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February 24, 2000

MEMORANDUM TO: Samuel J. Collins, Director  
Office of Nuclear Reactor Regulation

FROM: Ashok C. Thadani, Director *M. V. Thadani*  
Office of Nuclear Regulatory Research

SUBJECT: USER NEED REQUEST ON THE ACCEPTABILITY OF THE  
ARRHENIUS METHODOLOGY FOR ENVIRONMENTAL  
QUALIFICATION (EQ) FOR LOCA AND POST-LOCA ENVIRONMENTS

In a memorandum dated November 25, 1997, NRR requested RES to perform appropriate research and provide independent confirmation of the applicability of Arrhenius methodology to meet the environmental qualification (EQ) requirements for LOCA and post-LOCA environments. RES was requested to support the NRR reviews of licensees' requests for (1) power uprate amendments, (2) reevaluation of qualified life of electric equipment due to plant modifications and changes, and (3) license renewal technical reports on EQ.

My response memorandum to you, dated July 13, 1998, noted that RES would initiate a two-phase research approach to address the subject issue. Our response also stated that based upon the results of the Phase 1 research program, a determination would be made if a Phase 2 study is warranted.

As part of Phase 1, RES convened an expert panel to independently assess the use of Arrhenius methodology and the need for additional research. The panel members were Dr. Kenneth Gillen of Sandia National Laboratories, Dr. Salvatore Carfagno, a consultant (formerly with Franklin Research Institute), and Dr. Montgomery Shaw of the University of Connecticut. The panel members provided their independent reports on the use of Arrhenius methodology. We also had an opportunity to review a technical report submitted by the Nuclear Utility Group on Environmental Qualification (NUGEQ) outlining the industry's views on the subject matter. Members of the RES technical staff also reviewed the plant specific calculations (Monticello and Hatch nuclear power plants) provided by the licensees, that justified the use of Arrhenius methodology.

Based on the overall Phase 1 research effort, the following conclusions are drawn:

1. The Arrhenius methodology has been studied extensively over the past few decades and has been shown to be a valid means of modeling temperature effects and for evaluating thermal degradation of polymers, with some limitations. These limitations include: (i) Arrhenius methodology is applicable only if the thermal degradation of the polymer involved is dominated by a single reaction within the temperature range of interest; Arrhenius extrapolation between different transition regions should be avoided;

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(ii) there may be significant uncertainties in the activation energy used (i.e., activation energies measured in air are used to model accident environments, and these may be different from those in steam environment); (iii) oxygen diffusion limitations are not accounted for in the Arrhenius model; and (iv) moisture effects are not accounted for in the Arrhenius model.

2. Arrhenius methodology can be used to evaluate the effects of varying temperature conditions provided that it is based on the principle of cumulative damage to the polymers involved.

3. There is a general agreement that an adequate technical basis exists to justify the application of the Arrhenius methodology for integrated time-temperature equivalent analysis as used in recent licensee submittals. In spite of its limitations, the Arrhenius methodology is applicable for analyzing the effects of small deviations in time-temperature profiles to meet EQ requirements for LOCA and post-LOCA environments.

These conclusions are based on (1) the review of individual panel member reports, (2) the NUGEQ report, (3) the discussions with technical experts (from both NRR and RES), and (4) the discussions at a public meeting held on June 29, 1999, to discuss the Arrhenius methodology. Attached are the following supporting documents:

1. Dr. Gillen's report dated March 1, 1999.
2. Dr. Carfagno's report dated August 6, 1999.
3. Dr. Shaw's report, dated June 15, 1999.
4. NUGEQ report dated January 1999.
5. Dr. Shaw's review comments, dated March 1, 1999, on the NUGEQ report.

The consultants' reports identify a broad range of limitations with the overall EQ process and suggest several topics for future research. These topics include A Study of Risk Significance of LOCA Simulation as a Function of Time After the Start of LOCA, and An Investigation of Moisture Effects on Equipment Operability.

It is beyond the current scope of the user need to implement these types of long-range research programs to alleviate concerns with the overall EQ process. However, in a separate forum, RES staff will discuss these recommendations with cognizant NRR staff and determine whether further research is warranted.

From reviews of the licensees' submittals, we note that deviations in the actual vs. required temperature profiles are relatively minor with respect to the overall conservatism that is inherent in the EQ methodology and in the margins that it provides to account for thermal effects. Typically, EQ test temperatures are much more severe than the plant-specific accident profiles. Also, in their analyses the licensees have avoided time-temperature extrapolation among different transition regions of the material properties and activation energies involved.

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RES in consultation with the NRR staff has concluded that the use of Arrhenius methodology is acceptable for the reviews of licensee requests for (1) power uprate amendments, (2) reevaluation of qualified life of electric equipment due to plant modifications and changes, and (3) license renewal technical reports on EQ. The staff has also concluded that a Phase 2 study, involving tests and evaluation of samples of naturally aged and artificially aged insulating materials and cables under LOCA and post-LOCA conditions, is not warranted because the technical basis is sufficiently complete.

By transmittal of this memorandum and attachments, RES considers that the requested information in the NRR memorandum of November 25, 1997 has been provided and the User Need should be considered as closed.

Attachments: As stated

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Attachments: As stated

DOCUMENT NAME: G:\vora\ARRCOLLINS1wpd.wpd

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March 1, 1999

Final Letter Report- Consulting for Brookhaven National Laboratory

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## I. INTRODUCTION

This report summarizes work done to support three tasks requested by Brookhaven National Laboratory. The first task involved presenting a talk at the 26<sup>th</sup> Water Reactor Safety Information Meeting on "Limitations of the Arrhenius Methodology" and writing a paper on this topic for inclusion in the Conference Proceedings. A slightly modified version of this paper is included in Section II of this report. The second task involved consulting on the experimental conditions for Brookhaven to use in order to best duplicate Sandia historical combined environment aging with sequential aging conditions. The document generated in support of this effort is included in Section III. The third task involved writing comments critiquing 1) the use of the Arrhenius method for LOCA and post-LOCA situations and 2) the Nuclear Utility Group on Equipment Qualification position paper titled "Acceptability of Arrhenius Methodology to Analyze LOCA and Post-LOCA Environments". Section IV contains these comments.

## II. LIMITATIONS OF THE ARRHENIUS METHODOLOGY

### II.1 Background

The Arrhenius methodology is commonly used to analyze thermal aging data and to extrapolate the data to temperatures outside the range of experimental temperatures. In nuclear power plants, it has been used extensively for polymeric materials and components both as a means of simulating degradation caused by decades of ambient aging and as a method for compressing time scales during LOCA and post-LOCA simulations. In this paper, we describe some of the problems that can result in non-Arrhenius behavior, potentially leading to apparent changes in the Arrhenius activation energy  $E_a$  with temperature. Since changes in  $E_a$  with temperature can significantly influence predicted lifetimes at temperatures below the lowest experimental conditions used in the Arrhenius analysis, methods are needed for determining whether the  $E_a$  changes in the extrapolation region. For polymers that are dominated by oxidation effects, we have introduced the first approach capable of achieving this objective. It is based on the use of ultrasensitive oxygen consumption measurements. For the interested reader, more detailed discussions on the problems associated with the Arrhenius approach and on the use of the ultrasensitive oxygen consumption method to test the Arrhenius extrapolation assumption have been published previously [1-2].

### II.2 Discussion

Whenever oxygen is available during the aging of polymeric materials, oxidation chemistry typically dominates the degradation. For the simplest possible example, suppose a polymer  $P$  chemically reacts directly with oxygen dissolved in the polymer, leading to a degradation product  $D$ . In chemical kinetic terms, we write this reaction as



where classical chemical rate theory gives the rate constant  $k$  in terms of  $E_a$ , the absolute temperature  $T$  and the universal gas constant  $R$  as

$$k \propto \exp\left[\frac{-E_a}{RT}\right] \quad (\text{II.2})$$

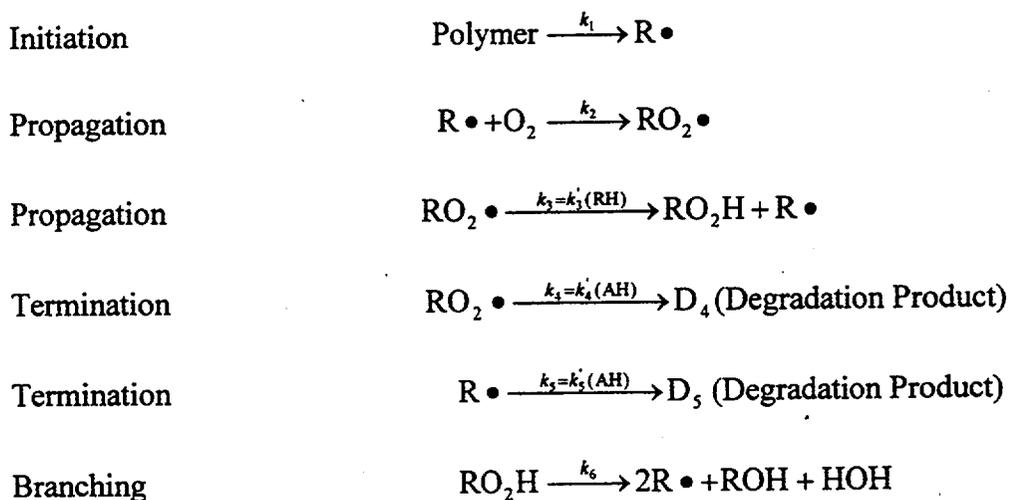
Since mechanical properties are typically destroyed after oxidation of 1-2% of the polymer, the concentration of  $P$  will remain essentially unchanged during the degradation. This leads to the following expression for the rate of oxygen consumption and, equivalently, the rate of growth of the degradation product  $D$

$$\frac{dO_2}{dt} = \frac{dD}{dt} = k[O_2][P] = k' = A \exp\left[\frac{-E_a}{RT}\right] \quad (\text{II.3})$$

Equation (II.3) implies that the rate of degradation and the rate of oxygen consumption will be given by the same Arrhenius dependence on temperature and that this dependence will not change as the temperature is changed ( $E_a$  remains constant). If we therefore measure failure times at various aging temperatures for a property related to the buildup of degradation products and plot the log of the failure time versus inverse absolute temperature, we would expect linear behavior. Figure II.1 shows such a plot for an EPDM material. In this plot, the induction (failure) times for several properties are in agreement and consistent with Arrhenius behavior (the  $E_a$  of 116 kJ/mol is derived from the slope of the line through the experimental results). From the figure, it is clear that the experimental time required for obtaining data at the lowest temperature probed by conventional measurements (111°C) is approximately 2 years. To make predictions at lower temperatures, it is assumed that the Arrhenius behavior remains constant, so that the linear behavior can be extrapolated (dashed line). This leads to a prediction of a 55,000-year lifetime at 25°C. Although a long lifetime is predicted at room temperature from the extrapolation shown in Fig. II.1, it is clear that the distance of extrapolation is very large relative to the data range. This means that a drop in  $E_a$  below 110°C could have a profound effect on the extrapolated prediction. Thus, without a method for determining whether  $E_a$  remains unchanged, little confidence exists in such extrapolations.

It turns out that there are numerous phenomena that can lead to changes in  $E_a$  as the temperature changes [1]. Perhaps the easiest to understand comes from the fact that the oxidation chemistry underlying degradation is seldom as simple as that described by eqs. (II.1) – (II.3). In fact, the simplest realistic kinetic scheme for the oxidation of stabilized polymers is given by the following set of chemical reactions [1,3,4]

#### Scheme II.1. Classical oxidation scheme.



Although this scheme has similarities to the earlier scheme ( $\text{O}_2$  is used up by the second reaction eventually resulting in the creation of degradation products  $\text{D}_4$  and  $\text{D}_5$ ), kinetic

analysis leads to very different conclusions concerning the constancy of  $E_a$ . By applying steady-state analyses to the free radical species and ROOH, one obtains [1]

$$\phi = \frac{d[\text{O}_2]}{dt} = \frac{C_1[\text{O}_2]}{1 + C_2[\text{O}_2]} \quad (\text{II.4})$$

where

$$C_1 = \frac{k_1 k_2}{k_5} \quad (\text{II.5})$$

$$C_2 = \frac{k_2(k_4 - 2k_3)}{k_5(k_3 + k_4)} \quad (\text{II.6})$$

At low concentrations of  $\text{O}_2$

$$\frac{d\text{O}_2}{dt} = \frac{k_1 k_2 [\text{O}_2]}{k_5} \frac{\exp\left[\frac{-E_1}{RT}\right] \exp\left[\frac{-E_2}{RT}\right] \exp\left[\frac{-\Delta H_s}{RT}\right]}{\exp\left[\frac{-E_5}{RT}\right]} \quad (\text{II.7})$$

implying that the effective activation energy  $E_{\text{eff}}$  is given by

$$E_{\text{eff}} = E_1 + E_2 + \Delta H_s - E_5 \quad (\text{II.8})$$

where  $\Delta H_s$  is the heat of solution for oxygen in the polymer. It is clear from eq. (II.8) that a constant effective value of  $E_a$  is predicted for low oxygen concentrations. On the other hand, at high oxygen concentrations, eqs. (II.4) – (II.6) lead to

$$\frac{d\text{O}_2}{dt} = \frac{k_1(k_4 + k_3)}{(k_4 - 2k_3)} \quad (\text{II.9})$$

which, in general, predicts that the effective  $E_a$  will change with temperature. In addition, kinetic analysis of the rate of product formation gives for example

$$\frac{dD_4}{dt} = \left[ \frac{k_4}{k_4 + k_3} \right] \frac{d\text{O}_2}{dt} \quad (\text{II.10})$$

This result predicts not only non-constant values of  $E_a$  for the degradation product  $D_4$  regardless of whether the oxygen concentration is low or high, but also differences in the values of  $E_a$  dependent upon which species ( $\text{O}_2$  consumption,  $D_4$  production) are being followed.

Although the above discussion indicates that non-Arrhenius behavior and differing values of  $E_a$  for different degradation variables might be anticipated from more realistic kinetic schemes, eqs. (II.9) and (II.10) show that the changes of the effective  $E_a$  with temperature may not be large if  $E_4$  is similar to  $E_3$  and  $E_1$  is considerably larger than either of the other two. This is in fact often the case, implying that the non-Arrhenius character may only show up as a gradual change with temperature. Nonetheless, given the large extrapolations often carried out, even a slowly changing  $E_a$  may have profound effects on extrapolated predictions.

Another important mechanism that can lead to non-Arrhenius behavior involves diffusion-limited oxidation (DLO). At the high temperatures typically used for accelerated laboratory experiments, the consumption of dissolved oxygen in the polymer will often occur faster than the oxygen can be resupplied by diffusion from the surrounding air-atmosphere. Although oxidation at the sample surface will be at equilibrium and unaffected by the presence of DLO effects, the amount of oxidation will drop at positions deeper within the sample. Important DLO effects are commonly observed for typical, air-oven aging studies of numerous elastomers, as illustrated by comprehensive studies on SBR [5], nitrile [6], neoprene [5,6], EPDM [7,8] and hypalon [9]. Even though the importance of DLO effects has a complex dependence on time and temperature, these studies show that tensile elongation measurements are typically consistent with Arrhenius behavior. The reason stems from the fact that oxidative degradation of most elastomers leads to hardening of the material. If DLO effects are present, the hardening is greatest at the sample surface. Cracks would be expected to initiate at the hardened surface during tensile testing. Once initiated, if these cracks immediately propagate through the material, the tensile elongation will be determined by the surface degradation, which represents the true equilibrium oxidation rate (uninfluenced by DLO effects). Therefore, quite accidentally, tensile elongation measurements often lead to Arrhenius behavior even in the presence of important DLO effects. If cracks do not immediately propagate through the material, non-Arrhenius behavior can often be observed, as noted for a Kerite hypalon jacket material [9]. Similarly, properties that depend on the entire sample cross-section will not be amenable to Arrhenius analyses when DLO effects are important [2, 9].

Several other mechanisms can lead to important non-Arrhenius behavior. If, for instance, two distinct oxidation pathways underlie the degradation of a material, the mechanism of lower  $E_a$  will become dominant when the temperature drops sufficiently. This lower  $E_a$  mechanism will not be apparent until the Arrhenius degradation plot begins to curve at lower temperatures, therefore representing an unanticipated surprise if the curvature starts in the extrapolation region. Another problem can occur when the data region or the extrapolation range encompasses a polymer transition region, such as the crystalline melting point region characteristic of many EPDM and crosslinked polyolefin materials [1]. Several non-Arrhenius complications can arise from antioxidant interactions, caused by such things as solubility changes with temperature and various evaporation effects [10,11].

From the above discussion, it is apparent that many possible phenomena can result in non-Arrhenius behavior. It is therefore clear that methods need to be developed to provide more confidence in extrapolated predictions. We will describe one viable method of accomplishing this, involving the use of ultrasensitive oxygen consumption measurements, after we briefly review the concept of time-temperature superposition. The formalism used for time-temperature superposition analysis is needed and is ideally suited for discussing the ultrasensitive oxygen consumption approach.

Earlier in Fig. II.1, we used one processed point (the induction time) per temperature to test the Arrhenius equation. This means that most of the data generated versus time at each temperature were eliminated from the analysis. However, if the rate of degradation is constant at each aging temperature, an important consequence is the expectation that the time-dependent degradation curves at any two temperatures will be related by a constant multiplicative factor. This means that the curves at different temperatures should have the same shape when plotted versus the log of the aging time. Normalized elongation results for a nitrile rubber at five different aging temperatures [2] are consistent with this picture, as seen in Fig. II.2. Instead of selecting only one point per temperature for the analysis, we apply the principle of time-temperature superposition [1,2,9,12]. We first select the lowest temperature (64.5°C) as the reference temperature. Then for each set of data at a higher temperature  $T$ , we multiply the experimental times by a constant shift factor,  $a_T$  chosen to give the best overall superposition with the reference temperature data ( $a_T = 1$  at the reference temperature). The results of this procedure are shown in Fig. II.3, where the time-axis gives the superposed results at the reference temperature. Unlike the analysis given in Fig. II.1, this approach utilizes every raw experimental point and yields empirical shift factors that can then be tested by models such as the Arrhenius. If, in fact the empirical shift factors are consistent with the Arrhenius equation, then they would be given by

$$a_T = \exp\left(\frac{1}{T_{ref}} - \frac{1}{T}\right) \quad (\text{II.11})$$

This would predict that a plot of  $\log(a_T)$  versus inverse temperature would give linear behavior. When the empirical shift factors are plotted in this fashion in Fig. II.4, such linear behavior is in fact observed, with a corresponding  $E_a$  of approximately 90 kJ/mol determined from the slope. To make predictions at temperatures lower than 64.5°C ( $a_T = 1$ ), the normal procedure would then be to extrapolate (dashed line extension). For instance the extrapolated  $a_T$  at 22°C would be  $\sim 0.01$ , implying a lifetime approximately 100 times longer than at 64.5°C.

Given the distinct possibility that non-Arrhenius effects will be important for the extrapolations shown by the dashed lines in Figs. II.1 and II.4, it would be extremely useful to have methods that give more confidence in any attempted extrapolations. At the lowest temperatures utilized for conventional measurements (111°C for the EPDM material, 64.5°C for the nitrile material), several years of aging were required to see

measurable property changes. Thus any technique that accesses lower temperatures must be an ultrasensitive monitor of the degradation. In addition, it needs to measure a property closely correlated to the chemistry dominating the mechanical degradation. One approach that we have developed for thermally oxidized materials involves ultrasensitive oxygen consumption measurements based on gas chromatography techniques [2]. With experimental care, this approach results in sensitivity capabilities of better than  $10^{-13}$  mol/g/s, which typically allows access to temperatures corresponding to expected mechanical property lifetimes of greater than 100 years. One might expect the oxygen consumption rate to be closely related to the tensile elongation since 1) oxidation chemistry is expected to dominate the degradation and 2) surface oxidation leads to the initiation of cracks that quickly propagate and therefore determine the elongation.

To confirm this correlation for the nitrile material, the oxygen consumption rate measurements (Fig. II.5) are made at temperatures overlapping the temperatures used for the mechanical property experiments (96°C, 80°C and 72°C) as well as at lower temperatures in the extrapolation region (52°C, 40°C and 23°C). The oxygen consumption results of Fig. II.5 were integrated and then time-temperature superposed at 64.5°C so that the shift factors could be directly compared with the mechanical property shift factors given earlier in Fig. II.4. The resulting oxygen consumption shift factors are plotted as the triangles shown for the nitrile data on Fig. II.6. The results show that the higher temperature oxygen consumption results are consistent with the mechanical property shift values, offering evidence that the two properties are dependent upon the same underlying chemistry. Since the oxygen consumption shift factors at the three lower temperatures are reasonably consistent with an unchanged Arrhenius slope (dashed line) in the extrapolation region, these results offer increased confidence in the validity of the extrapolation.

Similar oxygen consumption measurements spanning the temperature region where conventional measurements were made and continuing into the lower temperature "extrapolation regions" were made for the EPDM material (left set of triangles in Fig. II.6) and for a neoprene material (triangles in Fig. II.7). For the neoprene material, the results indicate that the Arrhenius behavior determined at high temperatures can be extrapolated with confidence all the way down to room temperature. For the EPDM material, the oxygen consumption measurements at 111°C and above give shift factors consistent with the conventional results ( $E_a \sim 118$  kJ/mol), but a change in mechanism leads to an activation energy reduction to  $\sim 82$  kJ/mol below 111°C. Therefore, the straight-line extrapolation used in Fig. II.1 is not warranted and the predicted EPDM lifetime is significantly reduced.

### II.3 Conclusions

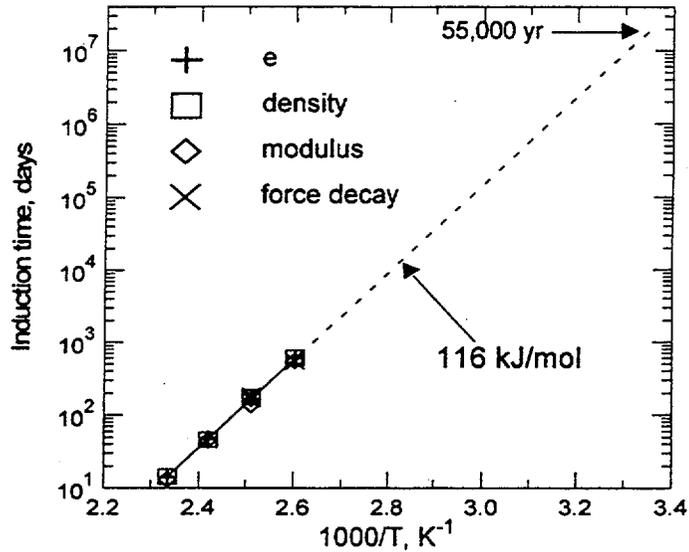
The Arrhenius methodology has been utilized for many years to predict polymer lifetimes in various applications. Unfortunately, there are numerous potential limitations associated with this methodology, many of which can lead to non-Arrhenius behavior. This section reviews several of these limitations, including a brief mention of diffusion-limited oxidation (DLO) effects and a more extensive discussion of the implication of

changes in the effective Arrhenius activation energy  $E_a$  or in the dominant reactions as the temperature changes. Changes in  $E_a$  or in the dominant reactions with temperature can happen for any material, making extrapolations beyond the experimental temperature range problematic. Unfortunately, when mechanistic changes occur, they invariably result in a reduction in effective Arrhenius activation energy, leading to lower than expected material lifetimes. Thus it is critically important to derive methods for testing the Arrhenius extrapolation assumption. One approach that we have developed involves ultrasensitive oxygen consumption measurements. Some results from the application of this approach are reviewed.

