Elevated Temperature Testing and Validation of Long-Term Performance for Polyethylene Piping Materials

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In order to design for thermoplastic, composite or multilayer piping applications, the long-term strength of the particular thermoplastic material or composite or combination of materials needs to be established. This is necessary because thermoplastic and many composite and multilayer piping products demonstrate time dependent strength properties due to their viscoelastic responses. To properly design using such materials and to ensure adequate service life for the plastic piping, some type of long-term testing method must be used. This testing method, along with some type of mathematical analysis of the resulting data must allow a projection of the estimated long-term strength at or near the projected service life limits required for the particular application.

For pressure piping applications with thermoplastic, composite and multilayer piping products there are three similar but differing analysis methods that have been developed and modified over the past fifty years. These are the American Society for Testing and Materials' (ASTM) D2837, "Standard Test Method for Obtaining Hydrostatic Design Basis for Thermoplastic Pipe Materials or Pressure Design Basis for Thermoplastic Pipe Products," ASTM D2992, "Standard Practice for Obtaining Hydrostatic or Pressure Design Basis for "Fiberglass" (Glass-Fiber-Reinforced Thermosetting-Resin) Pipe and Fittings," and the International Organization for Standardization (ISO) 9080-2012, "Plastics piping and ducting systems–Determination of the long-term hydrostatic strength of thermoplastics materials in pipe form by extrapolation." These test methods set out analysis procedures for the development of long-term strength projections based on the stress rupture testing of specimens of thermoplastic, composite and multilayer piping.

The commonly used thermoplastic piping materials are viscoelastic materials and demonstrate time dependent physical properties. These include un-plasticized polyvinyl chloride (u-PVC), polyethylene (PE), chlorinated polyvinyl chloride (CPVC), polypropylene (PP), polybutylene (PB), cross-linked polyethylene (PEX), acrylonitrile-butadiene-styrene (ABS), and the various fluoropolymers (polyvinylidene fluoride (PVDF), tetrafluoroethylene (TFE), ethylene-chloro-tri-fluoroethylene (ECTFE) and perfluoro-alkoxy (PFA)). Stress rupture test data of pressure piping products, when analyzed and plotted on a logarithmic basis, produces a straight-line plot over short testing times. This enables a linear or multi-linear regression analysis to be carried out and the long-term strength of these materials to be projected to 100,000 hours and also to 438,000 hours (50-years). This is the basis for the ASTM and ISO test methods.

One of the underlying assumptions of ASTM D2837 and D2992 is that there is only a single failure mechanism occurring. This is generally true of the vinyl polymers and also for the fluoropolymers. It may not be true depending on the basic material properties of polyethylene, polypropylene, and cross-linked polyethylene. Polyolefin materials will exhibit a change in the failure mode from a ductile failure to a brittle or slit type failure depending on the fundamental material properties of the particular grade and on the environmental conditions used for the testing. This transition from ductile to brittle failure mechanisms can vary tremendously. When this change in failure mode occurs, there is a drastic change in the slope of the regression line of the long-term stress rupture testing. The projected long-term strength of the particular material decreases rapidly as the testing is continued or if the testing is done at higher temperatures. Figure 1 shows an example of hydrostatic stress rupture curves (log time vs. log hoop stress) for a typical polyvinylchloride (PVC) pressure piping compound.

