13-A-493-PATRAM

Cane Fiberboard Degradation within the 9975 Shipping Package during Long-Term Storage Application

W. L. Daugherty[1], K. A. Dunn[1], E, R. Hackney[2]
[1]Savannah River National Laboratory, Aiken SC
[2]Savannah River Nuclear Solutions, Savannah River Site, Aiken SC

Abstract

The 9975 shipping package is used as part of the configuration for long-term storage of special nuclear materials in the K Area Complex at the Savannah River Site. The cane fiberboard overpack in the 9975 package provides thermal insulation, impact absorption and criticality control functions relevant to this application. The Savannah River National Laboratory has conducted physical, mechanical and thermal tests on aged fiberboard samples to identify degradation rates and support the development of aging models and service life predictions in a storage environment. This paper reviews the data generated to date, and preliminary models describing degradation rates of cane fiberboard in elevated temperature – elevated humidity environments.

Background

Celotex® cane fiberboard is used in the 9975 shipping package between the outer 304L stainless steel drum and the lead shielding (Figure 1), and provides three safety functions: thermal insulation to limit internal temperature during a fire, criticality control and resistance to package crushing. The 9975 shipping package is part of the approved storage configuration for nuclear materials in the K-Area Complex (KAC) at the Savannah River Site. The fiberboard must retain its properties within certain ranges to perform as required. Several properties of interest to demonstrate acceptable long-term performance of the material include dimensional stability, moisture absorption/retention, density, compressive strength, thermal conductivity and specific heat capacity.

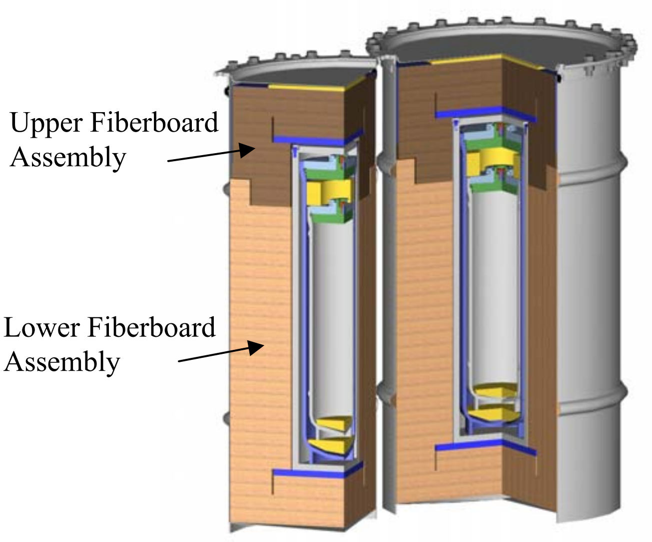


Figure 1. Cross section of 9975 shipping package.

Samples are conditioned in support of several specific tests. Thermal tests are performed to measure thermal conductivity and specific heat capacity. The thermal conductivity is measured on two sample orientations; the axial orientation measures the conductivity of heat perpendicular to the fiberboard layers (axial heat flow within the package), and the radial orientation measures the conductivity of heat parallel to the fiberboard layers (radial heat flow within the package). Compression test samples are tested in either of two orientations, with the applied load either parallel or perpendicular to the fiberboard layers. Physical measurements are made for small samples (~5 cm cubes) in each conditioning environment.

Samples have been taken from several different packages, with a range of package histories. Duplicate samples from multiple package sources have been conditioned to identify the range of variability. Table 1 summarizes the maximum conditioning times for each environment.

Baseline and post-aging results of mechanical and thermal testing have been reported previously [1-3]. Additional data have since been collected, and the cumulative data set has been analyzed for the development of an aging model.

Table 1. Summary of maximum sample aging times prior to testing.

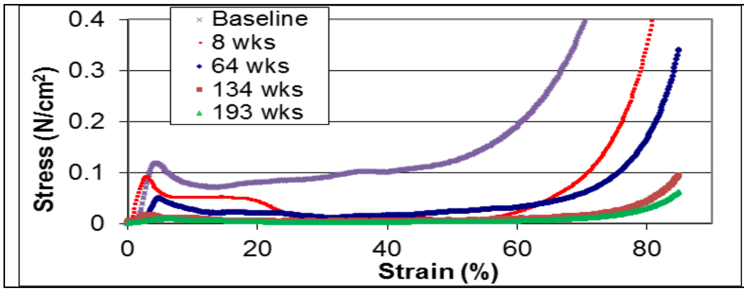
	Maximum aging time (weeks) for			
Environment	Thermal Conductivity	Specific Heat Capacity	Compression Strength	Physical Properties
121 ºC oven	255	258	193	275
102 ºC oven	304	—	200	334
85 ºC oven	337	368	211	367
85 ºC 30% RH	192	196	98	210
85 ºC 70% RH	22	22	23	19
71 ºC 50% RH	112	32	64	114
52 ºC oven	337	379	133	312
52 ºC 70% RH	80	17	64	90
25 ºC 70% RH	—	—	8	—
10 ºC refrigerator	—	—	—	288
-10 ºC freezer	—	—	—	288