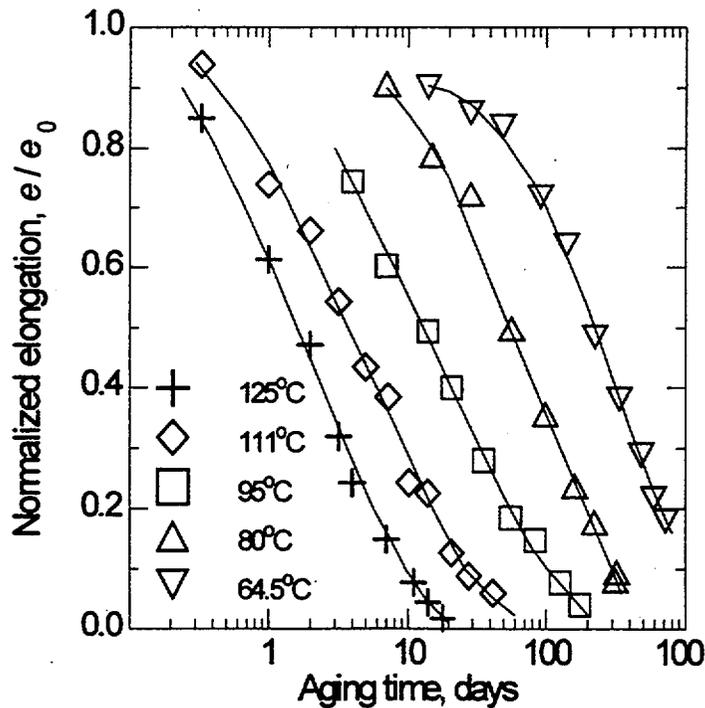
#### II.4 References

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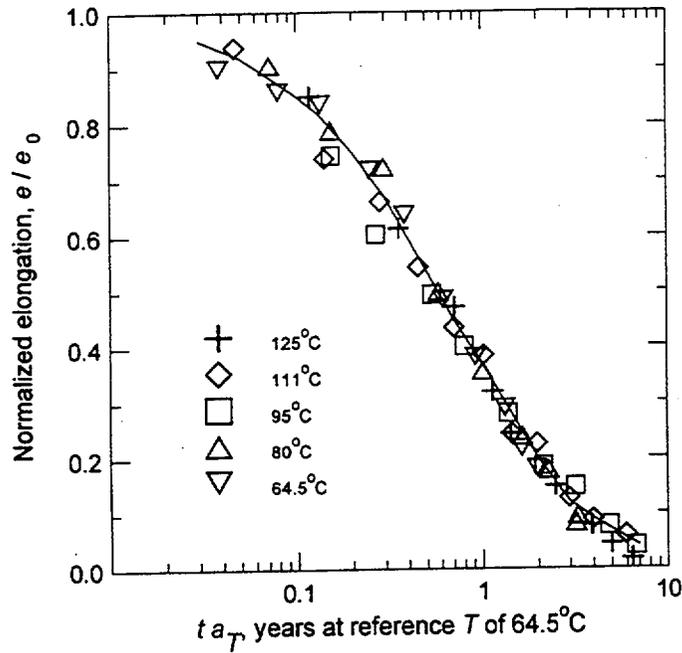
## II.5 Figures



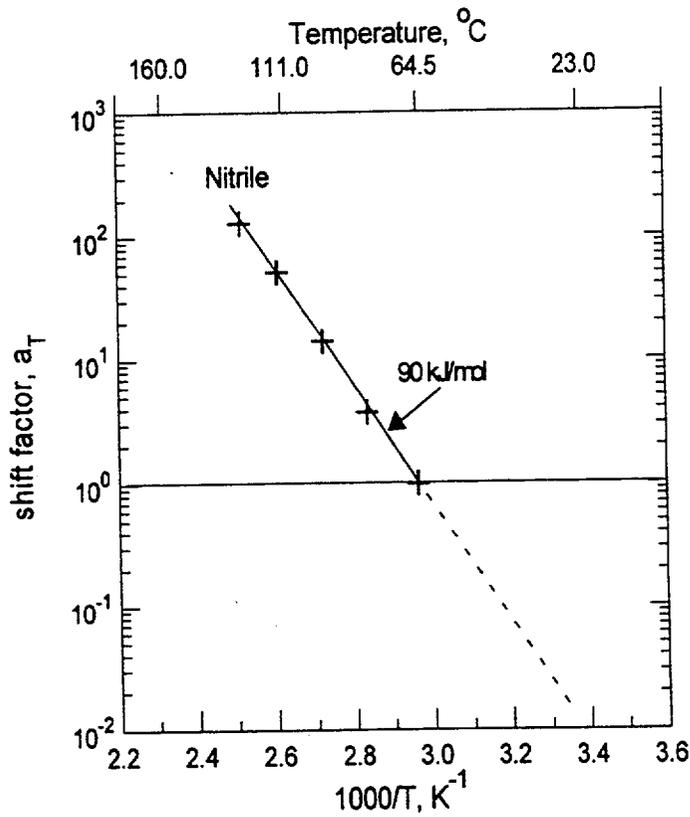
**Figure II.1.** Arrhenius plot of the log of the induction times for the indicated experimental variables versus the inverse absolute aging temperature for an EPDM seal material. The data show Arrhenius behavior with an  $E_a$  of 116 kJ/mol. An extrapolation of this behavior (dashed line) to 23°C predicts a room temperature lifetime of 55,000 years.



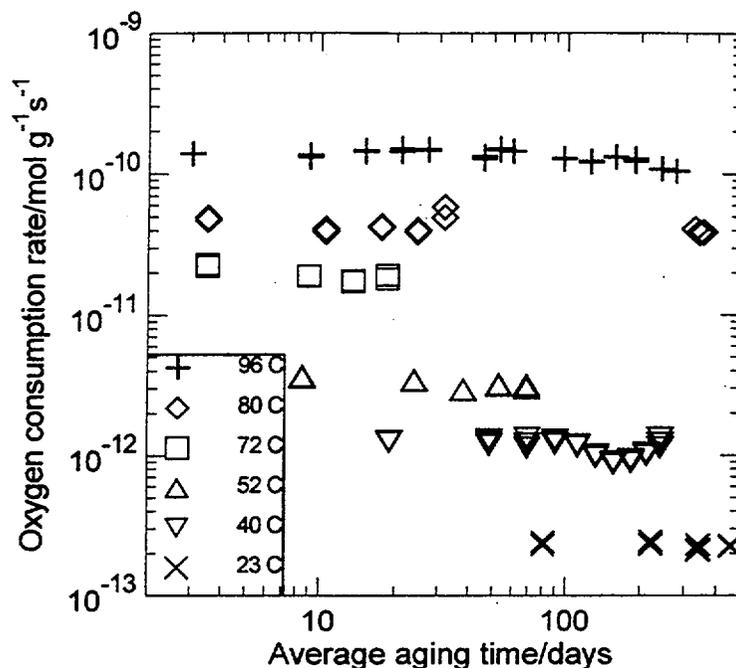
**Figure II.2.** Ultimate tensile elongation ( $e$ ) of a nitrile rubber normalized to its unaged value ( $e_0$ ) versus air-oven aging time and temperature.



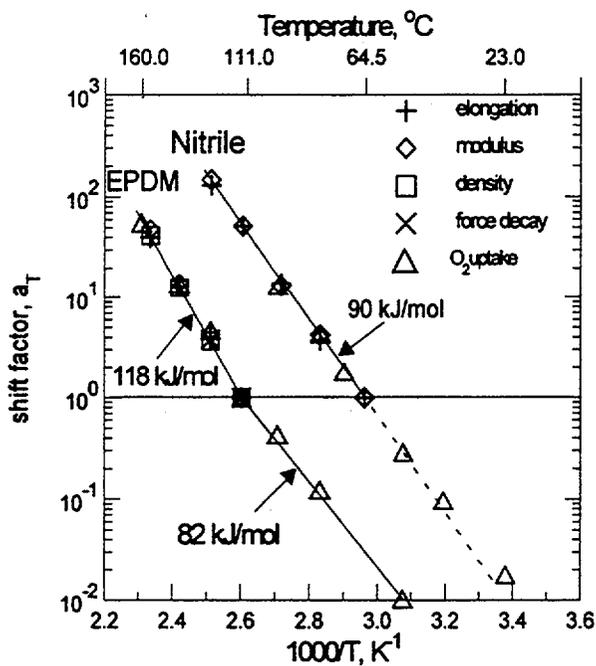
**Figure II.3.** Time-temperature superposition of the data from Fig. 2 using empirically derived shift factors,  $a_T$ .



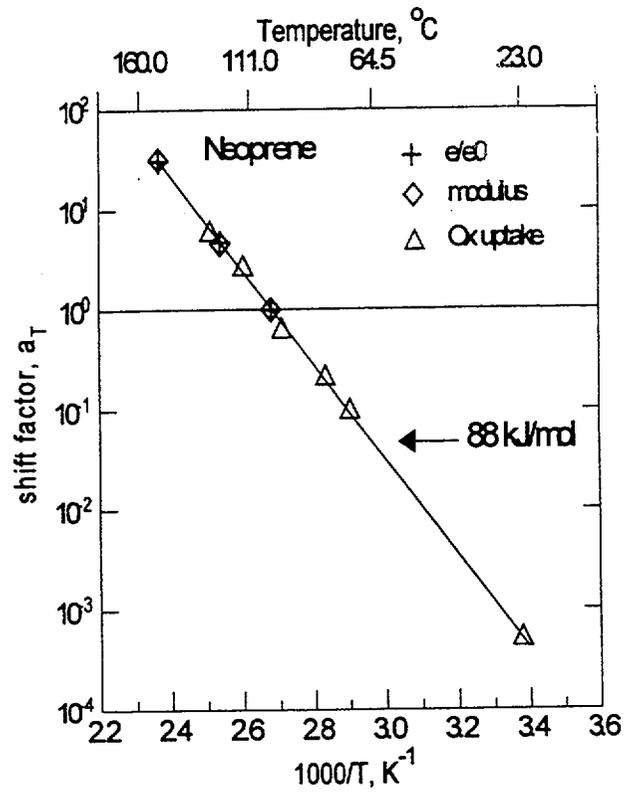
**Figure II.4.** Arrhenius plot of the empirical values of  $a_T$  used to achieve the superposition shown in Fig. II.3.



**Figure II.5.** Oxygen consumption rates for the nitrile rubber as a function of time at the indicated temperatures.



**Figure II.6.** Arrhenius plot of the empirical values of  $a_T$  for the indicated conventional parameters and for oxygen consumption measurements (triangles) for the EPDM and the nitrile for materials. The results are normalized ( $a_T = 1$ ) to a reference temperature of 64.5°C for nitrile and a reference temperature of 111°C for EPDM.



**Figure II.7.** Arrhenius plot of the empirical values of  $a_T$  for the indicated conventional parameters and for oxygen consumption measurements (triangles) for a neoprene material.

### **III. COMMENTS ON BNL PROPOSED "DUPLICATION" OF JACOBUS AGING CONDITIONS**

#### **III.1 Background**

BNL is planning a series of tests on electrical cables with EPR insulation and CSPE (Hypalon) jackets to investigate the cause of failures noted in tests previously performed at Sandia by Jacobus [1]. The BNL objective for the preaging is to simulate as closely as possible the condition of the SNL cables after their aging. Due to time and facility constraints, Sandia's long-term (up to 9 months) combined environment ( $\sim 70$  Gy/h at  $\sim 98^\circ\text{C}$  for the 9 month exposures- Appendices A and B of ref. 1) preaging cannot be exactly duplicated, forcing BNL to use higher-acceleration sequential aging exposures (3.5 months of temperature followed by  $\sim 10$  days of radiation). This section represents an attempt to estimate the consequences of this faster sequential exposure on the objective of simulating SNL's preaging. A major concern is the distinct possibility that the more accelerated BNL conditions (especially the radiation exposure) may lead to important diffusion-limited oxidation (DLO) effects for the overall CSPE jacket material. If this occurred, little oxidation would occur towards the inside of the overall jacket, implying that the EPR insulations and any individual CSPE jackets surrounding the insulations would see little oxidation during radiation exposure.

The analyses will begin by first presenting results showing that the aging of CSPE jacketing materials is fairly generic, both in thermal-only and in radiation environments. This means that aging and material property results for CSPE can be estimated from literature results with reasonable confidence, allowing the calculations presented below to be done without the need for extensive measurements on a given manufacturers CSPE material.

#### **III.2 Oven-aging of CSPE materials**

We have investigated six CSPE (hypalon) cable jackets in thermal-only and combined radiation-thermal conditions (an Anaconda Flameguard inner jacket and outer jackets from Anaconda Flameguard, Kerite FR, Rockbestos Firewall III, Samuel Moore Dekoron and Eaton Dekoron cables). Their behavior is quite similar versus temperature and dose rate as shown for the Anaconda Flameguard inner jacket and the Kerite FR jacket in previous publications [2-4]. This similarity in oven-aging environments for five of the materials is shown in Fig. III.1. This figure plots the log of the time for the ultimate tensile elongation to decrease to 100% as a function of inverse temperature. The five materials have comparable decay times at each temperature and show linear (Arrhenius) behavior with similar slopes. The average Arrhenius activation energy for the five materials is 25.5 kcal/mol, corresponding to the line drawn on the figure. This generic behavior allows us to create a rough plot of the average elongation result expected for these materials at  $98^\circ\text{C}$  (the temperature used for the 9 month combined aging exposure at SNL). Figure III.2 shows this result. From this figure, it is clear that 9 months of oven aging at  $98^\circ\text{C}$  will drop the elongation of these CSPE materials to around 100%. If BNL wants to simulate this thermal-aging component in 3.5 months, they will be required to

use a temperature of  $\sim 108.4^{\circ}\text{C}$  ( $227^{\circ}\text{F}$ ). After such a simulation, the elongation of a typical CSPE jacket should therefore be around 100%.

### III.3 Radiation-aging of CSPE materials

For combined environment radiation plus temperature aging, "generic" behavior is again observed for CSPE jacket materials. Evidence for this conclusion was shown earlier for the Anaconda Flameguard inner jacket and the Kerite FR outer jacket in published reports [3,4]. In addition, we have been collecting data on the other four CSPE materials mentioned above under the following four combined environments: 1100 Gy/h at  $90^{\circ}\text{C}$ , 60 Gy/h at  $80^{\circ}\text{C}$ , 60 Gy/h at  $100^{\circ}\text{C}$  and 150 Gy/h at  $60^{\circ}\text{C}$ . Under each of these conditions, these four materials gave similar results within  $\sim \pm 20\%$ . The average results for the dose required to lower the elongation to 100% is plotted on Fig. III.3 versus the aging dose rate (the numbers adjacent to the symbols denote the aging temperature). Combined environment results for the Anaconda Flameguard inner CSPE jacket are also plotted in this figure. These results are then analyzed with our time-temperature-dose rate superposition shifting procedure [3, 4] using an activation energy of 25.5 kcal/mol in order to derive predicted results versus dose rate at  $25^{\circ}\text{C}$ . Figure III.4 shows the predicted results at  $25^{\circ}\text{C}$ . If BNL uses 2500 Gy/h (250 krad/h) to simulate the radiation aging part of the SNL exposure, Fig. III.4 shows that  $\sim 1.3$  MGy (130 Mrad) dose would be required to drop the elongation to 100%. Since a dose of  $\sim 46$  Mrad (9 months at 7 krad/h) was used during the SNL combined environment aging exposure, BNL would require an approximately 7.7 day exposure at 250 krad/h to achieve a similar dose. It should be noted that the required 46 Mrad dose is  $\sim$  one third of the dose (130 Mrad) needed to reach an elongation of  $\sim 100\%$  for room-temperature radiation exposures. Since we saw earlier (Figure III.2) that the thermal portion of a sequential simulation results in an elongation drop to  $\sim 100\%$ , one can predict that the thermal only part of the BNL sequential simulation will be  $\sim 3$  times more severe than the radiation portion.

Similar to the superposition results at  $25^{\circ}\text{C}$  given in Fig. III.4, we can time-temperature-dose rate shift the raw data of Fig. III.3 to a  $98^{\circ}\text{C}$  reference temperature; the results of this procedure are shown in Fig. III.5. The conditions used for combined environment aging at SNL (70 Gy/h plus  $98^{\circ}\text{C}$ ) are indicated on this figure. Since the SNL aging conditions are located in the region where the dose-rate effects curve drops rapidly due to its eventual asymptotic approach to thermal-only domination, it is clear that the SNL combined environment conditions are dominated by thermal effects. Under the SNL combined environment aging conditions, the degradation occurs quite rapidly, requiring only  $\sim 0.16$  MGy (16 Mrad) for the elongation to reach 100%. Given that the actual combined environment dose of  $\sim 46$  Mrad is  $\sim 3$  times larger, the modeling results in Fig. III.5 would predict severe degradation of the CSPE jackets under SNL aging conditions. This supposition is consistent with the BIW CSPE elongation results (dead beyond  $\sim 25$  Mrad) and the severe hardening (500- 1500 MPa) observed from Jacobus' 9-month modulus profiling results [1]. Confirming that the sequential BNL aging gives similar elongation and modulus profiling results would offer some evidence that the sequential exposure reasonably simulates the combined exposure.

### III.4 Possible importance of diffusion-limited oxidation (DLO) effects

Another issue that potentially impacts the more rapid sequential aging approach proposed by BNL is the possibility that diffusion-limited oxidation (DLO) will be more likely. For cables in an oxygen-containing environment, each material will contain a certain concentration of dissolved oxygen (determined by the oxygen solubility coefficient). If during aging, the dissolved oxygen is used up faster by reaction than it can be replenished by diffusion from the surrounding, oxygen-containing atmosphere, the internal oxygen concentration will drop. This DLO effect can lead to reduced or non-existent oxidation in interior parts of the cable (e.g., inside portions of jackets and insulations). For cables aged under nuclear power plant conditions, the degradation rates are slow enough such that equilibrium oxidation will often occur throughout the cable jackets and the insulations. Under accelerated conditions, DLO effects can become important, leading to accelerated simulations that do not properly reflect the chemistry occurring under ambient aging conditions. In this section, we will estimate the importance of DLO effects for the original combined environment conditions used by SNL and for the two sequential conditions proposed by BNL.

It is possible to get reasonable estimates of the importance of DLO effects from estimates of the oxygen consumption rate  $\phi$  and the oxygen permeability coefficient  $P_{Ox}$  appropriate to the aging environment. For a commercial CSPE material, Seguchi and Yamamoto determined  $P_{Ox}$  at 21.3°C to be  $\sim 9.2 \times 10^{-11}$  ccSTP/cm/s/cmHg with an activation energy of 8.7 kcal/mol [5]. For the three temperatures of current interest (25°C, 98°C and 108°C), this leads to  $P_{Ox}$  values of  $1.1 \times 10^{-10}$ ,  $2.0 \times 10^{-9}$  and  $2.75 \times 10^{-9}$  ccSTP/cm/s/cmHg, respectively. For the same material in a radiation environment of 2 kGy/h at ambient temperature (assume 25°C), Seguchi and co-workers [6] found  $\phi \sim 7.2 \times 10^{-6}$  ccSTP/Gy/g, which can be used directly for the BNL room temperature radiation exposure. For the SNL combined environment exposure, we will assume that the oxygen consumption scales as the dose rate effect. Thus, from Fig. III.5, we estimate that  $\phi$  under SNL conditions is given by

$$\phi \approx \frac{1.3 \text{ MGy}}{0.16 \text{ MGy}} (7.2 \times 10^{-6}) \approx 5.9 \times 10^{-5} \text{ ccSTP/Gy/g}$$

Based on some limited work conducted at Sandia on the Kerite FR CSPE jacket, we estimate that  $\phi$  for thermal aging at 110°C is  $\sim 1.6 \times 10^{-6}$  ccSTP/s/g. Using the estimated average 25.5 kcal/mol activation energy for oven-aging of CSPE, this leads to a  $\phi$  of  $\sim 1.4 \times 10^{-6}$  ccSTP/s/g at the BNL sequential temperature of 108.4°C.

With the above estimates for  $\phi$ , it is now possible to make a second comparison of the importance of the two sequential environments that will be used by BNL to simulate the SNL combined environment. For 3.5 months at 108.4°C, the total oxygen consumed is estimated to be

$$\phi \sim (1.4 \times 10^{-6} \text{ ccSTP/s/g}) \left( \frac{3600 \text{ s}}{\text{h}} \right) \left( \frac{730 \text{ h}}{\text{month}} \right) (3.5 \text{ month}) \sim 13 \text{ ccSTP/g}$$

For the 460 kGy dose at room temperature and 2500 Gy/h,

$$\phi \sim (7.2 \times 10^{-6} \text{ ccSTP/Gy/g}) (4.6 \times 10^5 \text{ Gy}) \sim 3.3 \text{ ccSTP/g}$$

Comparison of the two results leads to the conclusion that the thermal-only environment is approximately 4 times more severe than the room-temperature radiation exposure, consistent with the earlier estimate of ~3 times based on expectations from average elongation results.

We can now use the above results to estimate the importance of DLO effects for the various aging conditions. The appropriate equation for the depth of a material that will be oxidized from one side is given by [7]

$$l_c = \left( \frac{\alpha_c p P_{Ox}}{4(\beta+1)\phi} \right)^{0.5} \quad (\text{III.1})$$

where  $l_c$  represents the depth at which the total oxidation is 90% of the oxidation corresponding to totally homogeneous aging,  $p$  is the oxygen partial pressure in the atmosphere and  $\alpha$  and  $\beta$  are model parameters. For thermal aging situations,  $\beta$  is typically close to unity [8], implying [7] that  $\alpha_c/(\beta+1) \sim 2$ ; for radiation aging,  $\beta$  is typically around 10 to 20 [7,9], implying [7] that  $\alpha_c/(\beta+1) \sim 7$ . For the SNL combined environment situation where thermal may be 3 to 4 times more important than radiation, we assume that  $\alpha_c/(\beta+1) \sim 3$ . For the experiments conducted at SNL,  $p$  is 13.2 cmHg. If the BNL experiments are conducted near sea level,  $p$  will be ~16 cmHg. Table III.1 summarizes the various parameters necessary to the calculations for the three environmental conditions of interest.

Table III.1. Summary of parameters used for the DLO estimates.