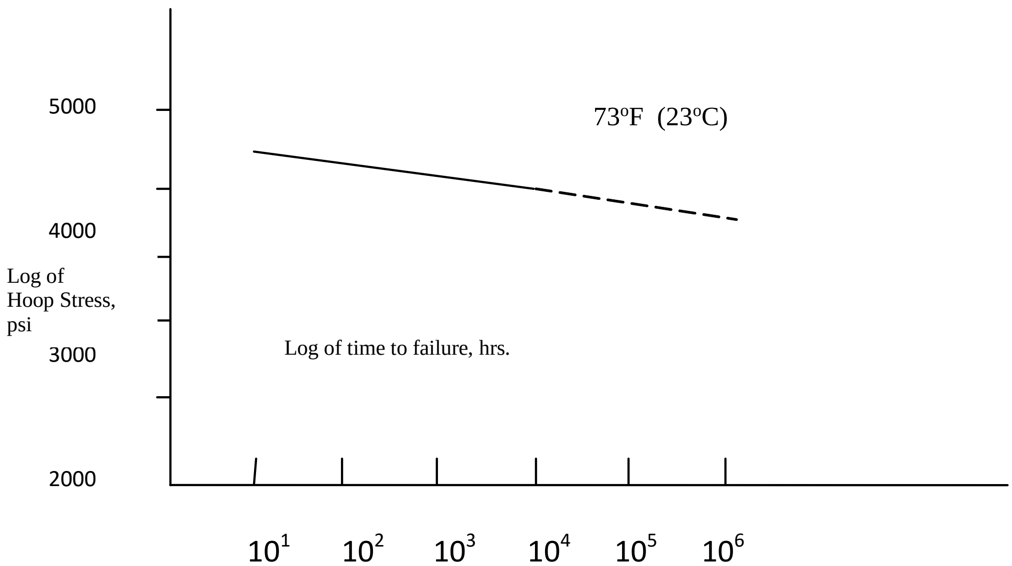

Figure 1: Typical Stress Rupture Testing Curves for a Polyvinylchloride Pipe Compound

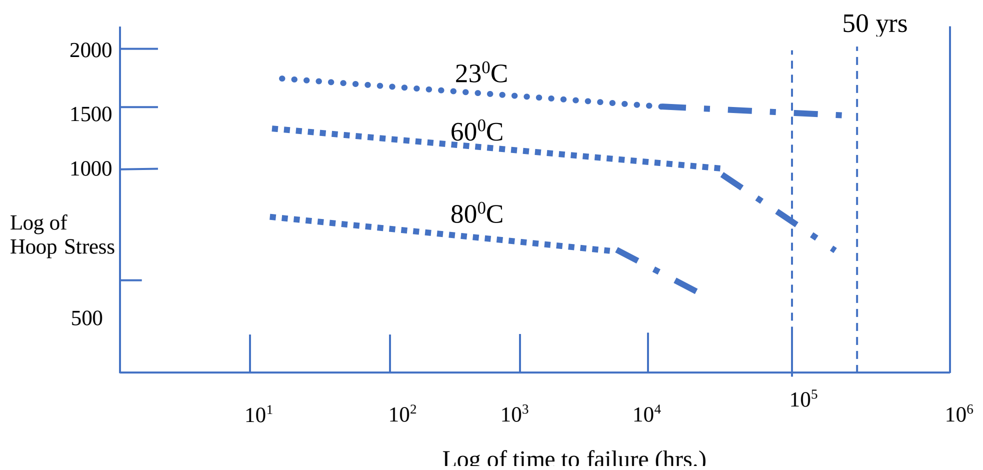

Figure 2: Hypothetical Stress Rupture Testing Curves for a Polyethylene Pipe Material

Figure 2 shows an example of hydrostatic stress rupture curves (log time vs. log hoop stress) for a hypothetical polyethylene piping material where elevated temperature testing demonstrates this change in failure mechanism. Figure 2 shows the development of a second type of failure mechanism (brittle or slit failures) for the higher temperature testing data (60ºC and 80ºC). The ambient temperature test data (23ºC) will show a similar downturn of the curve as a similar transition from ductile to brittle failure mechanism also occurs over time. But this does not happen until much longer test times beyond the 10,000 hours typically used to evaluate these materials. Figure 2 demonstrates how changes in temperature accelerate the onset of the transition from a ductile failure mechanism to a brittle or slit failure mechanism for polyethylene materials.

Changes in the fundamental properties of a polyolefin material, such as molecular weight, molecular weight distribution, long chain branching, density or degree of crystallinity, can also affect the onset of this change.

Changes in the testing temperature causes two distinct changes to the stress rupture testing curves. Again because of the viscoelastic nature of these materials as the temperature is increased the tensile strength decreases. That is, at higher temperatures, the portion of the curve representing the ductile behavior of the material demonstrates a lower hoop stress value and a lower projected long-term strength.

