Composite Materials for Hazard Mitigation of Reactive Metal Hydrides

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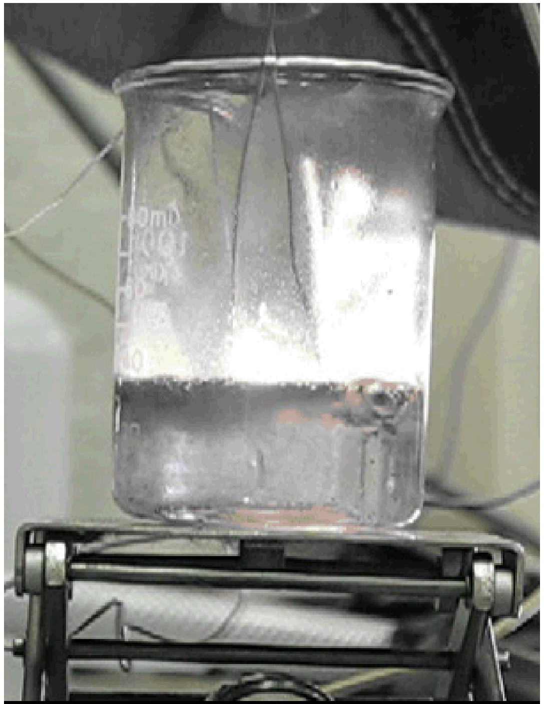
Unmitigated



Mitigated

Sandia has been working on hazard mitigation for several years.

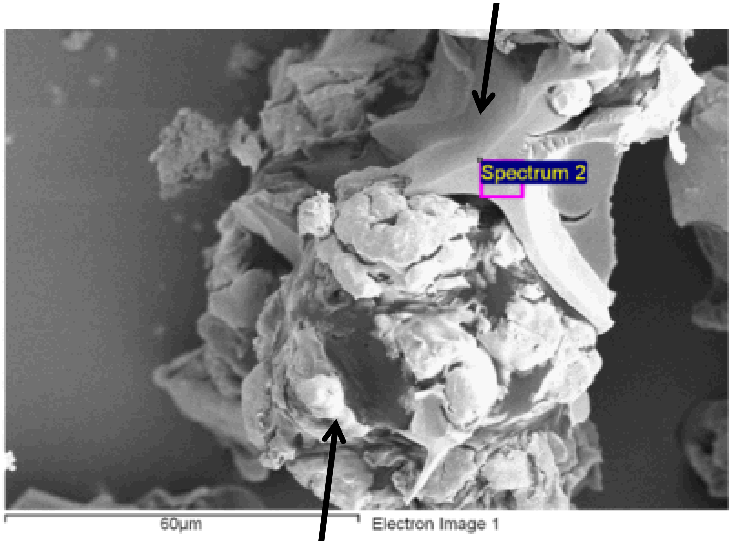
- CO_2 treatment of sodium alanate (SA).
  - Good for disposal but not for normal use.
- Tank liner to encapsulate bulk volume of SA during accident.
  - Liner materials showed too much interaction with the SA.
- Composite mixture of SA with mitigating material.
  - Normal operation until accident, then mitigation.

→ Purpose: Increase safety to enable wide-spread deployment of reactive metal hydride-based hydrogen storage materials.

Outline

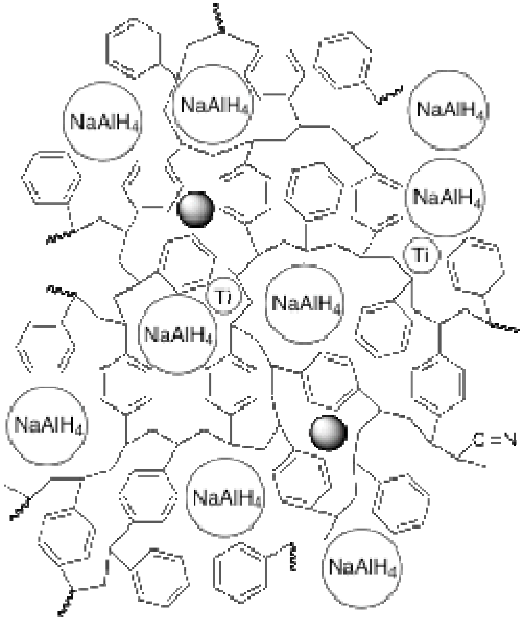
- Materials Development
- Experimental
- Discussion
- Conclusions

The composite is a mitigating material mixed with the active material.



Polymer (polystyrene)

Metal Hydride ($NaAlH_4$)



The mitigating material should:

- Slow the reaction rate,
- Stop the penetration of oxygen, and/or
- Absorb the heat of reaction.

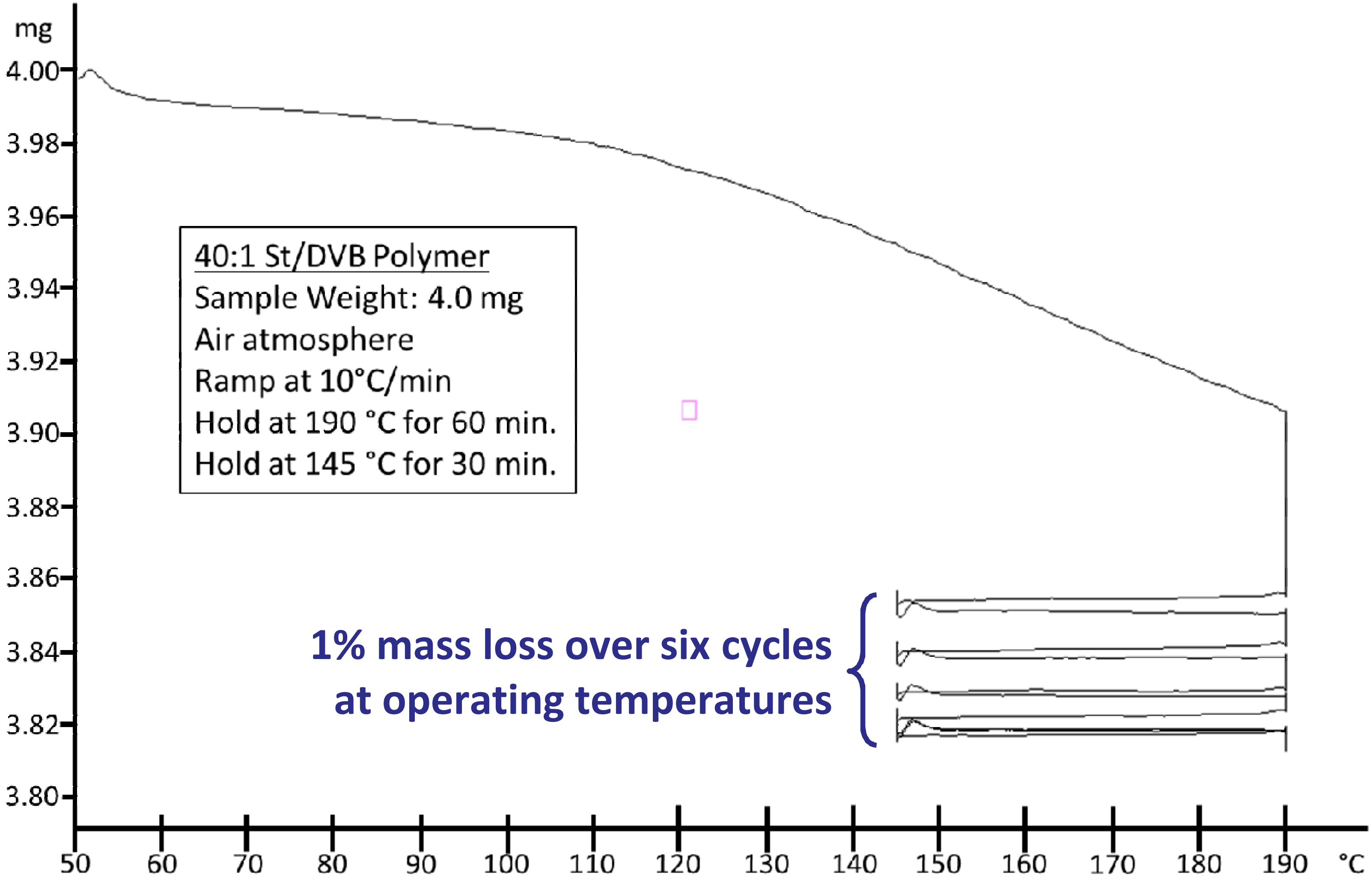
Without affecting the H_2 storage function during normal operation.