Aging Condition	SNL-98°C+70 Gy/h	BNL-108.4°C	BNL-RT+2500 Gy/h
$\phi$ , ccSTP/s/g	1.15e-6	1.4e-6	5e-6
$P_{Ox}$ , ccSTP/cm/s/cmHg	2e-9	2.75e-9	1.1e-10
$p$	13.2	16	16
$\alpha_c/(\beta+1)$	3	2	7
$l_c$	1.04 mm	0.99 mm	0.2 mm

Assuming a typical CSPE density of ~1.6 g/cc, an example calculation of  $l_c$  (eq. III.1) for the SNL conditions is

$$l_c = \left( \frac{3(13.2\text{cmHg})(2 \times 10^{-9} \text{ ccSTP/cm/s/cmHg})}{4(1.15 \times 10^{-6} \text{ ccSTP/g/s})(1.6\text{g/cc})} \right)^{0.5} = 1.04\text{mm}$$

Table III.1 summarizes the  $l_c$  values for the three experimental conditions of interest. Because of uncertainties in the values used for the calculations due to the assumptions needed and the expectations of variability in CSPE compounds, the  $l_c$  results are probably within  $\pm 30\%$  of actual values. Therefore the SNL combined environment experiment and the BNL thermal experiment will have  $l_c$  values of  $\sim 1 \pm 0.3$  mm. Since CSPE outer jackets have typical thicknesses of  $\sim 45$  mil (1.1 mm), minor DLO effects may occur for such outer jackets. Since individual CSPE jackets add another 15 mil (0.4 mm) to the overall aging thickness followed by an additional 30 mil (0.8 mm) for the EPR insulation, there is a great likelihood of DLO effects by the time the EPR insulation is reached for both experiments. For the BNL radiation aging at room temperature, the estimated  $l_c$  of  $\sim 0.2 \pm 0.06$  mm guarantees important DLO effects for all layers of the cable (even for a 1/C cable comprising a 15 mil (0.4 mm) CSPE jacket covering the EPDM insulation).

The calculations above imply that DLO effects may be possible for the outer CSPE jackets under the SNL combined environment aging conditions. In general, the modulus of CSPE materials increases in both thermal and radiation environments when oxygen is available, but increases much more slowly in the absence of oxygen (see Fig. 13 of Ref. 2). Thus, it may be possible to see evidence of DLO effects from modulus profiles taken after cable aging. Jacobus did this for the 9-month samples of Okonite, Dekoron and BIW (Appendix H of Ref. 1). The resulting modulus values for all of the CSPE jackets (overall, primary and bonded) were quite high (500-1500 MPa vs. 5-18 MPa for unaged materials) throughout their cross-sections, with no obvious indication of DLO effects. The very high values of modulus correspond to severe degradation, consistent with extremely low expected elongation values (see Figs. 11 and 17 of Ref. 2). It is possible that DLO effects were present but were masked by the extreme level of degradation. In other words, even though aging in the absence of oxidation leads to much slower increases in modulus (Fig. 13 of Ref. 2), severe aging could eventually cause the modulus in inert regions to rapidly increase. The key point to make is that SNL's aging conditions led to severely hardened material throughout all cross-sections of CSPE materials. When BNL's sequential simulation is completed, modulus-profiling comparisons would offer an excellent means of testing whether the spatial distribution of mechanical properties is similar. In other words, the important DLO effects predicted for the BNL radiation simulation could lead to very different modulus profiles after the sequential aging exposure. If, for instance, the modulus of the CSPE near or bonded to the EPR was much lower than the 500-1500 MPa found in the SNL experiments, the response of the cable to the subsequent LOCA simulation might be quite different. In particular, this much smaller step change (if observed) in modulus at the interface between CSPE and EPR could affect such things as crack propagation across the interface, adhesion/debonding, etc.

Even though the modulus profile results for the 9-month EPR insulations are essentially unchanged from their unaged values (Appendix H, Ref. 1), this does not provide evidence

on the importance of DLO effects for the EPR. This is because the modulus of EPR materials is relatively insensitive to radiation [10] and thermal [11] environments until the end-of-life is reached (which is beyond the aging conditions used in the SNL experiments).

### III.5 Conclusions

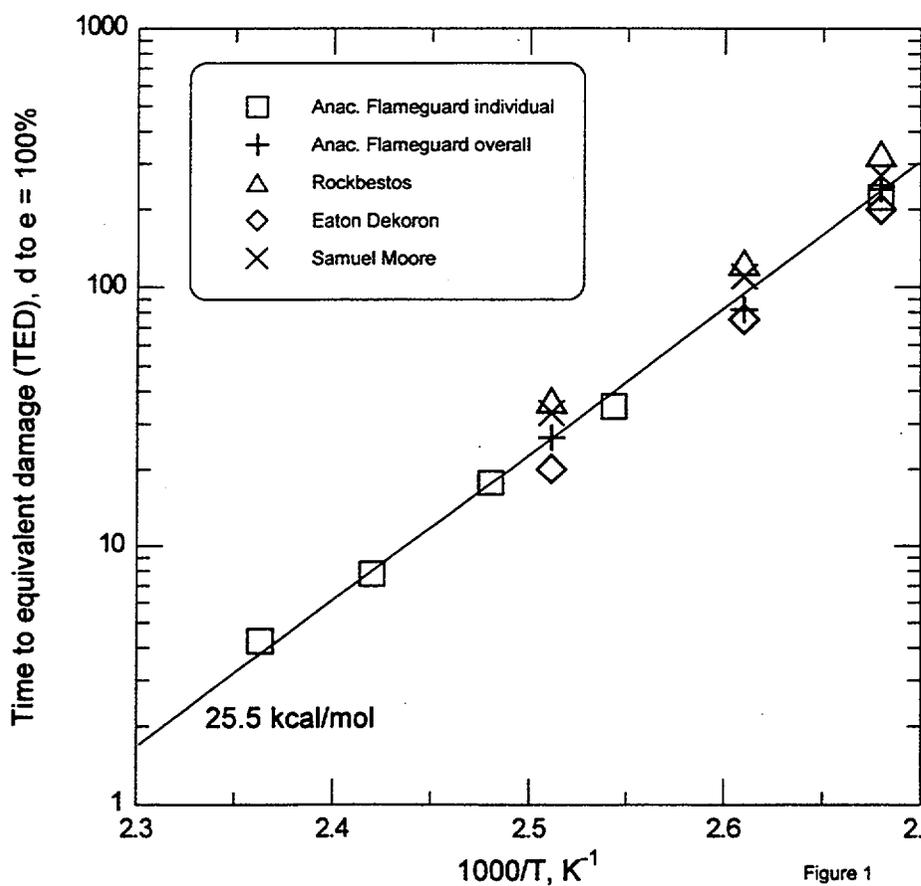
If BNL wants to simulate the combined environment 9-month conditions used by SNL (70 Gy/h plus 98°C) with shorter term sequential experiments (at 2500 Gy/h for radiation and for 3.5 months for temperature), their conditions should entail 7.7 days at 2500 Gy/h and 3.5 months at 108.4°C. Since CSPE materials age in a reasonably generic way, it is possible to conclude that the above BNL thermal-only exposure should decrease CSPE elongation to ~100% and the BNL room-temperature radiation exposure should be ~3 times less severe. Estimates of oxygen consumption during the two sequential exposures leads to a similar conclusion (thermal aging is ~4 times more severe than radiation aging). By combining estimates of the oxygen consumption rate with estimates of the oxygen permeability coefficient, it is concluded that diffusion-limited oxidation (DLO) effects will be extremely important for the BNL radiation aging conditions and may play a minor role for both the SNL combined environment conditions and the BNL thermal aging exposure. Modulus profiles of the 9-month cables from the SNL study indicated uniform and severe hardening of the CSPE materials, which offers some evidence against important DLO effects. This severe hardening is also consistent with the severe mechanical degradation (elongation ~ 0) found in the SNL study. It is hoped that the BNL procedure of exposing cables to the two environments in sequence (radiation followed by thermal is often more severe and would therefore be the recommended sequence), will lead to mechanical degradation comparable to that observed by SNL. Tensile tests on sacrificial sections of cable could be used to confirm such mechanical degradation. In addition, modulus profiles across the BNL aged cable specimens showing severe hardening across the entire cross-sections of CSPE materials would offer evidence for the equivalence of mechanical property distributions after aging.

### III.6 References

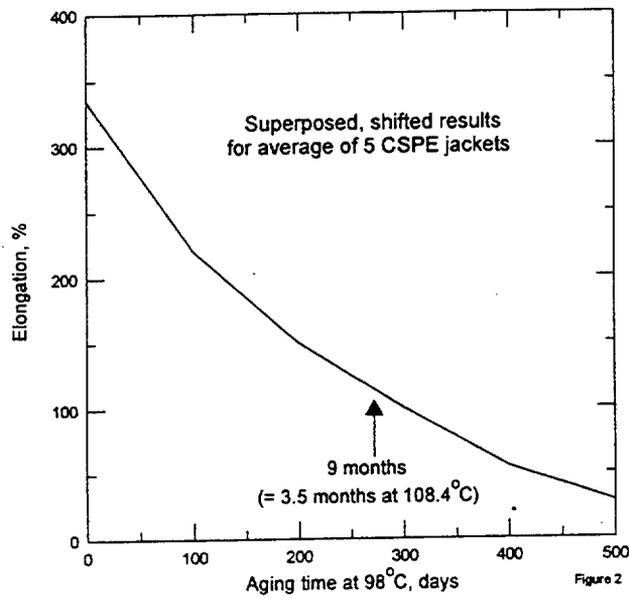
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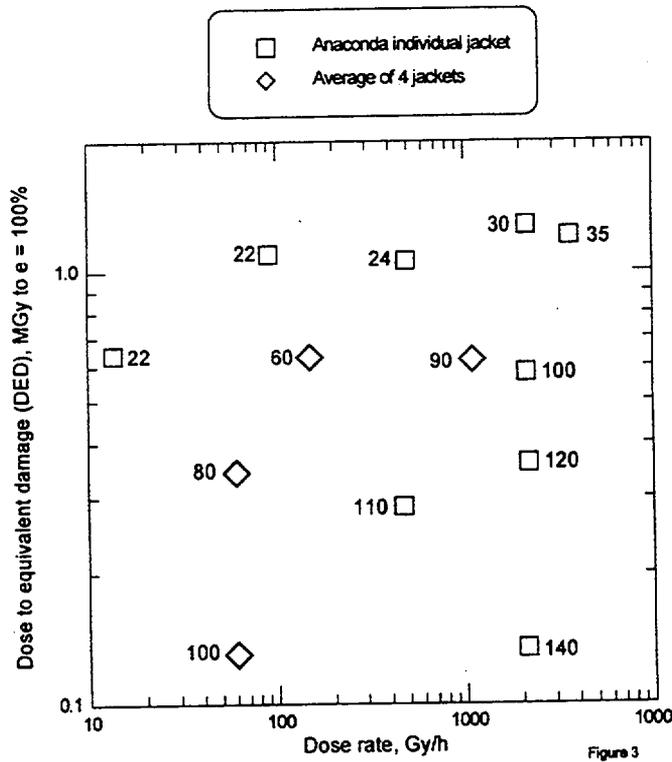
### III.7 Figures



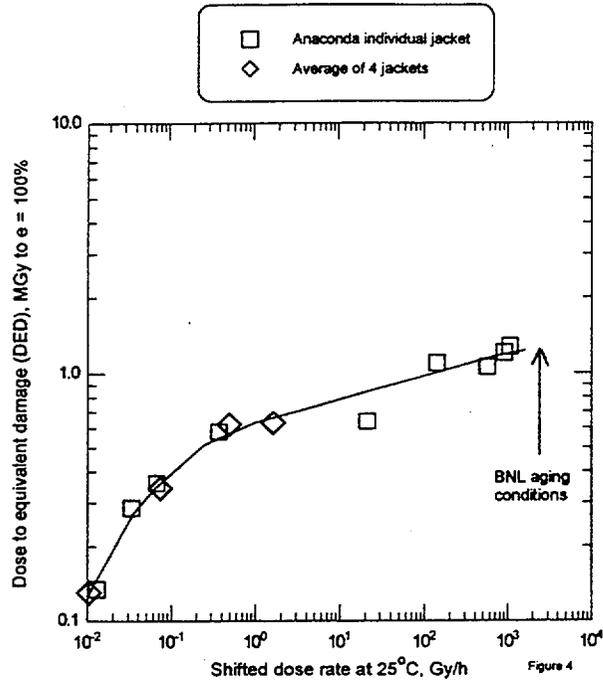
**Figure III.1.** Arrhenius plot of the times required for the elongation of the 5 indicated CSPE cable jackets to decrease to an ultimate tensile elongation of 100% versus inverse absolute aging temperature.



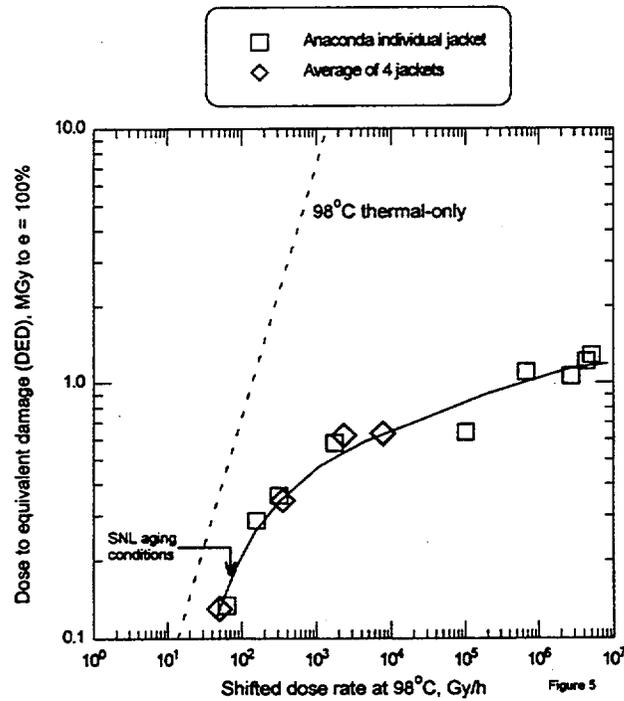
**Figure III.2.** Superposed, shifted results at 98°C for the average tensile elongation decay of the five CSPE materials.



**Figure III.3.** Average result for the dose required to lower the tensile elongation to 100% versus combined environment aging conditions (the numbers next to the symbols denote the aging temperature in °C)



**Figure III.4.** Predicted dose-rate effects at 25°C by shifting the CSPE combined environment results using the time-temperature-dose rate superposition approach.



**Figure III.5.** Predicted dose-rate effects at 98°C by shifting the CSPE combined environment results using the time-temperature-dose rate superposition approach.

## IV. ACCEPTABILITY OF THE ARRHENIUS APPROACH FOR LOCA AND POST-LOCA ENVIRONMENTS

### IV.1 Background

There has been a long history of licensees using the Arrhenius method together with existing accident qualification test results to establish qualification for test profiles that do not envelope the plant-specific LOCA profiles. The NRC has some concerns about the applicability of the Arrhenius methodology when used to analyze differences between equipment qualification (EQ) LOCA test profiles and actual plant LOCA profiles. In particular, there are concerns about the use of Arrhenius for the LOCA and post-LOCA phases of accidents when it is being used for (1) power uprate amendments, (2) reevaluations of qualified life of electrical equipment due to plant modifications and changes, and (3) license renewal technical reports on EQ. The main purpose of this section is to probe the issues relevant to the use of Arrhenius in such instances and try and determine if any of the issues are potentially significant.

One of the consultants for this project, Sal Carfagno, has already issued a report titled "Use of the Arrhenius Equation to Compare the Thermal Aging Of LOCA Profiles"[1]. In addition, The Nuclear Utility Group on Equipment Qualification recently issued a report titled "Acceptability of Arrhenius Methodology to analyze LOCA and Post-LOCA Environments [2]. In the interests of not being too repetitive in areas where I agree with these two reports, I will concentrate on areas where I disagree or on issues not discussed in these two reports. For convenience, I will generally follow the order of the subsections under Ch. 6 titled Technical Considerations in the NUGEQ Report [2].

### IV.2 General Arrhenius Information

Reference 2 starts by presenting a simple picture of the Arrhenius model. Unfortunately the chemistry proposed is so simple that it is seldom a valid description of the actual chemistry underlying degradation. This was pointed out in Section II.2 above, which gave a simplified oxidation scheme often used as a starting point for describing oxidative degradation mechanisms (Scheme I.1). This led to situations such as eqs. (II.9) and (II.10), where temperature-dependent effective activation energies would often be expected. Even so, the fact that the initiation rate constant ( $k_1$ ) often has a much larger value of  $E_a$  than the other rate constants implies that any temperature-dependent changes will be minor over the typical range of temperatures used for accelerated aging studies. This is probably the main reason that behavior approximating the Arrhenius model is often observed in accelerated aging simulations. Since LOCA and post-LOCA simulations use temperatures in the range used for typical accelerated aging exposures, small (usually unnoticed) temperature-dependent  $E_a$  values will not greatly impact these simulations. If, on the other hand, the accelerated aging results were extrapolated to much lower temperatures in order to make long-term predictions, changing  $E_a$  values could have a large impact on the predictions. In summary, I agree with most of the conclusions in the NUGEQ section titled "General Arrhenius Information", even though the kinetic description is too simplistic.

### IV.3 Arrhenius for Varying Temperature Conditions

Both the NUGEQ report [2] and Carfagno's review [1] conclude that you can use the Arrhenius approach for analyzing varying temperature conditions, based on the underlying principal of cumulative damage. I totally agree, but with an added important qualifying statement. I believe that the Arrhenius approach is a viable method for analyzing varying temperature conditions as long as careful testing of the Arrhenius assumptions underlie the experimental data. By careful testing, I refer to the time-temperature superposition approach discussed in Section II.2 above. The idea behind the Arrhenius approach is that raising the temperature will increase the degradation rate by a constant factor. This implies that the relationship between the times corresponding to a certain amount of degradation on the degradation curves at the two temperatures will be given by this constant multiplicative factor, independent of the amount of degradation. This is often the case – see for instance Fig. II.2 above and Fig 2 of reference 2. This is equivalent to saying that Arrhenius plots at different constant amounts of degradation will give identical values for the Arrhenius activation energy  $E_a$ .

When constant acceleration occurs, the degradation curves will have identical shapes (within the experimental uncertainty) when plotted versus the log of the time- see Fig. II.2. Then for each set of data at a higher temperature  $T$ , we multiply the experimental times by a constant shift factor,  $a_T$  chosen to give the best overall superposition with the reference temperature data ( $a_T = 1$  at the reference temperature). The results of this procedure are shown in Fig. II.3, where the time-axis gives the superposed results at the reference temperature. Unlike the often-used analysis given in Fig. II.1 (only a single processed data point at each temperature), this approach utilizes every raw experimental point and yields empirical shift factors that can then be tested by models such as the Arrhenius. If, in fact the empirical shift factors are consistent with the Arrhenius equation, then they would be given by

$$a_T = \exp\left(\frac{1}{T_{ref}} - \frac{1}{T}\right) \quad (IV.1)$$

This would predict that a plot of  $\log(a_T)$  versus inverse temperature would give linear behavior if Arrhenius were valid.

When raising the temperature increases the overall degradation by a constant amount (time-temperature superposition holds), a cumulative damage model will be valid. This means that if aging is done at one temperature for a given time and then switched to another temperature, the rate of degradation will immediately change by the constant multiplicative factor relating the two temperatures. The hypothetical data in Fig. IV.1 illustrates this concept. The two curves shown at temperature  $T_1$  and  $T_2$  are related by a constant multiplicative factor of 2 and therefore have the same shape when plotted versus log of the aging time. If aging occurs for 3 hours at the higher temperature  $T_1$ , the degradation level reaches 0.91 for this hypothetical data. If the temperature is then

switched to the lower temperature  $T_2$  for 8 hours, the degradation will start at the 0.91 level on this temperature curve and proceed down this curve for an additional 8 hours. The final degradation (solid circle on the  $T_2$  curve) will correspond to 14 hours at  $T_2$  since 3 hours at  $T_1$  is equivalent to 6 hours at  $T_2$ . The order of the aging clearly makes no difference- 8 hours at  $T_2$  followed by 3 hours at  $T_1$  will end up at the 7-hour point on the  $T_1$  curve (solid square) which gives the same overall damage as 14 hours at  $T_2$ .

When time-temperature superposition does not hold, cumulative damage models and the use of Arrhenius for varying temperature conditions are invalid. This is easily seen looking at the hypothetical data shown in Fig. IV.2. In this case the shapes of the curves change with temperature when plotted versus log time, implying that time-temperature superposition is impossible and that the "Arrhenius" activation energy will change with degradation level. In this case 3 hours at  $T_1$  followed by 8 hours at  $T_2$  will give a different result when the sequence is reversed to 8 hours at  $T_2$  followed by 3 hours at  $T_1$ , as shown by the end points (solid circle and solid square) on the two curves. In actuality, when time-temperature superposition is invalid, analyses like those shown on Fig. IV.2 cannot even be made. This is because the non-superposition says that the chemistry underlying the degradation at the two temperatures must be different. Therefore, it is hard to rationalize using one temperature to simulate what is occurring at the other temperature.

#### IV.4 Activation Energy at Accident Conditions

I agree with the NUGEQ comments that most activation energies are derived at temperatures that are typically close to those used for LOCA tests. However, most activation energies are derived in air-oven aging experiments, implying that they represent the activation energies appropriate to oxidation chemistry. Even in the presence of important diffusion-limited oxidation effects, the activation energies derived may still represent oxidation as noted in Section II.2 above. This observation complicates the use of these activation energies for LOCA situations. The complications depend upon the particular scenario of interest. If air is present during the simulated LOCA, use of the literature activation energies will probably be appropriate. If air is not present during the simulated LOCA, the proper activation energy to use would be one derived under inert aging conditions. However, since it is likely that the inert activation energy is greater than the activation energy appropriate to oxidation, use of the lower activation energy will be conservative for the accelerated parts of the LOCA simulation. For the "reverse Arrhenius" portions of the LOCA simulations, the times will be short enough such that the effects should be minimal. Of course, the worst case situation is when air is present during the actual LOCA, but air is absent during the simulated LOCA. In this case, the damage occurring during the simulation may be much less than would actually occur during the real LOCA [3]. Whether this is important depends upon whether enough oxygen is trapped at the start of a real accident and how fast this concentration would decrease with time. Since any trapped oxygen would immediately start reacting with all sorts of materials (metals, polymers, etc.), the concentration of oxygen during the LOCA may quickly decrease, but this is unproven conjecture on my part. The actual situation will depend upon the total amount of oxygen trapped initially

and the rates of its consumption by a multitude of materials, too complex a problem to ever hope for an answer.

#### IV.5 Changing Activation Energy

As pointed out in Section IV.3 above, a changing activation energy with degradation level is inconsistent with the Arrhenius assumption of a constant acceleration of the effective overall reactions when the temperature is increased. When the activation energy changes with degradation level such as the Raychem results shown in Fig. 3 of the NUGEQ report [2], I therefore question the use of any models based on Arrhenius. NUGEQ's conclusion that a change to higher activation energy for this material with degradation would be in the conservative direction sounds reasonable at first and may actually turn out to be correct. However, since the non-superposition of the results at the two temperatures implies that the chemistry is different at the two temperatures, this seems to say that any "simulation" at the elevated temperature would not really simulate the chemistry occurring at the lower temperature. The consequences of this situation are unclear. This situation also brings out an interesting paradox. It is often difficult to determine whether published Arrhenius activation energies come from good analyses that use time-temperature superposition or from inferior analyses that use only a single point from each degradation curve. The values are then used without knowing the care taken in deriving the values. When a manufacturer takes more care and publishes the entire curves, if the curves do not superpose, he may be "penalized" for being forthright about his results.

