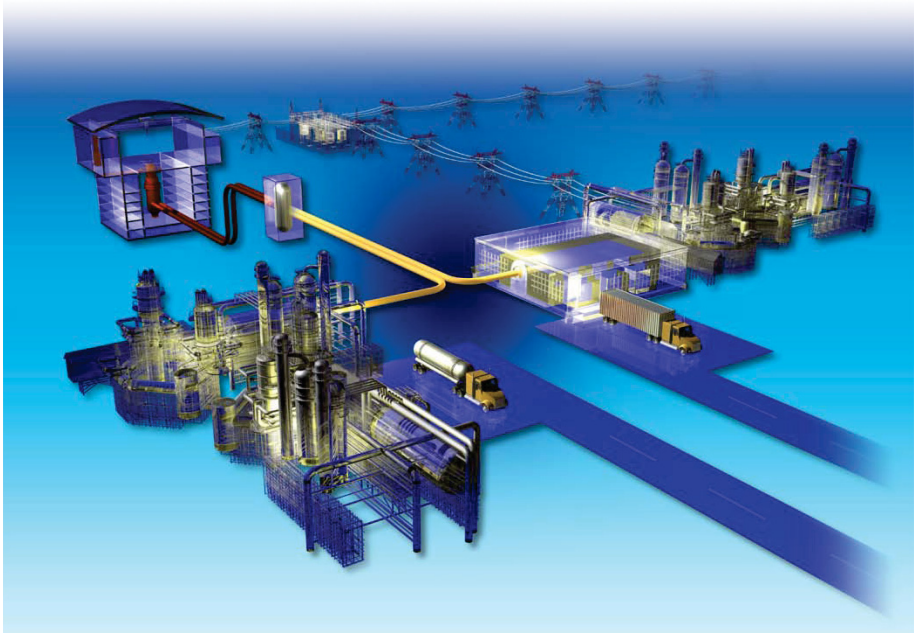
INL/EXT-10-18880

Status of Graphite Oxidation Work

Rebecca E. Smith

May 2010



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ABSTRACT

Data were developed to compare the extent of structural damage associated with high temperature exposure to an air leak. Two materials, NBG-18 graphite and unpurified PCEA graphite have been tested as of this report. The scope was limited to isothermal oxidation at a single temperature, 750°C. Ambient post-oxidation compression strength testing was performed for three levels of burn off (1%, 5%, and 10% mass loss) for two leak scenarios: 100% air and 10% air in helium. Temperature, gas flow, and dynamic mass loss oxidation conditions were monitored and recorded for each sample. The oxidation period was controlled with flow of inert gas during the thermal ramp and upon cool down with a constant 10 liter per minute flow maintained throughout furnace operation. Compressive strengths of parallel un-oxidized samples were tested to assess the relative mass loss effects. In addition to baseline samples matching the un-oxidized dimensions of the oxidized samples, two sets of mechanically reduced samples were prepared. One set was trimmed to achieve the desired mass loss by removing an effectively uniform depth from the geometric surface of the sample. The other set was cored to produce a full penetration axial hole down the center of each sample.

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Status of Graphite Oxidation Work

1. INTRODUCTION

Nuclear reactor design engineers prompted interest in partial air oxidation as a consideration for graphite material selection. A recoverable air leak suggests that graphite exposure to oxygen in a high temperature helium cooled nuclear reactor is limited far below the catastrophic scenario of graphite immersion in air (21% oxygen with 79% nitrogen) at or near reactor operating temperature, but well above the chronic exposure to acceptable (ppm) levels of contaminant oxidants in the helium during normal operation. The objective of this study has been to improve the understanding of graphite mechanical performance under conditions where the graphite is exposed to a significant fraction of air in flowing helium, similar to convective flow in a leak recovery scenario.

Graphite grade selection for testing was based on prospective use and immediate availability. The intent has been to build an information base where there are limited existing data. NBG-18 and unpurified PCEA grades were available and therefore were tested first. A small quantity of purified PCEA has been recently received and will be tested next. Testing of HLM, NBG-17, and IG-110 or PGX will follow as determined by interest and availability. These materials reflect the range of grain size, source materials, and fabrication processes associated with currently produced nuclear grade graphite.