The change in failure mechanism generally represents the effects of chemical-oxidative attack on the polymer material. This process is dependent on the temperature at which the test is carried out. With very few exceptions, the rate of reaction increases with an increase in the temperature. In 1889, Arrhenius pointed out that a reasonable equation for the variation of the rate constant of a chemical reaction with temperature would be the following:

Equation 1:

$$\frac{d \ln k}{d T} = \frac{Ea}{RT^2}$$

Where
k is the rate constant for the reaction
T is the temperature (degrees Kelvin)
Ea is the activation energy of the reaction
R is the gas constant
ln is the natural logarithm

If Ea is not temperature dependent, Equation 1, upon integration, yields the following:

Equation 2:

$$\ln k = \frac{-Ea + \ln A}{RT}$$

Where A is the constant of integration

This equation is also written as the following

Equation 3:

$$k = Ae^{-\in/kT}$$

Where k is the average rate constant for the reaction
A is the per-exponential factor, frequently termed the frequency factor and is independent of temperature
$\in$a (Ea) is the Arrhenius Activation Energy and provides a value for some characteristic energy that must be added to the reactants for the reaction to occur.

From Equations 2 and 3 it follows that a plot of the logarithm of the rate constant against the reciprocal of the absolute temperature should be a straight line. The slope of the plot will yield the activation energy of the reaction and the frequency factor can be found from the intercept.

As the equations imply, reaction rates increase as the temperature increases. A useful rule of thumb is that the reaction rate doubles for every 10^{o}C increase in the temperature of the reaction.

Because the basic failure mechanism of brittle failure in polyolefin piping materials is a chemical process (chemical oxidative attack on the polymer backbone) then this process will follow the Arrhenius equation and occur much faster at elevated temperatures. This allows accelerated testing at elevated temperatures to be used to model and project the longer-term ambient temperature behavior. This has been well demonstrated experimentally by the polymer industry over the past fifty years.

Thus, when a polyolefin pipe material is evaluated by linear regression analysis in order to project the long-term strength (i.e. ASTM D2837), this projection is only valid with certain boundaries. Where a second failure mechanism is known to occur then a straight forward extrapolation of the 10,000-hour test data will give an erroneous long-term value at 100,000 hours and at 438,000 hours (50 years). The long-term strength of the material will be significantly overestimated and there develops a significant risk of early failure of pipe made with this material depending on the stresses and environmental factors encountered in service. Where a change in the physical state of the material occurs over the range of temperatures tested the linear regression analysis cannot be applied. A change in the physical state of the material would be a phase transition, reaching the glass transition or changes in the crystallinity of the material.

TEST METHODS FOR DETERMINING LONG TERM HYDROSTATIC STRENGTH

ASTM D2837, "Standard Test Method for Obtaining Hydrostatic Design Basis for Thermoplastic Pipe Materials or Pressure Design Basis for Thermoplastic Pipe Products," describes a procedure for analyzing stress rupture pipe test data in order to extrapolate a long-term strength value for the piping product being tested. ASTM D2837 is the preferred method for establishing the Hydrostatic Design Basis (HDB) for thermoplastic pipe materials throughout North America and also for much of Central America and South America. ASTM D1598, "Standard Test Method for Time-to-Failure of Plastic Pipe Under Constant Internal Pressure," describes how to test individual pipe specimens and is applicable to both thermoplastic and reinforced thermosetting/resin pipe materials. ASTM D2837 requires that a minimum of 18 failure points as well as a specific distribution of failure points be obtained to develop a full hydrostatic stress rupture curve for a material at a specific temperature. This distribution is shown in Table 1.

Table 1: Required Minimum Distribution of Failure Points

Hours	Failure Points
< 1000	At least 6
10 to 1000	At least 3
1000 to 6000	At least 3
After 6000	At least 3
After 10,000	At least 1

Thus, to develop a full stress rupture plot at ambient temperature at least 18 failure points distributed over 10,000 hours must be obtained. Spreading the failures out over three log decades as required by ASTM D2837 adds to the statistical significance of the linear regression analysis. It also provides an opportunity to look for indications of the occurrence of a second failure mechanism. The occurrence of a second failure mechanism increases the variance in the data.

For materials that demonstrate a single failure mechanism during stress rupture testing and meet the analysis requirements in D2837, establishing the long-term hydrostatic strength is a simple matter of performing a linear regression analysis of the test data as per D2837 and PPI TR-3 and extrapolating the 100,000-hour intercept of the projected failure data. However, with some materials there exists the potential of a second failure mechanism occurring which invalidates the fundamental assumption of D2837 and in turn, PPI TR-3, that there is only one failure mechanism occurring. With these types of materials (polyethylene, polypropylene, crosslinked polyethylene, for example) additional testing requirements have been introduced to ensure the validity of the long-term strength projection.