Test Data

Compression Tests

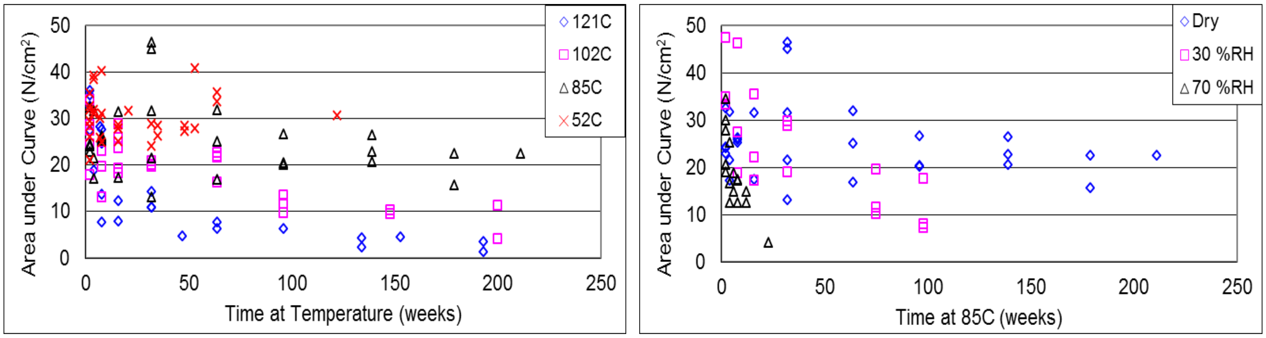
Unlike the thermal and physical tests, compression testing is destructive – each sample can be tested only once. Therefore, these samples become increasingly important after extended conditioning periods as fewer conditioned samples remain for future testing. Compression testing has been performed following aging for as long as 4 years in some environments.

Typical compression stress-strain curves are shown in Figure 2 for samples aged in the 121 ºC dry environment. A range of behaviors has been observed during compression testing (varying shape of the stress-strain curve). The integrated area under the stress-strain curve up to a strain of 40% is used as a metric for quantifying and comparing the performance of different samples. This metric provides a relative measure of the energy absorption capability of the sample. The 40% strain level is arbitrary, but provides a consistent point of comparison. This metric is summarized in Figure 3 for parallel orientation samples from several aging environments.



Aging Period (wks)	Area under Curve to 40% Strain (N/cm^2)
0	32.8
8	13.7
64	7.6
134	2.3
193	1.2

Figure 2. Engineering stress-strain compression curves for typical fiberboard samples aged and tested in the parallel orientation at 121 ºC

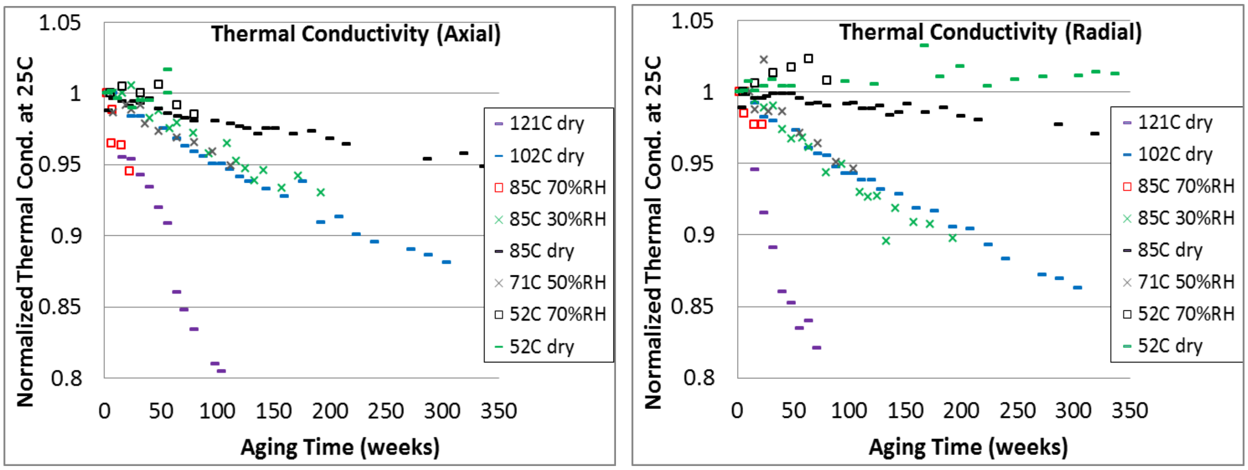


(a) (b)

Figure 3. Area under the stress-strain curve up to 40% strain, for parallel orientation compression test samples. Samples in (a) were conditioned in dry environments, at the temperature noted. Samples in (b) were conditioned at 85 ºC, at the humidity levels noted.

