Advanced Oxidation & Stabilization of PAN-Based Carbon Precursor Fibers

June 11, 2015

Status as of early April 2015

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Project ID: LM006

OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Overview

Timeline

Phase **I – Basic Science**

- Completed in 2011

Phase **II – Scale Up**

- Start 2011
- End 2015

Barriers

- High cost of carbon fiber
- Long conventional processing times for oxidative stabilization are the bottleneck in carbon fiber conversion
- Inadequate supply base for low cost carbon fibers/high volume production

Budget

- FY2014 $1,500,000
- FY2015 $1,500,000

Partners

- **ORNL** (Host site), carbon fiber production, analysis and characterization, recipe development.
- **RMX Technologies** (Experimental site), atmospheric plasma and hardware development.

Relevance and Objectives

- **Phase I: Produce multiple tows of carbon fiber meeting minimum program specifications using oxidation residence time of 40 minutes or less.**
  - Oxidation is the bottleneck in production often requiring 80 to 120 minutes. By developing a 2-3X faster oxidation process, higher throughput can be achieved.
  - This phase is Complete.
- **Phase II: Demonstrate Phase I capability at Pilot Scale.**
  - This will involve multiple tows and larger tows at less than 35 min residence time (increased throughput).
  - This phase is In Progress.
- **Current Project Year Objectives (FY15):**
  - Verify plasma oxidation approach at 1 ton/year through testing.
  - Optimize Large Reactor performance and prepare for further scale-up.

FY15 Milestones

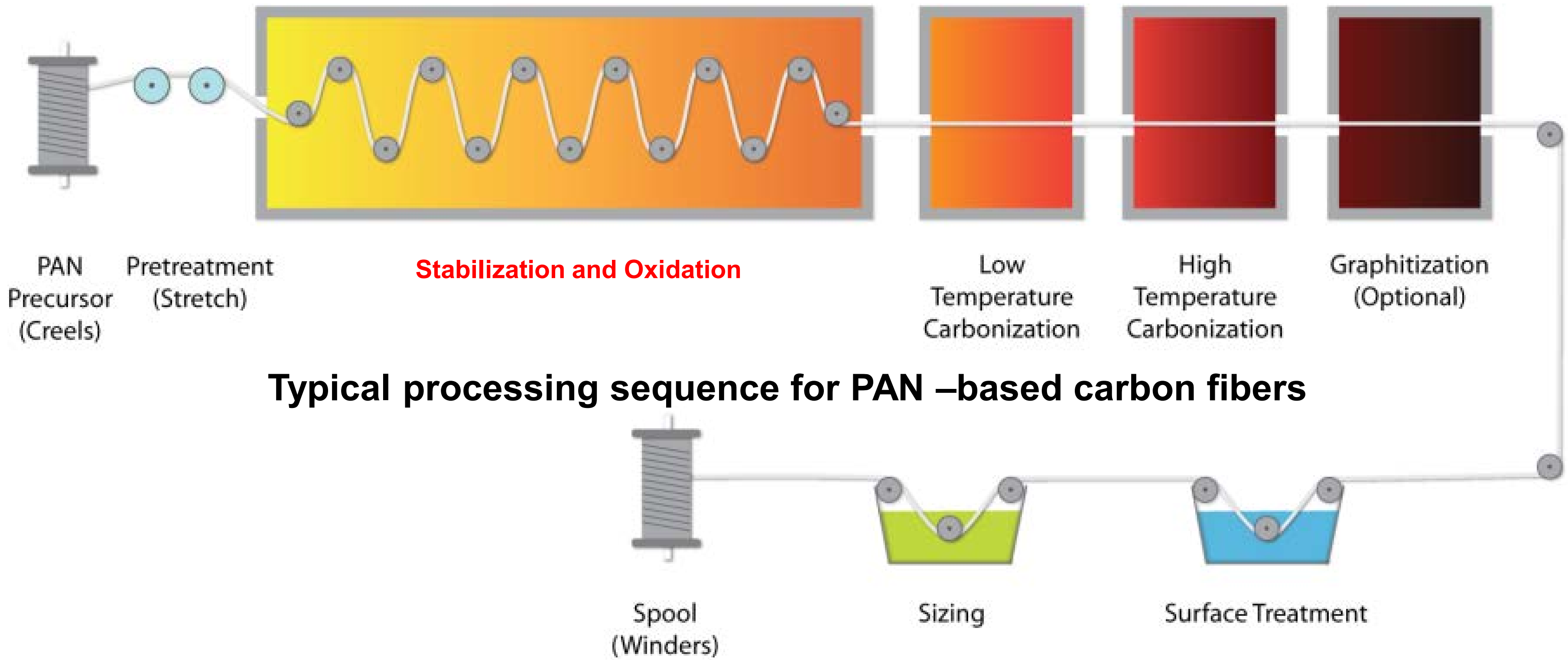
Date	Milestone	Status
December 31, 2014	**M1:** Capacity Test 1: Double the capacity of the 1 ton/year plasma oxidation oven from 2 tows to 4 tows of 20,000+ filaments per tow. Carbonized tows must meet 250 ksi strength and 25 Msi modulus.	**Complete**
March 31, 2015	**M2:** Robustness Test: Process two 20,000+ filament tows continuously for at least 8 hours of continuous operation with no equipment failures or breaks in fiber. Oxidized fiber will have a minimum density of 1.35 g/cc.	**Complete**
June 30, 2015	**M3:** Variability Test: Plasma oxidize four 20,000+ filament tows. Variability across all tows will be analyzed. The mean values of the oxidized mechanical properties should not vary more than ±20% and the density not vary more than ±3%.	**On-Track**