ASTM D2992, "Standard Practice for Obtaining Hydrostatic or Pressure Design Basis for "Fiberglass" (Glass-Fiber-Reinforced Thermosetting-Resin) Pipe and Fittings," describes a similar procedure for analyzing stress rupture test data for glass reinforced thermosetting resin piping and fittings products in order to extrapolate a long-term strength value for the products being tested. ASTM D2992 offers two procedures: static and cyclic. The static procedure is similar to ASTM D2837 with slightly modified data analysis. The cyclic testing requirements were added because of the susceptibility of fiberglass reinforced piping to cyclic fatigue.

Prior to 2012, The International Organization for Standardization (ISO) published a similar testing method; Technical Report ISO/TR 9080: "Thermoplastics pipes for the transport of fluids -- Methods of extrapolation of hydrostatic stress rupture data to determine the long-term hydrostatic strength of thermoplastics pipe materials." TR9080:1992 required testing of a minimum of 30 samples at each of three temperatures (for example, 20°C, 60°C and 80°C) and included a graphical methodology to estimate the ductile to brittle transition at 20°C in order to extrapolate the long-term 50-year strength.

ISO updated ISO/TR9080 to a Standard Specification. The current version is ISO 9080:2012 - "Plastics piping and ducting systems–Determination of the long-term hydrostatic strength of thermoplastics materials in pipe form by extrapolation." ISO 9080 requires the testing of a minimum of 30 specimens at each of two or more temperatures (for example, 20°C, 60°C and 80°C). A multilinear regression and knee detection computer algorithm analyzes the three data sets. The computer program replaces the graphical method and calculates the potential for a brittle to ductile transition and then projects the 50-year lower confidence limit of the predicted long-term strength using that algorithm.

VALIDATION OF POLYETHYLENE PIPE COMPOUNDS

In order to address the possibility of a loss of ductility in polyethylene piping compounds, the Hydrostatic Stress Board of the Plastics Pipe Institute developed the validation testing concept to ensure that polyethylene piping products would remain ductile to 100,000 hours and not undergo a ductile to brittle transition leading to premature failures due to Slow Crack Growth (SCG), while in service. This validation testing protocol is included in ASTM D 2837 and PPI Technical Report TR-3, "Policies and Procedures for Developing Hydrostatic Design Basis (HDB), Hydrostatic Design Stresses (HDS), Pressure Design Basis (PDB), Strength Design Basis (SDB) and Minimum Required Strength (MRS) Ratings for Thermoplastic Piping Materials or Pipe."

A “substantiation” of the 23°C regression to 50-years for PE piping grades is required in ASTM D 2513, “Standard Specification for Polyethylene (PE) Gas Pressure Pipe, Tubing, and Fittings.” The protocol requires additional stress rupture testing at elevated temperatures to confirm that the polyethylene piping compound remains ductile throughout the time frame of the extrapolation of the ambient temperature testing data. It is this extrapolation to 100,000-hours, which is used to establish the LTHS and the resulting HDB cell classification.

The original validation methodology adopted in the late 1980’s employed the “Rate Process Method,” which uses the development of brittle failures at three sets of conditions comprising three elevated temperatures and three different stress levels. The three-coefficient rate process equation is used to calculate the minimum test time for a target test stress and test temperature to validate linearity.

Equation 3: $$\log t = A + \frac{B}{T} + \frac{C \log S}{T}$$

Where:
- t = time, hours
- T = absolute temperature, °K (°K = °C + 273)
- S = hoop stress, psi
- A, B, C = constants

There was an alternative validation method, where if no brittle failures were observed in testing at 80°C within a 6,000-hour time frame, the LTHS value developed per ASTM D2837 at 23°C was considered validated.

In the mid 1980’s bidirectional shift functions were developed for high density polyethylene (HDPE) and medium density polyethylene (MDPE) piping materials analyzed by Popelar, Kenner and Wooster. Popelar’s work was among four methodologies used to establish the duration of short-term elevated temperature stress rupture testing required to confirm the 100,000-hour long-term hydrostatic strength or to confirm the 50 year (438,000 hour) long-term hydrostatic strength.