Thermal Tests

Thermal conductivity data for typical samples in each environment are summarized in Figure 4. For ease of comparison, the thermal conductivity data for each sample are normalized to the first measurement taken after conditioning began.



(a) (b)

Figure 4. Thermal conductivity data measured at 25 ºC mean temperature for each aging environment. Each data set is normalized to its first conditioned value. Axial orientation samples are shown in (a), and radial orientation samples are shown in (b).

The specific heat capacity data can show a significant degree of scatter from one trial to the next. Accordingly, the results are averaged over all samples and trials for a given conditioning interval and test temperature. A summary of these averaged data is shown in Figure 5.

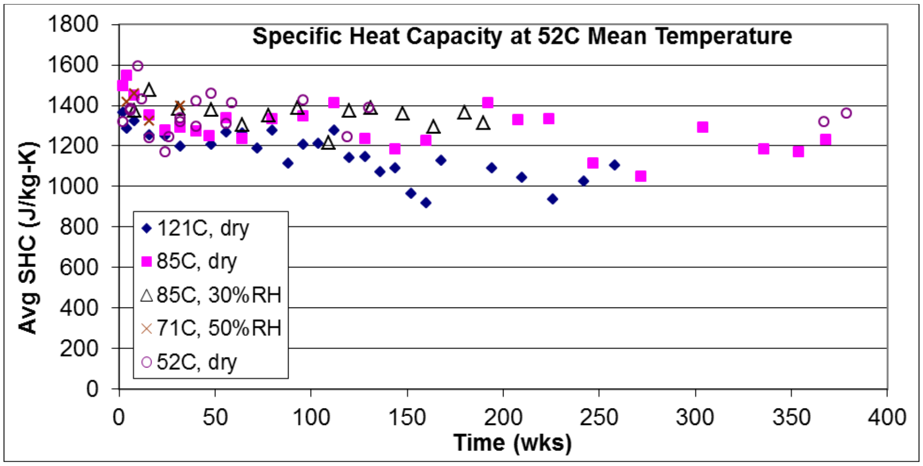


Figure 5. Specific heat capacity data at a mean temperature of 52 ºC for each aging environment.

Physical Tests

Sample weight and dimensions in each aging environment have been tracked. In order to better compare samples and highlight changes among samples with different initial property values, the properties (weight, density, and height) of each sample are normalized to their initial conditioned value. The normalized values are summarized in Figures 6-8.

For samples conditioned at temperatures of ≥71 ºC, a continuous weight loss (beyond an initial change due to moisture loss / gain) is observed. The rate of weight loss is greater with higher temperatures and with increased humidity. In the 52 ºC dry environment, a slight decrease in weight is observed, superimposed on a stronger seasonal variation. No significant change in weight was observed at low temperatures (10, -10 ºC). Samples from the different material sources behave similarly, with about the same rate of weight loss in a given environment.

Density data for the physical property samples are shown in Figure 7. For samples conditioned in dry ovens at 102 and 121 ºC, a continuous decrease in density is observed. Within each of the humid environments at 71 and 85 ºC, a continuous density decrease is observed. At 52 ºC 70% RH, there is no significant change in density over time. Above 52 ºC, the rate of density loss is greater for higher temperatures and higher humidity levels. Comparable rates of density loss are observed for the various material sources within each environment. Qualitatively, dimensional changes in each environment follow those described for density. The change in height tends to be significantly greater than the change in length or width for a given environment.

