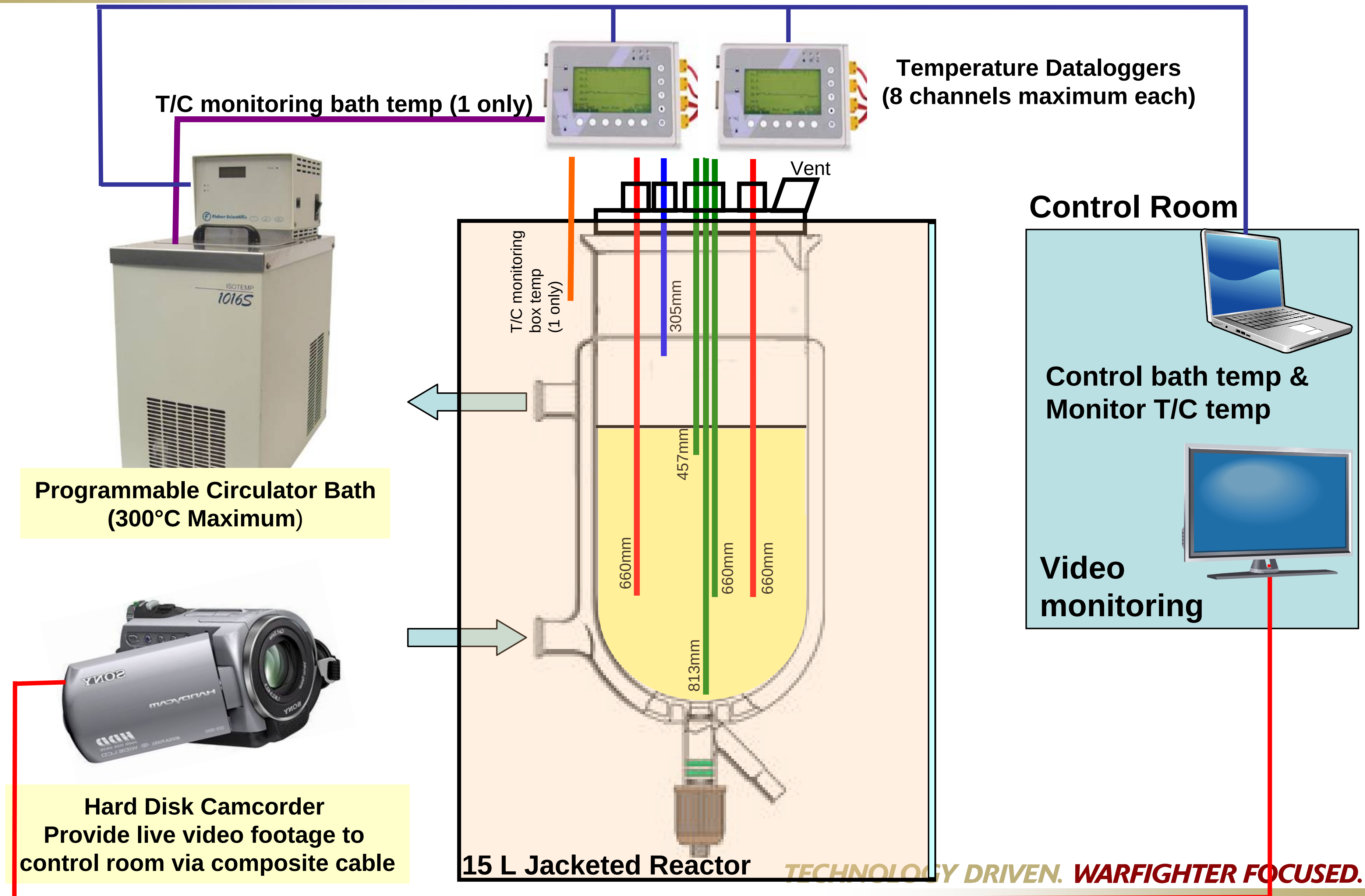
- ARDEC tests observed discoloration at 140°C and self-heating at 145°C using a 3°C /hr ramp rate

Confirmation with Larger Tests

- **Cookoff tests**
  - **Multiple scales (1-L and less)**
  - **Similar self-heating temperature 145-155°C**
  - **Mild Response**
  - **Conduct scale up testing in large vessel**
  - **What about larger scales?**

- **12-Liter cookoff test**
  - **Conduct in 15-L jacketed reactor**
  - **Heat with silicon oil at rate of 3.3°C/hr**
  - **Performed by BAE at Holston with Army consultation**
  - **Further demonstrate**
    - ✓ **Reaction is independent of size**
    - ✓ **F-K or Semenov models predictions are too conservative**
  - **Geometry more comparable to production melt kettles than 1-L spherical flask**