FY15 Milestones

Date	Milestone	Status
September 30, 2015	**M4:** Process four simultaneous tows of 48,000+ filaments each and demonstrate that densities exceeding 1.34 g/cc can be achieved and that fiber mechanical properties will not vary by more than 30% and fiber densities will not vary by more than 6%.	**On-Track** **(procurement of 48k precursor tows is nearly complete)**
September 30, 2015	**Go/No-Go M6:** Capacity Test 2: Process four simultaneous tows of 48,000+ filaments each to test exothermic capacity of the plasma oxidation oven. Tows should exceed 1.34 g/cc density and mechanical properties not vary by more than 20%.	**On-Track** **(procurement of 48k precursor tows is nearly complete)**
September 30, 2015	**M5:** Process Correlation: Analyze and correlate process parameters to fiber properties and determine relationships between them. This correlation is necessary for further scale-up to demonstration level. Energy balance analysis will also be undertaken.	**On-Track**

Approach Background

Conventional PAN Processing



Major Manufacturing Costs	
Precursor	43%
Oxidative stabilization	18%
Carbonization	13%
Graphitization	15%
Other	11%

Not selling price

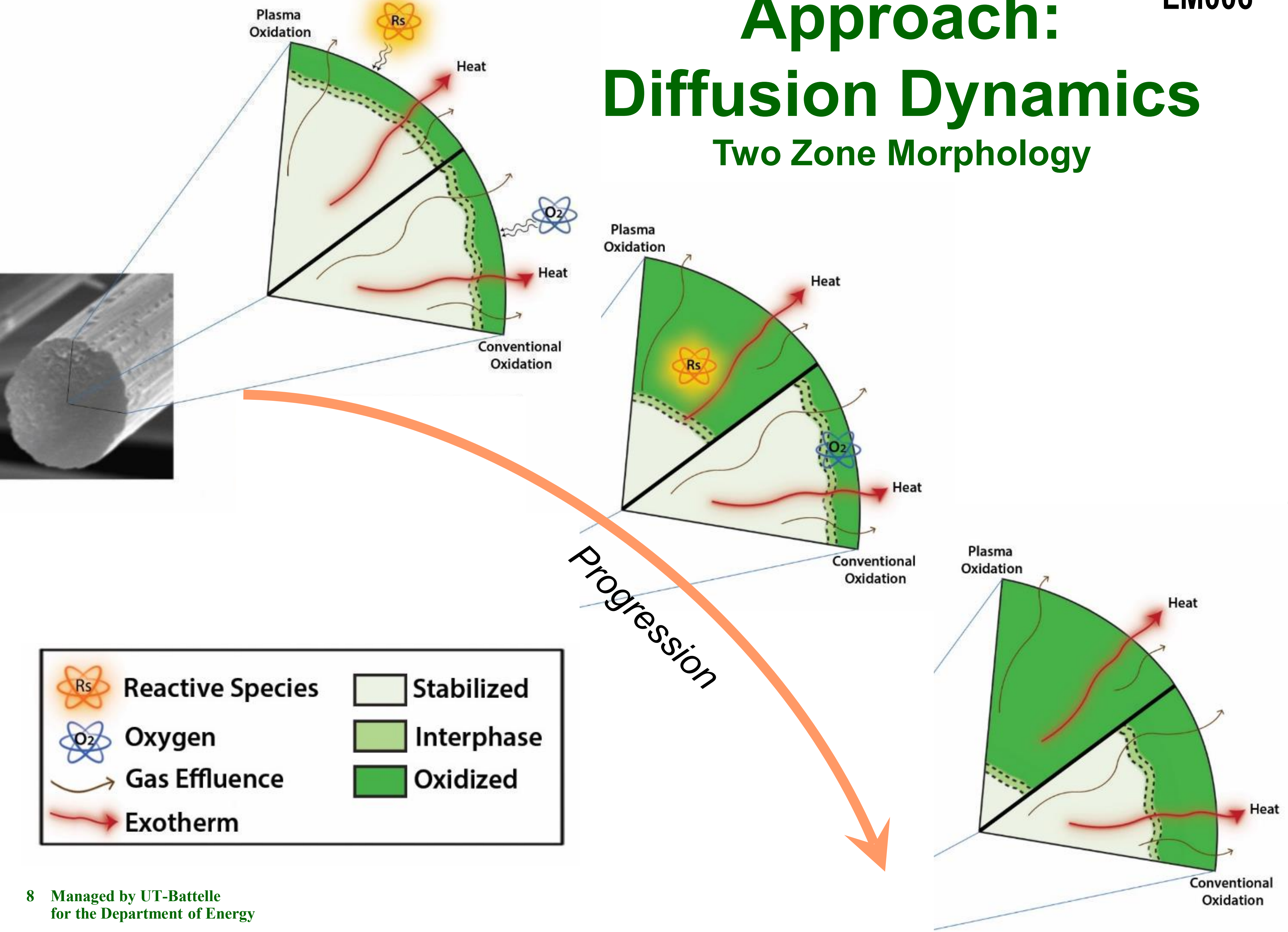
- Automotive cost target is $5 - $7/lb
- Tensile property requirements are 250 ksi, 25 Msi, 1% ultimate strain
- ORNL is developing major technological breakthroughs for major cost elements