Popelar, Kenner and Wooster related the stress rupture performance of polyethylene materials measured at elevated temperatures to that occurring at the operating or reference temperature of the system by using the classical time-temperature superposition principle, whereby elevated temperature data are translated along both the time axis (horizontal shifting) and the stress axis (vertical shifting) to form a smooth master curve. The amount of the shift at each temperature establishes the shift function. A necessary condition for the validity of this procedure is that the resulting bidirectional shift function must be independent of the specific mechanical test. The shift functions for both HDPE and MDPE were found to be essentially identical. Popelar developed two reduction equations, one for temperature reduction factors and a second for stress reduction factors.

Popelar's work provides the following shift functions:

Equation 4: $$\alpha\tau = \exp[-0.109\,(T - TR)] \qquad \beta\tau = \exp[0.0116\,(T - TR)]$$

The time to failure t_f of PE depends upon the applied stress (σ) and the temperature (T).

Where $\sigma(TR) = \sigma(T)\,\beta\tau$ and $t_f(TR) = t_f(T)/\,\alpha\tau$

Where T = testing temperature (^oK), TR = reference temperature (^oK) and (T - TR) is the difference between the two temperatures.

σ (TR) = stress at the reference temperature
σ (T) = stress at the testing temperature
t_f (T) = time to failure at the testing temperature
t_f (TR) = time to failure at the reference temperature

Popelar proposed in his paper, that times to failure of 650 hours at 80^0C would be sufficient to establish the 50-year Hydrostatic Design Stress at 20^oC. He also stated that these shift functions could consolidate data irrespective of type of MDPE or HDPE gas pipe material and that this signified that these functions are universal for these materials.

In addition to Popelar's published papers, the "Extrapolation Time Limits" and the "Rule of Thumb," published in ISO Technical Report TR-9080:1992, as well as extrapolation studies published by Nobuaki Nishio were also used to analyze the accelerated testing requirements. In ISO Test Report TR-9080 the time limits (t_e) for which extrapolation is allowed are bound to temperature dependent values. The time t_e includes the testing time. ISO TR 9080 contains a table, which gives the extrapolation time factor (K_e) as a function of δT based on the following equation:

Equation 5: $\delta T = T_{max.} - T_S$

Where $T_{max.}$ is the maximum test temperature, and T_S is the service temperature.

The extrapolation time t_e can be calculated using the following equation:

Equation 6: $t_e = K_e\, t_{max}$

Table 2: Relation between δT (= $T_{max.}$- T_S) and K_e in TR 9080

δT (^0K) >	**δT (^0K) $\leq$**	**K_e**
0	10	1
10	15	3
15	20	5
20	25	9
25	30	16
30	35	28
35	40	50

In the instance where t_{max} is equal to 8760 hours (1 year), K_e indicates the maximum allowed extrapolation time (t_e) in years. Table 2 from TR 9080 indicates the extrapolation time limit (t_e)

in years as a function of the maximum test temperature (T_{max}) and the service temperature (T_S) from 20^0C inclusive up to 25^0C (not included), from 25^0C inclusive up to 30^0C (not included), and so on, provided the maximum test time (t_{max}) at $T_{max.}$ is at least 8760 hours. The ISO TR9080 extrapolation time limits were used to extend the 80^0C stress rupture testing results to estimate long term 20^0C service life. However, it must be noted that ISO TR9080 did not allow an extension beyond a temperature difference of 40^0C nor beyond a ratio of 1:50.

ISO TR 9080 also cited an accepted rule of thumb of a 2.5 to 3.0 increase in time per each 10^0C increase in temperature. Using these values, times to failure to confirm the 20^0C LTHS intercepts at 100,000 hours and 50 years (438,000 hours) were calculated. Similar values for elevated temperature stress rupture times to confirm the 60^0C LTHS intercepts of 100,000 hours and 50 years were also calculated.

Similar stress and time reduction factors were also calculated by Nobuaki Nishio in a 1983 paper, "A Theory on Stress-and Temperature-Dependence of the Life of Polyethylene". In this paper, Nishio showed that the phenomenon of stress cracking is closely related to the phenomenon of creep through a study of the stress-strain relationship. Long term strength is shown to be related to long term stress conditions or long-term strain condition. Long term stress is proportional to the hoop stress and long- term strain is proportional to the bending strain or to point loading. Constant strain results in creep failure. Constant strain causes stress crack failures or slow crack growth failures.