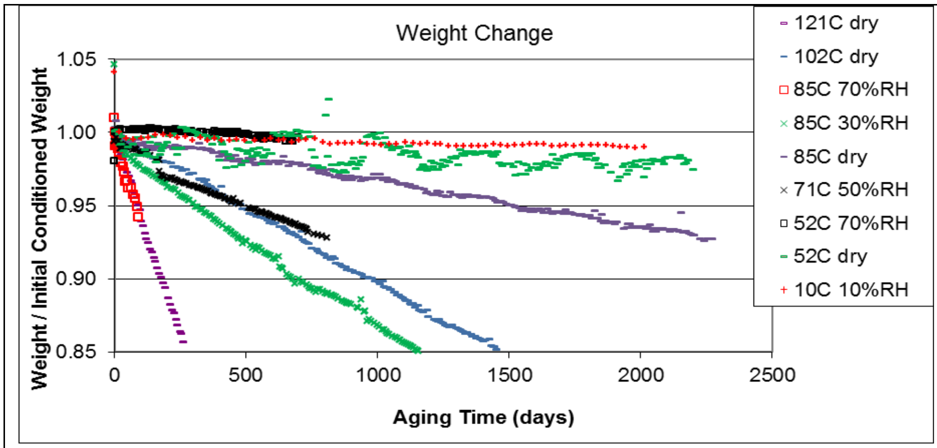


Figure 6. Weight data for physical property samples in the identified environments.

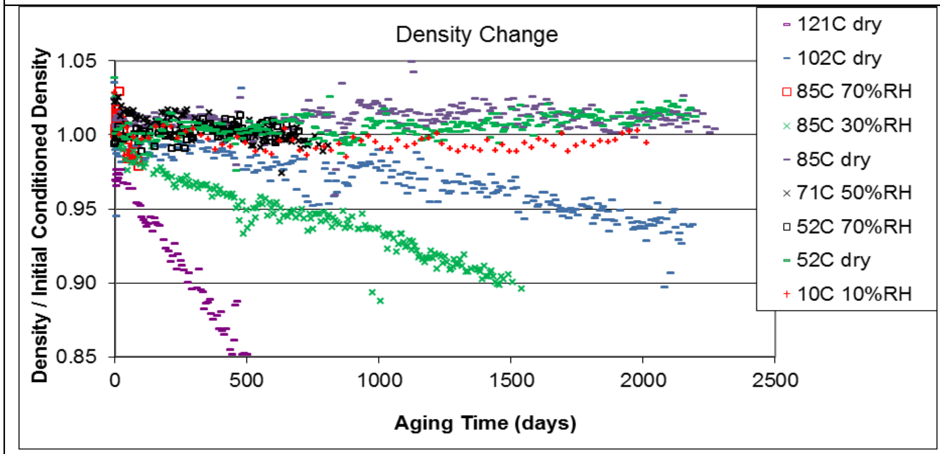


Figure 7. Density data for physical property samples in the identified environments

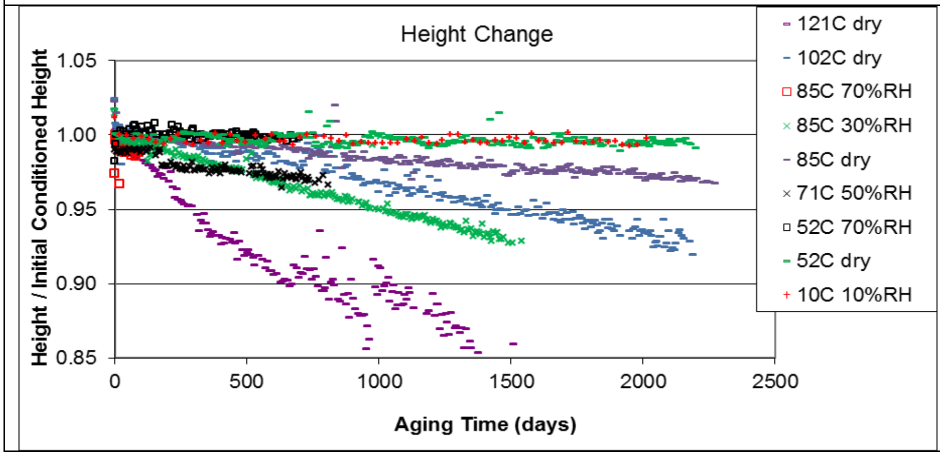


Figure 8. Height data for physical property samples in the identified environments

Analysis

No significant degradation has been observed in fiberboard assemblies from conforming packages (i.e. packages without excessive moisture and/or mold) examined following up to 7 years storage in KAC. The typical package stored in KAC contains a modest amount of moisture within the fiberboard assembly, and has an internal heat load significantly less than the 19 watt rating of the package.

The ambient temperature within KAC can vary seasonally, or due to changes in HVAC status. The normal ambient temperature in KAC is less than 32 °C (90 °F), even in the summer. However, with loss of ventilation, the maximum ambient temperature increases to 58 °C (137 °F), and the corresponding shield temperature can reach 91 °C (196 °F) with 19 watts internal heat load. The maximum fiberboard temperature is assumed to be similar to this shield temperature. With normal ventilation conditions, the fiberboard temperature should generally remain below ~66 °C (150 °F) for all packages. For a typical ambient temperature of ~29 °C (85 ºF) and an internal heat load of 10 watts or less, the maximum fiberboard temperature is expected to be about 46 °C (115 ºF).