#### IV.6 Activation Energy During Steam Conditions

The effect of steam during the LOCA on the degradation and the activation energy is an important question. Carfagno expressed several concerns with humidity effects in his report [1], including the absence of a practical humidity-aging model for chemical (hydrolysis) effects and various physical effects caused by swelling, crack propagation, etc. As pointed out in the NUGEQ report [2], we actually suggested and used literature results to successfully test a general approach for humidity aging predictions approximately 20 years ago [4]. We started by assuming the simplest possible hydrolysis degradation reaction (water reacts with polymer  $P$  giving a degradation product  $D$ ). This leads to

$$\frac{dD}{dt} = k[H_2O][P] \quad (\text{IV.2})$$

where  $[H_2O]$  and  $[P]$  represent the concentration of water dissolved in the polymer and the concentration of polymer, respectively. It turns out that solubility isotherms for water are exceedingly complex when plotted versus water partial pressure surrounding the material, as illustrated for a silicone material [5] in Fig. IV.3. The situation becomes much less complex when the sorption isotherms are plotted versus relative humidity, as seen in Fig. IV.4. If the results shown in Fig. IV.4 are analyzed at various constant

relative humidity values and plotted on an Arrhenius plot, it turns out that the concentration of water has an Arrhenius dependence on temperature given by

$$[H_2O] \propto \exp\left[\frac{-\Delta H_s}{RT}\right] \quad (IV.3)$$

where  $\Delta H_s$ , the heat of solution at constant RH, is independent of RH (see Fig. IV.5). Therefore eq. (IV.2) analyzed at constant RH becomes

$$\frac{dD}{dt} = k[H_2O][P] \propto \exp\left[\frac{-\Delta H_s}{RT}\right] \exp\left[\frac{-E_a}{RT}\right] \propto \exp\left[\frac{-E_a - \Delta H_s}{RT}\right] \quad (IV.4)$$

This means that degradation experiments analyzed at constant RH should be Arrhenius, which was verified by literature results on a polyurethane potting compound [6], as shown in Fig. IV.6. Since this work, other reports confirming that hydrolytic degradation analyzed at constant RH follows the Arrhenius model have appeared, including work on a polyester material [7] and on a cellulose [8].

These results have several interesting implications. First of all, as pointed out in the NUGEQ report [2], the hydrolysis activation energies are similar to the range found for normal thermoxidative aging. Since LOCA experiments use thermoxidative activation energies and entail ~100% RH conditions throughout the experiment, any hydrolysis reactions should be accelerated properly and in concert with the normal degradation reactions. Another observation is that the water solubility at constant RH typically increases with increasing temperature, as was the case for the silicone material (data shown in Fig. IV.4). This implies that the physical swelling effects caused by moisture absorption will be larger when the LOCA temperature is higher than the actual temperature. Since this will be the case for the post-accident operating time (PAOT) portion of the LOCA where there might be some concern over physical effects, the larger swelling for the simulation actually could represent some conservatism.

Another issue that could influence hydrolytic (chemical) effects during the accelerated PAOT part of LOCA is diffusion-limited hydrolysis (DLH) effects, which are analogous to the diffusion-limited oxidation (DLO) effects discussed in Section II above. Water permeability coefficients tend to be orders of magnitude higher than oxygen permeability coefficients [9]. In addition, at the elevated temperatures used for the PAOT portion of LOCA, the water partial pressure in the saturated steam environment will be an order of magnitude higher than oxygen partial pressures appropriate to air aging. Given these facts, eq. III.1 shows that as long as hydrolytic consumption rates are not too large relative to oxygen consumption rates, DLH effects may not be too important. Finally, most of this discussion may be largely academic, since humidity-sensitive materials are not typically chosen by suppliers for nuclear power plant applications.

NUGEQ refers to our report NUREG/CR-2763 [3] comparing 96-hour air-oven aging results at 145°C with a 145°C steam exposure for the same 96-hour period, noting that

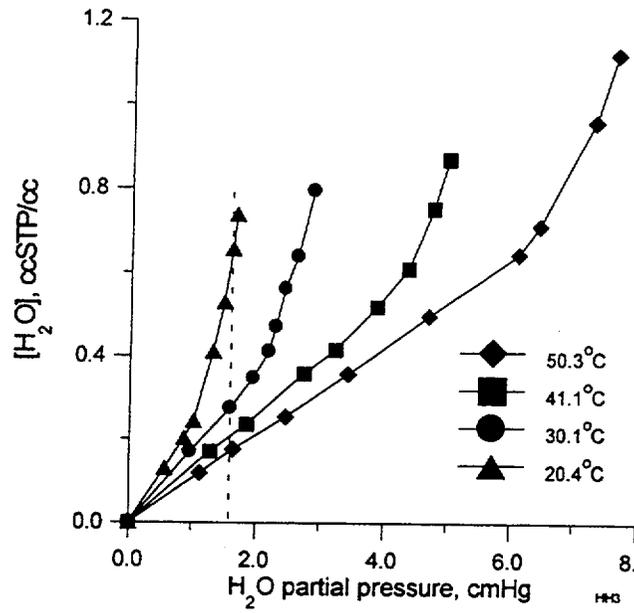


Figure IV.3. Water isotherms for a silicone rubber material from ref. 5.

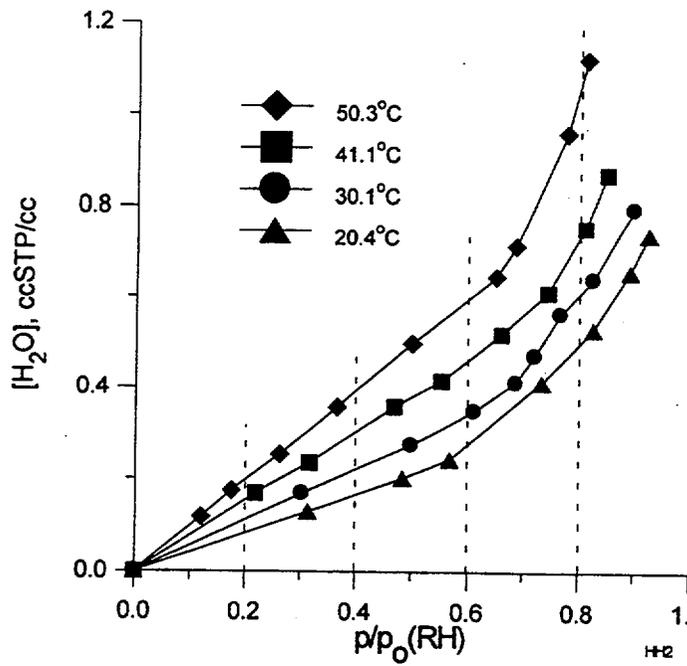
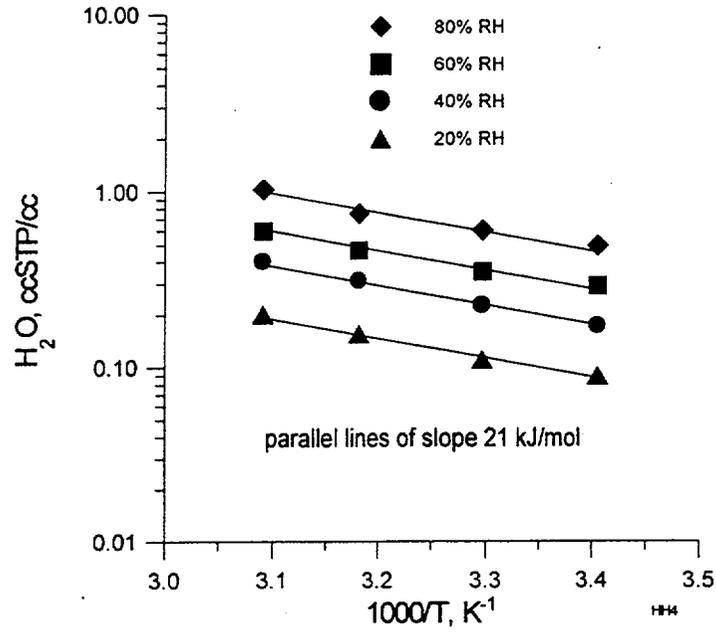
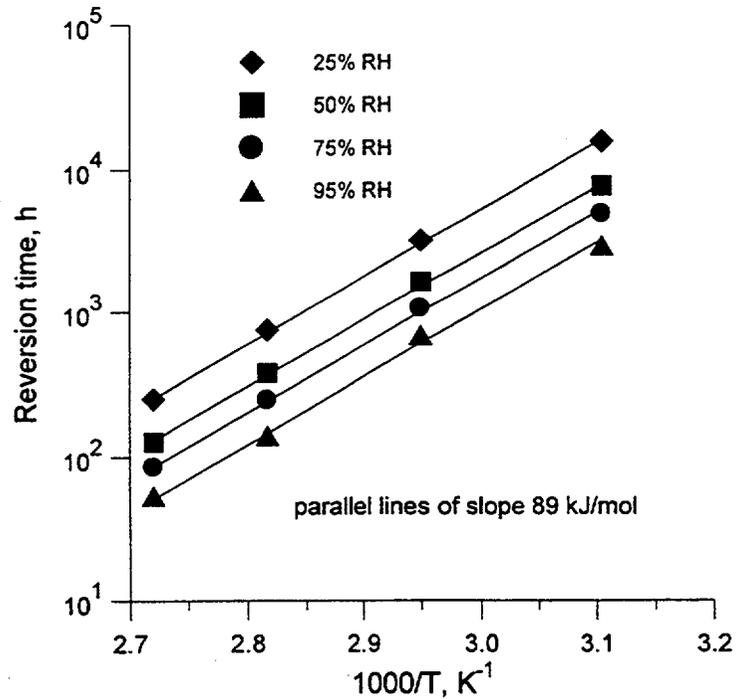


Figure IV.4. A replot of the data from Fig. IV.3 vs. relative humidity (RH).

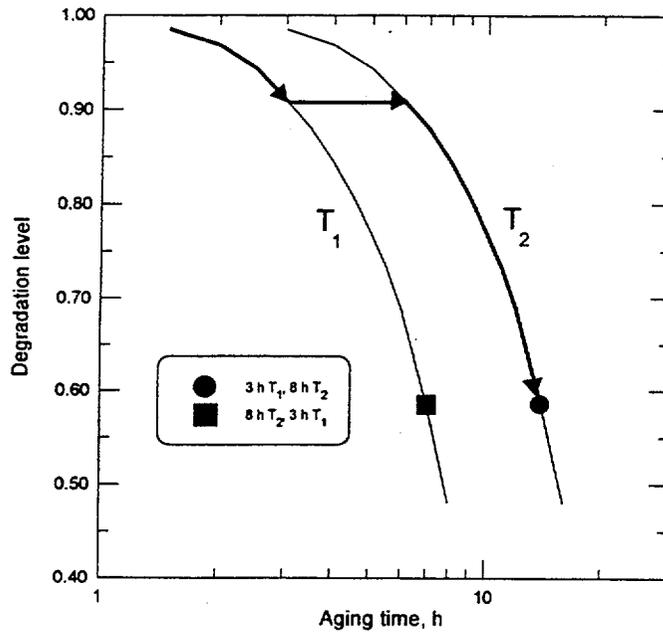


**Figure IV.5.** Log of the water solubility for the silicone material plotted versus inverse temperature at the four indicated RH levels.

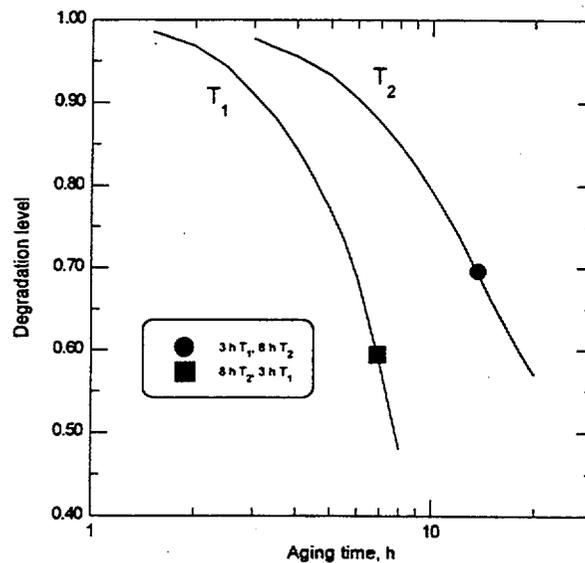


**Figure IV.6.** Plot of the log of the reversion times for a polyurethane potting compound versus inverse temperature at the four indicated values of RH.

## IV.8 Figures



**Figure IV.1.** Hypothetical superposable degradation data at two temperatures plotted versus log time. The total degradation is independent of the order of sequential steps from one temperature to the other.



**Figure IV.2.** Hypothetical non-superposable degradation data at two temperatures plotted versus log time. The total degradation depends on the order of sequential steps from one temperature to the other.

we concluded a reasonable correlation of the results. It is important to add, however, that our LOCA exposure experiment contained a partial pressure of oxygen essentially equal to that found under the air-oven aging conditions. Quite different results occurred when inert LOCA aging was compared to air-oven aging.

NUGEQ's arguments on the meaning of the JAERI results (Figs. 10-12 of reference 2) were somewhat unconvincing to me, given the scatter in the results. For instance, for the air aging in Fig 10, the results at 140°C (solid triangles) dropped faster than the 160°C data (solid squares), making any conclusions concerning shifting of these data ridiculous.

The only other comment concerns a comment by Carfagno [1] in his Section 6.3. He mentioned his irritation with Monticello's claim "that the test profile enveloped the required profile by a margin of 11.8 days." I agree with Carfagno's comment and suggest that no ambiguity on such statements would exist if the margin was stated as a percentage (5.5% for the Monticello case). The beauty of the cumulative damage approach (equivalent time) is that such comparisons can always be made and stated as a percentage.

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**Subject:** *Final Report by S. Carfagno on Use of Arrhenius  
E.Q. Research Program, JCN W6465*

Dear Satish:

Enclosed is a copy of the final report by Dr. Sal Carfagno on his work related to the use of Arrhenius. This report incorporates comments he received during our June 29, 1999 meeting.

If you have any questions, please contact me.

Sincerely,

A handwritten signature in black ink, appearing to read "Robert Lofaro".

Robert Lofaro  
Engineering Mechanics and Infrastructure Group

RL/jmf99L27  
Enclosures  
Copies to: (w/o Encls.)  
S. Carfagno  
C.R. Kempf  
R. Hall  
J. Taylor  
J. Vora, NRC

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**USE OF THE ARRHENIUS EQUATION TO COMPARE THE THERMAL AGING OF LOCA  
PROFILES**

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February 6, 1999

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## SUMMARY

Use of the Arrhenius equation to demonstrate that the thermal aging associated with a LOCA test profile exceeds the thermal aging of a required accident profile is investigated for four different types of deviation between the test profile and the required profile. The profiles are compared by calculation of equivalent thermal aging times, at the same reference temperature, for selected time intervals of the test profile and a comparable interval of the required profile. If the equivalent thermal aging of the test interval exceeds the equivalent thermal aging of the required profile interval, the test is satisfied the accident thermal aging requirement. The method can also be used to compare the relative thermal aging associated with two required profiles, in lieu of comparing each of them directly to the LOCA test profile. This procedure is sometimes used when an existing required profile is changed due to rerating (or uprating) of a plant's power level.

In many applications, the equivalent thermal aging analysis is used to demonstrate that a relatively short LOCA test satisfies the requirements of a much longer required profile; in such cases, if equipment is vulnerable to the effects of humidity in the LOCA environment, it must also be demonstrated that the effects of humidity on the functional capability of the equipment are adequately simulated by the LOCA test.

Evaluation of each of the four types of deviation is discussed; and the information necessary to determine their acceptability is outlined. Most of the acceptance criteria are qualitative, as it is not feasible to translate the evaluation into quantitative measures.

Comments are given on five utility reports in which thermal aging equivalency analysis was used to demonstrate that deviations between required accident profiles were within the conditions encompassed by existing qualification programs. A review of a NUGEQ report on the use of the Arrhenius method for analyzing LOCA environments is given in Appendix D.

General background information is included on the Arrhenius equation and its use for thermal aging calculations, limitations of its application to LOCA profile analysis, and humidity effects in the LOCA environment.

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## 1 Introduction

This report has been prepared in partial fulfillment of a task to provide technical support for "use of the Arrhenius Methodology for the LOCA and post-LOCA phases of the accident in cases where it is being used for (1) power uprate amendments; (2) reevaluations of qualified life of electrical equipment due to plant modifications and changes; and (3) license renewal technical reports on EQ. This research effort is intended to provide independent confirmation of the validity for the use of the Arrhenius Methodology for the LOCA and post-LOCA phases of the accident."

The Arrhenius equation has been used to calculate 'equivalent thermal degradation' at reference temperatures so that the thermal degradation of different LOCA temperature profiles can be compared. Usually, the intent is to demonstrate that equipment qualification conducted in accordance with one profile is still acceptable when plant changes cause the temperature of the revised LOCA profile to exceed the temperature of the original profile over certain intervals of time. The Arrhenius equation may also be used to recalculate the qualified life of equipment in accordance with actual plant service conditions that may be either less severe or more severe than the conditions assumed in the original qualified life determination. In those cases where the actual service conditions are less severe than those assumed originally, the qualified life may be recalculated to satisfy the requirements of license renewal.

In accordance with the last sentence in the task statement quoted above, this report is devoted primarily to application of the Arrhenius equation to the analysis of LOCA profiles.

## 2 Background

### 2.1 LOCA Conditions

The qualification of safety related equipment for service in nuclear power plants requires two fundamental procedures: aging of a sample of the equipment to simulate any significant degradation that takes place in normal service and testing the equipment under simulated LOCA<sup>1</sup> conditions. This report is concerned primarily with the LOCA simulation. To plan a LOCA simulation, it is necessary to specify the equipment, its safety function and the time during which the function is required, plus a definition of the LOCA environment where the equipment is located in the plant. The LOCA environment is obtained from thermo-hydraulic calculations that determine the profiles of temperature and pressure as functions of time following the rupture of a line carrying water or steam; calculation of the radiation environment; definition of the composition of the atmosphere at the equipment's location; and, in cases where a chemical spray is used as one of the mechanisms for mitigating the effects of a LOCA, specification of the spray intensity, its chemical composition, and its duration. The atmospheric composition may initially be air or largely nitrogen (for inerted environments), but the concentration of water vapor quickly increases after the start of an accident. The vapor condition is usually saturated, although for some line breaks it may initially be superheated for a relatively short time; consequently, the relative humidity is high most of the time after a LOCA starts.

### 2.2 Scope of Evaluation

Basically, an equipment qualification (EQ) program is required to demonstrate that the equipment is capable of performing its specified safety function, under the predicted service conditions, and for the required time. The effect of radiation exposure is usually simulated separately from the steam/chemical spray exposure; and its evaluation is excluded from consideration in this report. Furthermore, consideration of the chemical spray will also be excluded; and it will be assumed that simulation of the LOCA pressure profile is a secondary concern. The adequacy of the test chamber atmosphere during LOCA testing, particularly the partial pressure of air (which affects the rate of oxidation), is also considered to be outside the scope of this report. Consequently, the concerns that will be addressed are simulation of the LOCA temperature profile and the effect of humidity, with minor comments on the effect of rapid pressure rises.

Temperature deviations between LOCA test conditions and required conditions have been analyzed using the Arrhenius equation as a model for the rates of chemical reactions; a comparable practical model for humidity effects is not available. A ground rule of the analysis in this report is that use of the Arrhenius equation for reaction rate is acceptable for correlating the rates of reaction at different temperatures in LOCA environments. Background information from Ref. 7 on accident temperature equivalency is included in Appendix A; and background information on humidity effects from the same reference is given in Appendix B.

Notes on the Arrhenius equation, its use as a model for accelerated thermal aging, and the uncertainties associated with its use in equipment qualification are discussed in Appendix C.

### 2.3 Description of Accident Profiles

Before describing how the Arrhenius equation is used to analyze LOCA profiles, it is necessary to define the profiles that will be compared. Figure 1, page 4b, illustrates three LOCA profiles. The vertical scale is temperature, and the horizontal scale is time after the start of a LOCA; the time scale is not linear, and the labeled times are intended simply to illustrate typical times at key

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<sup>1</sup>In this report, LOCA is used as a generic reference to all pipe breaks, including steam line and high energy line breaks, that result in the release of large amounts of energy.

points of the profile: the initial rapid temperature rise typically takes place in seconds, the time at the highest temperature levels may last several hours, the test duration may be about 10 days, and the required safety function capability may be anywhere between an hour and a year. The use of 100 days in Figure 1 illustrates a common intermediate safety function requirement. About 4 days after the start of a LOCA, the temperature falls to a relatively low level, labeled  $T_{eq}$ ; the portion of the profile at this temperature is frequently referred to as the 'tail.' The dashed curved line represents the calculated temperature profile; it is usually a curve that encompasses the temperature profiles for several different line breaks so that a single test can qualify equipment for all of the encompassed breaks. The solid curved line is obtained by adding a temperature 'margin' to the calculated curve, thereby obtaining (as will be explained in the next paragraph) the LOCA required profile that must be simulated. The third profile, consisting of straight lines, is the LOCA test profile. Ideally, the test profile temperature should at all times be equal to or greater than the temperature of the required profile. It is the main objective of this report to suggest guidelines for evaluation of deviations in which the test profile falls below the required profile.

Margin is the word used in EQ to define increments applied to environmental and operational parameters in a test to increase the severity of the test. The purpose of using margins is to account for experimental errors in performing tests, to account for differences between installed equipment and the tested sample, and to contribute to the conservatism of the qualification process. In this report, the only margin that will be considered is the temperature margin. In a list of **typical** margins, IEEE Std 323-74 gives the value 15 °F. In deciding what margin should be applied to the calculated profile to obtain the required profile, any excess conservatism already included in the calculated profile, especially if it is one that encompasses the profiles for several pipeline breaks, may be used to reduce (or possibly eliminate) the temperature margin.

### 3 Types of Deviation between Required and LOCA Test Profiles.

Starting with the principle that the LOCA test must demonstrate operability for the entire period that the safety function may be required, four types of deviation between the required LOCA profile and the test profile can be identified. These deviations are labeled by the letters A, B, C, and D in Figure 1; and they have the following descriptions:

- A. The rapid rise to peak temperature takes place more slowly in the test than is predicted by the thermo-hydraulic calculations.
- B. The peak temperature attained in the test is lower than the peak temperature of the calculated profile.
- C. The test profile falls below the required profile in a temperature range below the peak temperature.
- D. The test duration is shorter than the required operating time.

The Arrhenius equation has been used for degradation equivalency analyses to demonstrate that the test profile is more severe than the required profile in spite of any deviations of the type described above. The aging equivalency analysis has also been used when the required profile has been modified as a consequence of increasing the power level at which the plant is operated, a process referred to as **rerate** by some utilities and **uprate** by others. The term **uprate** will be used in this report to be consistent with the Task statement quoted in Section 1. In the case of uprate, assuming that equipment has already been qualified in accordance with the required profile for the lower power level, it suffices to show that the uprate required profile is not more severe than the required profile for the lower power level. Figure 1 will apply to this case as well if the 'LOCA test profile' is interpreted as being the profile for the lower power level and the 'required qualification profile' is interpreted as being the uprate profile.