Recently we have been searching for mitigating materials that can accomplish this.

- Requirements:
  - Able to form a cross-linked polymer matrix to act as a “scaffold” for the active material.
  - Able to be polymerized in situ with the active material.
  - Able to withstand the operating environment.
  - Has a mitigating feature.

- Candidates:
  - Polystyrene + divinyl benzene (DVB)
  - Siloxane (-R_2SiO-)
  - Polystyrene+DVB -siloxane mixtures

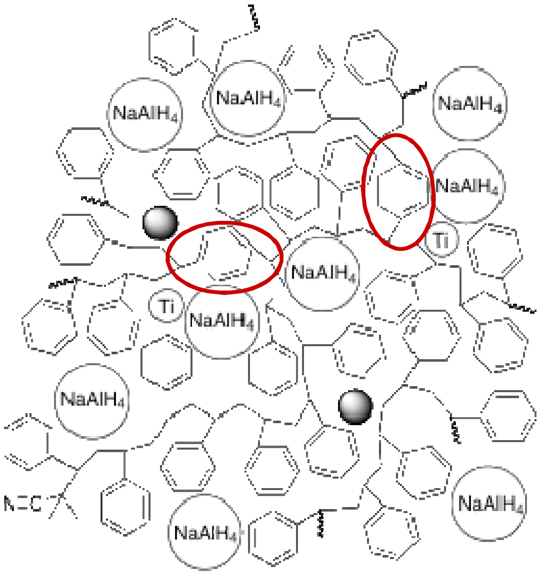
Polystyrene + DVB by itself is thermally stable at temperatures needed for system operation.



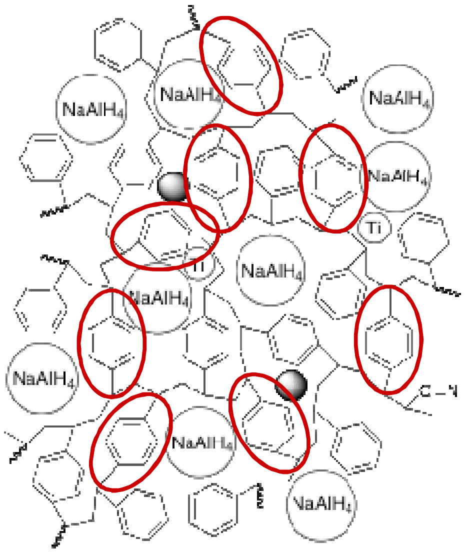
40:1 St/DVB Polymer
Sample Weight: 4.0 mg
Air atmosphere
Ramp at 10°C/min
Hold at 190 °C for 60 min.
Hold at 145 °C for 30 min.

1% mass loss over six cycles at operating temperatures

Different degrees of crosslinking can change the matrix and bulk mechanical properties.



High sty:dvb ratio (10:1)



Low sty:dvb ratio (3:4)

Lower Cross-linking Density

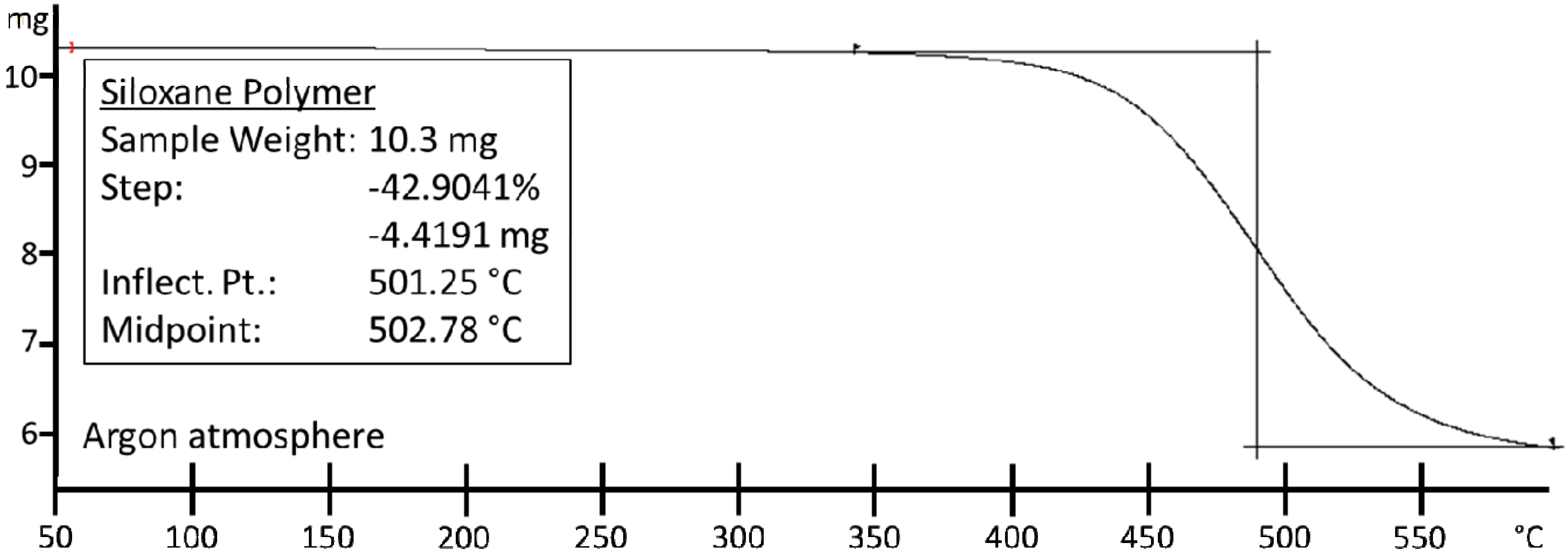
Flexible matrix, tough material
→ holds together

Higher Cross-linking Density

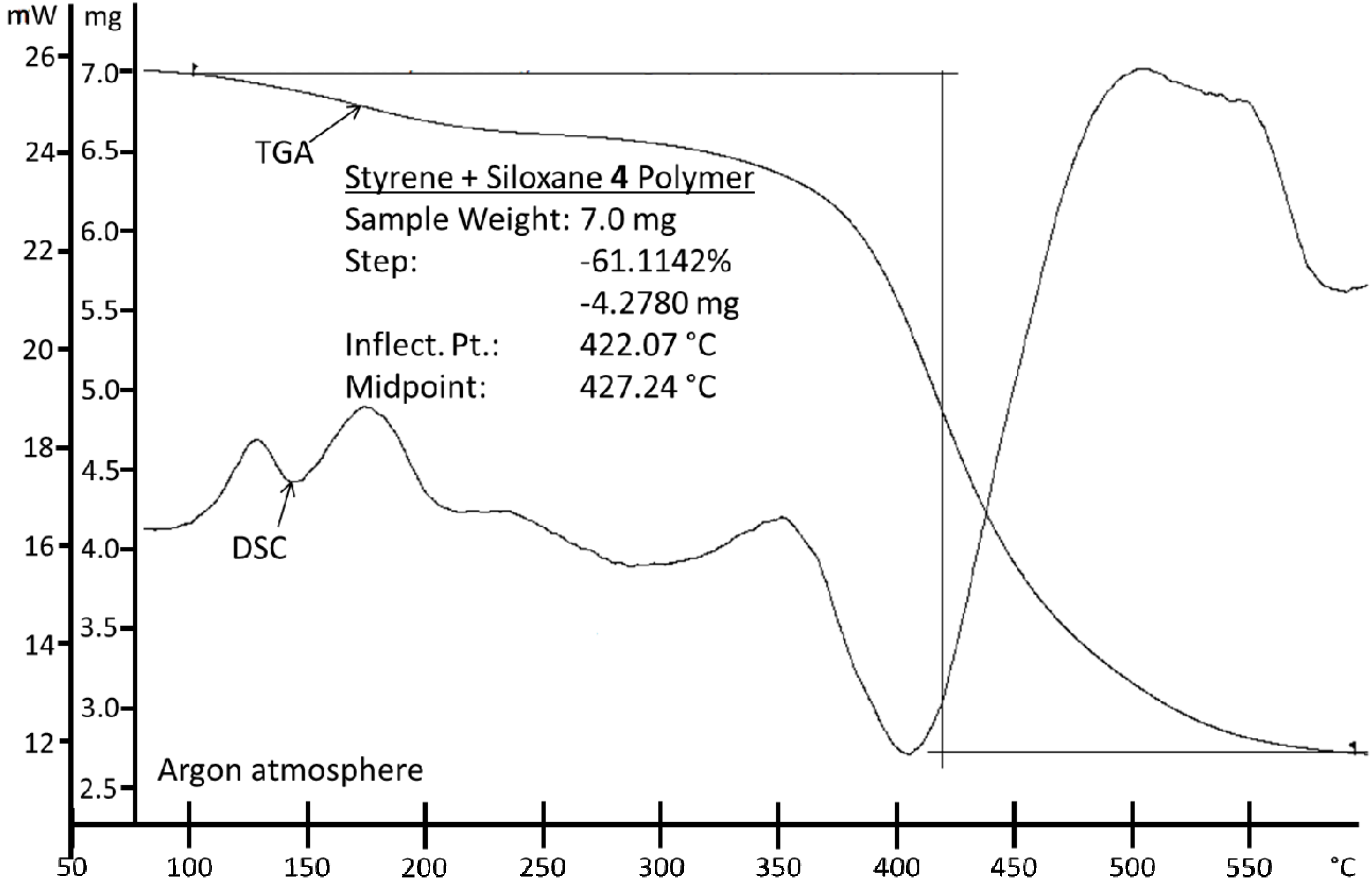
Stiff matrix, brittle material
→ easily crushed