Approach
Plasma-Based Oxidation

- Lower the cost of carbon fiber to remove the cost barrier to commercial applications.
- Develop a faster oxidation process to remove the bottleneck of carbon fiber conversion.
- Maintain carbon fiber properties compared to conventional.
- Utilize atmospheric pressure plasma based oxidation.

Approach: Diffusion Dynamics

Two Zone Morphology



Technical Accomplishments

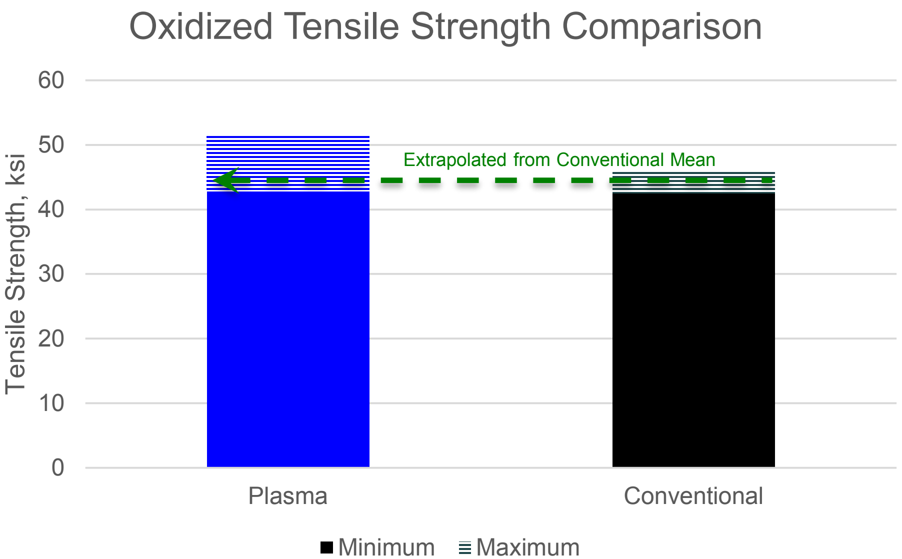
Summary

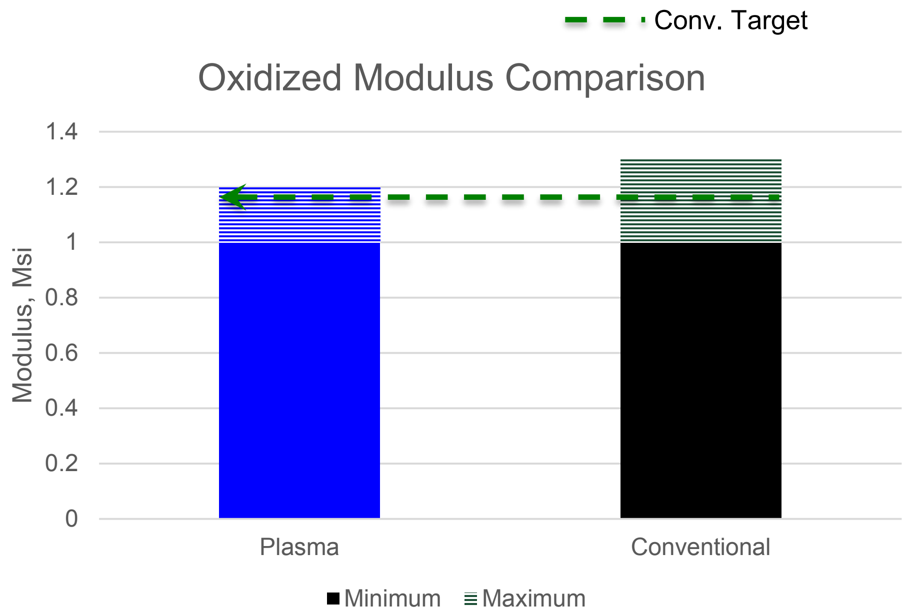
- Proven that plasma oxidation works with the Large Reactor.
- 1 ton/year Large Reactor has been operational for over a year with hundreds of hours of successful operational time. Plasma system has proven robustness.
- Successfully demonstrated plasma oxidation with 3 industry clients to date utilizing their precursor.
- Continue to optimize process and equipment – have not yet determined full potential of this technology/equipment.
- All results presented here are with 24k BlueStar* commodity grade precursor. Conventional references are from work performed at ORNL with the same precursor. Mechanical properties based on optical microscopy.
- This round of testing looked at three different stretch conditions (other conditions held constant) during plasma oxidation with **4 x 24k tow processing for each condition**. Then conventional carbonization was performed at ORNL at a variety of conditions to determine the best carbonization conditions. The following data captures *all* oxidation and carbonization results, not just the optimal cases.