To date, all the packages removed from storage for destructive examination have contained cane fiberboard. They had been held in storage for periods ranging from ~5 months to 7 years. The consistent trend indicates the storage environment is sufficiently mild to preclude significant degradation over this time period, although baseline data from these specific cane fiberboard assemblies are not available for comparison. In contrast, the environments used for accelerated aging of the test samples described in this report are more severe than typical KAC storage conditions. This difference is necessary in order to observe degradation and develop models for predicting service life in advance of unacceptable degradation occurring in KAC.

The 9975 SARP notes that the package does not provide an air- or water-tight seal. However, a properly closed drum does provide a significant degree of isolation of the fiberboard from the ambient environment [4]. Accordingly, any moisture originally in the fiberboard assembly will likely remain in the package for a long time. A typical fiberboard assembly will have a moisture content of ~6 – 16 %WME (wood moisture equivalent) or ~7 – 13 wt%. This moisture content will define the relative humidity within the package.

The fiberboard within a heated package will develop temperature and moisture gradients. Moisture will tend to migrate to the cooler regions of the fiberboard, while the total moisture content will change very slowly (if at all).

An indication of the moisture gradient that can exist in service is seen in an instrumented test package that has been conditioning at elevated temperature. It contained an internal heat source of 12 watts (creating a temperature gradient in the fiberboard), and was held in a chamber at 61 ºC. Before conditioning, the fiberboard moisture content in this package ranged from 13 – 15 %WME along the ID, and 16 – 18 %WME along the OD. After conditioning for 57 weeks, the fiberboard moisture content was a maximum of 6.4 %WME along the ID, and ranged from 12 – 22 %WME along the OD. Some regions of the bottom of the lower fiberboard assembly had significantly higher moisture content. Thus, a significant amount of the moisture within this package had migrated from the inner (hotter) regions near the shield to the outside and bottom.

A variety of temperature / humidity combinations should be considered in conjunction with understanding the range of conditions within KAC to adequately identify a limiting service life. For instance, for an ambient temperature of 32 °C (90 °F), the maximum fiberboard temperature of ~66 °C (150 °F) will occur along the ID surface, in conjunction with relatively low moisture content. The higher moisture concentrations (corresponding to a relative humidity of ~75% or greater) will tend to occur along the OD surfaces which are close in temperature to the ambient value of ~32 °C or less. Other intermediate temperature / moisture combinations should also be considered, including the milder temperatures that would accompany heat loads less than 19 watts.

In the laboratory testing, there are two contributions to property changes – immediate, reversible changes due to change in moisture content, and irreversible changes due to degradation. When a sample is placed in an environment, there may be a change in moisture content as the sample comes to equilibrium with the environment (typically within ~1 day for smaller samples, or after many weeks for a full assembly). Reversible changes likely to occur due to moisture change include the following.

- Thermal conductivity and specific heat capacity will decrease as moisture content decreases. This effect is reported in the literature [5] for wood products (and by extension is applicable to fiberboard) and is observed in the laboratory data.
- Physical properties (weight, density, dimensions) all decrease as moisture content decreases.

In addition to short-term moisture effects, longer term changes may occur as a result of degradation. The literature identifies that slow pyrolysis occurs at modest temperatures [6]. In addition to water vapor, compounds from pyrolysis are evolved at temperatures as low as 95 ºC (203 ºF). This is strongly evidenced by samples conditioned at 121C, with an immediate weight loss of 8-10% (moisture loss), followed by an additional 15 – 20 %/year weight loss. At the higher temperature and humidity levels, the samples also change visually. The samples darken, and the coarse fibrous appearance changes to a finer particulate texture.

Degradation Models

Aging models have been constructed based on the observed changes in several fiberboard properties, including weight, height, and thermal conductivity (axial and radial). The models are based on the average behavior of all samples, and do not reflect the minor variation among packages or samples. Specific steps of model development are illustrated for the change in weight.

1. The data are normalized, to show the relative decrease in each property over time (see Figure 6 for normalized weight change).

2. It is observed that very similar rates of change occur for 102 °C dry, 85 °C 30%RH and 71 °C 50%RH environments, and that these 3 environments fall close to a common straight line in humidity – temperature space. This same line includes the environment of 59 °C 70%RH. It is assumed that the average behavior in these 3 test environments (3.6 %/year decrease in weight) is also valid for an environment of 59 °C 70%RH.