2. EXPERIMENTAL DESIGN

The experimental design for this graphite oxidation work expanded upon the release of American Society for Testing and Materials (ASTM) Standard D7542-09, "Standard Test Method for Air Oxidation of Carbon and Graphite in the Kinetic Regime." The protocol and equipment for isothermal oxidation at 750°C with 10 L per minute gas flow were adapted for use with helium to meet the requisite partial air environment, 10% air in helium, without losing the original nitrogen–100% air capability. In order to achieve consistent levels of 1, 5, or 10% burn off, the system was configured and reprogrammed to automate gas flow and provide for cooling in inert gas to facilitate recovery of oxidized samples for subsequent ambient compressive strength testing.

The basic sample test matrix is illustrated in Table 1.

Table 1. Graphite oxidation compressive strength test matrix.

	NBG-18 in 100% air	**PCEA in 100% air**	**NBG-18 in 10% air**	**PCEA in 10% air**	**NBG-18 cored**	**PCEA cored**	**NBG-18 trimmed**	**PCEA trimmed**
0% mass loss	—	—	—	—	—	—	3 samples	3 samples
1% mass loss	3 samples	3 samples	3 samples	3 samples	3 samples	3 samples	3 samples	3 samples
5% mass loss	3 samples	3 samples	3 samples	3 samples	3 samples	3 samples	3 samples	3 samples
10% mass loss	3 samples	3 samples	3 samples	3 samples	3 samples	3 samples	3 samples	3 samples

NOTE: Shaded blocks require sample oxidation at 750°C in 10 L per minute overall mass flow.

Strength testing was performed under ASTM C695-91(2005), "Standard Test Method for Compressive Strength of Carbon and Graphite." To satisfy this standard, the sample sizes for this work deviate from the 25.4 mm diameter by 25.4 mm long sample dimensions identified in ASTM D7542-09. To achieve the necessary ratio of height to diameter (allowed to vary between 1.9 and 2.1) for the compressive strength test, the height of the cylindrical sample was doubled; before mass loss, samples for this work were 25.4 mm diameter by 50.8 mm long. Samples were conditioned at 100°C for 3 hours before testing and stored in a dry box before oxidation and before strength testing to control exposure to moisture. Each sample was tested to failure under ambient conditions.

Unoxidized samples with 0% mass loss were tested to establish baseline compressive strength performance for these materials. Two sets of samples were machined to new dimensions, or mechanically reduced, for comparison of strength performance for similar levels of mass loss. Mechanically trimmed samples provide a physical basis for the shrinking core oxidation model by removing a uniform quantity of material from the sample exterior to achieve the desired mass loss. Mechanically cored samples have full penetration axial holes drilled through the center; these were intended to provide an inverse perspective on the shrinking core.

2.1 Oxidation System

The oxidation system was initially assembled to enable Idaho National Laboratory (INL) participation in the round-robin testing for the development of ASTM D7542-09. Mass measurement, environmental control, environmental monitoring, and data collection are coordinated by recipe input at the computer interface. The schematic in Figure 1 illustrates the basic orientation and function of system components.