BlueStar was one of the last third party sources of PAN precursor at the time of purchase.

Technical Accomplishments

Oxidized Mechanical Properties





- Oxidized mechanical properties are generally equivalent to conventional.
- 4-tow plasma processing variation across tows for three stretch conditions:

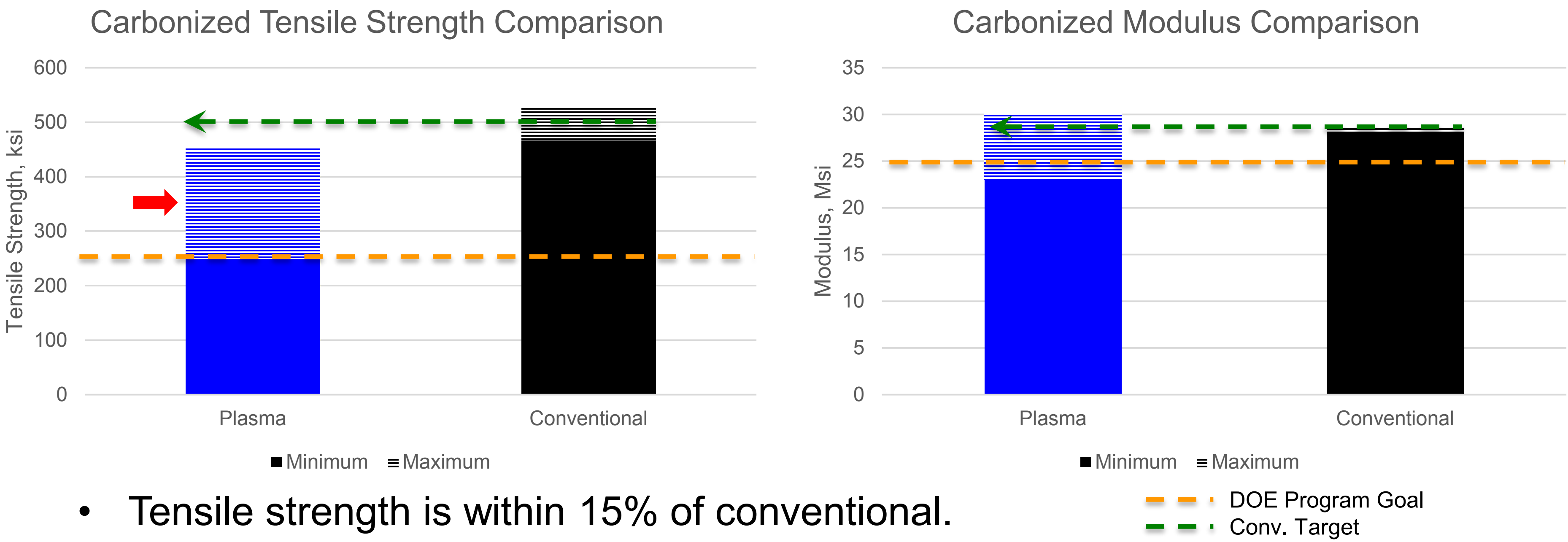
Variation	Reqt.*	Cond. 1	Cond. 2	Cond. 3
Density, %	≤±3.0	+0.8/-1.1	+0.9/-1.4	+0.4/-0.4
Tensile Strength, %	≤±20	+3.5/-6.6	+6.3/-4.8	+1.1/-1.0
Modulus, %	≤±20	~0	+9.1/-9.1	~0
Strain, %	≤±20	+6.1/-6.0	+15.1/-10.1	+4.3/-8.7

Actual stretch conditions are not presented here.

*DOE Project Requirement – Maximum permissible variation based on M3.