In the next section, the method of calculating equivalent thermal aging times at a reference temperature will be described; then, in Section 5, each of the four types of deviation will be discussed.

## **4 Use of the Arrhenius Equation to Compare the Thermal Aging of Different LOCA Profiles**

### **4.1 Introduction**

The analysis is based on the assumption that the Arrhenius equation applies under LOCA conditions over the entire range of LOCA temperatures and that the activation energy applicable in normal service conditions is also applicable under LOCA conditions. Both of these assumptions are questionable; and making them introduces uncertainties in the analysis. With regard to activation energy, it is possible that the choice of the value that applies in normal service is conservative because the oxygen concentration in the LOCA environment may be lower than it is in the normal plant environment, in which case thermal degradation would be expected to proceed more slowly under LOCA conditions than in normal service (at the same temperature). In that case, the equivalent thermal degradation calculated for the LOCA profiles using the normal service activation energy would be overestimated. This is particularly true for equipment in inerted containments. However, this potential conservatism is somewhat obviated if the analysis is used to compare similar LOCA profiles, i.e., if the thermal degradation in two profiles is overestimated by the same amount, the conservatism disappears.

In addition to the concern with activation energies, the Arrhenius equation applies only to thermal effects and, therefore, does not account for humidity effects, which can be significant.

Acknowledging these reservations, application of the Arrhenius equation to LOCA profiles is described in the following section for the case in which a required LOCA profile is compared with a LOCA test profile; then, in Section 4.3, its application to other profile comparisons is discussed.

### **4.2 Equivalent Thermal Aging Analysis for Test and Required Profiles**

To compare the thermal aging associated with different LOCA profiles, the Arrhenius equation is used to translate the actual time history of a LOCA profile, or a portion of it, to an equivalent time at a reference temperature. If the same reference temperature is used for different profiles, the equivalent times provide a means of comparison: the longer the equivalent time, the greater the equivalent thermal degradation.

The Arrhenius equation strictly allows us to calculate the times taken at different temperatures for the same amount of reaction to occur; thus, the reference to equivalent times. Since the Arrhenius equation relates reaction rate to temperature and the progression of time may be thought of as aging, the equivalent times can also be called equivalent thermal aging times. And since thermal aging usually causes degradation that affects the functional capability of equipment, it has become common practice to call the process equivalent degradation analysis. To emphasize that the analysis addresses only thermal effects and that aging does not necessarily cause degradation, the term equivalent thermal aging analysis is preferable.

The method of evaluating the relative thermal aging of the required and LOCA test qualification profiles is illustrated in Figure 2, where the required temperature exceeds the qualification temperature over a limited time interval. The procedure is to select an evaluation interval that encompasses the deviation and divide it into segments, not necessarily of the same duration. Figure 2 illustrates a case in which the evaluation interval is the same for both the LOCA test profile and the required profile; however, the analysis is frequently applied to required profile intervals that are longer (sometimes

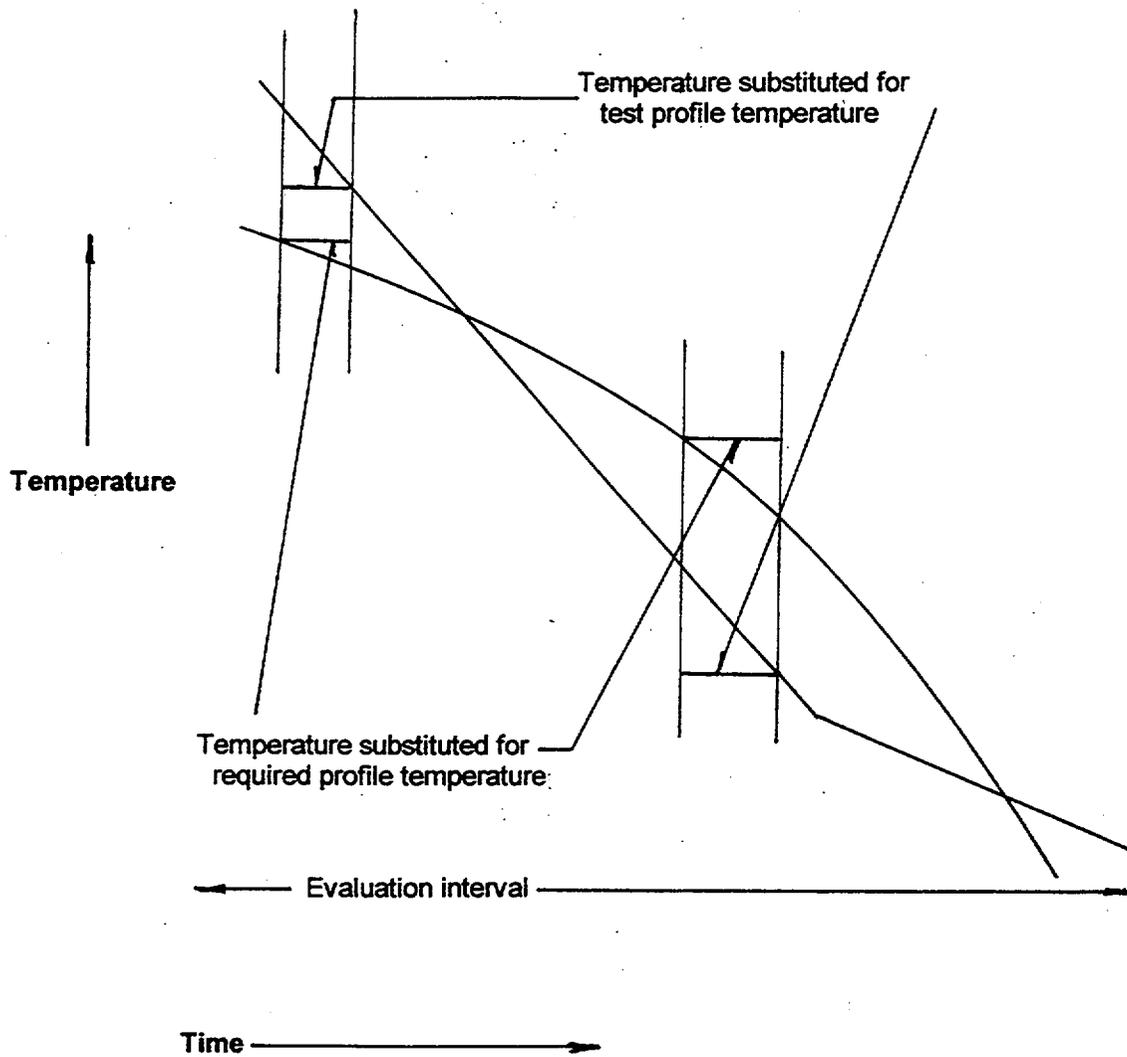


Figure 2 Typical segments used for Arrhenius calculation of equivalent required and test LOCA times at a reference temperature.

much longer) than the comparable LOCA test profile. In each segment the test profile and the required profile are replaced by constant-temperature steps such that the test profile step is always below the actual test profile and the required profile step is always above the actual required profile. This procedure of approximating the profiles is conservative because the required profile is made more severe and the test profile is made less severe. The thermal aging that occurs at the temperature level of each segment is converted, by use of the Arrhenius equation, to an equivalent aging at a reference temperature, which may be either higher or lower than the range of temperatures in the evaluation interval. For example, some utilities have chosen the low temperature that exists a long time after an accident has started; and at least one utility has chosen the peak accident temperature for its reference.

The calculation for a typical segment follows:

The Arrhenius equation for the equivalent time at the reference temperature is:

$$t_t = t_a \exp[(E/k)(1/T_{ref} - 1/T_t)]$$

where

$t_t$  = equivalent LOCA test time at reference temperature (h)

$t_a$ = segment time interval (h)	<u>Sample Values</u> 1.0 h
-----------------------------------	-------------------------------

$E$ = activation energy (eV/molecule)	0.8 eV/molecule
---------------------------------------	-----------------

$k$  = Boltzmann's constant =  $8.617 \times 10^{-5}$  eV/(K molecule)

$T_{ref}$ = reference temperature (K)	160 °F = 71.1 °C = 344 K
---------------------------------------	--------------------------

$T_t$ = temperature of test profile step (K)	200 °F = 93.3 °C = 366 K
--	--------------------------

The only requirement for the units of time are that  $t_{ref}$  and  $t_t$  have the same units, here chosen to be hours. Using the sample values given at the right, above, we find that the value of the equivalent test time  $t_t$  is 5.1 h.

We can find the equivalent time,  $t_r$ , at the reference temperature for the **required** step temperature  $T_r$ , by rewriting the Arrhenius equation as follows:

$$t_r = t_a \exp[(E/k)(1/T_{ref} - 1/T_r)]$$

Letting  $T_r$  have the sample value of 180 °F = 82.2 °C = 355 K, we find  $t_r$  to be 2.3 h.

As expected, since  $T_t > T_r$ , we find that  $t_t > t_r$ , i.e., in this segment the test profile corresponds to more thermal aging than the required profile. The reverse will be true in a segment where  $T_t < T_r$ .

To demonstrate that the test profile corresponds to more thermal aging than the required profile over the entire evaluation interval, it must be shown, as a minimum that:

$$\text{sum of } t_t > \text{sum of } t_r$$

when the sums are taken over all segments within the LOCA test interval and the corresponding required profile interval.

In addition to satisfying this minimum requirement, one must also consider the effect of humidity. If the evaluation interval is relatively short, say several hours, and the required profile interval is not significantly longer than the corresponding test profile, the effect of humidity may be considered to be adequately simulated by the test. However, when the required profile evaluation interval is very long, say 100 days, and the corresponding test interval is much shorter, say 1 or 2 days, there remains the need to demonstrate that there will be no significant humidity effect on the equipment performance during the long required period of functional capability. It is not feasible to provide a quantitative criterion for evaluation of the humidity effect. The first requirement is to evaluate the vulnerability of the equipment to humidity under LOCA conditions for the period of required functional capability.

Another factor to consider is the ratio of the required profile interval to the corresponding actual test interval, which may be called the acceleration factor. The larger this factor, the more difficult it is to evaluate the humidity effect, because it is then necessary, short of other supporting humidity effects data, to extrapolate the performance during a relatively short test period to the performance during a long period of required functional capability. In this case, there is no simple substitute for analyzing all relevant data and reaching a judgment as to whether humidity can have a significant effect on functional capability during the required period.

#### 4.3 Other Profile Comparisons

The comparison of a required profile directly with the test profile has been discussed in the preceding Section 4.2; another approach is to compare a modified profile with an existing profile. This may happen when the required profile has been modified as a consequence of increasing the power level at which the plant is operated, a process referred to as **rerate** by some utilities and **uprate** by others. For simplicity, the term **uprate** will be used in this report. In the case of uprate, assuming that equipment has already been qualified in accordance with the required profile for the lower power level, it suffices to show that the uprate required profile is not more severe than the required profile for the lower power level. To distinguish the two required profiles, the profile for the lower power level (for which equipment qualification programs exist) will be called the **qualified** profile and the other as the **uprate** profile. Figure 1 will apply to this case as well if the 'LOCA test profile' is interpreted as being the **qualified** profile and the 'required profile' is interpreted as being the **uprate** profile.

For this type of profile comparison, it is essential to confirm that the LOCA test profile satisfies the required profile at the lower power level, because any conclusion reached on the basis of comparing two required profiles hinges on the validity of the existing qualification. It is also possible to obtain misleading indications of conservatism by this process, particularly if the analysis is applied to a long interval. For example, as discussed in the review of one utility's analysis in Section 6.3, a margin of 11.8 days was claimed for the thermal degradation equivalency when, in fact, the total duration of the LOCA test was only 3 days.

#### 4.4 Self-heating and Thermal Lag Considerations<sup>2</sup>

For equipment that has negligible self-heating, thermal lag may prevent the temperature of critical internal materials and parts from reaching the peak environmental temperature, during a LOCA test, before the environmental temperature begins to decrease. In such cases, thermal lag analysis may justify a deviation of Type B, in which the peak test temperature does not envelope the peak plant-specific LOCA profile temperature (as described in Section 5). However, when there is significant self-heating, internal components of the equipment may reach temperatures that exceed the peak environmental temperature; and the analysis of degradation equivalency becomes more complicated.

Figure 3, taken from Ref. 8, illustrates the case of a 300-hp motor, in which the motor winding temperature reached levels more than 50 °F higher than the peak environmental temperature. In cases like this one, it is necessary to confirm that the test conditions allowed critical internal components to reach the temperatures that would be attained in a test without deviations from the required profile and that such temperatures last for the duration that would apply in a test without deviations. If either of these conditions, i.e., temperature level and duration, is not satisfied in the test, then any degradation equivalency analysis (DEA) must consider the vulnerability of critical internal components to the higher temperatures and durations that would apply in a test without deviations. Any deviation can be justified only if the DEA, supplemented by data and analysis of self-heating and thermal lag, demonstrates that vulnerable internal materials and parts were adequately tested.

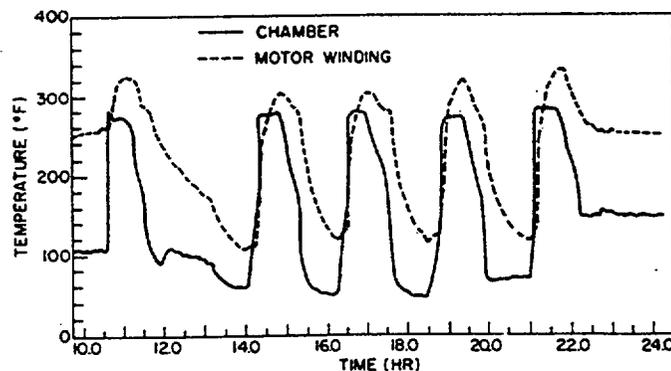


Figure 3 Chamber and motor-winding temperature during LOCA test of 300-hp motor. (From Ref. 8.)

<sup>2</sup>Although one of these subjects, the effect of thermal lag, is mentioned in Section 5 (in the discussion of Deviation Type B), this section was added after reviewing the NUGEQ report discussed in Appendix D.

## 5 Discussion of Deviations Between Required and Test LOCA Profiles

As summarized in Section 7, several different pairs of profiles may be compared but for simplicity, the following discussions are limited to comparing a required profile to a test profile. The application to other pairs of profiles listed in Section 7 should be obvious.

**Deviation Type A:** The rapid rise to peak temperature is slower during the test than predicted by thermo-hydraulic calculations.

This deviation occurs frequently because of the difficulty of achieving very rapid temperature rises in LOCA test facilities. It is a concern only for equipment that may be vulnerable to a very rapid pressure/temperature transient.<sup>3</sup> For most equipment a slower than required temperature rise should not be a concern because the rise time is too short for appreciable heat transfer to the equipment under test. One possible exception is found in NRC Information Notice 97-45, Supplement 1, Ref. 6, which reports erratic indications from high-range radiation monitors caused by currents induced in associated coaxial cables when they are exposed to extreme temperature transient conditions.

Aside from temperature considerations, some equipment may be vulnerable to the pressure transient. There have been instances in which the equipment enclosure has collapsed as a consequence of the pressure transient. Even if the enclosure is not sealed, openings may be too small to accommodate rapid equilibration between interior and exterior pressures. It is during this transient that moisture in the LOCA test environment may be forced into the equipment; once pressure equilibrium occurs, moisture enters equipment primarily by the slower process of diffusion. Although the greatest lack of pressure equilibrium occurs during the initial transient, lack of equilibrium may also exist during subsequent drops in the environmental pressure.

There is no simple criterion for evaluating the acceptability of deviations of Type A. It is necessary to consider the magnitude of the deviation and the vulnerability of the equipment to rapid temperature/pressure transients and moisture intrusion. Deviations of Type A will probably be of concern for relatively few types of equipment.

**Deviation Type B:** The required peak temperature exceeds the peak temperature of the qualification profile.

This type of deviation is usually limited to relatively short intervals on the order of an hour. The main concern is whether any critical part of the equipment is vulnerable to causing malfunction if it were exposed to the higher required temperature for the time of interest. For interior parts that are more thermally isolated from the environment, the deviation will probably not affect functional capability because of the temperature lag between the interior and exterior of the equipment. [Appendix A5.4 of Ref. 7 discusses thermal lag analysis.] There could be an effect if a vulnerable part is at or near the surface of the equipment and the deviation is large enough in magnitude and duration. Again, the coaxial cable mentioned in Ref. 6, may be an example of equipment that could be affected by this type of deviation.

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<sup>3</sup>The term 'transient' is used in this report to mean the initial rapid pressure/temperature rise in the LOCA profile (seconds); thus, it is distinguished from use of the term in reference to the entire profile up to the time equilibrium exists (days).

As with deviations of Type A, it is not feasible to identify a simple, quantitative criterion for evaluating the acceptability of deviations from the peak required temperature. It is necessary to investigate any known information concerning the susceptibility of the materials and parts of the equipment to temperatures between the qualification and required temperatures, taking into account the magnitude and duration of the deviation.

**Deviation Type C:** The test profile falls below the required profile in a temperature range below the peak temperature.

This type of deviation can be evaluated exactly as described in Sections 4.2 and 4.3.

The minimum criterion of acceptability is that the equivalent thermal aging time of the LOCA test profile be greater than the equivalent thermal aging time for the required profile. As pointed out in Section 4.2, it is also necessary to consider humidity effects, especially when the required profile interval is much longer than the comparable test profile interval.

**Deviation Type D:** The test duration is shorter than the required operating time.

This deviation exists for practically all equipment qualification programs in which the equipment is required for more than a few days following the start of an accident. The equivalence of thermal aging during the test is compared with the thermal aging of the required profile in the same way that the comparison is made for deviations of Type C; and the discussion of Type C deviations applies to Type D as well. However, Type D deviations are outside the scope of the task covered by this report and will therefore not be discussed further.

## 6 Comments on Utility Reports

### 6.1 Ref. 1, Equivalent Temperature Evaluation for Equipment in Containment, CA-97-176, Rev 2, Monticello Nuclear Generating Plant, March 25, 1998.

Ref. 1 was prepared to "correct [a small] error that was detected in the bounding profile for 1880 MWt." It documents Arrhenius calculations used to extend the duration of the accident profiles at a reference temperature, thereby obtaining equivalent accident thermal aging times. The reference temperature was chosen as 135 °F as this is the average drywell temperature over the life of the equipment prior to the occurrence of an accident. The original EQ LOCA "composite curve" bounded all postulated pipe break events for a power level of 1670 MWt; and the original LOCA test profile presumably encompassed this composite curve. To demonstrate that the existing equipment qualification satisfies the requirements of rerate conditions associated with the higher power level of 1880 MWt, the Arrhenius method was used to calculate equivalent thermal aging times of the time history curves of individual accidents for the 1880-MWt power level; and it was shown that these equivalent thermal aging times are shorter than the equivalent thermal aging time of the composite curve for the 1670-MWt power level. It is concluded that equipment qualified for the 1670-MWt level is also qualified for the 1880-MWt level.

Additional comments concerning the analysis and the conclusions are included in the discussion (in Sections 6.2 and 6.3) of Monticello References 2 and 3.

### 6.2 Ref. 2, Qualified Life Evaluation for Containment EQ Components, Calculation CA-98-105, Rev 0, Monticello Nuclear Generating Plant, March 25, 1998.

The analytical method used for calculating equivalent thermal aging times at reference temperatures appears to be consistent with the method described in Section 4.2. The method was used to calculate the thermal aging equivalents of the accident test curve and the composite 1880 MWt curve at a reference temperature of 135 °F; and the acceptance criterion was that the test profile provide greater thermal aging than the required profile during the operating time of the device tested.

The analysis appears to be acceptable with respect to thermal effects, especially in view of some conservatisms: the containment atmosphere is inert during the entire accident period; and the analysis was conducted for a power level of 1.02 x 1880 MWt, although the license amendment request is for 1775 MWt. However, the document does not address humidity and spray effects. On page 2, Ref. 2 cites Ref. 7 as justification for use of the "Arrhenius methodology ... [as] an accepted evaluation technique...for extending the duration of the test profile." However, as shown in Appendix A, while Ref. 7 acknowledges that the approach has been used to support long-term operability in post-LOCA environments, it concentrates on describing the limitations of the approach. In fact, its summary statement is that "the application of the Arrhenius equation to LOCA conditions involves large uncertainties and, at best, gives only crude estimates of equivalencies."

Ref. 2 also states (page 2) that, "The NRC has accepted the use of the Arrhenius Model for selected evaluations of equipment." However, while the NRC accepts use of the Arrhenius equation for analysis of thermal aging in normal service and acceleration of the LOCA tail, its position on use of the Arrhenius equation to calculate equivalent thermal aging where temperatures of the plant required accident profile exceed temperatures of the qualification profile does not seem to be established at this time.

Although it does not have a significant bearing on the subject of this report, it is noted that the meaning and justification for a statement (bottom of page 2 and continuing at top of page 3) is not obvious: "Once drywell temperature drops below 135 °F,...no further aging due to thermal characteristics will occur." Thermal aging may occur at any temperature, although the rate decreases as temperature is decreased.

### **6.3 Ref. 3, Environmental Qualification Calculation File FRR-49D, Rev. 0, Monticello Nuclear Generating Plant, no date.**

Ref. 3 gives a sample calculation of rerate environmental condition changes for an electrical connector. The body of the report is a good summary of the qualification file, reaching the conclusion that certain connectors are "environmentally qualified for 20 years of normal service plus accident and 1 year post-accident conditions" provided an O-ring is replaced periodically as specified.

Of particular interest is Appendix 1, Accident Degradation Equivalency, which describes how a three-day test "was more degrading for the connectors than would be the required profile." Since the first 24 hours of the test encompassed the required profile, the equivalency analysis was applied only to the period after the first 24 hours, which was 49.27 hours of LOCA testing at 255 °F. The Arrhenius equation was used to show that this period was equivalent to 226.8 days at 160 °F. Applying the same method to the required profile, it was shown that 5.9 days at 229.6 °F plus 5.0 days at 157.2 °F is equivalent to 215 days at 160 °F, which is 11.8 days less than the equivalent LOCA test time. It was concluded "that the test profile enveloped the required profile by a margin of 11.8 days."

In view of the significant uncertainties associated with the equivalency analysis (see Appendix A), the accuracy of an extrapolation by a factor of 110 (226.8 days x 24 hours/day / 49.27 hours) probably exceeds considerably the claimed margin of 11.8 days. Presumably, the 1-year post-accident qualification is justified by the post-LOCA thermal aging listed on p 6 of the report, claimed to be equivalent to 1 year at 200 °F, which is listed on p 6 of the report.

As in References 1 and 2, there is no discussion of the effects of humidity during 1 year following the start of an accident, a matter which is of particular importance for connectors.

### **6.4 Ref. 4, Drywell Accident Temperature Profile Comparison - Extended Power Uprate, Calculation Number SINH 97-004, E.I.Hatch Nuclear Plant, signed by Darrel G. Howard, 6-7-97.**

This report documents a degradation equivalency analysis to demonstrate that existing equipment qualification is acceptable for the accident temperature profile under power uprate conditions, which exceeds the existing EQ profile by up to 7 °F during a period of approximately 1 hour beginning 1 hour after the start of an accident. This deviation corresponds to condition C in Figure 1, page 4b. The analysis was conducted for four sets of conditions: reference temperatures of 250 and 150 °F, each at activation energies of 0.5 and 2.28 eV.