3. A curve is fit to rate of change vs temperature for 3 environments – 52 °C 70%RH, 59 °C 70%RH and 85 °C 70%RH (Figure 9). A binomial provides a good

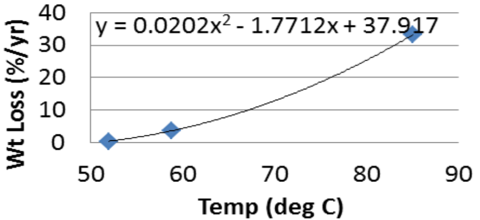


Figure 9. Weight loss vs temperature at 70%RH

fit, and represents the variation with temperature at a constant relative humidity of 70%.

4. A curve is fit to rate of change vs temperature for 4 dry environments – 52 °C dry, 85 °C dry, 102 °C dry and 121 °C dry (Figure 10). An exponential relationship provides a good fit, and represents the variation with temperature at a low value of relative humidity (<10%).

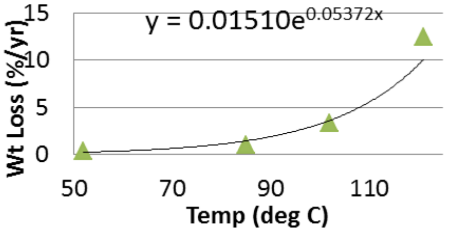


Figure 10. Weight loss vs temperature for dry environments

5. The two curve fits developed for the two relative humidity extremes are used to predict the temperatures at which specific rates of change will occur (e.g. a 1% rate of weight loss is predicted at 78 °C for low relative humidity, and at 54 °C for 70% RH).

6. For the temperature pairs identified in the above step, linear interpolation is used to identify combinations of intermediate temperature and relative humidity values that should provide the same rate of change. Lines of constant rate change are plotted on a graph of relative humidity vs temperature (Figure 11). Based on the very low rates of weight loss at 52 °C (dry and 70 %RH), it is assumed that there is no significant change in weight at lower temperature environments.

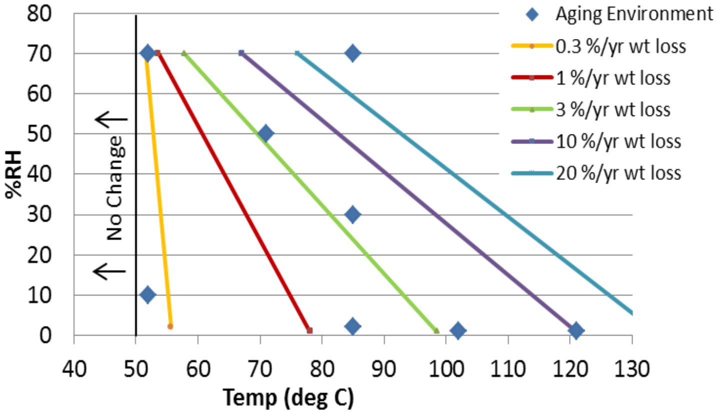


Figure 11. Weight loss model

7. Linear interpolation for intermediate relative humidity values is validated by considering the rates of change for 85 °C at the 3 relative humidity levels (~2%, 30% and 70%). An exponential curve is fit to the rates of change from these 3 environments, and that curve used to calculate the relative humidity for which specific rates of change are expected. Values from this fit are plotted in Figure 12 ("+" symbols), and show good agreement with the lines of constant rate change. In addition, Figure 12 shows the actual rates of weight loss for each environment, for comparison to the model estimates. For a given combination of temperature and relative humidity within the envelope provided by the data, the graph provides an estimate of the rate of change in fiberboard weight.

Additional aging models for height, and thermal conductivity (radial orientations) are shown graphically in Figures 13 – 14. Each of these models was developed through the same process described above for weight. For the thermal conductivity model, the observed rate of change was positive in both 52 °C environments. To facilitate modeling, the 52 °C dry rate of change was not included, and the 52 °C 70%RH rate of change was adjusted to -0.0001 %/year.