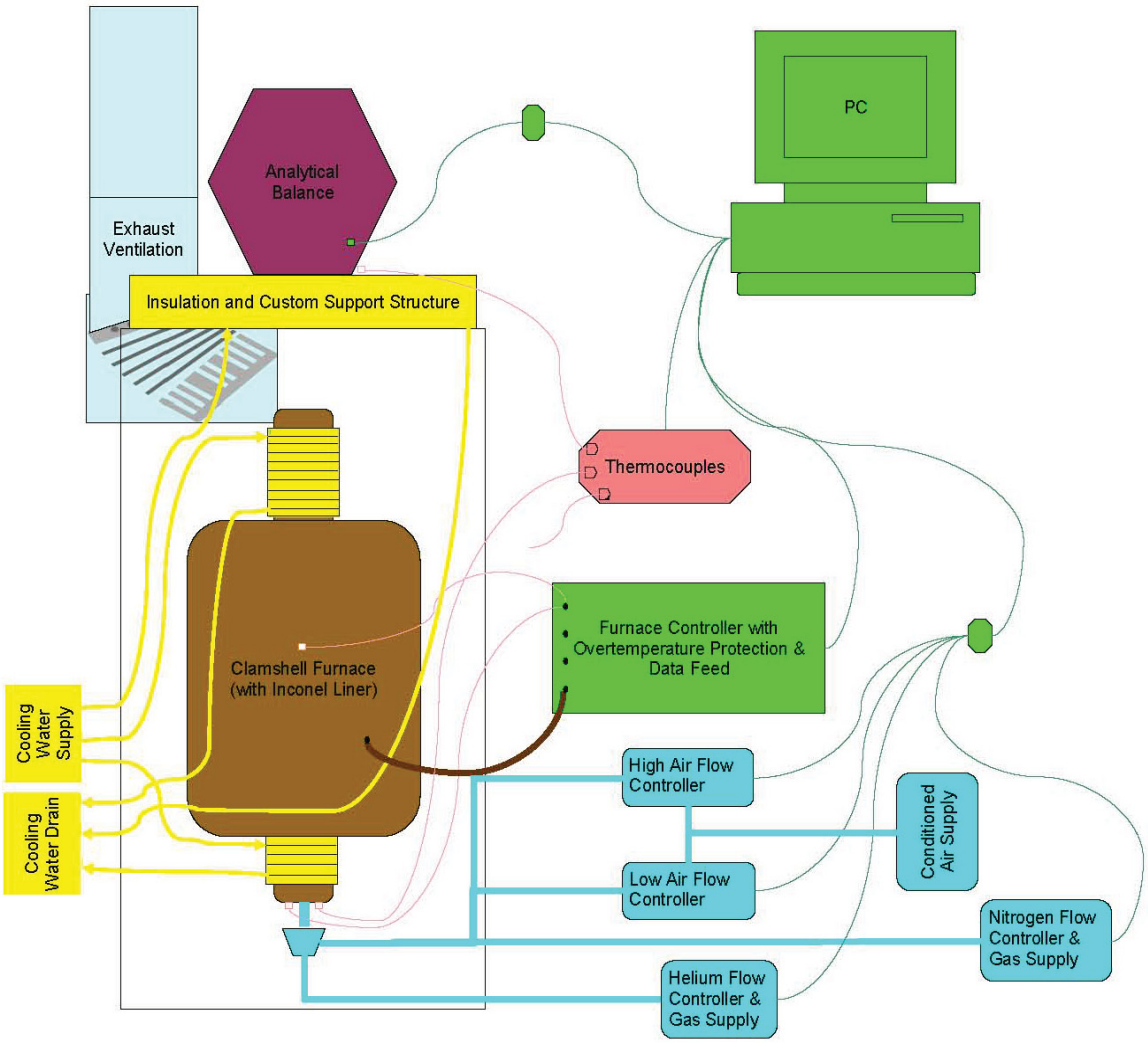

Figure 1. Schematic of graphite oxidation system.

When the helium and low flow air lines were installed, they were integrated with the existing nitrogen and (higher flow) air gas flow control. The gas inlet was fitted with a sintered metal filter (in addition to the bed of silica gel at the base of the furnace to promote plug flow conditions) to facilitate mixing

between helium and nitrogen or helium and air as needed throughout furnace operation. The furnace controller was replaced with a newer model to allow fully automated temperature and gas control to be integrated with mass measurement and data collection, thus providing for inert gas flow during a cooling period after isothermal oxidation. The inert gas cooldown period and the capacity for prolonged fractional air-in-helium runs were facilitated with the addition of a gas cart (supplying gas from up to eight gas cylinders at a time).

Samples are oxidized one at a time, suspended into the furnace from the hook at the base of the analytical balance to allow real time tracking of oxidative mass loss. The platinum wire basket and thin platinum suspension wire are shown with a graphite sample in Figure 2.

Figure 2. Suspension wire and basket with graphite sample.