12L Cookoff Configuration



Video Stills from 12-L Cookoff Test

Circulating Bath = 160 °C
Melt Temperature = 150 °C

Circulating Bath = 162 °C
Melt Temperature = 163 °C

Circulating Bath = 163 °C
Melt Temperature = 170 °C

T_{melt} (°C)	Observation
135	Bubbling, discoloration, and convection
140	Onset of self-heating, vigorous mixing
150	Smoke, expulsion of material Sample heating at 3x the ramp of the circulating bath
>150	Heating continued; Majority of explosive expelled T_{melt} increased to greater than 300°C

12-L Cookoff Post-test Analysis

- Coating of fine yellow powder
- Considerable ejected material and splatter
- No evidence of burning or equipment damage

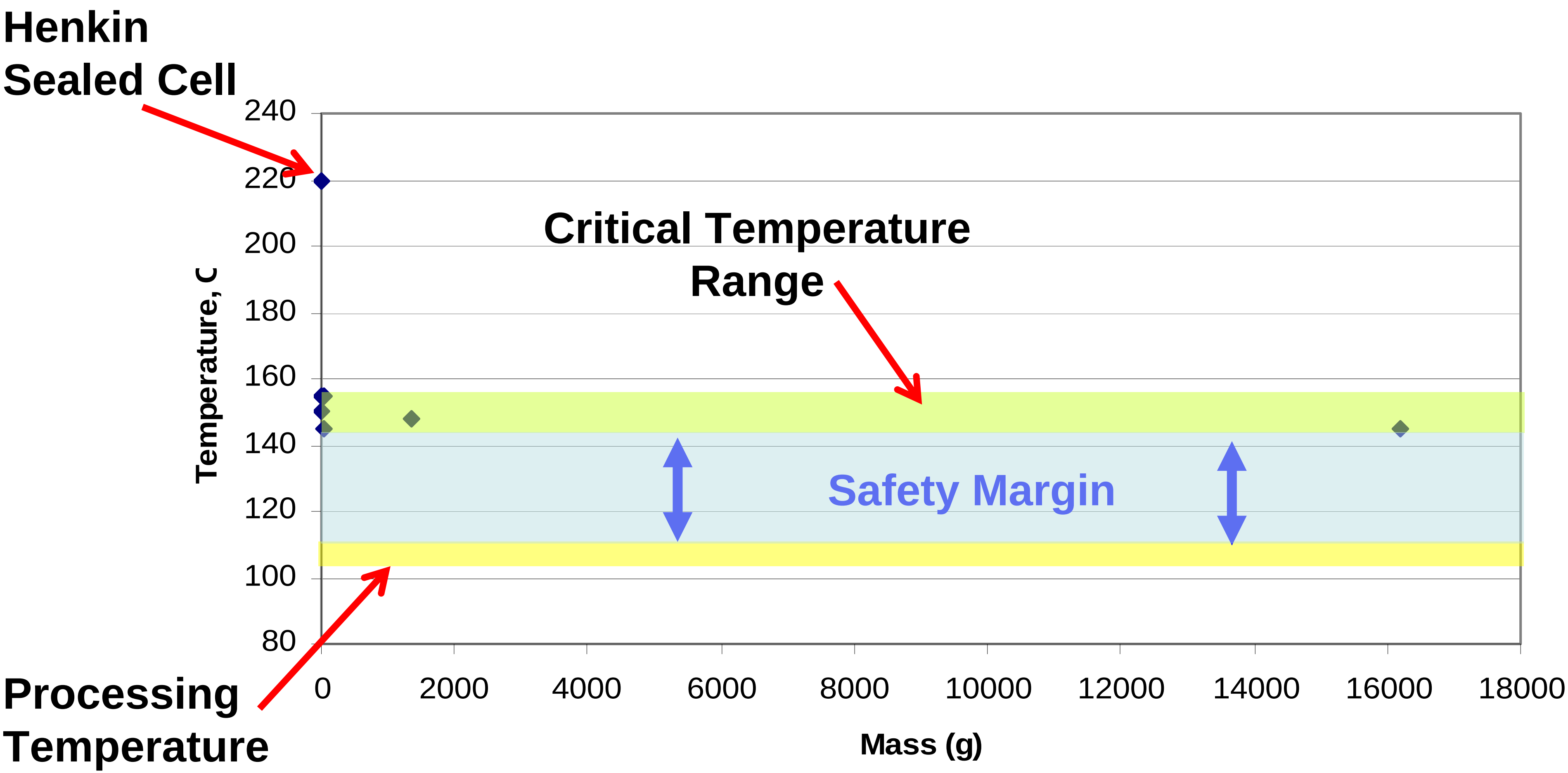
- **Reactor**
  - Undamaged
  - Coated in ejected material
- **Thermocouples still functional**