Technical Accomplishments

Carbonized Mechanical Properties



- Tensile strength is within 15% of conventional.
- Modulus is equal or better than conventional.
- 4-tow processing variation across tows for three *oxidized* stretch conditions:

Variation	Cond. 1	Cond. 2	Cond. 3
Tensile Strength, %	+4.7/-5.6	+13.0/-29.0	+16.8/-9.1
Modulus, %	+8.6/-8.8	+9.1/-17.8	+5.7/-4.3
Strain, %	+9.4/-6.2	+11.2/-13.2	+15.9/-12.1

Actual stretch conditions are not presented here.

The large variation in plasma-based tensile strength is due multiple carbonization conditions at ORNL.

Technical Accomplishments

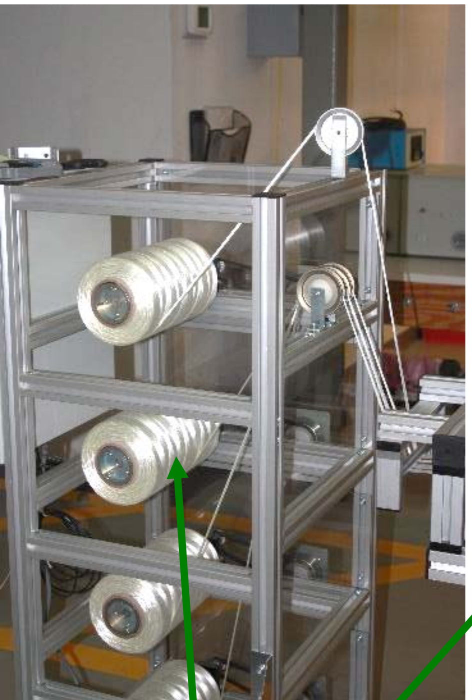
Carbonized Mechanical Property Results (12 of 47)

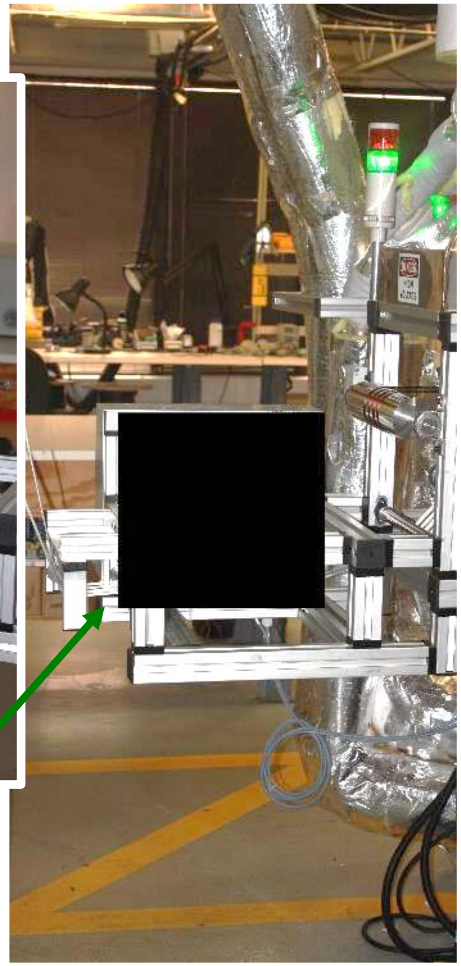
	Sample	Density g/cc	Diameter µm	Tensile Strength ksi	Modulus Msi	Strain %
	DOE Program Goal			*250*	*25*	*1*
	Conventional 1	*1.80*	*7.02*	*467.3*	*28.6*	*1.48*
	Conventional 2	*1.80*	*7.27*	*528.5*	*28.2*	*1.69*
Stretch Condition 1	MTR20075A-1	1.79	7.18	376.8	27.6	1.26
Stretch Condition 1	MTR20075A-3	1.78	7.15	328.4	29.8	1.04
Stretch Condition 1	MTR20075B-3	1.78	6.37	417.9	29.9	1.30
Stretch Condition 1	MTR20075C-3	1.80	7.35	402.6	25.1	1.47
Stretch Condition 2	MTR20077A-2	1.79	7.07	399.4	28.0	1.32
Stretch Condition 2	MTR20077B-1	1.78	7.43	366.9	27.5	1.24
Stretch Condition 2	MTR20077C-1	1.78	7.91	251.0	21.1	1.10
Stretch Condition 2	MTR20077D-3	1.79	6.87	396.6	26.1	1.41
Stretch Condition 3	MTR20078A-11	1.80	6.83	357.9	25.7	1.27
Stretch Condition 3	MTR20078C-5	1.79	6.64	352.5	28.4	1.16
Stretch Condition 3	MTR20078D-1	1.80	6.56	443.4	28.5	1.41
Stretch Condition 3	MTR20078D-4	1.80	6.63	453.0	26.5	1.53