2.2 Compressive Strength Test

Uniaxial compressive strength tests were performed as illustrated in Figure 3. The materials test equipment shown is operated by trained personnel and its use is shared with other organizations at the INL. The compressive strength testing for the graphite oxidation work did not require application specific adaptations for graphite sample testing.

Figure 3. Compressive strength test configuration.

3. RESULTS

To date, graphite oxidation testing has been conducted on two materials: NBG-18 and unpurified PCEA. Results are compared to facilitate material selection based on strength and air leak related design constraints.

3.1 Oxidation Trends

Kinetic theory indicates three regimes of air oxidation performance defined by the specific reaction environment: (1) lower temperature oxidation with adequate oxygen supply (and product gas removal) leads to chemically controlled bulk oxidation throughout the graphite; (2) higher temperature or diminished oxygen availability leads to oxidation governed by (oxygen and product gases) diffusion through the pores of the graphite; and (3) above some temperature (or below some oxygen availability level) the oxidation rate is dominated by the gas diffusion at the surface of the graphite.

The Arrhenius equation describes the chemically controlled reaction rate and can be written as

$$r = k_0 \cdot P_{O2}^{\,n} \cdot \exp(-E_a/RT) \quad (1)$$

where r represents the oxidation rate; k_0, a rate constant; P_{O2}, the partial pressure of oxygen; R, the gas constant; and T, the temperature. Note that k_0 defines the oxygen dependence of the frequency factor, A, as indicated in

$$A = k_0 \cdot P_{O2}^{\,n} . \quad (2)$$

The scope of this work was limited to the collection of data at a single oxidation temperature, 750°C, so Equation 1 cannot be fully defined with these data. The direct comparison of oxidation rates is therefore illustrated with mass loss with exposure time in Figure 4. The bottom two curves (PCEA in

yellow and NBG-18 in blue) reflect the more rapid mass loss observed in 100% air. The top two curves (PCEA in orange and NBG-18 in pink) show that in a helium environment with only 10% air the oxidative mass loss rate is significantly reduced. In each case, the unpurified PCEA is oxidized more rapidly than the NBG-18, as expected because of the catalytic effect of the contaminants in the unpurified material.

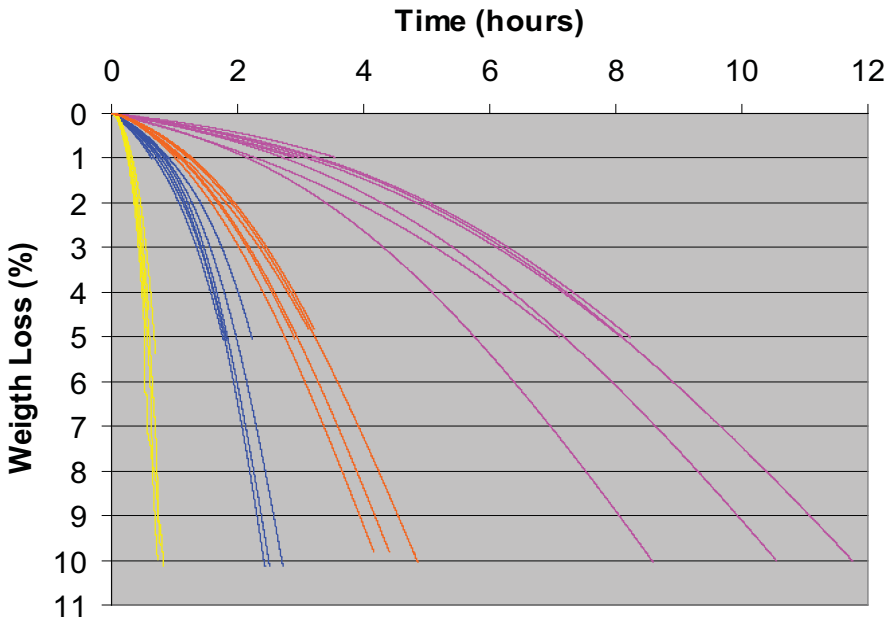

Figure 4. Oxidation rates for unpurified PCEA and NBG-18 in 100% air and 10% air.