◯ Red circles indicate **styrene cross link** between polystyrene chains

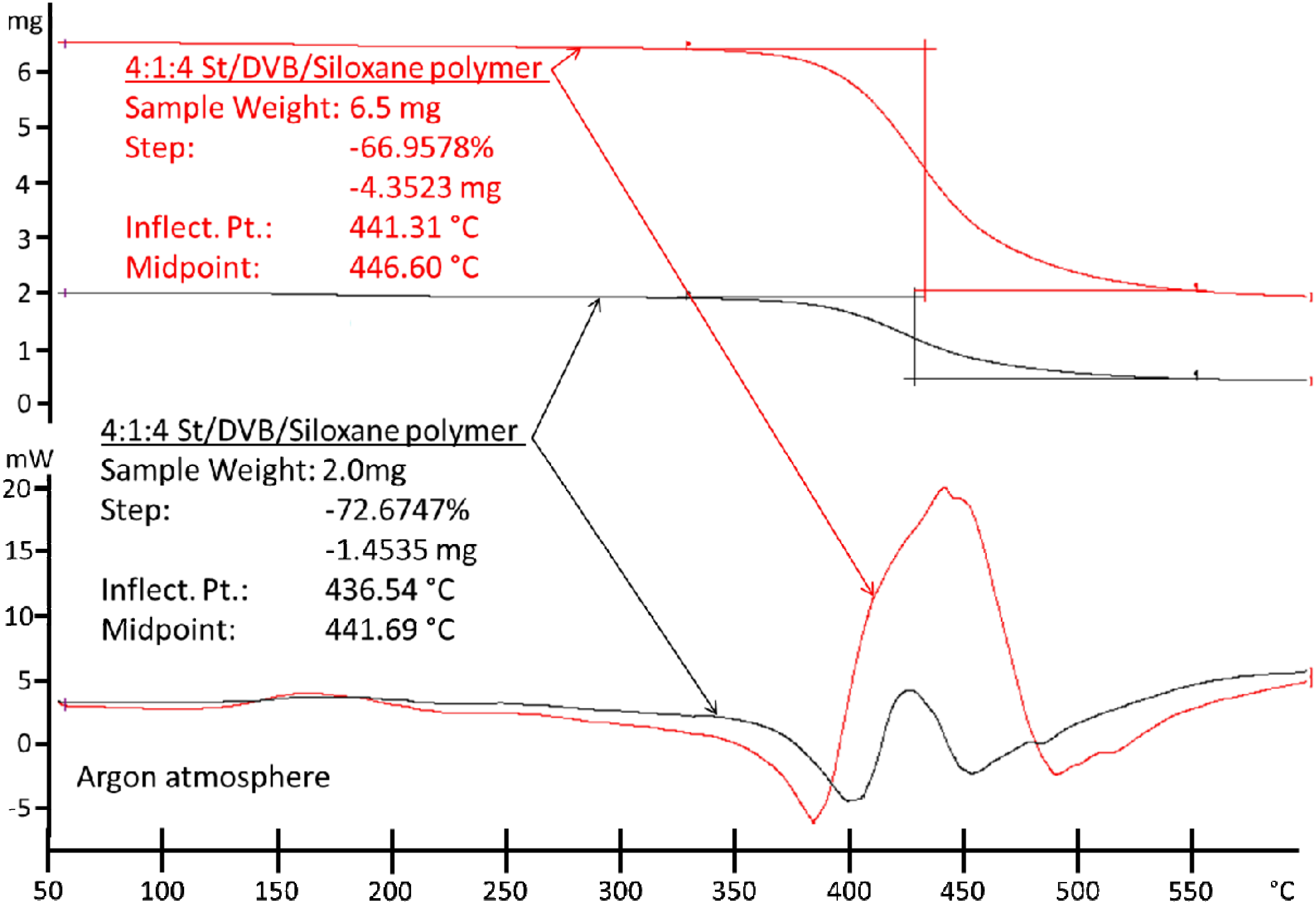
Siloxane is also stable, and does not begin to decompose until nearly 350 C.



DVB:Styrene at a 1:1 ratio mixed with Siloxane begins to lose mass at lower temperatures, with the majority occurring near 350 C.



When DVB:Styrene is at a 4:1 ratio and mixed with Siloxane, the material is stable to nearly 350 C.



4:1:4 St/DVB/Siloxane polymer
Sample Weight: 6.5 mg
Step: -66.9578%
-4.3523 mg
Inflect. Pt.: 441.31 °C
Midpoint: 446.60 °C

4:1:4 St/DVB/Siloxane polymer
Sample Weight: 2.0mg
Step: -72.6747%
-1.4535 mg
Inflect. Pt.: 436.54 °C
Midpoint: 441.69 °C

Argon atmosphere

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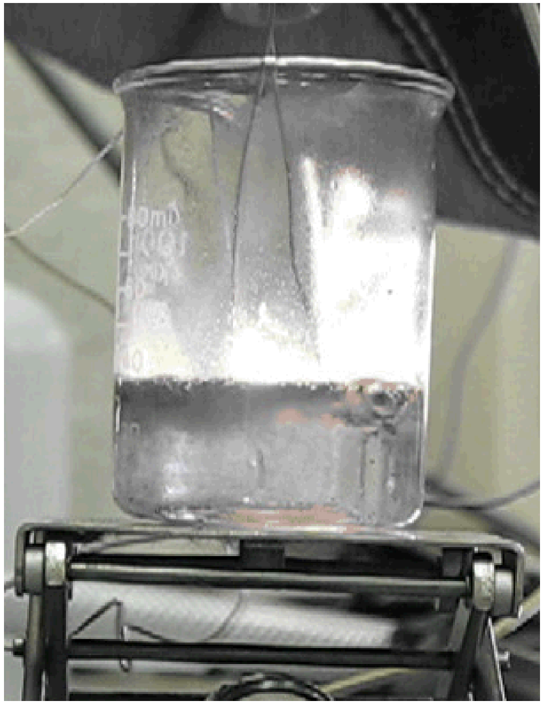
Qualitative experiments visually compare mitigated and unmitigated pellets and powder dropped into water.