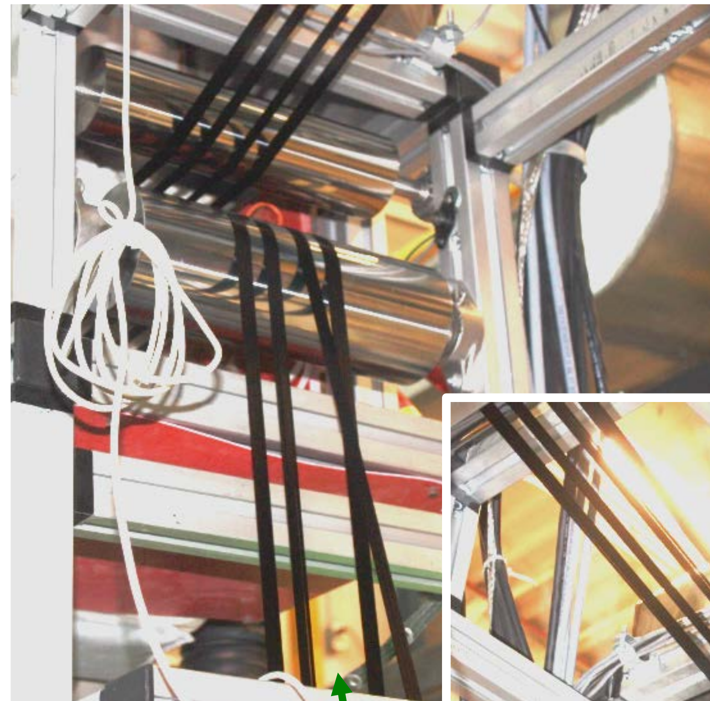
All plasma oxidation processing was completed with 4 x 24k tows.

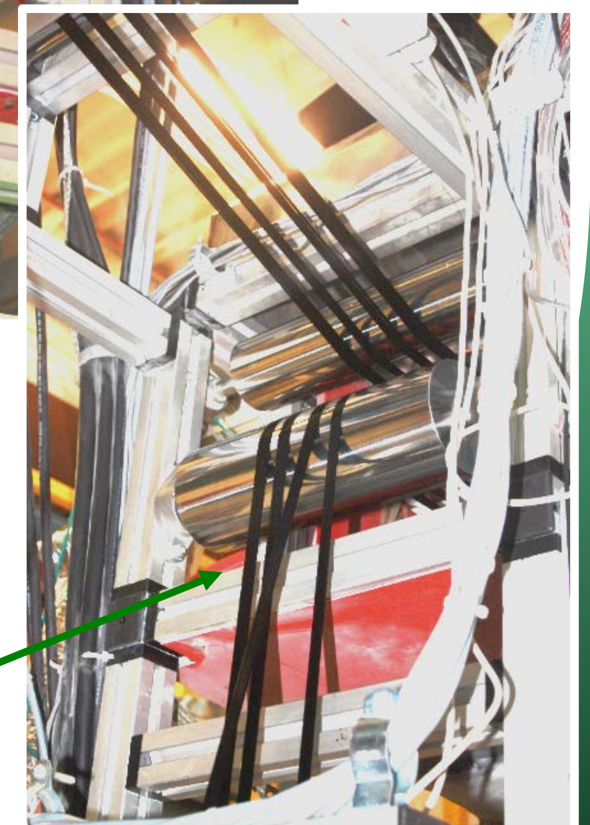
Technical Accomplishments

Images of 4-tow Plasma Oxidation Processing









Virgin Precursor → Oxidized Fiber

Technical Accomplishments

Commercialization

- Plasma oxidation advantages have been demonstrated to 3 private companies in the past 7 months – each using their proprietary precursor.
  - One *large tow* PAN precursor company.
  - One *small tow* PAN precursor company.
  - One non-PAN precursor company.
- All results are proprietary to the company.
- Demonstrated unique performance and economic advantages in all three cases.
- All three have expressed interest in buying plasma oxidation ovens once it has been demonstrated at a larger scale (hundreds of tons).

Response to FY14 Reviewers

- **Questions 1-6** contained all **positive reviews**.
- The single criticism was related to the lower mechanical properties from the Small Reactor (single processing zone reactor used for technology development – still in standby condition today). The Large Reactor, now in use, is a multi-zone processing oven. It represents a large step forward in methods and equipment, and has produced superior results. This has been directly addressed in the data presented here.

Collaboration and Coordination

RMX TECHNOLOGIES

- RMX Technologies – subcontracting industry partner for plasma technology and overall engineering.
- RMX is leading commercialization effort and working to establish industry partnerships to scale up and commercialize plasma oxidation.
- RMX has been awarded a $2M DOE/VTO grant (VT Incubator) to scale plasma oxidation further.