Where published Arrhenius data are available, and assuming both 100% air oxidation and 10% air oxidation are within the chemically controlled bulk oxidation regime, the order of the oxidation reaction can be assessed. For PCEA, there are no such published data at this time. However, for NBG-18, one reference provides Arrhenius data produced by the method established in ASTM 7542-09.[1] For NBG-18, n, was estimated at 0.69. Indicated values of n for air oxidation of other nuclear grade graphite materials in air in the range from 0.54 to 1.3, with 0.75 being typical for H-451 and IG-110, so the value appears to be a reasonable approximation.[2,3,4,5]

3.2 Compressive Strength Trends

Stress-strain curves were plotted for all samples tested, and the compressive strength at failure was determined for each.

The performance of strength, S, with oxidation is commonly related to density, ρ, according to Equation 3 (empirically derived), where the subscript "$_0$" indicates the value of unoxidized material:

$$S/S_0 = \alpha\,(\rho/\rho_0)^{\beta}\,. \tag{3}$$

At initial conditions, $S/S_0 = 1$ and $\rho/\rho_0 = 1$ imply that the value of α must be unity. The application of this strength-density relation is often simplified with the constant volume assumption shown in

$$\rho/\rho_0 = m/m_0 = 1 - x \text{ for constant } V \tag{4}$$

where $x = (m_0 - m)/m_0$.

This assumption is consistent with the bulk oxidation observed in the chemically controlled oxidation regime. On the other hand, the surface diffusion limited oxidation regime is expected to produce a volume

reduction reflected by the shrinking core model. For a consistent basis of comparison, constant volume is assumed throughout these data in the presentation of these results. Conditions necessary for the surface diffusion limitation to dominate would require a much higher temperature (>1,300°C).[6] Also, the data for the mechanically trimmed samples provide a measure of the error introduced with this assumption.

Figure 5 illustrates the results for NBG-18 graphite using S0 = 88.39 MPa, the average strength of the three NBG-18 samples with 0% mass loss. Note that the fitted equations for 10% air oxidation and 100% air oxidation data essentially superimpose. Figure 6 shows the results for the unpurified PCEA graphite where S0 = 62.54 MPa, the average strength of the three unpurified PCEA samples with 0% mass loss. Although the scatter in the PCEA data provide for a poor fit, the suggestion that the 10% air oxidation environment leads to slightly less strength loss for the same mass loss in the 100% air environment is consistent with the theory that the preferential oxidation of the sample exterior protects the strength of the remaining (shrinking) core. For either material, the error associated with the constant volume assumption is reasonably small, for volume changes less than ~5% the effect is no greater in magnitude than the observed variation among unoxidized samples of the same dimensions.