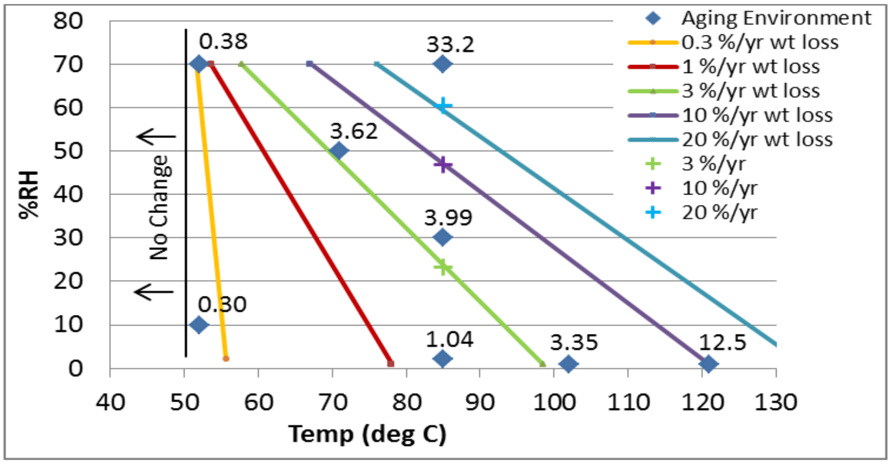


Figure 12. Weight loss model, with interpolated comparison points at 85C (+ symbols). Lines represent contours of equal rate of weight loss. Numerical values are the average degradation rates of aged samples.

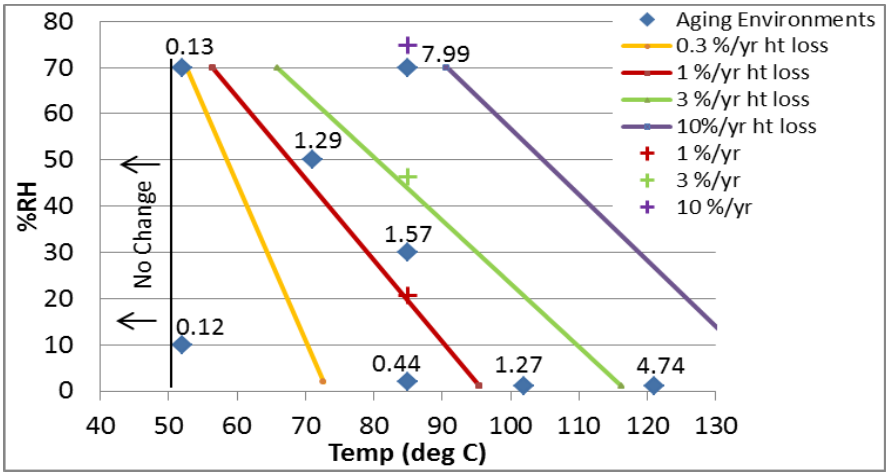


Figure 13. Height loss model, with interpolated comparison points at 85C (+ symbols). Lines represent contours of equal rate of height loss. Numerical values are the average degradation rates of aged samples.

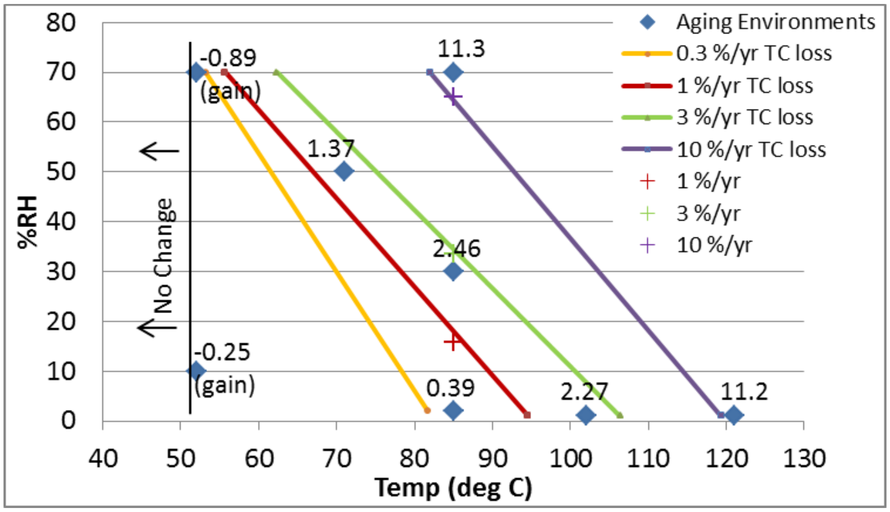


Figure 14. Thermal conductivity, radial orientation model, with interpolated comparison points at 85C (+ symbols). Lines represent contours of equal rate of thermal conductivity decrease in the radial orientation. Numerical values are the average degradation rates of aged samples.