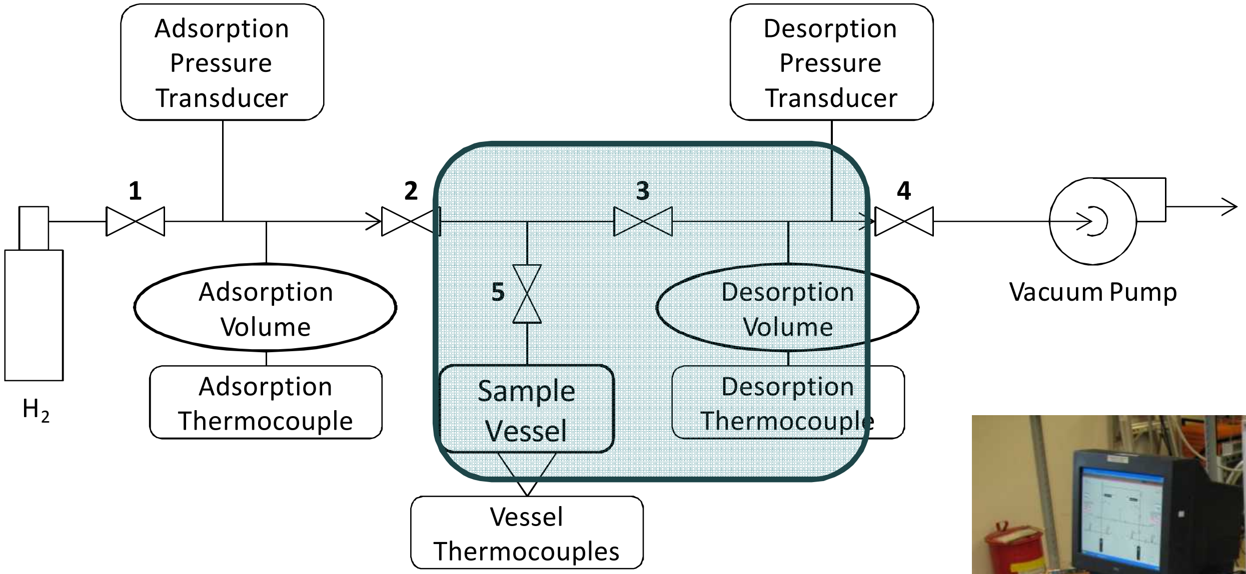
Unmitigated powder



Composite powder (polystyrene-DVB mixture)

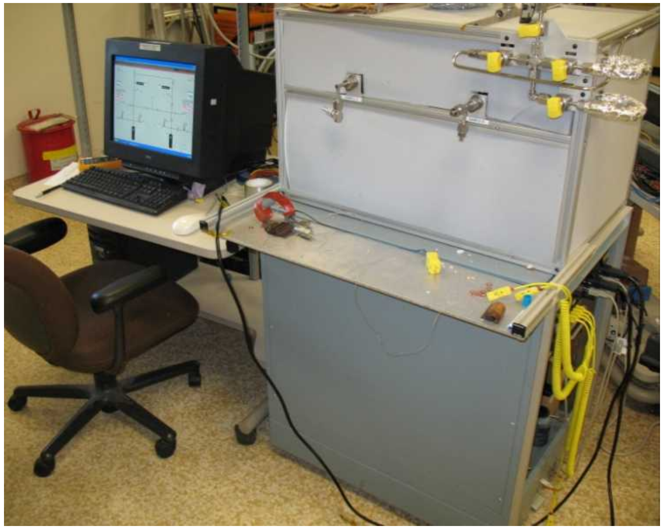
Qualitative experiments visually compare mitigated and unmitigated pellets and powder dropped into water.

Hydrogen adsorption/desorption cycling at normal operating temperatures tests the capacity and durability of the composite material.

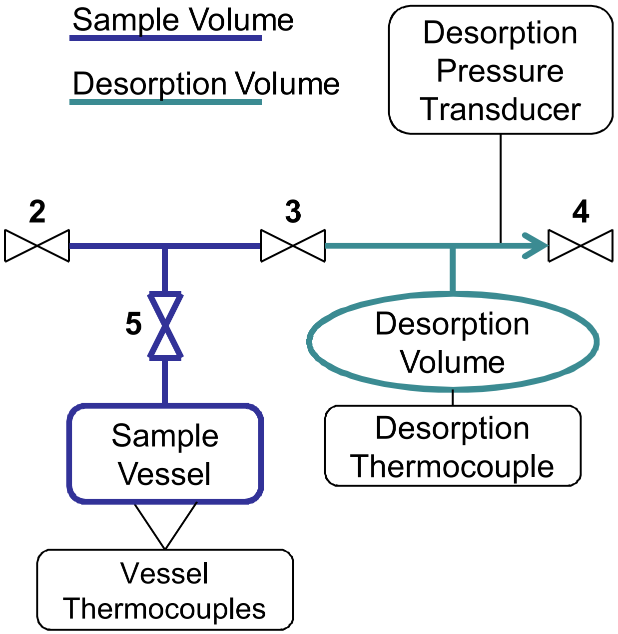


Cycling conditions:

- Adsorption: 30 min at 145 C;
  1900 psia (130 bar) supply pressure.
- Desorption: 60 min at 190 C; to vacuum.
- Number of cycles set by user.



Capacity was calculated by applying the ideal gas law to the desorption volume.



$$\text{[illegible]} = \frac{\text{[illegible]}}{\text{[illegible]}}$$

Ideal gas law is applied to the desorption volumes, initially at vacuum.

$$\text{[illegible]}_{\text{[illegible]}_2} = \frac{\text{[illegible]}_{\text{[illegible]}_2}}{1000\,\text{[illegible]}}\,\text{[illegible]}_{\text{[illegible]}}\left(\frac{\text{[illegible]}_{\text{[illegible]}}}{\text{[illegible]}_{\text{[illegible]}}} + \frac{\text{[illegible]}_{\text{[illegible]}}}{\text{[illegible]}_{\text{[illegible]}}}\right)$$

The gas desorbed is calculated at each time step.

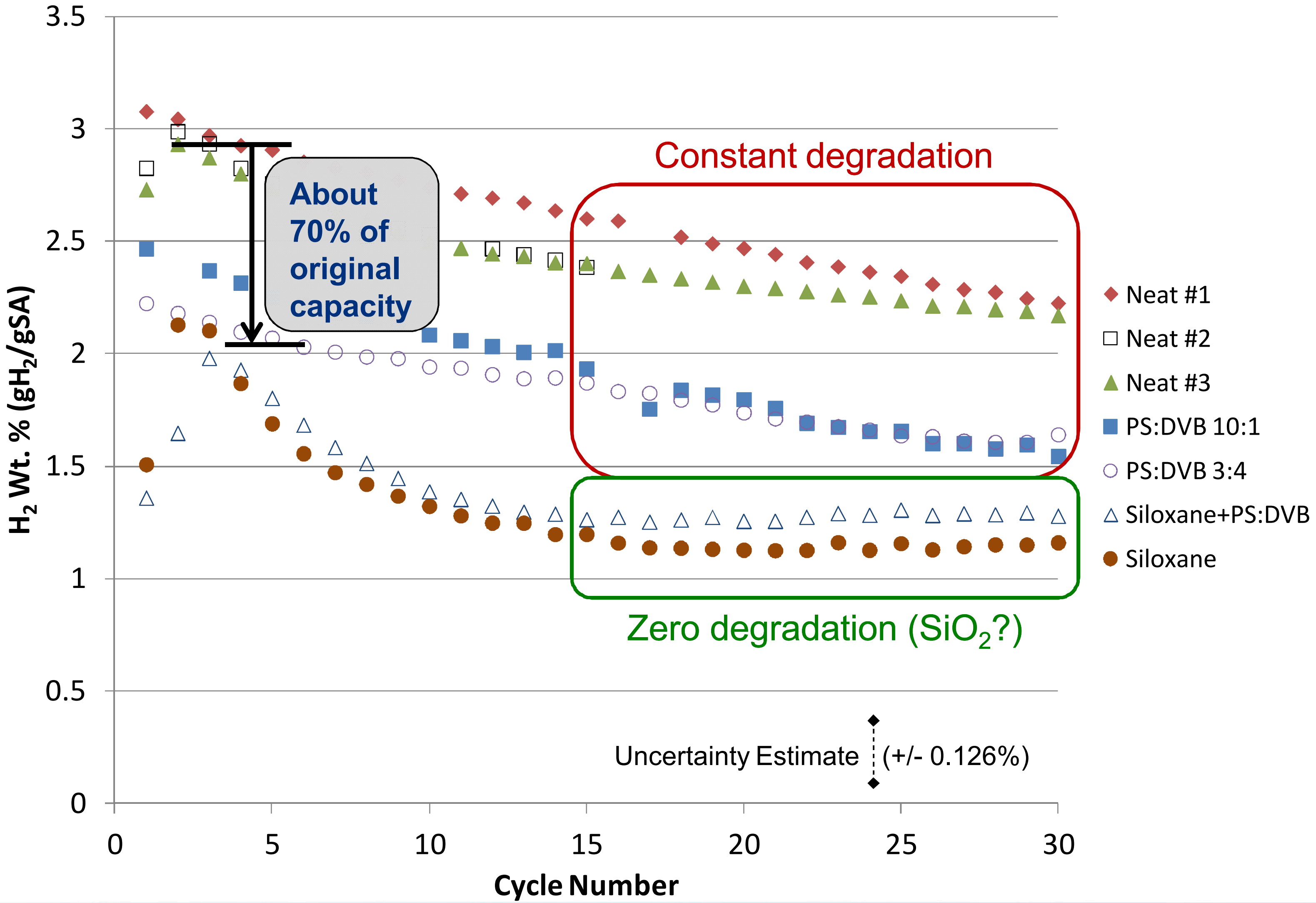
$$\text{[illegible]}_{\text{[illegible]}_2,\text{[illegible]}} = \text{[illegible]}_{\text{[illegible]}_2}\Big|_{\text{[illegible]}} - \text{[illegible]}_{\text{[illegible]}_2}\Big|_{\text{[illegible]}0}$$

The weight percent is based on the mass of metal hydride.