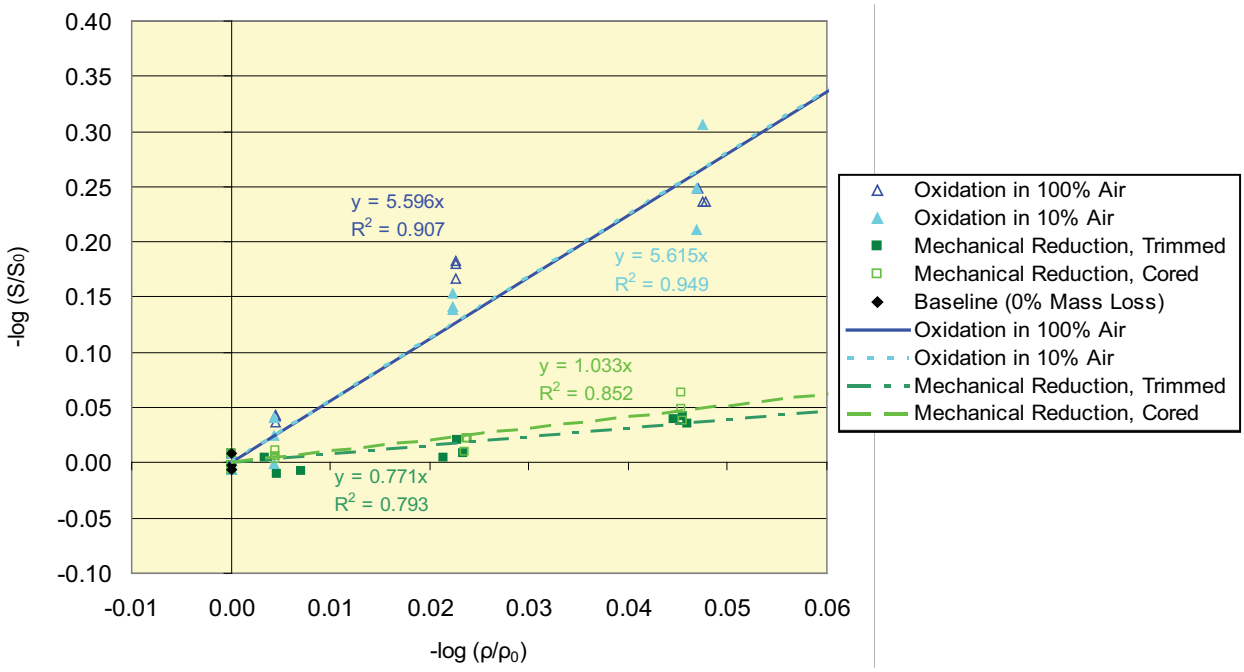

Figure 5. NBG-18 compressive strength results.

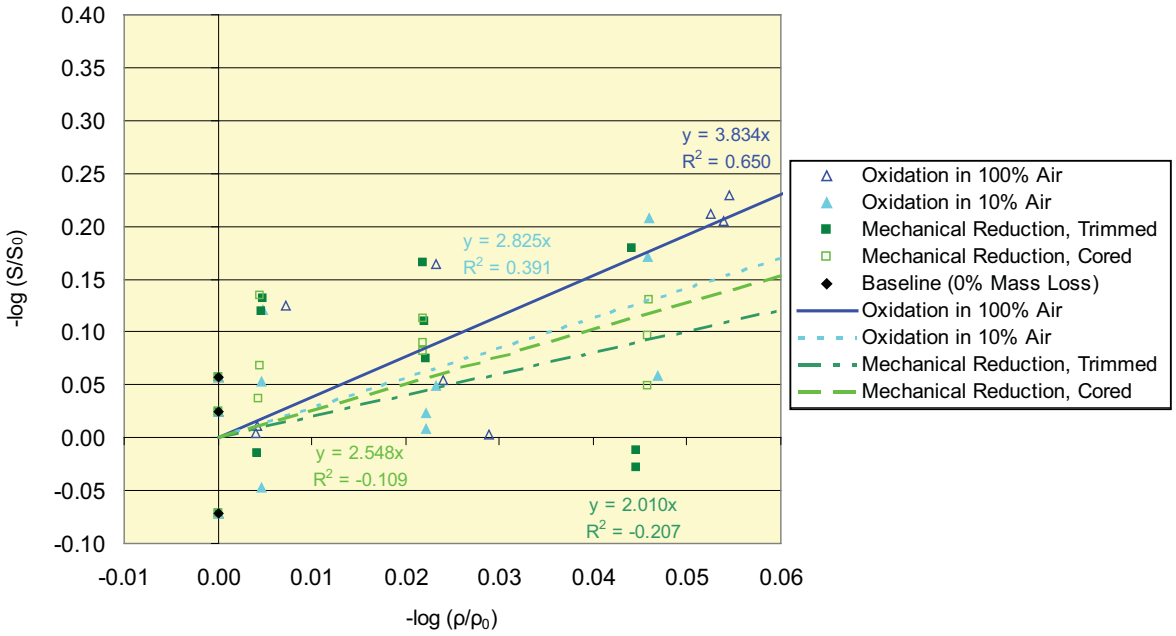

Figure 6. Unpurified PCEA compressive strength results.