A further consideration in the implementation of any acceptance criterion is that degradation will not occur uniformly throughout the fiberboard. The temperature gradient across the side wall of the fiberboard assembly is modest. For a 19 watt load in a 3013 container, the maximum steady state temperature difference across the fiberboard and drum (in the radial direction) is calculated to be 26 °C (47 ºF). Coincident with this thermal gradient, there will tend to be a moisture gradient in the opposite direction (higher moisture content in the lower temperature regions). Since degradation rates are typically dependent on the temperature and moisture content, any gradient in these conditions within the fiberboard assembly will produce a corresponding gradient in the degradation rate. In some cases, the opposite effects of these two gradients may offset each other. More likely, there will be a partial offset, but a net difference in degradation rate across the fiberboard.

The fiberboard environment within the 9975 packages stored in KAC will vary. The temperature and temperature gradient within a package will vary with the ambient temperature and internal heat load. The moisture content of the fiberboard will largely be determined by the initial fiberboard condition (barring significant water intrusion during service), and the distribution of that moisture will be driven by the temperature gradient.

With an ambient temperature of 29 °C and a maximum internal heat load, the maximum fiberboard temperature will be ~57 °C (along the ID surface). Based on data from instrumented packages, the temperature along the fiberboard OD is ~22 °C cooler than the ID, or ~35 °C for an ambient temperature of 29 °C. The total moisture content will vary from package to package, but it might be assumed that the typical package will have no more moisture than would be absorbed from the air at 24 °C and 100% RH. Without any redistribution of moisture, the elevated service temperatures would reduce the relative humidity inside the package to ~55% along the fiberboard OD surface and ~17% along the fiberboard ID surface. These are two environments that might exist along the OD or ID surfaces of 9975 packages. The intermediate fiberboard regions would be at intermediate environments. The overall degradation rate would be an average over a continuum of local behaviors for a range of intermediate environments.

In reality, moisture within the package will re-distribute. Moisture levels near the ID surface will be further reduced, while the OD surfaces will become wetter. In addition, there will likely be a net transfer of moisture from the central elevations to the bottom of the fiberboard if a significant heat load is present. In local regions where the moisture level increases further (e.g. above 55% RH), fiberboard weight, density, compressive strength and axial thermal conductivity are expected to decrease at a faster rate.

These changes will have a local (near-surface) effect only, since the moisture extremes will be local. The property limits are developed as bulk average properties. It is judged that even with local surface regions degrading at a significant rate, the overall average rate of change in the bulk fiberboard property will still be low. This judgement is supported by observation of packages removed from service after up to 7 years storage in KAC. Examination of these packages has shown a range of fiberboard properties (density, thermal conductivity, specific heat capacity and compression strength) consistent with that of un-aged fiberboard, with no discernable change in the fiberboard exterior surface compared to the rest of the assembly.

Conclusions

Thermal, mechanical and physical property data for cane fiberboard samples have been summarized following aging in several environments (elevated temperature and/or humidity) for periods up to ~7 years. Most of the aging environments are bounding to the conditions expected within the 9975 shipping package during storage in KAC. Initial models have been developed from this data to provide estimates of degradation under potential storage conditions for several fiberboard properties, including thermal conductivity, weight loss and height change.

Additional data continue to be collected to permit future refinements to the models and assumptions. The prediction of service life for packages stored in KAC would utilize the degradation rate models developed within this report, along with specific allowable ranges on each property under consideration. For potential storage environments, package service life is dependent on the most limiting service life estimate based on each of the relevant fiberboard properties.

References

[1] WSRC-TR-2004-00523, "Baseline Mechanical Property Data for Model 9975 Package Celotex® Material", W. L. Daugherty, December 2004

[2] WSRC-TR-2007-00441, "Properties for Fiberboard in Model 9975 Package Following Environmental Conditioning – FY07 Status Report", W. L. Daugherty, November 2007

[3] PVP2010-25118, "Aging Model for Cane Fiberboard Overpack in the 9975 Shipping Package", W. L. Daugherty and S. P. Harris, Proceedings of the ASME 2010 Pressure Vessels and Piping Division / K PVP Conference PVP2010, July 18-22, 2010, Bellevue, Wa

[4] PVP2010-25087, "Effects of Moisture in the 9975 Shipping Package Fiberboard Assembly", W. L. Daugherty, K. A. Dunn, J. L. Murphy and E. R. Hackney, Proceedings of the ASME 2010 Pressure Vessels and Piping Division / K PVP Conference PVP2010, July 18-22, 2010, Bellevue, Wa

[5] DOE/USDA-21697/1, ORNL/Sub/87-21697/1, "Thermal Properties of Wood and Wood Panel Products for Use in Buildings", A. TenWolde, J. D. McNatt and L. Krahn, September 1988

[6] FPL Report #2136, "Theories of the Combustion of Wood and Its Control a Survey of the Literature", F. L. Browne, Forest Products Laboratory, USDA