Under each of the four conditions, the equivalent time under uprate conditions was less than the equivalent time under conditions of the existing EQ profile; therefore, it was concluded the existing EQ profile is more severe than the uprate profile and equipment qualified in accordance with the existing EQ profile is also qualified under uprate conditions.

[Note: The report is somewhat confusing because it refers to the existing EQ profile as the "present accident profile," i.e., **requirement**, and refers to the "new accident profile," i.e., the uprate profile, as the **test** profile. And the conclusion is stated by saying that the "Test...does not meet requirements," which is a confusing way of saying that the uprate profile is less severe than the existing EQ profile.]

The thermal degradation analysis is conducted conservatively because the profiles are broken up into segments in which the uprate temperature is always higher than the actual uprate profile temperature, and the existing EQ temperature is always less than the actual EQ profile temperature. (Refer to Figure 2, page 5b.)

In view of the short period (~1 hour) of the deviation and its small magnitude (up to 7 °F), the analysis in this report is an acceptable justification for acceptance of existing qualification for the uprate conditions.

#### **6.5 Ref. 5, Analysis, Calculation, or Justification to Support Qualification, EQ-CL021, Rev. 34, Illinois Power Company, Clinton Power Station Unit 1, signed 5/6/91.**

The purpose of the analysis in this report is to establish a qualified life for Rosemont pressure transmitters and to demonstrate that a 68.7-h LOCA test qualified the transmitters for 100 days of operability after the start of a LOCA.

The LOCA equivalency calculations were made using the Arrhenius equation, but the pages of the report in which the calculations were documented were not available for review. From the available pages (C1 through C23), it was noted that the reference temperature used was the peak LOCA test temperature of 318 °F, instead of the lower long-term temperature used in the Monticello and Hatch calculations. As noted in Section 4.2, the choice of reference temperature does not affect the relative thermal aging in the two profiles compared. A LOCA test dwell of 8.275 h at 318 °F was shown to be longer than the equivalent time at 318 °F for the first 24 h of plant LOCA at temperatures lower than 318 °F. And it was shown that the balance of the LOCA test, 58 h at 265 °F plus 2 h at lower temperatures, had a 318-°F equivalent greater than the equivalent of 99 days of two plant LOCA profiles: one at 150 °F for 99 days and the other profile with a ramp from 185 °F to 104 °F during 99 days.

As with the Monticello and Hatch analyses (Sections 6.1 through 6.4), there is a concern that the calculations have considerable uncertainty for large extrapolation factors, which in this case was 99 days of plant LOCA time vs approximately 60 h (2.5 days) of test time, i.e., an extrapolation factor of 40. In addition, the long term effect of humidity is not adequately addressed. For example, para 4.7 on page C21.1 shows that corrosion could be a concern for the stainless steel isolator components. The resolution of this concern in para 4.7 is not clear: it seems to relate the qualified life of the critical component (with a thickness of 0.001 in.) to the time it would take for the entire thickness to be consumed by corrosion. However, isn't it possible that malfunction might occur well before the entire thickness corrodes away?

Qualified life calculations documented in the report reveal use of one of the best thermal aging procedures found in equipment qualification programs: the equipment was aged for 107.7 days at 203 °F (95 °C), assuming an activation energy of 0.78 eV. In different zones of the plant, the qualified life was 18 to 48 years, depending on the normal service in the zones. In three zones (H-6, H-11, and H-12), the qualified life was re-evaluated to accommodate a period of 3.5 years during which the service temperature exceeded the value assumed originally, with the consequence that the qualified lives in those zones was reduced. Although qualified life during normal service is not within the scope of the

assigned task, the procedure was reviewed because it involves an analysis similar to the LOCA equivalency analysis; the procedure was found to be acceptable.

For the benefit of others who may review this report, certain things that confused this reviewer will be pointed out. In the table on page C18, the second column gives the duration of various service temperatures in "Hrs/Yr" and the third column is labeled "Equivalent Hours at Ref. Temp. 203 F/40 hrs." What was done was effectively to multiply the (1-year) numbers in the second column by 40 to obtain the equivalent times for 40 years; then the equivalent hours at 203 °F were calculated (listed in the third column).

Another confusing statement appears at the top of page C19, it reads:

Total equivalent hours = 2149.043 hours = greater than 40 yrs

The meaning is that 40 years of normal service are equivalent to 2149.043 h at 203 °F; but, since thermal aging was conducted for 107.7 days (2585 h) at 203 °F, the thermal aging is equivalent to 48.11 y of normal plant service, as shown by the calculation that follows the above statement in the report.

## 7 Evaluation Criteria

### 7.1 Introduction

Based on the discussion in Section 5, a summary of evaluation criteria is given here for each of the four types of deviation between accident profiles. Using the definitions given below, the comparison may be between any pair of accident profiles in the following table:

<u>CANDIDATE PROFILE</u>	<u>REFERENCE PROFILE</u>
test	original required
modified (including uprate)	qualified
modified (including uprate)	test

The reference profile is one for which acceptance has been established; and a candidate profile is one to be evaluated. The various profiles are defined as follows:

<b>original required</b>	the profile that encompasses the temperature/pressure curves for all the pipe breaks for which equipment is to be qualified
<b>modified</b>	a required profile that has been modified to account for changes in assumptions concerning the accident conditions, or to accommodate an uprate to a higher plant power level
<b>qualified</b>	a required profile, either the original required profile or a modified profile, that has been verified to have been qualified by the accident simulation test
<b>test</b>	the profile achieved during the accident simulation test

### 7.2 Criteria

**Deviation Type A:** The rapid rise to peak temperature is slower during the test than predicted by thermo-hydraulic calculations.

1. Evidence that the equipment is not vulnerable to rapid temperature rises or, if it is, evidence that the test adequately accounts for the temperature transient effect.
2. Evidence that the equipment is not vulnerable to rapid pressure rises or, if it is, evidence that the test adequately accounts for the pressure transient effect.
3. Evidence that the equipment is not vulnerable to moisture intrusion during the pressure transient or, if it is, evidence that the moisture effect is adequately accounted for by other test data.

**Deviation Type B:** The required peak temperature exceeds the peak temperature of the test profile.

1. Evidence that no critical part or material in the equipment is vulnerable to changes during the period of test temperature deficiency that differ significantly from the type of changes that occur at temperatures encompassed by the test.
2. Lacking the evidence of Item 1, then evidence that temperature lag prevents vulnerable parts from being affected by the higher temperature of the required profile.
3. Thermal equivalency analysis is acceptable if evidence of either Items 1 or 2 is documented.

**Deviation Type C:** The test profile falls below the required profile in a temperature range below the peak temperature.

1. Thermal equivalency analysis is acceptable to account for thermal effects, with the requirement that the thermal equivalent of the test interval must exceed the thermal equivalent of the comparable required profile interval.
2. If the test and candidate profile intervals analyzed for thermal equivalency have approximately the same real-time duration, humidity effects are not a concern.

NOTE: This criterion always requires that the candidate profile interval be compared to the comparable actual test interval, even if the thermal equivalency analysis has been used to compare a modified profile to a qualified profile (see second row of above table).

3. If the ratio of real-time intervals (required/test) is large, evidence must be provided that humidity effects are accounted for by other test data. The note of Criterion 2 applies here as well.

**Deviation Type D:** The test duration is shorter than the required operating time.

Although this type of deviation is not within the scope of the task addressed in this report, it is observed that Steps 1 and 3 of Deviation Type C apply.

## 8 Suggestions for Research to Resolve Open Issues

Two suggestions are made to help resolve issues that remain with respect to the use of the Arrhenius method to analyze deviations between LOCA test profiles and required profiles: 1) an investigation of whether risk analysis can provide a basis for allowing greater flexibility in simulating the balance of the LOCA profile following rigorous simulation of the first few days of the LOCA, and 2) a review of the literature and any other data that can be found on the effect of moisture on equipment in a LOCA environment.

It is suggested that further study of the Arrhenius method should be excluded from consideration; the reasoning is given in Appendix E, which is an extract from Ref. 10, which gave an overview of research needs more than 15 years ago. That extract also provides other considerations to aid in the selection of research topics.

### 1. Study of Risk Significance of LOCA Simulation As a Function of Time After the Start of a LOCA.

As previously suggested and discussed elsewhere in this report (see Appendix D and Appendix C, page 12), a study of the risk significance of LOCA simulation as a function of time offers the prospect of justifying emphasis on the first few days of the simulation and allowing greater flexibility in the simulation of the balance of the LOCA profile. Ref. 8 provides an introduction to such an investigation.

The idea is illustrated in Figure 4, in which the vertical axis represents the risk that termination of the LOCA test at a corresponding point on the time axis would give an erroneous result, i.e., the test might result in a false indication of 'passing.' Another interpretation of the vertical axis could be the risk significance (of danger to the public) of terminating the LOCA test at the corresponding point of the time axis. If such a risk analysis proves feasible and an acceptable risk level can be defined, the study could define the time during which LOCA simulation must be rigorous, beyond which the simulation could be terminated or, at least, simulated with greater flexibility in procedure.

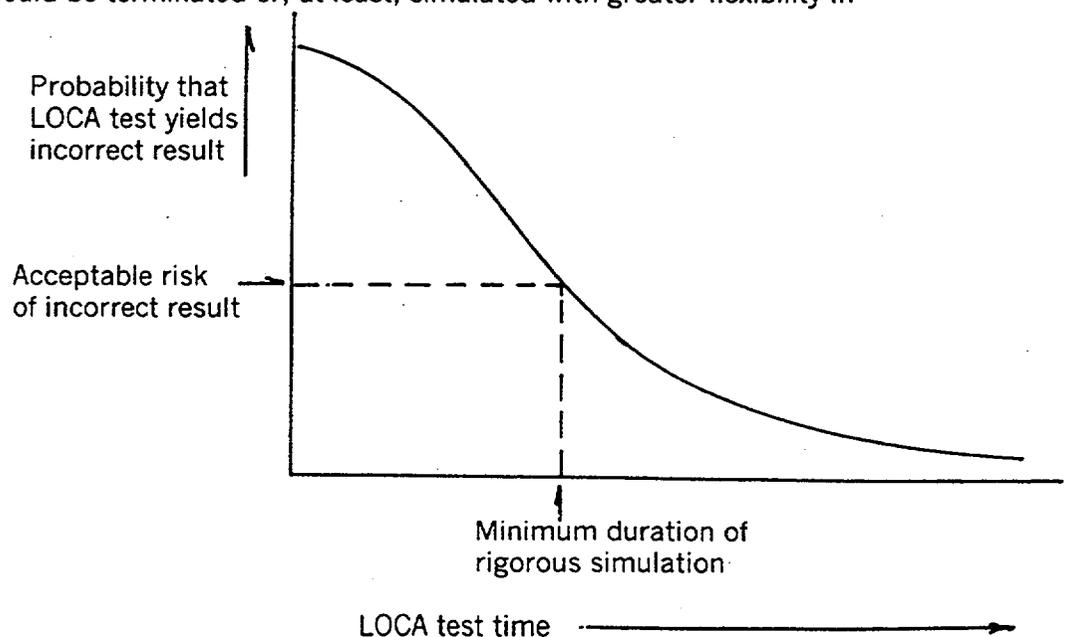


Figure 4 Use of risk analysis to determine minimum duration of rigorous LOCA simulation.

If a risk significance study were successful, it would reduce the concern with some of the deficiencies of the analytical techniques being used to justify deviations of the test profile from the required profile. While such deficiencies are discussed to some extent in this report (see, for example, Section 4.1 and Appendix C), the ground rules for the task included acceptance of the Arrhenius method; and the deviations were analyzed accordingly.

## 2. Investigation of Moisture Effects on Equipment Operability

It is suggested that a study of moisture effects be initiated with a review of the literature and any unpublished data that can be obtained. The literature review conducted as an early component of the overall BNL research program has limited information on moisture effects, partly because it was almost entirely limited to published literature. Moisture was a contributor to failure in LOCA qualification performed during the last 30 years, but little published information of such failures exists. Moisture has also contributed to failures observed during the recent BNL cable research. There are indications that moisture contributed to equipment failure during the Three-Mile-Island incident, but it appears that little information is available in readily available documents. Before a task of this type is undertaken, there should be an effort to establish whether a significant amount of previously unavailable information can be obtained.

The importance of this review would depend partly on the outcome of the risk significance research suggested. If the risk significance of LOCA simulation is shown to be negligible after the first few days, simulation of moisture effects for long periods beyond the first few days would be of secondary importance.

## 9 References

1. Equivalent Temperature Evaluation for Equipment in Containment, CA-97-176, Rev 2, Monticello Nuclear Generating Plant, March 25, 1998.
2. Qualified Life Evaluation for Containment EQ Components, Calculation CA-98-105, Rev 0, Monticello Nuclear Generating Plant, March 25, 1998.
3. Environmental Qualification Calculation File FRR-49D, Rev. 0, Monticello Nuclear Generating Plant, no date.
4. Drywell Accident Temperature Profile Comparison - Extended Power Uprate, Calculation Number SINH 97-004, E.I.Hatch Nuclear Plant, signed by Darrel G. Howard, 6-7-97.
5. Analysis, Calculation, or Justification to Support Qualification, EQ-CL021, Rev. 34, Illinois Power Company, Clinton Power Station Unit 1, signed 5/6/91.
6. NRC Information Notice 97-45, Supplement 1: Environmental Qualification Deficiency for Cables and Containment Penetration Pigtails, Feb. 17, 1998.
7. Nuclear Power Plant Equipment Qualification Reference Manual, TR-100516, P. Holzman and G. Sliter, Electric Power Research Institute, 1992.
8. Qualification of Motors for Nuclear Power Generating Stations, S. P. Carfagno, R. L. Ferguson, and M. Sheets, presented at IEEE Winter Power Meeting, New York, January 1974.
9. Equipment Aging - An Overview of Status and Research Needs, S. P. Carfagno, Franklin Research Center, presented at NRC Workshop on Plant Aging, Bethesda, MD, August 4, 1982.

## Appendix A EPRI Information on Accident Temperature Equivalency

Ref. 7, Nuclear Power Plant Equipment qualification Reference Manual, P. Holzman and G. Sliter, TR-100516, Electric Power Research Institute, 1992.

Since this reference has been quoted as justification for using the Arrhenius equation for calculating extended equivalent LOCA test durations, it is useful to quote pertinent parts of the document. The relevant part of the document is Appendix A5.3, Limitations of Arrhenius Model for Accident Temperature Equivalency. Some statements from this Appendix are quoted below:

The Arrhenius method has...been employed to relate accident test temperatures to postulated accident conditions. This analysis is often called a "thermal degradation equivalency evaluation." ...

If the Arrhenius model and activation energy value are applicable to the test and accident temperatures, then the model may arguably be used in various ways to draw correlations between the accumulated thermal damage occurring during various phases of loss-of-coolant accident (LOCA) testing. This approach has been principally used to support long-term operability in post-LOCA environments when it is desirable to have a test duration be shorter than the actual required operability time. ... It is common practice to argue that [a] higher test temperature...can be viewed as an accelerated version of the actual [lower] post-LOCA temperature...

Several technical concerns have been identified with the use of this model for the purpose of analyzing LOCA conditions. The principal concern relates to the use of an activation energy value derived in air for this application, since the correct activation energy value for LOCA steam test conditions may be different. Post-LOCA, the actual containment atmosphere may be oxygen rich or oxygen poor, depending on the use of inerting systems and other hydrogen control systems. Similarly, LOCA test chambers may be purged of air at the start of the accident simulation to achieve the initial temperature ramp. The air/oxygen level in the test chamber is particularly important when acceleration of the postaccident operability period is attempted using the Arrhenius model, since...oxygen reactions are often critical to material degradation and chemical reactions. Since activation energies have not been measured under LOCA conditions, the applicability of the Arrhenius model to LOCA environments has not been definitely established. Finally, other degradation mechanisms (e.g., corrosion) occurring during long-term simulations may not be adequately accelerated by simply raising the test temperature. The degradation due to these mechanisms, singly or in combination with temperature, may not be addressed by the Arrhenius analysis....

...[The Arrhenius model] has also been used to analyze the equivalency between the LOCA time-temperature profiles. In this case, the analysis is used to develop a bounding artificial thermal profile based on a thermal equivalency with the LOCA test [pro]file. The approach has a number of limitations and cautions in addition to the problem with selecting an appropriate activation energy. In particular, the following should be recognized:

...Due to thermal lag effects, short-term high-temperature conditions are not experienced by internal devices...Consequently, the analysis will overestimate the degree of degradation that has occurred inside the equipment.

Due to changes in material properties with temperature, the analysis should not be used to extrapolate lower-temperature long-term effects to shorter times at higher temperatures. It should never be used to extrapolate results to temperatures substantially higher than the test temperatures.

The Arrhenius model addresses only thermal degradation; it does not account for other LOCA stresses, (e.g., the long-term effects of steam and chemical spray on sensitive equipment parts). If other time-dependent mechanisms are present (e.g., water absorption, electrical surface tracking, corrosion) and have not been addressed by Arrhenius or other correlations, they may be considered separately.

In summary, the application of the Arrhenius equation to LOCA conditions involves large uncertainties and, at best, gives only crude estimates of equivalencies.

## **Appendix B Humidity, Moisture, and Steam Effects.**

The following information is excerpted from pages 3-12 and 3-13 of Ref. 7.

### **Humidity and Moisture**

Humidity can cause degradation aggravate the effects of other stressors. Humidity causes corrosion and, at interfaces between dissimilar metals, galvanic effects. Corrosion can directly affect performance of metallic components. Electrical terminations and contact surfaces can be degraded by corrosive effects. The transfer of highly conductive corrosion products to other components can affect their electrical characteristics.

Humidity can directly degrade organic materials, weakening their physical, mechanical, and electrical properties and distorting their shapes. Hygroscopic materials, such as polyimide, are particularly vulnerable. The absorption of water in many organic materials is both a physical and a chemical process. Absorbed water can chemically combine with existing molecules and change the chemical formulation. Other absorbed water molecules not chemically reacting can cause swelling of material....

The presence of surface moisture significantly alters the resistivity and dielectric withstand potential of insulating surfaces. Humidity can aggravate thermal and radiation effects in electrical insulating materials. For example, moisture entering the crevices and pores produced by hardening and embrittlement lowers the material's insulation resistance and electrical breakdown strength. Terminal blocks are particularly sensitive to surface moisture effects.

### **Steam**

Exposure to high-temperature steam combines temperature and humidity effects. The condensation of steam on colder surfaces results in rapid heating of the cooler surface (condensing heat transfer). This heat transfer is much more rapid than exposure to hot air. The condensed moisture can further degrade equipment by collecting on the equipment surface or accumulating in undrained areas

### **Appendix C Use of the Arrhenius Equation in Equipment Qualification.**

The following pages are copies of notes used in a presentation to members of the NRC staff at a kickoff meeting for the task addressed in this report on September 29, 1998.

They explain the meaning of the variables in the Arrhenius equation, the assumptions that must be satisfied for its application, its application in determining the qualified life of safety-related equipment and in LOCA analysis, and the uncertainties associated with its application.

# USE OF THE ARRHENIUS EQUATION IN EQUIPMENT QUALIFICATION

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Prepared for Brookhaven National Laboratory

S. P. Carfagno

September 25, 1998

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## **USE OF THE ARRHENIUS EQUATION IN EQUIPMENT QUALIFICATION (EQ)**

- **the Arrhenius equation**
- **assumptions for application to thermal aging**
- **calculation of material life**
- **calculation of thermal aging conditions**
- **determination of activation energy**
- **application to EQ**
- **limitations for use in accelerated thermal aging**
- **limitations for use in acceleration of LOCA simulation**
- **the problem in perspective**

**ww\bn\larrineq2**

## THE ARRHENIUS EQUATION

$$r = dq/dt = A \exp(-E/kT)$$

where

**r** = the rate of a reaction, (mole/s): interpreted as the rate of degradation when the reaction is responsible for degradation

**q** = quantity of reactant (mole)

**A** = a material dependent constant ( $s^{-1}$ ), determined experimentally,

-called a frequency constant; is related to the frequency with which reactant molecules collide (in a gas)

- strictly, the units are mole/s since the units of r are mole/s

**E** = the activation energy (eV), determined experimentally

-it is basically the energy needed for the reactant molecules to produce a product molecule

-strictly, the units should be eV/molecule

**k** = Boltzmann's constant =  $0.8617 \times 10^{-4}$  (eV/K)

-as with E, the units are strictly eV/(K molecule)

**T** = absolute temperature (K)

In accordance with the Arrhenius equation, the rate of a reaction depends on the frequency with which reactant molecules meet; it depends exponentially on the energy needed for the molecules to react (the greater the activation energy, the slower the rate); and exponentially on the absolute temperature at which the reaction occurs (the higher the temperature, the faster the reaction).

#### **ASSUMPTIONS FOR APPLYING THE ARRHENIUS EQUATION TO THERMAL AGING**

- the aging that causes degradation is dominated by a single reaction
- the reaction rate is constant at constant temperature, which implies that:
- the frequency constant (A) and the activation energy (E) are constant
- for accelerated thermal aging, A and E must have the same values at the accelerated aging temperature as they do at the service temperature

## USE OF THE ARRHENIUS EQUATION TO CALCULATE THE LIFE OF A MATERIAL

- with the assumptions made, the Arrhenius equation can be integrated to yield:

$$q = A \exp(-E/kT)$$

- if we define Q as an end value of q, i.e., the amount of reaction that produces the limiting acceptable degradation, the above equation can be solved for L, or life, which is the value of t for  $q = Q$

$$L = (Q/A) \exp(E/kT_s)$$

where  $T_s$  is the temperature at which the reaction takes place, here chosen as the service temperature

NOTE. This equation has been used by some utilities to predict lives of thousands of years.