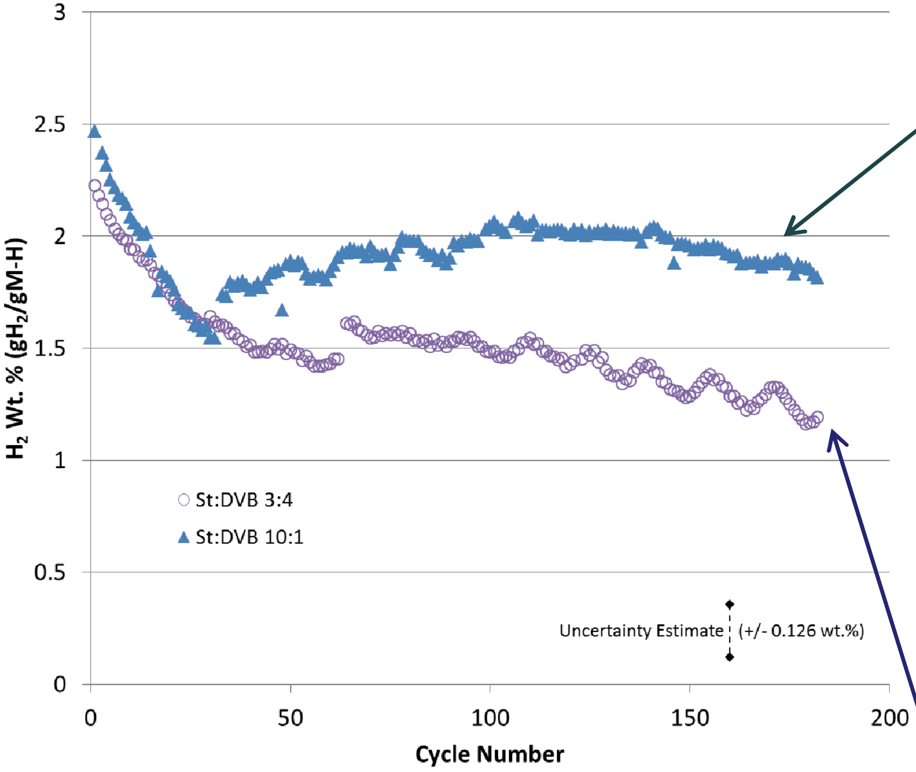
$$\text{[illegible]}\% = \frac{\text{[illegible]}_{\text{[illegible]}_2,\text{[illegible]}}}{\text{[illegible]}_{\text{[illegible]}\,h\,\text{[illegible]}}}$$

Does not include mass of the polymer additive

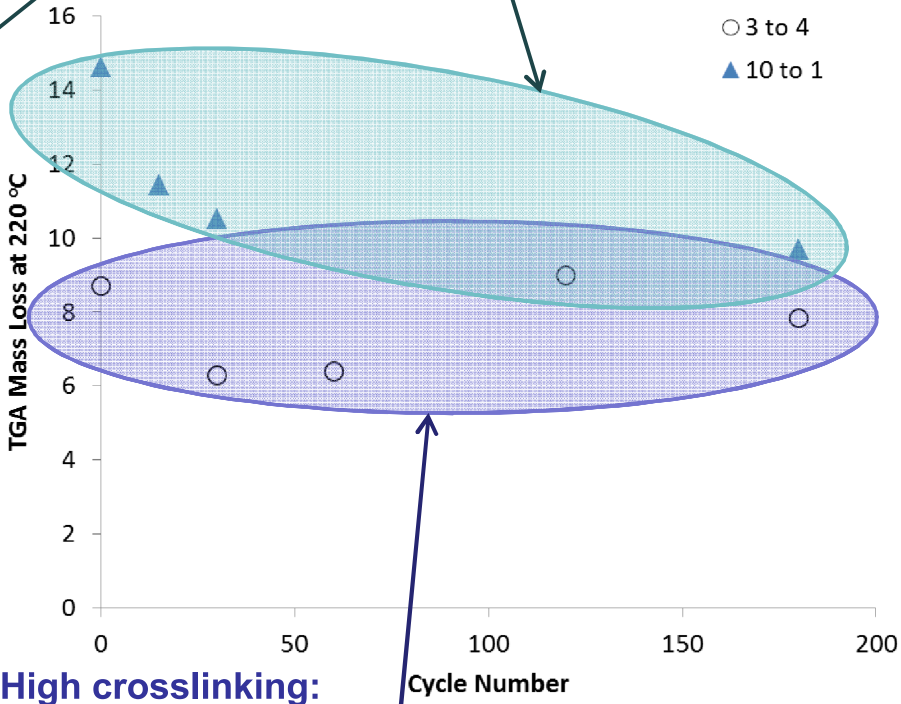
Addition of the mitigating material decreases the hydrogen capacity of the metal hydride and effects vary with number of cycles.



For the PS:DVB materials, higher crosslinking improves stability as shown upon repeated cycling.

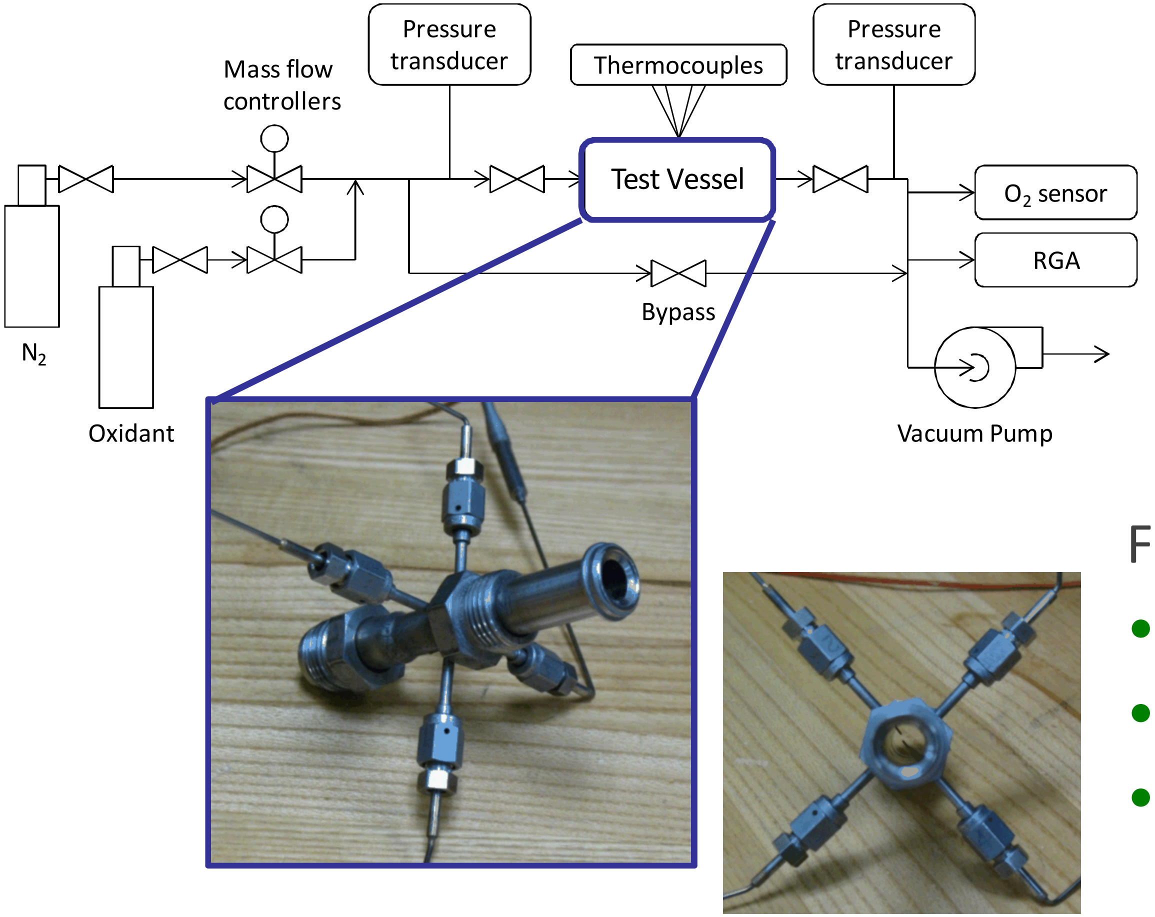


Low crosslinking:
- Material is degrading
- Decreasing mass loss
- Capacity recovers