Comparison of 1-L and 12-L Cookoff Tests on NIE

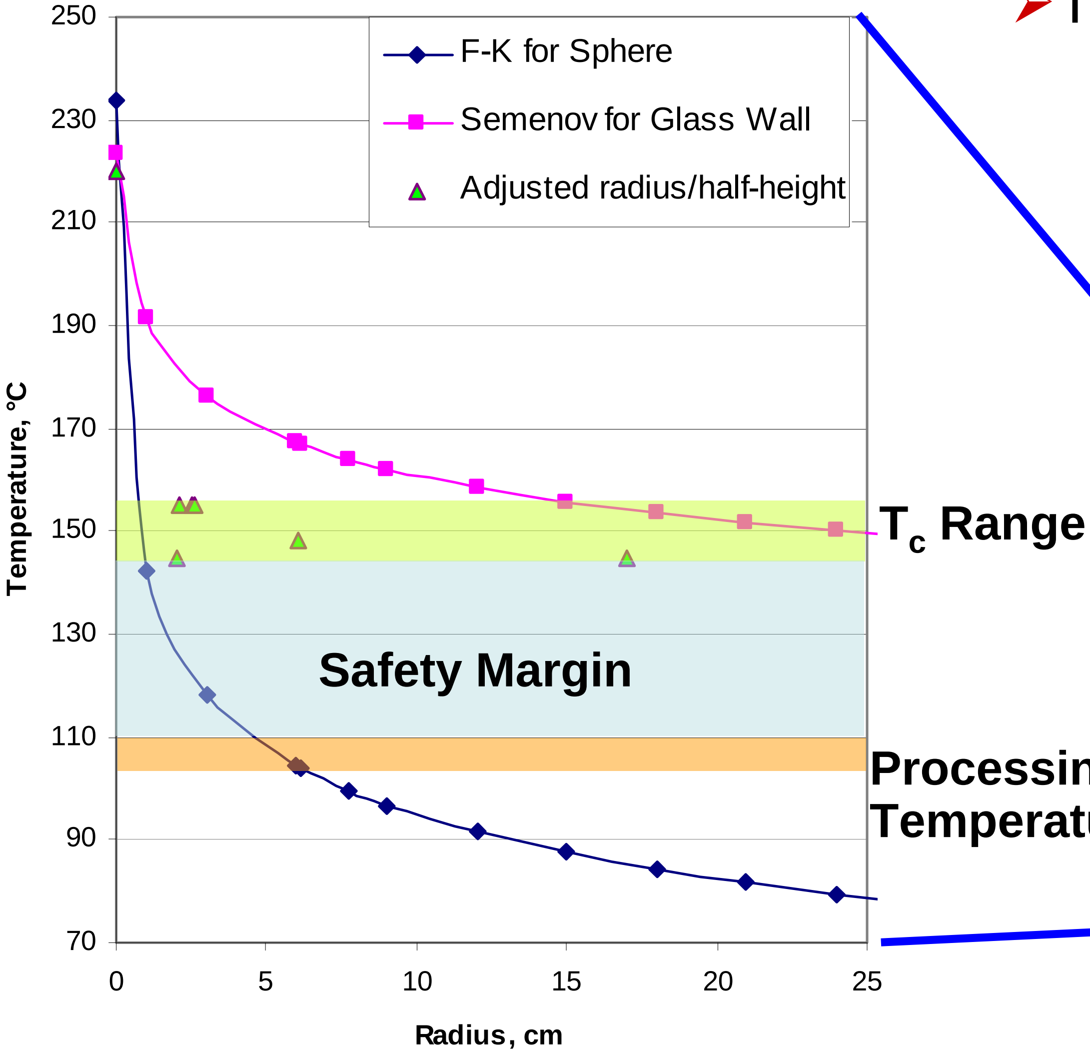
Set-up/Observation	1-L Test	12-L Test
Excess volume/head-space	Minimal	>25%
Venting	1 small flask neck	1 large, several small ports
Heating	Air	Silicone oil
Mixing/Convection	None	Significant
Ejection	Slow exudation	Rapid expulsion
Source of Self-heating	From center	Towards top
Temperature of self-heating	148 °C	145 °C
Violence of Event	None	None
Post-test	Fine yellow powder coating	Fine yellow powder coating