## CALCULATION OF THERMAL AGING CONDITIONS

- an equation for calculating thermal aging conditions is obtained by requiring that the degradation at the service temperature be the same as the degradation under accelerated aging conditions

$$Q_s = Q_a$$
$$At_s \exp(-E/kT_s) = At_a \exp(-E/kT_a)$$

- which yields

$$t_s/t_a = \exp(-E/k)(1/T_a - 1/T_s) = \exp(E/k)(1/T_s - 1/T_a)$$

- note that the frequency factor, A, has been eliminated; and the only material parameter is the activation energy, E

#### DETERMINATION OF ACTIVATION ENERGY - example for insulation material

- degradation reactions are complex
- an indirect measure of degradation, such as elongation (EI), is used
- the end point may be a minimum acceptable absolute elongation or a minimum acceptable fraction of the initial elongation
- if the assumptions of the Arrhenius model are satisfied, a plot of  $\ln L$  vs  $1/T$  will be a straight line, the slope of which is the activation energy, as seen from the following equations:
- $Q = A \exp(-E/kT)$

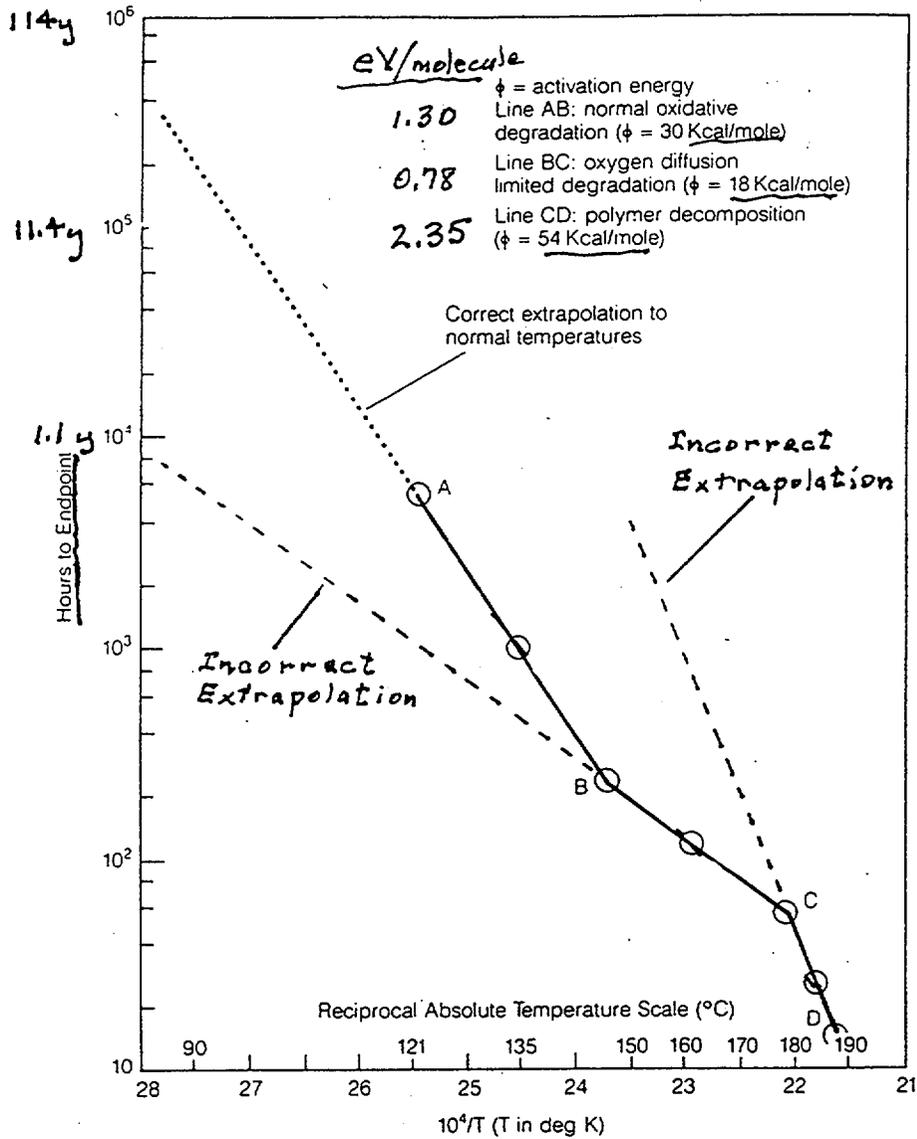
let  $Q = EI_{\text{end}}$ , the endpoint elongation; and  $t = L$ . Then:

$$L = (EI_{\text{end}}/A) \exp(E/kT)$$

$$\ln L = \ln(EI_{\text{end}}/A) + (E/k)(1/T), \text{ where the first term and } (E/k) \text{ are constants}$$

# EXAMPLE OF ACTIVATION ENERGY DETERMINATION

Adapted from Figure 4.3, page 4-12, Equipment Qualification Reference Manual, EPRI Report TR-100516, 1992, P. M. Holzman and G. E. Sliter.



**FIGURE 4.3** Single (heatshrink) material's differing activation energies in three temperature ranges

*(Modified)*

## HOW THE ARRHENIUS EQUATION HAS BEEN APPLIED IN EQ

- for accelerated thermal aging
  - $t_s$  is taken to be the qualified life and  $T_s$  is the service temperature
  - then,  $t_a$  and  $T_a$  are calculated
- for the acceleration of LOCA simulation
  - $t_s$  is the duration of the LOCA tail and  $T_s$  is the LOCA tail temperature
  - then, an abbreviated LOCA test time  $t_a$  and a higher LOCA test temperature  $T_a$  are calculated

## **LIMITATIONS FOR USE IN ACCELERATED THERMAL AGING**

- the degradation may not be dominated by a single reaction
- the activation energy may not be the same at the aging temperature as it is at service temperatures
- the activation energy is not known accurately
- the activation energy may be taken from tabulations of data for similar materials although minor differences in composition can cause significant differences in activation energy
- the activation energy may be determined by methods, such as thermogravimetric analysis (TGA), that have poor correlation with the activation energy in service
- oxygen diffusion limitations
- the components of an assembly have different activation energies
- service conditions differ from the conditions under which the activation energy was determined, e.g., the activation energy is determined for cable insulation, which is covered by jacket material in installed cables
- interactions among materials in equipment that are not taken into account, e.g., interaction of bonded insulation and jacket materials and corrosion at the conductor/insulation interface
- synergistic effects
- difficulty of accounting for weak links and hot spots



#### **LIMITATIONS FOR APPLICATION TO LOCA ACCELERATION**

- **activation energies for degradation under LOCA conditions are not generally known**
- **moisture effects may not be simulated adequately if the LOCA duration is shortened significantly by considering thermal degradation only**

## **THE PROBLEM IN PERSPECTIVE - THERMAL AGING**

- **the Arrhenius equation is probably the best basis for modelling thermal aging**
- **a major problem is that the Arrhenius equation is often the dominant basis for determining the qualified life of equipment; and the uncertainties associated with doing so tend to be overlooked**
- **the contribution of thermal aging to uncertainties in EQ, need to be evaluated in combination with all the other elements of EQ**

**For example, accurate knowledge of radiation exposure doses in normal service and the effect of phenomena such as dose rate effects in radiation aging may introduce uncertainties that exceed those of thermal aging. Also, the effects of moisture and vibration are difficult to include in an accelerated aging program.**

## **THE PROBLEM IN PERSPECTIVE - LOCA ACCELERATION**

- while use of the Arrhenius equation may not provide an acceptable technical basis for LOCA acceleration, it is possible that other considerations may be able to provide the basis
- if it is relatively easy to control a LOCA and assure public safety after the first several days of a LOCA, is it essential to simulate more than the first few crucial days of a LOCA in EQ?
- is it feasible to calculate the probability that a LOCA test gives an incorrect result (pass instead of fail) as a function of test duration relative to the time for which the safety function is required?
- if so, can we determine the required LOCA test duration based on a maximum acceptable risk of obtaining an incorrect result?

**Appendix D Review of Acceptability of Arrhenius Methodology to Analyze LOCA and Post-LOCA Environments, Nuclear Utility Group on Equipment Qualification, January 1999.**

NOTE: To distinguish between the document under review and the report of which this appendix is a part, the former is referred to as the '**document**' and the latter is referred to as the '**report**.'

This document was submitted for review after a draft of the report had been submitted to BNL; and it was reviewed primarily for technical content that would warrant a modification of the draft. The only change was the addition of Section 4.4 on degradation analysis when there is substantial self-heating of the equipment during a LOCA test.

**D1 General Comments**

Section 6.3, EQ Deficiencies, of the document is the one that correlates most closely with the research task; and the conclusions reached therein are largely consistent with positions discussed in this report. In fact, the document takes a more stringent position than that taken in this report on the case in which the peak plant LOCA profile temperature exceeds the peak LOCA test temperature. (See Comment 15.) There is disagreement, however, with regard to moisture effects which, unlike the position of this report, are concluded to be "...not significant during the post-transient period." (See Comment 15.)

The point of major interest was the discussion of risk analysis as a basis for the position that "...whether correct accident acceleration techniques have been used is not risk significant." This position is consistent with an approach that this reviewer has suggested (to BNL, NRC, and IEEE committees) for resolution of the LOCA acceleration issue. (See, for example, p 13 of Appendix C.) The technical discussions to support use of the Arrhenius method for degradation equivalency analysis (DEA) are not entirely convincing, but this concern would be obviated if risk analysis were to prove an adequate basis for the position that, if LOCA tests simulate the first few days of plant specific LOCA conditions with the conservatism and margins already dictated by standards and regulatory requirements, the specific procedure for simulating the balance of the LOCA duration is of secondary importance. Of course, this implies that compliance with LOCA test requirements during the first few days should be rigorous, and justification for exceptions should be based on firm data and analysis. As discussed in this report (Appendix A), use of the Arrhenius method involves significant uncertainties; and arguments to justify its use do not yield a satisfactory technical conclusion. Nonetheless, since the NRC accepts use of the Arrhenius method, several ways of applying it to the analysis of LOCA deviations are outlined in Section 5 of this report. If risk analysis can show that technical accuracy after the first few days of LOCA simulation is of secondary importance, it would relieve the concern of relying on the use of the Arrhenius method beyond the first few days.

The reference cited<sup>D1</sup> for the position on risk significance does not by itself provide the resolution of the LOCA acceleration issue, but it is a good starting point. In response to a request<sup>D2</sup> for "...recommendations on additional activities required to complete this task,"

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<sup>D1</sup> NUREG/CR-5313, Equipment Qualification (EQ) - Risk Scoping Study, Sandia National Laboratories, January 1989.

<sup>D2</sup> Letter of 1-20-99 from R. J. Lofaro (BNL) to S. P. Carfagno (consultant).

a new section 8 (replacing the old section 8, now renumbered 9) has been added to this report. Comments on the rest of the NUGEQ report follow.

ww\bn1\rep9901

## D2 Specific Review Comments

Each review comment is preceded by an indication of the place in the document to which the comment refers.

### 1. INTRODUCTION and RESULTS OF NUGEQ REVIEW, Sections 1 and 2.

No comment since the basis for statements in these sections is given in subsequent sections of the document.

### 2. Section 3. Risk Significance, first para, last sentence, p 3.

The statement that "...the uncertainties associated with using Arrhenius for accident analysis are relatively small..." is not consistent with the technical information given in this report. (See Appendix A.)

### 3. Page 4, middle of para at top of page.

It is stated that, "From a risk perspective, operability only needs to be demonstrated for a few days or possibly weeks." Further investigation of the risk approach should define the period of importance more precisely because the difference between *days* and *weeks* is significant. Since the Arrhenius method is sometimes applied to LOCA analysis for intervals of weeks and months, concerns about its use would not be obviated if risk analysis leads to the conclusion that demonstration of operability is risk significant beyond the first few days.

4. No technical comments are given for Section 4, International Practices, and Section 5, Regulatory Considerations, because these sections document existing and past *practices*, while the objective of the task covered by this report is to examine the **validity** of a past *practice*.

### 5. Section 6. Technical Considerations, p 4, last full sentence.

The statement that "...Arrhenius is not used .... at accident temperatures beyond those occurring during the accident simulation tests" is not consistent with the fact that this is one of the applications submitted by the NRC for review in this task. (See Section 3, Deviation type B, and Figure 1.) Statements in the para at the top of page 11, in particular, that "Arrhenius cannot be used to justify peak temperatures beyond those experienced in the accident simulation test," indicate that, if utilities do so, it is not considered acceptable. The position taken in this report (Section 5, Deviation Type B) is somewhat more relaxed than the one expressed by the quoted statement.

Section 6.3 of the document (see Comment 18) does make a passing reference to the use of thermal lag analysis when the "peak test temperature profile" does not envelope "the peak plant-specific temperature profile."

6. Page 13, bottom para, statement referring to standards that describe the Arrhenius method, including regression analysis.

Documentation of regression analyses of data used to obtain the activation energy of materials used in safety-related equipment is not generally available; but in the instances in which this reviewer has seen such analyses, they tend to illustrate the major uncertainties in the application of the Arrhenius method. (See Appendix C of this report.)

7. First para of Section 6.1.2, Arrhenius for Varying Temperature Conditions, p 17.

It is not clear under what practical conditions different temperature profiles will produce the same end point. Does this para imply, for example, that the elongation of insulation materials will recover during periods of temperature decrease after degradation during periods of temperature rise? My recollection<sup>D3</sup> is that some experiments have shown that an oscillating temperature will produce more degradation than a steady temperature.

8. Sentence beginning at bottom of p 19, "None of these conditions [possible variations in activation energy at high temperature and extrapolation through material phase transition regions] should exist when Arrhenius is applied to accident conditions since accident temperatures are typically within the temperature range used in the accelerated aging experiments used to define material activation energy values."

This generalization is too sweeping to be justified by the technical information presented in the document.

9. Page 20, para concerning thermal aging of Kapton and Neoprene.

With respect to Kapton, a major concern is its low resistance to moisture, i.e., even if concerns about thermal degradation were resolved, there would remain the concern about moisture effects. In fact, moisture effects are a concern with regard to DEA of LOCA profiles. (See also Comments 12 and 15.)

10. Page 20, last sentence in first para under 6.1.4, "This minimizes the potential for and significance of data extrapolations across phase transition boundaries."

The data in the document do not establish this conclusion.

11. Page 20, bottom paragraph continuing into page 21, leading to conclusion that "...there should be no concern about activation energies at the latter stages of the accident exposure being significantly lower than [n] pre-accident values."

Although the reasoning in this para is somewhat loose, it is not relevant to the task covered by this report, because the scope excludes the long-term dwell of the LOCA profile at low temperature. [In any case, since the para mentions Ken Gillen, another reviewer, comments on this material are best left to him.]

12. Page 21, sentence beginning at bottom of page and continuing to page 22, "For devices such as these whose internals remain isolated from the steam environment, thermal aging based activation energy values have direct applicability."

The concern about activation energy is secondary to the concern about the ability of the equipment to maintain "isolation" and avoid the electrical problems associated with moisture intrusion.

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<sup>D3</sup> EPRI NP-1558, A Review of Equipment Aging Theory and Technology, prepared by Franklin Research Center, September 1980.

13. Pages 22 through 25, review of Sandia and Japanese data to support the use of "thermal aging based activation energy values when performing Arrhenius analysis of accident conditions."

The concern about activation energies is secondary to the concerns about moisture effects, adequate analysis when the peak LOCA test temperature is lower than the peak plant profile temperature, and any analysis which equates a short test interval (within the scope of this task) to a much longer equivalent time of the plant profile. However, all of these concerns may be obviated if risk analysis proves able to demonstrate that LOCA simulation is of secondary importance beyond the first few days. (See also Comments 5 and 12.)

14. Page 26, next to last sentence, "The results indicate that degradation equivalency analysis errors for typical equipment and profile conditions are generally less than 10% and should not exceed 15% for limiting equipment and profile conditions."

This conclusion is inconsistent with the information in appendices A and C of this report; and it is inconsistent with the general impression obtained from the review of several utility DEAs, as reported in Section 6 of this report. For example, DEA was used by one utility (see Section 6.3 of this report) to extrapolate a 49-hour test to 227 days, a factor of 110; and another utility used DEA to extrapolate a test period by a factor of 40 (see Section 6.5 of this report). It is dubious that such large extrapolations can be done with small errors.

15. Section 6.2.1, pp 27-30, particularly a statement in the middle of the first para, "...it is concluded that such mechanisms [i.e., pressure-related and moisture-related degradation effects] are not significant during the post-transient period."

The information and the logic offered in this section are inadequate to justify this general conclusion. It is inconsistent with the observation in numerous LOCA tests that moisture was a significant factor in causing failures. Sometimes, the effect of moisture is not the consequence of a process that accumulates with time (e.g., diffusion) but one that takes place once thermal degradation has progressed far enough (e.g., electrical leakage or shorting following embrittlement of insulation). In this report, discussions of moisture effects may be found in Section 4.2, on page 9 in the discussion of Deviation Type C, and in Appendix B.

As with Comment 11, since this section references several Sandia reports, it may be best to depend on the review by Ken Gillen, a Sandia scientist.

16. Section 6.2.2 Self-Heating Effects and 6.2.3 Transient Analysis Considerations, pp 31-35:

These pages contain interesting information on self-heating and thermal lag, based on which a Section 4.4 has been added to this report.

17. Analyses on pp 38-43, comparing DEAs for environmental and equipment internal temperature profiles.

For cases in which the assumptions of this analysis apply, it is shown that little error is incurred if one uses the environmental temperature profile instead of the equipment internal temperature profile for DEA, and that the error is on the conservative side. This conclusion would not apply if there is substantial self-heating as illustrated, for example, in

## CONSIDERATIONS FOR ESTABLISHING THE SCOPE OF RESEARCH TOPICS AND THEIR RELATIVE PRIORITIES

### Correlation with Reduced Risk to the Public

Since the primary purpose of equipment qualification is to protect the public from potential hazards of operating nuclear power-generating stations, a primary consideration in selecting research topics is an evaluation of their potential contribution to enhancing public safety.

### Potential for Reducing the Cost of Qualification Without Compromising the Adequacy of Qualification

If more than one approach to a given aging problem is adequate to satisfy the demands of public safety, cost becomes a primary factor of comparison and selection. The relative cost of different acceptable approaches should be evaluated on an integrated basis, i.e., it is not sufficient to calculate only the cost of implementing a particular approach; another essential ingredient is the cost impact over the long term. The cheapest acceptable qualification procedure is not necessarily the most beneficial from the cost standpoint over the long run if it involves lower plant reliability, greater downtime, and the wasted time and cost associated therewith.

### Time Required to Achieve Practical Results

Another factor to consider in developing a comprehensive research program is the probable time required to obtain practical results from each research topic. It is necessary to estimate the length of time during which nuclear fission will continue to be a dominant source of energy before a different mechanism such as fusion or solar power becomes dominant. To be of value to the present nuclear industry, practical research results must be obtained within a time that is short by comparison with the probable lifetime of power generation by nuclear fission.

Obviously, research with a potentially fast payback is more attractive than research with a long-range payback; but the more basic research, the less likely it is to have a rapid payback. This consideration tends to reduce the value of long-range, fundamental research. The history of the development of aging theory and technology provides a benchmark by which to estimate the probable payback time of basic aging research. The Arrhenius theory was developed nearly 100 years ago and the first significant effort to apply it to the deterioration of electrical insulating materials took place not much over 30 years ago. Aging studies over the last 10 to 20 years have enhanced our understanding of the subject, but they have made little progress toward identifying procedures for quantitative simulation of equipment aging. Clearly, basic research on the degradation of materials is not likely to yield practical aging qualification procedures for complex equipment in a reasonable period. And in view of the much greater complexity of synergistic effects by comparison with the effects of single stresses, it appears altogether unjustified to expect significant advances from a reasonable investment of time and funds in research on synergistic effects. However, the importance of basic research in advancing the understanding of aging and synergistic phenomena should not be minimized. The foregoing discussion is intended to give us a realistic picture of the prospects. Basic research should be continued with due recognition of these prospects. If we recognize the time scale of basic research, it will not be required to offer fast turnaround to justify itself. This recognition will also reduce the temptation to make unjustified extrapolations of research findings, which result in their premature and potentially erroneous application.



June 15, 1999

Mr. Satish Aggarwal  
U.S. Nuclear Regulatory Commission  
TWFN M/S 10 E10  
11545 Rockville Pike  
Rockville, MD 20852

**Subject:** *Paper on Arrhenius by M. Shaw*

Dear Satish:

In support of the task on Arrhenius, Dr. M. Shaw has prepared a paper based on his research to date on the pitfalls of using Arrhenius for environmental qualification. A copy of the paper is enclosed for your information. We can discuss this work at the June 29<sup>th</sup> meeting.

Sincerely,

A handwritten signature in cursive script that reads "Robert J. Lofaro".

Robert J. Lofaro  
Engineering Mechanics & Infrastructure Group  
Environmental Systems Engineering Division

/pvg

cc: w/enclosure  
S. Carfagno  
K. Gillen, Sandia  
J. Taylor  
J. Vora, NRC/RES  
w/o enclosure  
M. Shaw, UConn

## Task 4: Evaluation of Arrhenius Pitfalls

Montgomery Shaw  
June 1999

### INTRODUCTION

Much has been written and verbalized concerning the application of the Arrhenius theory to prediction of the long-term aging of polymers. While the Arrhenius equation has received careful scrutiny for simple chemical reactions in the dilute gas phase [e.g., Johnston (1966)], its application to the aging of polymers is largely empirical. Although it is possible to express the degradation of hydrocarbon elastomers in terms of known free-radical pathways, the relative importance of competing reactions has not been investigated thoroughly even in comparatively simple system such as polyethylene. The validity of the use of empiricism for extrapolation is an unanswerable question; however, if the method can be found invalid, then some progress will have been made. For the Arrhenius relationship, invalidity can be phrased simply in terms of curvature in the Arrhenius plot.

For this reason, the investigation described here sought the answers to the following questions:

- Is there any empirical evidence for curvature in the Arrhenius plot?
- What are the limits on the importance of theoretical sources of curvature.

The term "curvature" refers to deviations from a linear relationship on the typical plot of  $\log(\text{rate})$  vs.  $1/T$ , where rate refers to reciprocal lifetime, replacement frequency, failure frequency, reciprocal time to a limiting property value, etc. The magnitude of the slope of such a plot will be proportional to the Arrhenius activation energy, which should be a constant. If the curvature is down (decreasing activation energy with temperature), the result will be a conservative estimate of lifetime. Positive curvature would thus be of most interest, as such would suggest that predictions of lifetimes would be too optimistic.

### EMPIRICAL EVIDENCE FOR CURVATURE

#### A. Search techniques

Web: Searches of the standard sources were conducted using the logic (Arrhenius *or* (Aging *and* Polymers)), limited to five years.

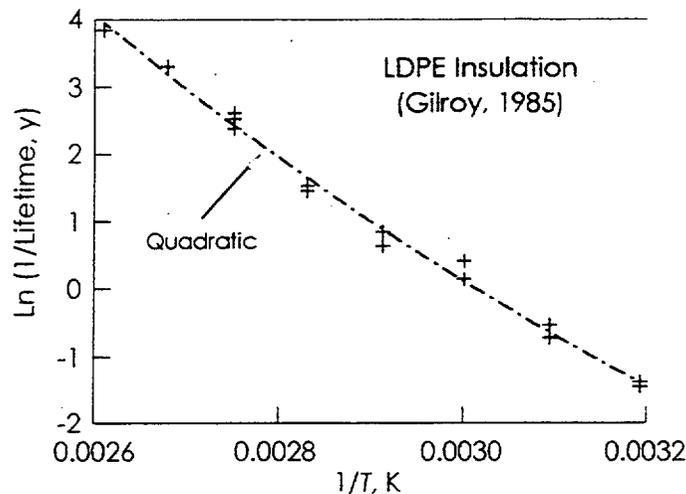
Data Bases: Searches were conducted on INSPEC (1987-1999), JREF(1983-1999), and Ei COMPENDEX (1980-1999)

Personal Literature Collection: The author has an extensive file of literature because of research activity in chemical stress relaxation (30 years), radiation aging (15 years) and water treeing (15 years).

*IEEE Transactions on Electrical Insulation*: As coeditor, the author handles most manuscripts on the aging of polymers. Some of these are never published. All are searched for new citations on aging. In addition, all articles over the past 30 years were searched for possibly fruitful citations.

Results: Hundreds of data sets using the Arrhenius relationship were found and examined; few were specifically aimed at finding curvature. However, a handful of reasonably complete sets of data were found.