High crosslinking:
- Stable material
- Constant mass loss
- Continued capacity reduction

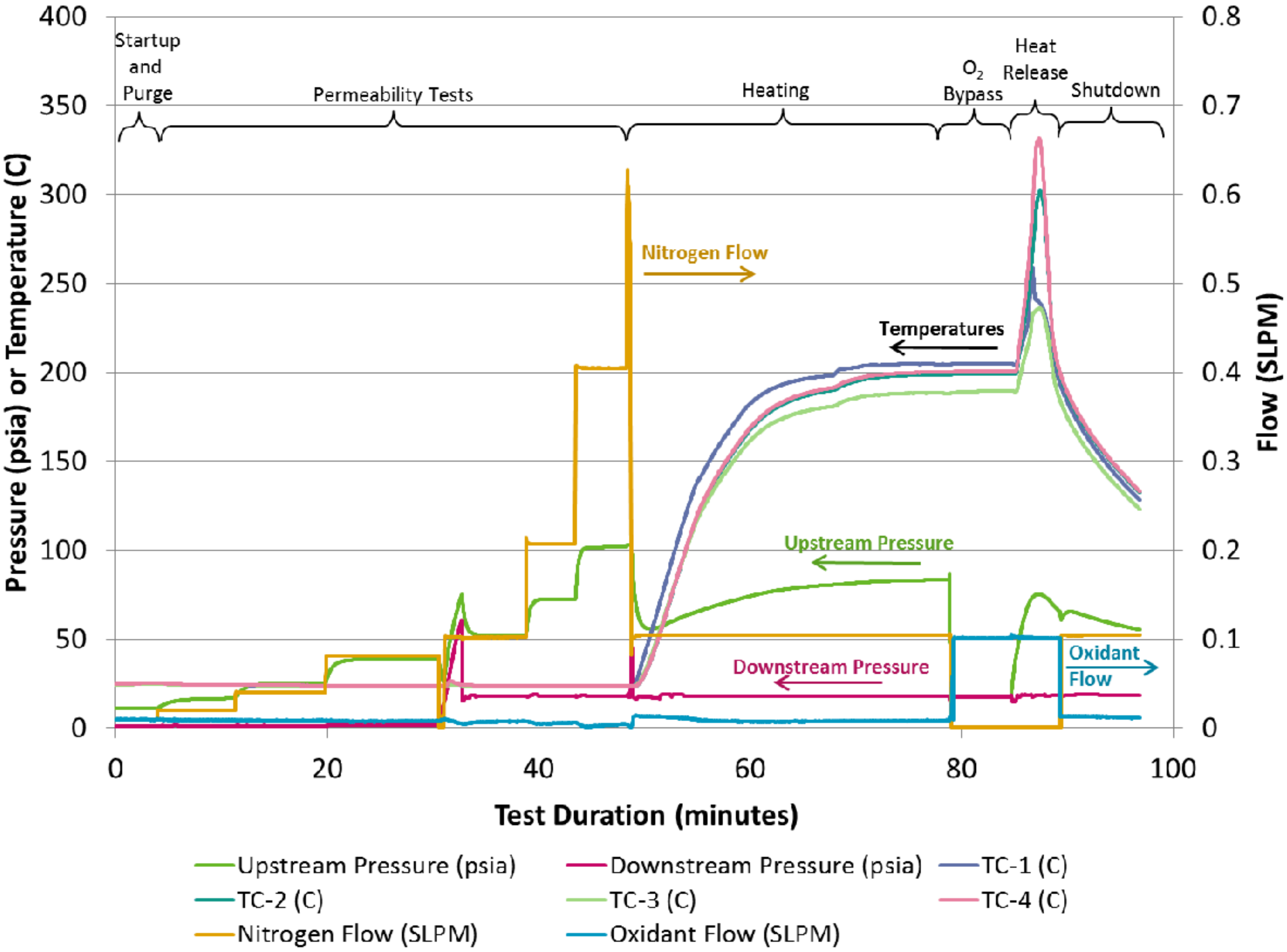
The heat released by the sample when exposed to flowing oxygen determines the mitigating material’s effectiveness.



Flow-through Conditions:

- 24% O_2, 75% N_2, 1% He
- 200 C at start
- 0.1 SLPM

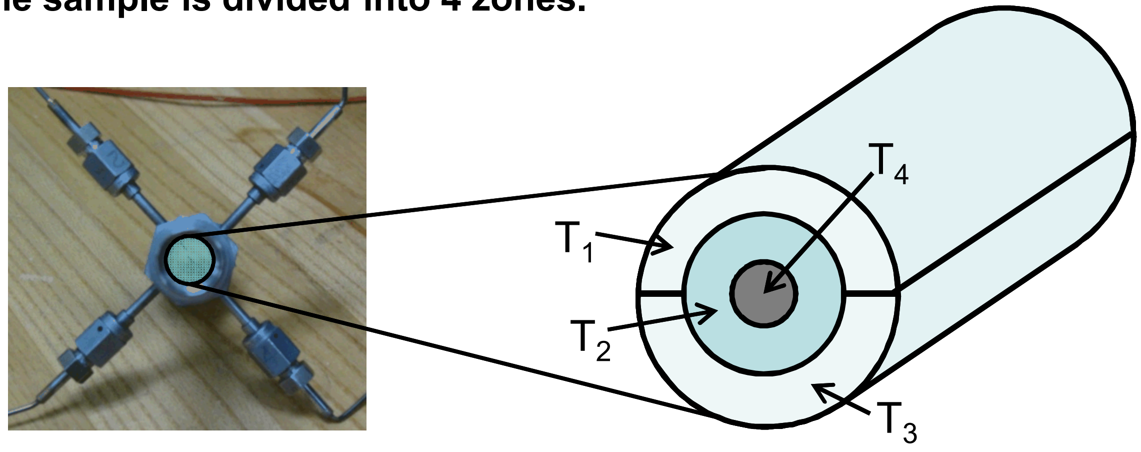
Overview of a typical heat release and permeability test.



Heat release was determined by applying thermodynamics to temperature measurements.

$$\text{[illegible]} = \text{[illegible]} + \text{[illegible]} + \cancelto{0}{\text{[illegible]}} \quad \text{[Joules]}$$

The sample is divided into 4 zones.