Critical Temperature vs Mass

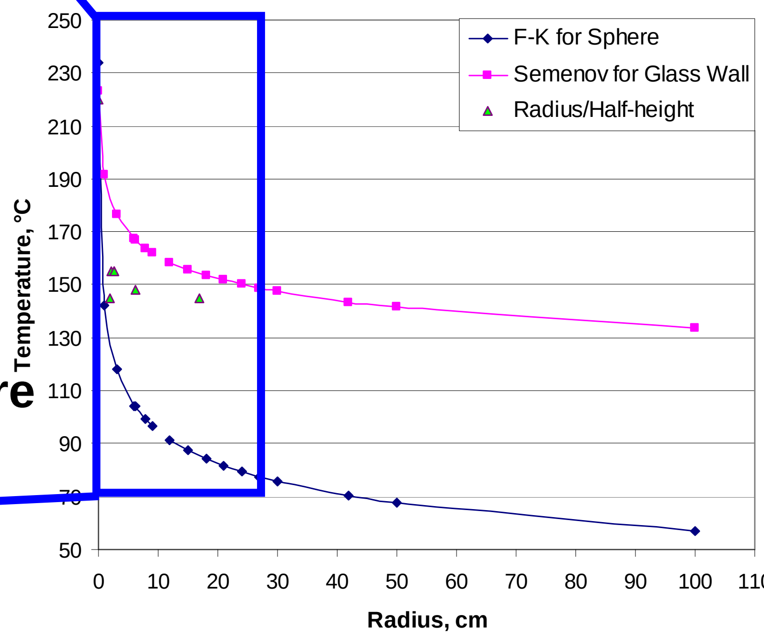
- Test results from 15 to 16,200 grams (36-lb) indicate no scaling effect



Critical Temperature vs Radius



- T_{crit} seems unaffected by size
  - **Shallow curve or horizontal line within error**
  - **T_c constant at 145±5°C**
  - **Henkin is the exception (sealed/confined)**



Conclusions and Recommendations

- Non-ideal formulations
  - F-K and Semenov models are often too conservative
  - Use of sealed, confined Henkin test questionable for predictive models
  - May not follow traditional scaling rules for critical temperature
  - May lack “catastrophic” event

- Formulation NIE
  - Despite the incorrectly predicted hazards, NIE is safe to process and handle on large production scales
  - Safety margin of 35°C realized
  - Recommend processing at lower end of range suggested

- For formulation development, conduct predictive calculations
  - **Best tool currently available**
  - If models suggest safe processing, it is definitely safe
  - If models predict “unsafe” operations, it may be worthwhile to investigate further

Questions?

References

1. MIL-STD-1751A. Safety and Performance Tests for the Qualification of Explosives (High Explosives, Propellants, and Pyrotechnics) December 2001.
2. McKenney, Robert L. Jr, and Krawietz, Thomas R., One-Liter Test: A Mid-Scale Safety Characterization Test for Melt-Castable Explosives, AFRL-MN-EG-TR-1999-7049, July 1999.
3. Wikipedia, the Free Encyclopedia. Retrieved April 5, 2009, from http://en.wikipedia.org/wiki/Catastrophe.
4. Dictionary.com. Retrieved April 5, 2009, from http://dictionary.reference.com/browse/catastrophe.
5. The American Heritage® Dictionary of the English Language: Fourth Edition. 2000. Retrieved April 5, 2009, from http://www.bartleby.com/61/60/C0156000.html.
6. Frank-Kamenetsky, D. A., "Calculation of Thermal Explosion Limits," *Acta Phisicochimica U.R.S.S.*, Vol. X, pp. 365-369, 1939.
7. Rogers, Raymond R., "Thermochemistry of Explosives," *Thermochimica Acta*, Vol. 11, pp. 131-139, 1975.
8. Zinn, J. and Mader, C. L., "Thermal Initiation of Explosives," *Journal of Applied Physics*, Vol. 31, No. 2, pp. 323-328 (1960).
9. Semenov, N. N., Chemical Kinetics and Chain Reactions, London: Oxford University Press, 1935.
10. Gibbs, Terry R. and Popolato, Alphonse, editors, LASL Explosive Properties Data, University of California Press, Berkeley, 1980.
11. Henkin, H., and McGill, R., "Rates of Explosive Decomposition of Explosives," *Industrial and Engineering Chemistry*, Vol. 44, p.1391, 1952.