Remaining Challenges and Barriers

- Demonstrate that plasma oxidation produced carbonized fiber that *meets or exceeds* conventional fiber properties.
- Prove to industry that plasma oxidation can *lower the cost* of carbon fiber through validated economics at scale.
- Further *scale-up* will be required to fully commercialize this technology - production scale is typically 1000 ton/year and greater.

Proposed Future Work

- FY15
  - Continue optimization of Large Reactor:
    - Verify fiber property variability of plasma oxidation process across processing width and time for both 24k and 48k tows.
    - Test mass scaling effect with larger tows.
    - Update data correlation for further scaling.

- FY15 (Possibly 1-2M into FY16 as carryover/no-cost extension)
  - Deliver equipment specification for a plasma oxidation oven for an advanced technology/demonstration pilot line appropriate for integration with the Carbon Fiber Technology Facility.

Summary

Relevance

- This technology will reduce the required oxidation time during conversion, and will reduce the production costs of carbon fiber.

Approach

- Develop an oxidation technology that addresses the diffusion time limitations of the conventional method and scale that technology sufficiently to demonstrate the success of this approach to the carbon fiber industry.

Technical Accomplishments

- Project well on schedule and on budget.
- Proven that plasma oxidation works with the Large Reactor.
- 1 ton/year Large Reactor has been operational for over a year with hundreds of hours of operational time.
- Successfully demonstrated plasma oxidation with 3 industry clients to date utilizing their precursor.
- Continue to optimize process and equipment – have not yet determined full potential of this technology/equipment.

Proposed Future Work

- Develop specification for 25 ton/year plasma oxidation oven for CFTF.

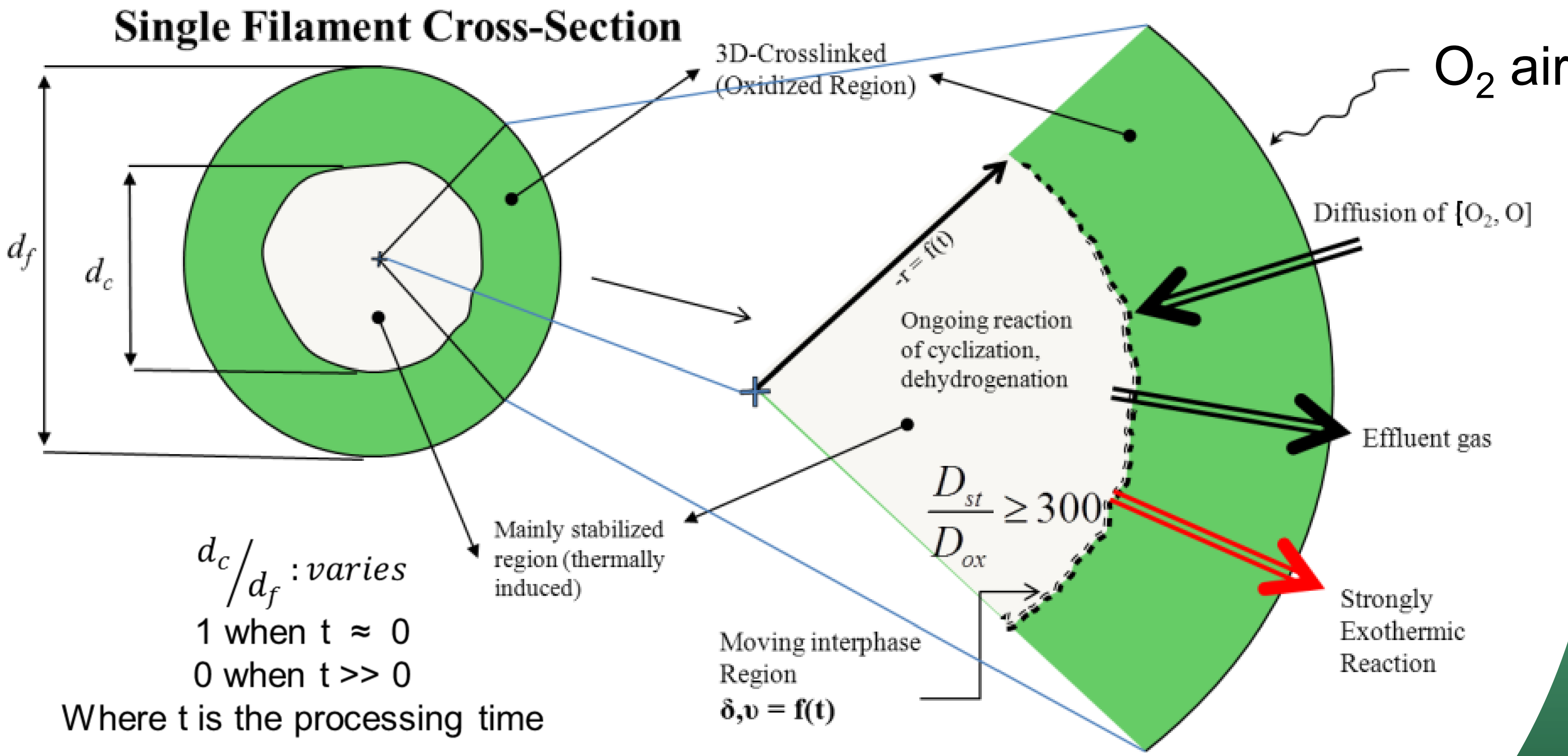
Thank you for your attention.