The calculations, performed by Nishio, showed that the time reduction ratio for time-to-failure testing due to an increase in testing temperature from 20^0C to 80^0C is between 1/5000 and 1/9000. While for stress cracking the extrapolation is between 1/3000 to 1/10,000. For brittle failures, the time extrapolation ranges from 1/3000 to 1/10,000; or a projected service life of 50 years reduces to between 44 and 146 hours of 80^0C testing.

APPLICATION OF SHIFT FUNCTIONS TO THE VALIDATION OF PE PIPING

The key property in the long-term testing of plastic piping materials is the retention of ductility. This is one of the basic assumptions of ASTM D 2837. In constant-tensile load testing the onset of the “ductile-to-brittle transition” is the important parameter. This corresponds to the area of the stress vs. time plot in which a downward inflection point or “knee” is observed. This represents the region of the stress-rupture plot in which ductile/creep deformation failure ends and brittle/stress cracking failure begins. The later this transition occurs, the better the resistance of the plastic material to Environmental Stress Cracking (ESC)/Slow Crack Growth (SCG) failure. Retention of ductile performance is the basis for the validation testing requirements for PE piping.

In the mid 1990’s a minimum of 200 hours on test at 176°F (80°C) or 70 hours on tests at 194°F (90°C) was proposed to confirm the Long-Term Hydrostatic Strength (LTHS) of polyethylene piping, which is the extrapolation to 100,000-hour LTHS at 73^0F (23^0C). Similarly, to validate the 140^0F (60^0C) Hydrostatic Design Basis (HDB) or the Long-Term Hydrostatic Strength (LTHS) values at 100,000 hours, a minimum of 11,300 hours of elevated temperature testing at 176°F (80°C) without any brittle failures or a minimum of 3,800 hours at 194°F (90°C) was proposed.

These proposed requirements were adopted into the PPI requirements and the ASTM D2837 requirements.

A minimum of 1000 hours on test at 176°F (80°C) or 300 hours on test at 194°F (90°C) without any brittle failures was proposed to confirm the extrapolation to reach 50 years (438,000 hours) at 73°F (23°C) for polyethylene piping. PPI TR-3 currently requires a minimum of 6000 hours at 176°F (80°C) or 2400 hours on test at 194°F (90°C) without any brittle failures

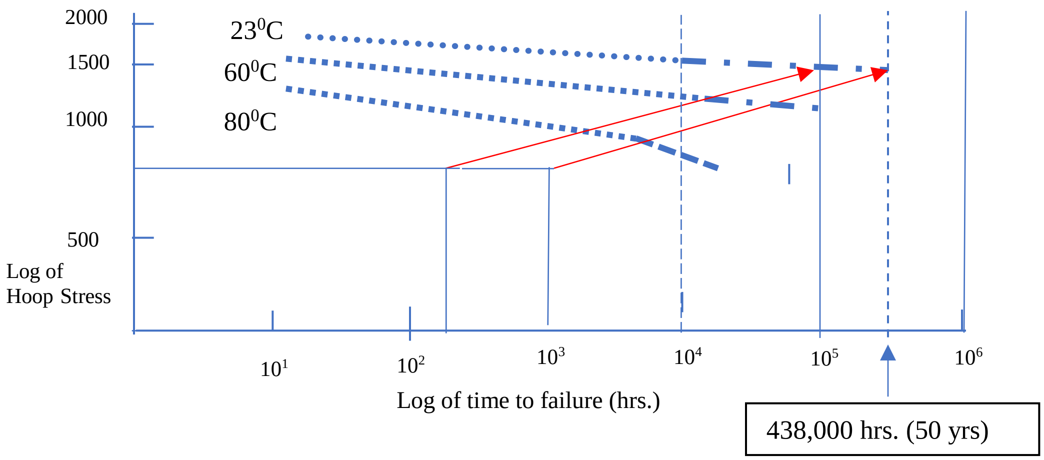

Figure 3: Graphical Representation of PE Validation Process for 23°C LTHS Using 80°C Testing