$$\text{[illegible]} = \sum_{\text{[illegible]}=1}^{4} \text{[illegible]}$$

$$\text{[illegible]} = \sum_{\text{[illegible]}=1}^{4} \text{[illegible]}$$

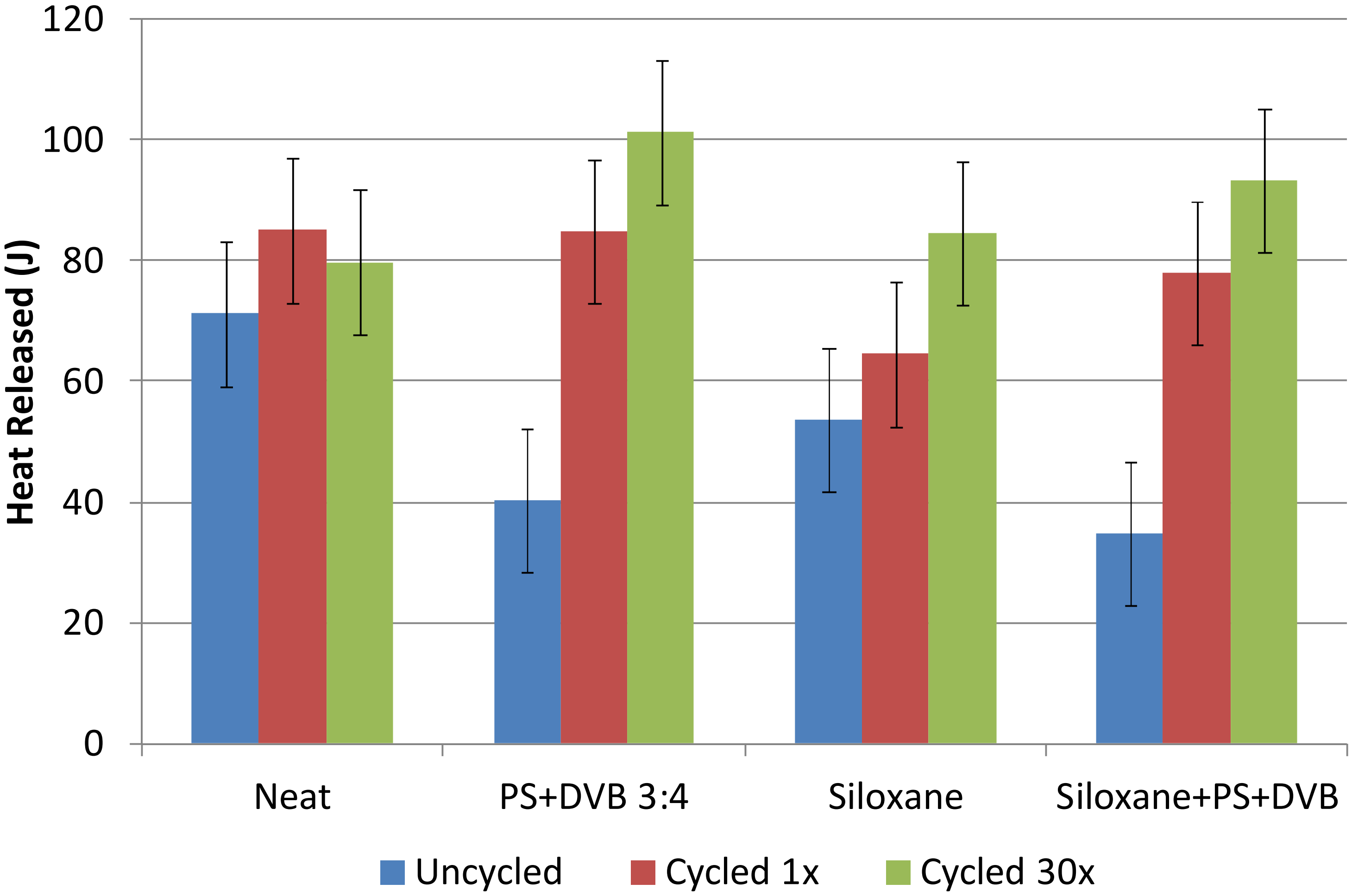
Solid: Heat absorbed by the solid from its initial temperature to its peak zone temperature.

$$\text{[illegible]} = \text{[illegible]}\left(\text{[illegible]} - \text{[illegible]}\right)$$

Gas: Heat absorbed by the gas flow from its inlet temperature to its zone temperature, added for every time step.

$$\text{[illegible]} = \sum_{\text{[illegible]}}^{\text{[illegible]} @ \text{[illegible]}} \frac{\text{[illegible]}}{\text{[illegible]}} \text{[illegible]}\left(\text{[illegible]} - \text{[illegible]}\right) \Delta \text{[illegible]}$$

The composites mitigate well initially, reducing heat release to between 49% and 75% of its original amount, but degrade under repeated cycling.



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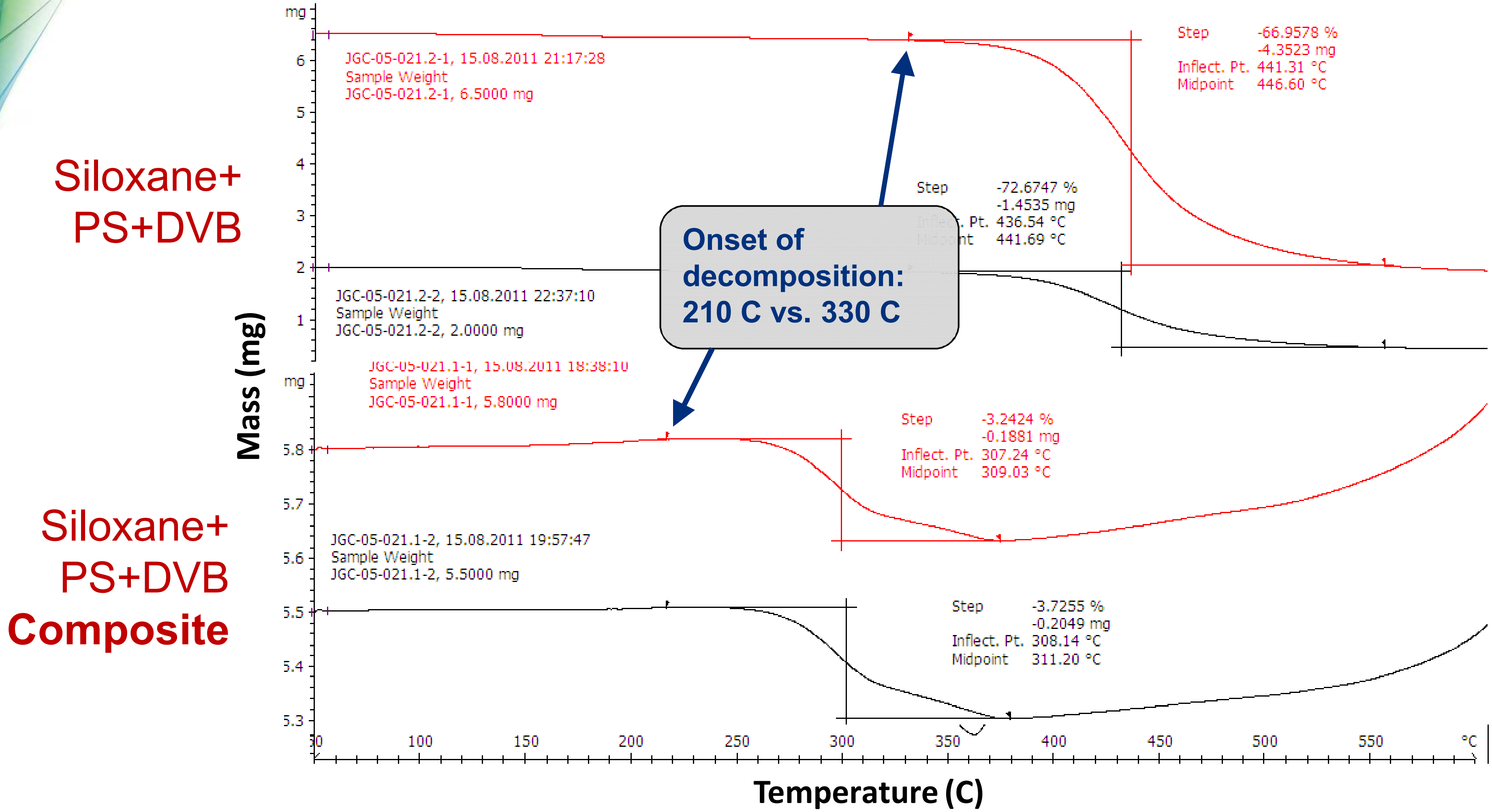
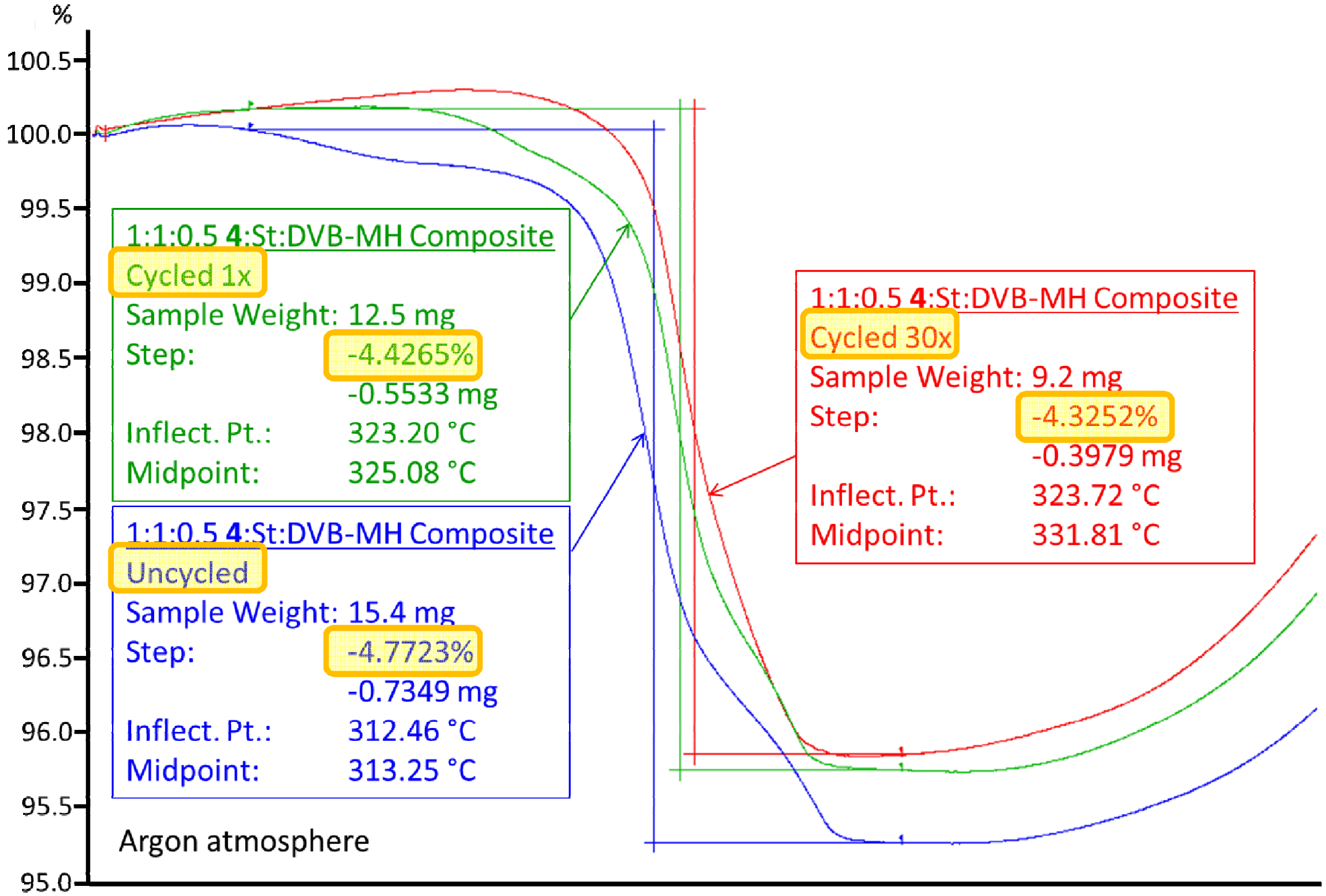
The polymers decompose at a lower temperature when mixed with the active material.