Questions?

Technical Backup Slides

Approach: Reduce PAN-Oxidation

Two Zone Morphology



d_c / d_f : *varies*

1 when t ≈ 0

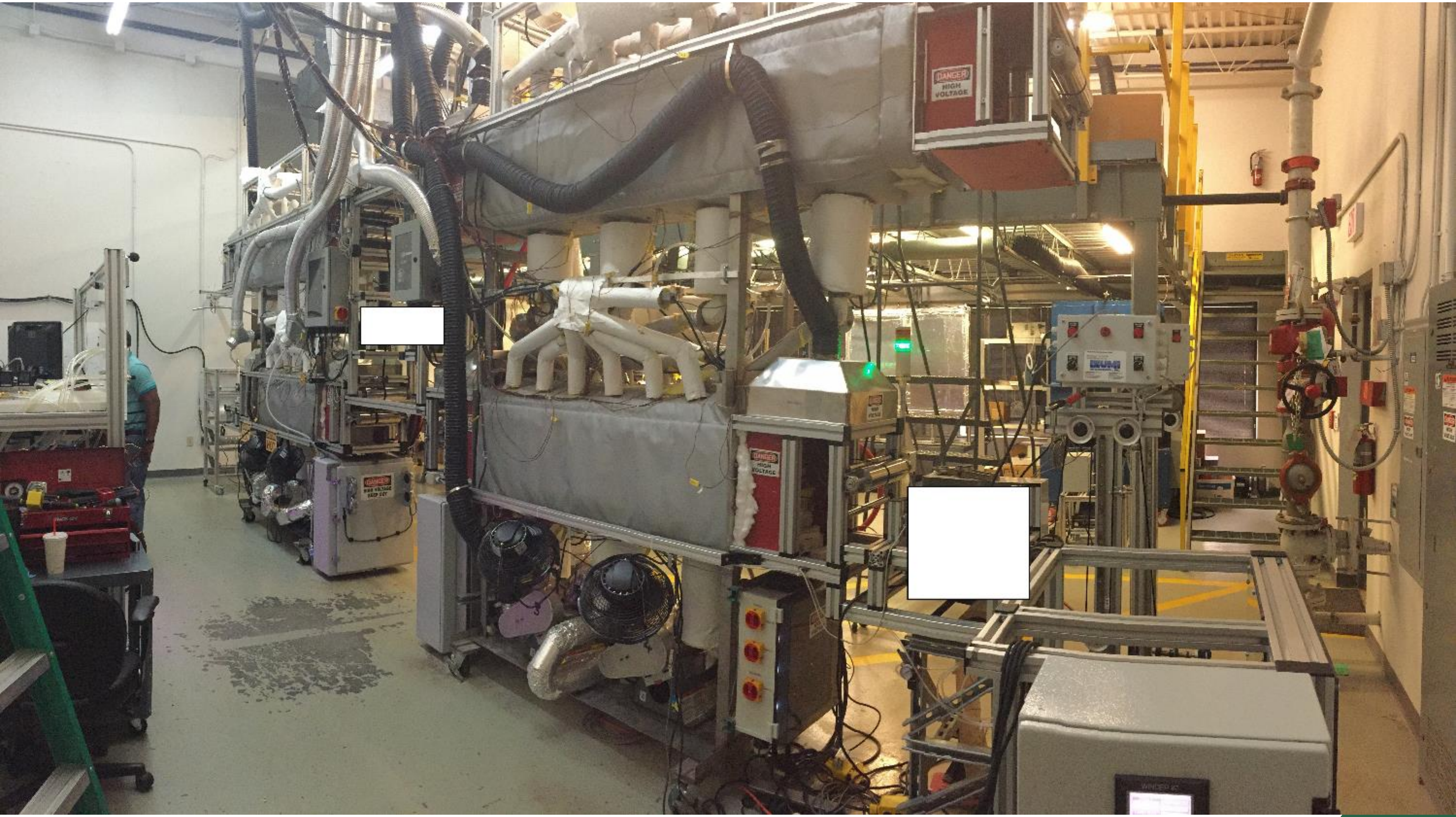
0 when t >> 0

Where t is the processing time

- Diffusion of oxygen to reactive sites is restricted, sequent reactions follow more slowly
- The limiting factor in the oxidative processing is the diffusion-controlled phase

Source: Felix Paulauskas - ORNL

The Large Reactor



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