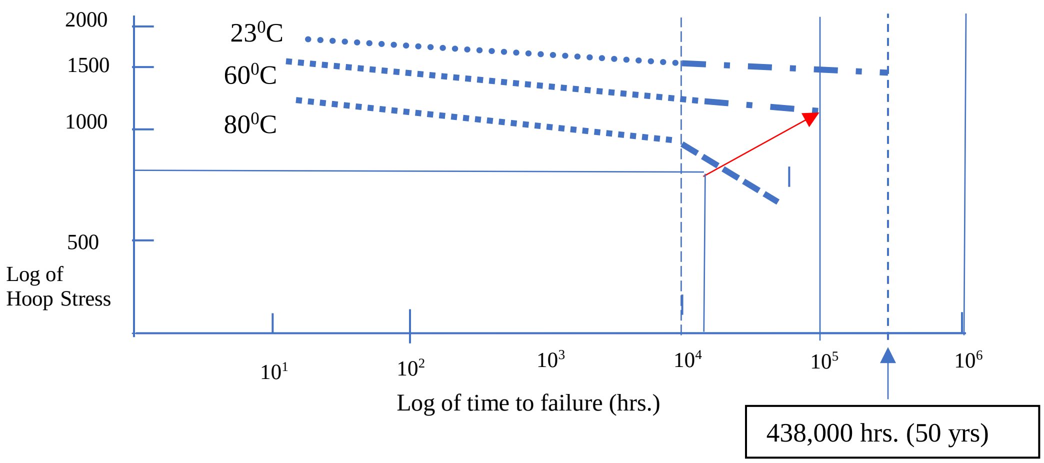

Figure 4: Graphical Representation of PE Validation Process for 60°C LTHS Using 80°C Testing

CURRENT VALIDATION METHODS

Currently, PPI TR-3 offers several methods to validate that the stress regression curve will continue without the occurrence of a "knee" out to 100,000 hours.

- A standard method for Validation of the Hydrostatic Design Basis (HDB), which provides stresses and minimum testing times for various HDB classes. These are shown in Table 3 and Table 4.

Table 3: Validation of 73°F (23°C) HDB

HDB to be Validated (psi)	193°F (90°C)		176°F (80°C)	
	Stress (psi)	Time (hrs.)	Stress (psi)	Time (hrs.)
1600	735	70	825	200
1250	575	70	645	200
1000	460	70	515	200
800	365	70	415	200
630	290	70	325	200
500	230	70	260	200

Table 4: Validation of 140°F (60°C) HDB

HDB to be Validated (psi)	193°F (90°C)		176°F (80°C)	
	Stress (psi)	Time (hrs.)	Stress (psi)	Time (hrs.)
1250	860	3800	970	11300
1000	690	3800	775	11300
800	550	3800	620	11300
630	435	3800	490	11300
500	345	3800	390	11300
400	275	3800	310	11300

- A Rate Process Based Method (RPM) for Validation of the HDB, which employs the original validation methodology adopted in the late 1980's. This procedure uses the development of brittle failures in elevated temperature testing at two different stress levels and the three-coefficient rate process equation to project a minimum test time for a third set of conditions.

- The ISO 9080 Based Method for Validation of 140oF (60°C)HDB, which provides specific instructions for testing for the development of brittle or slit type failures. The logarithmic average of the five highest testing times must exceed minimum specified times. These are shown in Table 5.

Table 5: Minimum Time (t_{max}) Requirements

Temperature to be Validated (°F)	193°F (90°C) Regression		176°F (80°C) Regression	
	Data Level (hrs.)	Min. t_{max}	Data Level (hrs.)	Min. t_{max}
250 (60oC)	E-6 (6000)	5500	E-10+ (>10,000)	17,000

- Determination of Elevated Temperature HDB When Brittle Failures Occur Before 10,000 hours. This procedure uses ductile failure data to determine the linear regression equation and then requires the development of data using brittle failures only and the application of the RPM cited above or another recognized rate process method protocol to calculate a brittle failure LTHS.

- Hydrostatic Design Basis Substantiation for PE Materials provides three procedures to further substantiate that the stress regression curve is linear to the 50-year (438,000-hour) intercept.
  - If the 140°F HDB has been validated, then the 73°F extrapolation is considered to be substantiated linear to 50 years.
  - Rate Process Method testing, where the 50-year intercept is used to solve the 3-coefficient rate process extrapolation equation and the six tested specimens exceed the projected minimum time without brittle failure.
  - When log average failure time of six test specimens at 176°F (80°C) surpasses 6000 hours or at l93°F (90°C) surpasses 2400 hours at a stress no more than 100 psi below where all failures are ductile.

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stress rupture data to determine the long-term hydrostatic strength of thermoplastics pipe materials."