Onset of decomposition: 210 C vs. 330 C

The chemical nature of the polymer is adversely affected in the composite.

The polymer is still present in approximately the same amount after cycling.



1:1:0.5 **4**:St:DVB-MH Composite
Cycled 1x
Sample Weight: 12.5 mg
Step: -4.4265%
-0.5533 mg
Inflect. Pt.: 323.20 °C
Midpoint: 325.08 °C

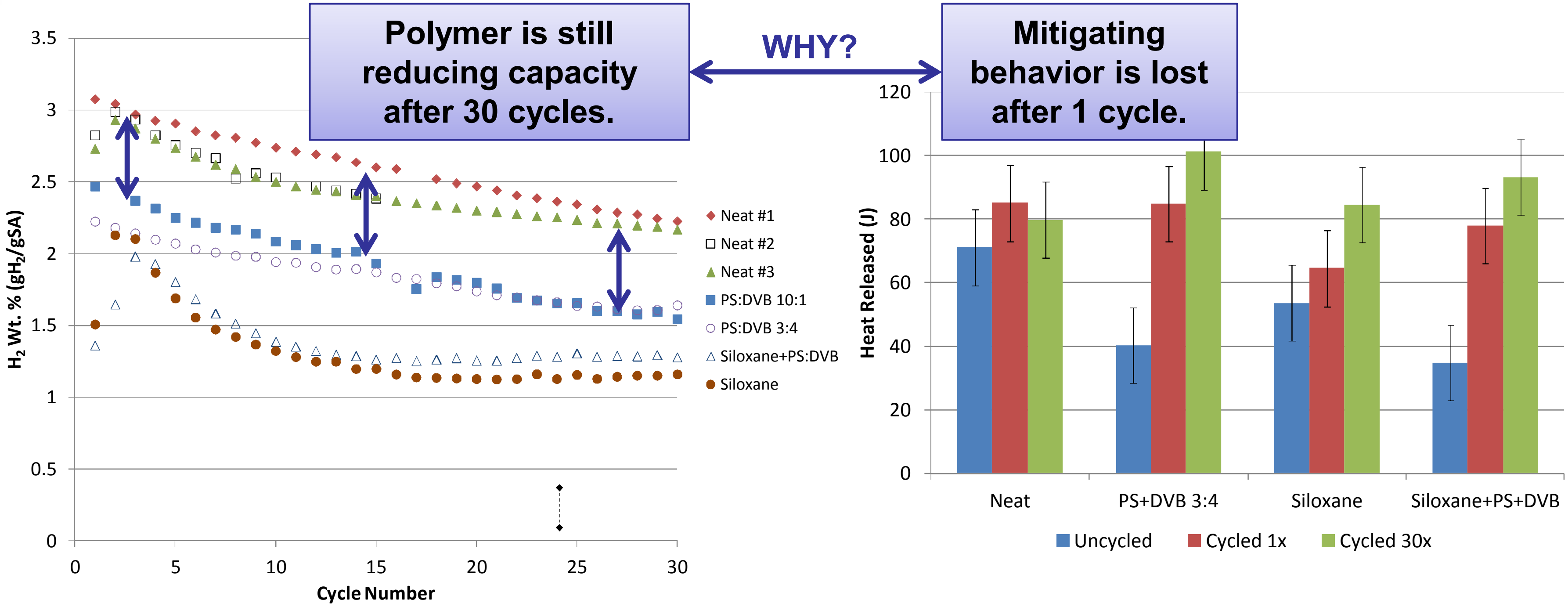
1:1:0.5 **4**:St:DVB-MH Composite
Uncycled
Sample Weight: 15.4 mg
Step: -4.7723%
-0.7349 mg
Inflect. Pt.: 312.46 °C
Midpoint: 313.25 °C

1:1:0.5 **4**:St:DVB-MH Composite
Cycled 30x
Sample Weight: 9.2 mg
Step: -4.3252%
-0.3979 mg
Inflect. Pt.: 323.72 °C
Midpoint: 331.81 °C

Argon atmosphere

The mechanical nature of the polymer in the composite is robust.

The cycling and heat release results seem to contradict each other.



Polymer is still reducing capacity after 30 cycles.

WHY?

Mitigating behavior is lost after 1 cycle.

Hypothesis: The mitigating and capacity-reducing functions are separate phenomena.

→ Capacity reduction effect is a mechanical one (blocking active sites).

→ Mitigating effect is a chemical one, and cycling is causing chemical changes.

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Conclusions

- Styrene-Siloxane-MH composites showed the best combination of durability and effectiveness.
- Addition of the polymer reduced the hydrogen capacity of the metal hydride to about 70% of its original capacity, most likely due to mechanical blocking of active sites.
- The composite materials mitigate well initially, reducing heat release to between 49% and 75% of its original amount.
- However, the composite materials are not robust under cycling conditions.
- Although the polymers are stable by themselves, they undergo a chemical change when mixed with the active material, causing them to decompose at a much lower temperature.
- Cycling causes additional chemical changes to the polymers that eliminates their mitigating property.

Suggested Future Work

- For mitigation, an approach to new materials that more-emphasizes *robustness* may be an effective strategy.
- Develop understanding of the interaction between the polymer and the hydride and the resulting chemical changes that occur both during synthesis and during cycling.
- The additive's interaction with the metal hydride may have unintended consequences that need quantification:
  - Bad: Possible introduction of contaminants into the H_2 stream as the polymer degrades.
  - Good: Stabilizing effect / reduction of degradation?

Acknowledgements

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Craig Reeder

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George Sartor, Ken Stewart

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Isidro Ruvalcaba, Jr.

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Continued collaboration will be a key to success!

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International collaboration

Sandia's Joe Pratt (8366) demonstrates his experimental method for determining what happens when metal hydrides are exposed to contaminants and oxygen during everyday use. His colleagues, Mayumi Tode (far left) and Nobuhiko Takeichi (seated), both from Japan's National Institute of Advanced Industrial Science and Technology (AIST), also work in the field of metal hydrides for hydrogen storage and were at Sandia/California recently as part of a DOE effort to encourage international collaboration in the area of hydrogen research. The work is considered part of Sandia's Research, Engineering and Applications Center for Hydrogen (REACH), an initiative that houses various hydrogen research activities on the grounds of the Livermore Valley Open Campus (LVOC).

(Photo by Dino Vournas)