A comparison can be made between the unpurified PCEA and the NBG-18 assuming that the general trends in the fitted data reflect the general performance of the respective materials. The results for both materials are plotted together in Figure 7 by normalizing the PCEA to the higher initial NBG-18 strength, S0 = 88.39 MPa, and forcing the fitted PCEA lines through the appropriate y-intercept instead of through the origin. The average initial bulk graphite density, ρ0, (calculated from measured sample masses in combination with height and diameter information) was 1.88 g/cm^3 for NBG-18, and 1.81 g/cm^3 for PCEA, close enough to yield a valid comparison.

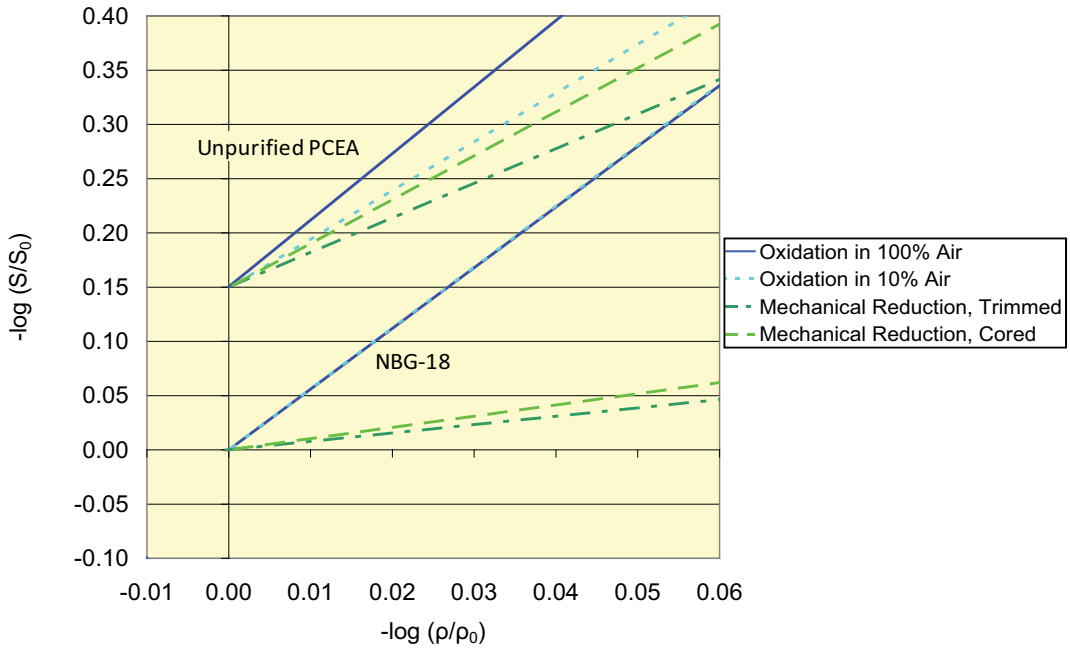

Figure 7. Comparison of strength performance of NBG-18 and unpurified PCEA.

Given the slopes of the respective lines, some tentative conclusions can be drawn. While the un-oxidized strength is greater for NBG-18 than for PCEA regardless of mechanical mass reduction, the unpurified PCEA appears to lose strength more gradually with oxidative mass loss than the NBG-18 for either the 100 or 10% air oxidizing environment. However, consider Figure 7 carefully in the context of both the oxidation rate performance illustrated in Figure 4 and any minimum structural strength criterion. Figure 7 correlates failure strength with mass loss, not with oxidation time; unpurified PCEA oxidizes so much more rapidly than NBG-18 that the remaining strength favors the NBG-18 for any oxidation exposure duration. Also, the remaining strength would likely be unacceptably poor for either material at or beyond the intersection of lines where strength performance with mass loss favors the unpurified PCEA.

4. CONCLUSION

The scope of this graphite oxidation work was established in May 2009 with the anticipation that a total of five graphite materials would be tested. The furnace system was adapted to include the capability to run with helium and low flow air in addition to the original nitrogen and air flow options. Operating software was developed to provide fully automated oxidation control from ambient start, to thermal stabilization in inert gas, to prescribed oxidative mass loss, followed by inert cooldown to near ambient finish. The graphite oxidation testing of NBG-18 and unpurified PCEA has been finished, and work continues with the testing of other materials.

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