One notable set resulted from the careful work at Bell Labs in the 70's and 80's on polyolefin oxidation by a number of scientists, including M. G. Chan, H. M. Gilroy, W. L. Hawkins, and J. B. Howard. This was a very serious effort to predict the lifetime of polyolefins (mostly polyethylene) targeted for wire insulation. Unfortunately, the crystallinity of most of these specimens was high, but the low-temperature aging of LDPE up to 4 years was judged relevant [Gilroy (1985)]. This set is plotted in Figure 1.



**Fig. 1.** Replot of data from Gilroy (1985) showing the initial failure times of a LDPE subject to thermal-oxidative aging in air over the temperature range 40-110 °C. The curve is a quadratic; the statistics are discussed in the text.

The curve through the data has a quadratic term that is significant at the 95% confidence level. Without the 4-yr data (two points), the curvature is not significant. The curvature is upward; thus, the Arrhenius analysis based only on the higher temperature part of the set would predict overly optimistic lifetimes.

Discussion of this result should address the following questions: (1) what error would be introduced in the lifetime at, say, 30 °C; and (2) what are the problems with this otherwise remarkable set? If one uses the Arrhenius analysis based only on data at temperatures of 70 °C and greater, then the predicted lifetime is 29 years at 30 °C. The

extrapolation of the quadratic to 30 °C (a 10 °C extrapolation) yields only 8 years. Thus for this material the Arrhenius method, if applied to quite normal qualification data, would yield a seriously overoptimistic estimate of the lifetime. As for the problems with this set, one could argue that the decreasing crystallinity with temperature could have exposed more material to aging and increased the diffusivity of oxygen leading to an increase in observed rate without any real change in chemical mechanism. Such an effect would be less dramatic in EP elastomers. As for the problems with the data, one notes that the “lifetimes” reported represent a truncated set of initial failure data. Thus an analysis based on this data makes the very severe assumption that the distribution is invariant with temperature. Clearly, even more complete sets of failure times should be gathered, a daunting task.

Two other sets of data should be discussed. One was generated by Celina et al. using head-space analysis for oxygen loss and evolution of CO and CO<sub>2</sub>. Results for

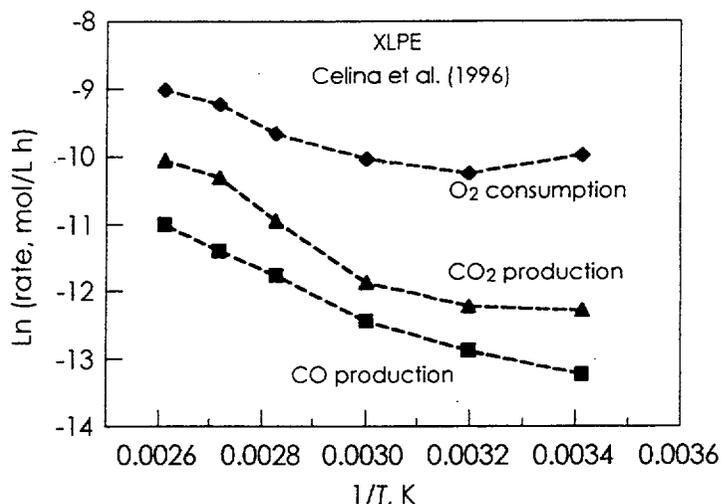


Fig. 2. Oxygen uptake and release of CO and CO<sub>2</sub> from XLPE. [Data of Celina et al. (1996)]

crosslinked polyethylene are displayed in Figure 2. The upward curvature is apparent; however, it proves significant only if all the results are pooled. The problem with pooling the results is that the three analyses are not independent: all three were drawn from the same ampoules placed in the same oven. This reduces the number of independent observations to 6, and the curvature disappears.

Extensive studies on the stabilization of polypropylene (PP) by Ciba Specialty Chemicals, Inc., notably those of Gugumus (1999), merit comment. End of life for PP films was assessed by brittleness on bending. Using this test, Gugumus found not only curvature, but inflection points over the range 40 – 140 °C. Aging data for unstabilized PP is shown in Figure 3.

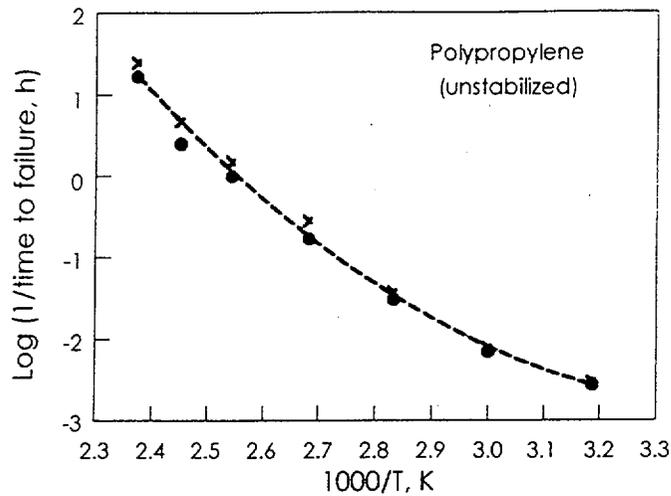


Fig. 3. Lifetime as judged by a flex test for unstabilized PP film of two grades. Data from Gugumus (1999)

## IMPORTANCE OF THEORETICAL SOURCES OF CURVATURE

### A. Non-Arrhenius rate equations

The development of rate expressions based on the notion of an activated complex with a Boltzmann probability has led to numerous refinements. The main theoretical development of concern to the validity of the Arrhenius method are the expressions with temperature-dependent frequency factors [e.g., Johnston (1966)]. These take the form:

$$k = aT^n \exp(-E/k_B T) \quad (1)$$

where  $n$  varies between  $-2$  and  $2$ , depending on  $T$  and  $E$ . These expressions do produce curvature in the Arrhenius plot.

To determine the seriousness of this curvature, we can take the derivative of Eq. 1 leading to

$$d \ln k / d(1/T) = -nT - E/k_B \quad (2)$$

The first term should be around  $-700$  (e.g.,  $n=2$ ;  $T=350$ ), while the second is typically  $-10000$  or more. Thus, the first term can be expected to be very hard to see, and will contribute very little to curvature.

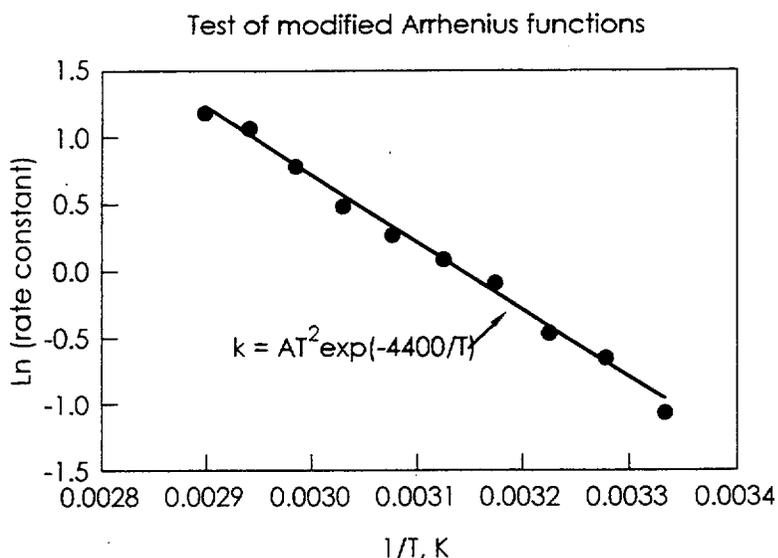
To illustrate this with a concrete example, some "data" were calculated using Eq. 1 with  $n=2$ . This is the curve shown in Figure 4. To this data a 1% random noise was added (to the natural logs). The curvature could not be detected with this data, either "by eye" or statistically.

In conclusion, the most severe examples of theoretical nonlinearity resulting from refinements of the Arrhenius would have a negligible effect on the observed Arrhenius behavior, in spite of much discussion [e.g., Crine et al. (1985)].

## B. Complex kinetics

Thermal oxidation of hydrocarbons follows many routes depending upon the temperature, structural details of the polymer, presence of catalysts and concentration of oxygen. While both scission and crosslinking can lead to loss of properties, a combination of both may help to preserve the material. Thus, attempting to connect specific kinetic pathways with loss of elongation must be done on a case-by-case basis, and with ample empirical evidence.

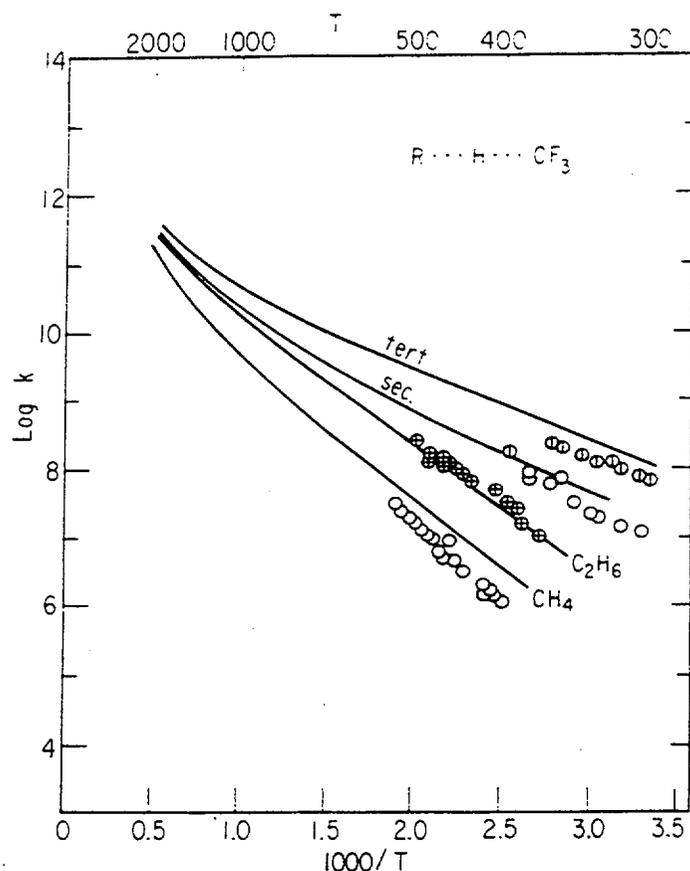
The general notion of activated processes does, however, suggest that as the temperature increases, higher energy pathways will become more important. This manifests itself in the so-called compensation principle, which states that the front factor in the Arrhenius expression should be nearly a universal constant for a given order of reaction.\* This is



**Fig. 4** Arrhenius plot of an extreme in the theory of activated rate processes that give a temperature-dependent frequency factors (Eq. 1)

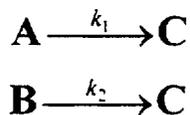
illustrated with Figure 5, which shows the second-order abstraction of hydrogen from various hydrocarbons (an early step in the oxidation scheme) by a trifluoromethyl radical. The more difficult abstractions show the higher activation energies, as expected, but also the lower rates. The implication of this is that if these reactions are running in parallel, the apparent activation energy will climb as temperature increases. In turn, the implication of this is that qualification done at high temperatures will predict lower-than-actual rates at low temperatures—the non-conservative result.

\* Other connections between A and E have been reported as well. See for example, Crine (1991).



**Fig. 5** Arrhenius plots for the reaction of trifluoromethyl radical with various hydrocarbons showing compensation principle (reactions with lower rates at low temperatures have higher activation energies).

To investigate the seriousness of this, two parallel first-order reactions were assumed to lead to scissions. The reaction scheme is thus:



where  $k_1$  and  $k_2$  are the two rate constants given by:

$$\begin{aligned} k_1 &= A_1 \exp(-E_1 / k_B T) \\ k_2 &= A_2 \exp(-E_2 / k_B T) \end{aligned} \quad (3)$$

As one option, the frequency factors  $A_i$  might be the same (compensation principle).

The question addressed was what the effect of qualification at temperature  $T_q$  would have on the prediction of the conversion of **A** and **B** to **C** at temperatures  $T < T_q$  (normal

Arrhenius) and  $T > T_q$  (reverse Arrhenius). An auxiliary question was the influence of changing temperature with excursions above  $T_q$ .

The apparent activation energy at the qualification temperature  $T_q$  was defined as

$$E_q = k_B \left. \frac{d \ln r}{d(1/T)} \right|_{T=T_q} \quad (4)$$

where  $r$  is the rate of reaction, assumed to be given by the expression:

$$r = \frac{dC}{dt} = -\frac{d(A+B)}{dt} = k_1 A + k_2 B \quad (5)$$

In these expressions  $A$  (no subscript) is the concentration of species A, and so on. The mass balance gives  $C = A_0 - A + B_0 - B$ , where the  $A_0$  and  $B_0$  are the initial concentrations. The expression for  $E_q$  becomes:

$$E_q = \frac{k_B}{r} \left. \frac{dr}{d(1/T)} \right|_{T=T_q} = \frac{AE_1 A_1 \exp(-E_1/k_B T_q) + BE_2 A_2 \exp(-E_2/k_B T_q)}{AA_1 \exp(-E_1/k_B T_q) + BA_2 \exp(-E_2/k_B T_q)} \quad (6)$$

This expression depends on (1) concentrations of reactants  $A$  and  $B$ , (2) qualification temperature  $T_q$  and (3) individual activation energies  $E_1$  and  $E_2$ .

The Arrhenius plot for the rate expression of Eq. 3 is shown in Figure 6.

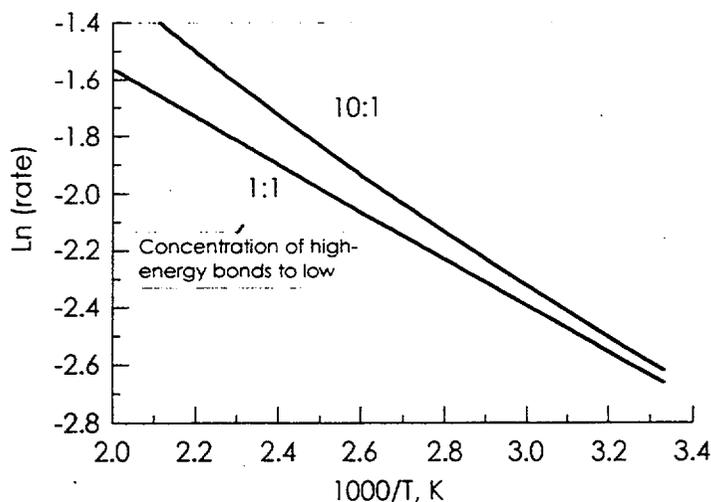


Fig. 6. Simulated Arrhenius plots for parallel reactions with 3:1 ratio of activation energy and the ratios of high- to low-energy bonds as shown.

Parallel reactions with equal concentrations and equal frequency factors give an Arrhenius plot that is essentially straight over a 200 °C temperature range. Only when

the relative concentration of high-energy bonds is increased does the expected curvature appear. However, this situation may not be unrealistic: the high-energy bonds could be the numerous methylene-ethylidene linkages in an EP elastomer, for example. These could undergo a cyclic rearrangement reaction with a high activation energy to give a scission.

The answer to the question concerning temperature- and concentration-dependent activation energies is clearly an almost unqualified yes; that is, reasonable assumptions can lead to mild curvature.

### C. Temperature excursions.

The question of the problems induced by temperature excursions as the polymer ages is somewhat more difficult to address. In applying data from an accelerated test to a lower temperature, the approach is often to use the property decay response from the accelerated test as an indication of what will happen at the lower temperature, but with the time appropriately adjusted using the Arrhenius equation. If the natural aging temperature is fluctuating, the times can be summed up for each temperature. Alternatively, an Arrhenius-equivalent temperature can be calculated, and the time shift done in one easy step. For constant activation energy processes, these are equivalent. A summary of these equations is provided in Table 1.

Table 1. Summary of equations used to predict natural aging from accelerated testing.

<p><b>Equivalent Time, fixed aging temperature.</b>  <math>t_{eq}</math> is equivalent time at <math>T_q</math>  <math>T_q</math> = qualification temperature  <math>T</math> = natural aging temperature  <math>t</math> = natural aging time  <math>E_q</math> = Activation energy at <math>T_q</math>  <math>k_B</math> = Boltzmann constant</p>	$t_{eq} = t \exp \left[ -\frac{E_q}{k_B} \left( \frac{1}{T} - \frac{1}{T_q} \right) \right]$
<p><b>Equivalent Time, varying aging temperature</b>  <math>t'</math> = dummy variable for integration</p>	$t_{eq} = \int_0^t \exp \left[ -\frac{E_q}{k_B} \left( \frac{1}{T(t')} - \frac{1}{T_q} \right) \right] dt'$
<p><b>Equivalent Temperature</b></p>	$T_{eq} = \frac{-E_q / k_B}{\ln \left[ \int_0^t \exp[-E_q / k_B T(t')] dt' \right] t}$

The real problem with temperature excursions occurs when they are large enough to generate significant rates for the high-activation-energy processes. To explore if this is likely to be worrisome, some simulations with the reaction scheme above were run. This was done by integrating the differential rate expression of Eq. 5 using either an apparent

activation energy or one that depends on temperature according to Eq. 6. The former is the "predicted," the latter, the "actual." The results are shown as concentration of product vs. time resulting from two temperatures. The scission concentration, which will presumably be monotonically related to the physical property of interest, will be the predictor for other temperatures after applying the Arrhenius shift to get the equivalent time. The activation energy will be  $E_q$ , given by Eq. 6. The actual concentration will be determined by the actual rates at the aging temperature.

Figure 7 shows what happens at  $T = T_q$ . This serves as the template for predicting the aging at another temperature by using the equivalent time given in Table 1.

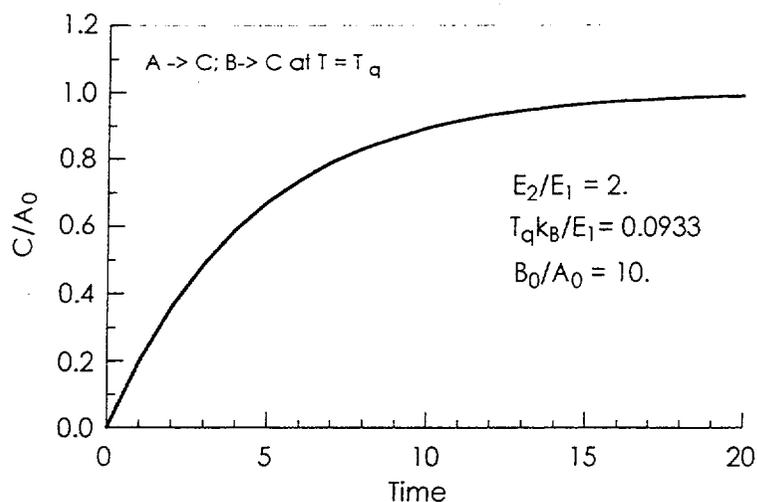


Fig. 7. Build up of scissions  $C$  at  $T = T_q$ .

The conditions for Figure 7 are such that most of the scissions result from the first reaction. Illustrated in Figure 8 are predicted and actual concentrations for

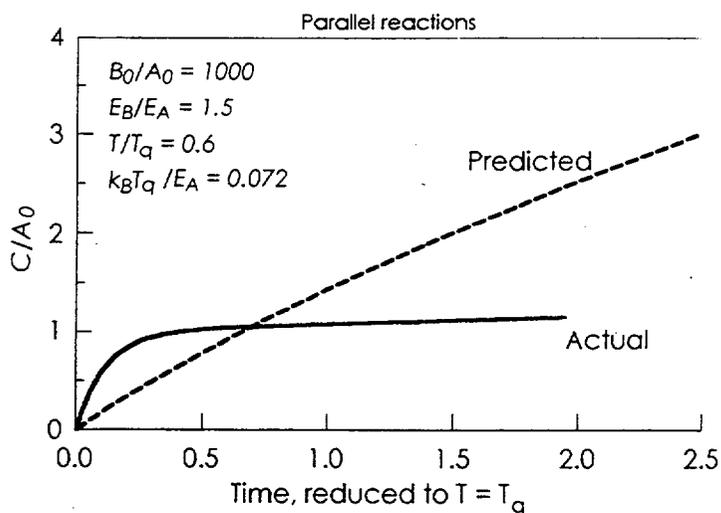
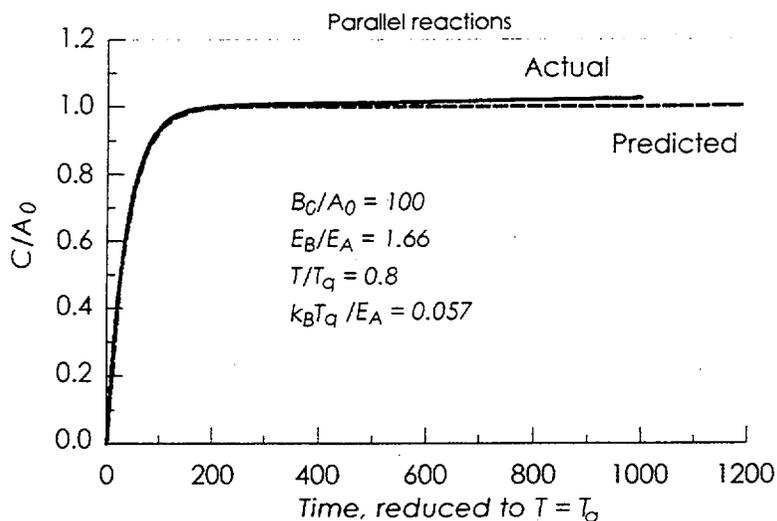


Fig. 8. Conversion in a parallel reaction scheme with extreme conditions. The qualification test is at a high temperature and the high concentration of the more-stable species (B), so the conversion marches to high levels. At the aging temperature, the reaction uses mostly the less-stable species (A). (B) is almost inert, and the reaction essentially stops.

somewhat extreme conditions to illustrate what can happen. The activation energy ratio of 1.66 (for example, 0.6 and 1.0 eV) and the initial concentration ratio of 100 (for example,  $A = 0.01$  and  $B = 1.0$  mol/L) were chosen to emphasize the curvature in the Arrhenius plot. The temperature ratio could represent an aging temperature of 300 K (23 °C) and a qualification temperature of 500 K (223 °C).

The actual conversion in this case exceeds the predicted at early times, but falls below the predicted as the less-stable species **A** is used up. The aging temperature is not high enough to convert much of the more stable **B** to product. The prediction, on the other hand, is for a reaction that parallels the situation at the qualification temperature, but at a lower rate.

Less extreme conditions produce results that are indistinguishable from each other; i.e., the Arrhenius method becomes a good one. This is illustrated in Figure 9.



**Fig. 9.** Conversion in a parallel reaction scheme with more normal conditions. The actual and predicted are virtually indistinguishable.

The conditions shown in Figure 9 might be a qualification temperature of 127 °C, and an aging temperature of 47 °C, activation energies of 0.6 and 1.0 eV for **A** and **B**, respectively, and concentrations of 0.01 and 1.0 mol/L, respectively. Although the actual degradation is slightly higher than the predicted, it is judged not significant.

#### D. Reverse Arrhenius

Reverse Arrhenius refers to using the Arrhenius method to predict aging at temperatures that exceed the qualification test temperature. The technical concerns for this are the same as that for lower temperatures—the opening of reaction pathways that were not present during qualification.

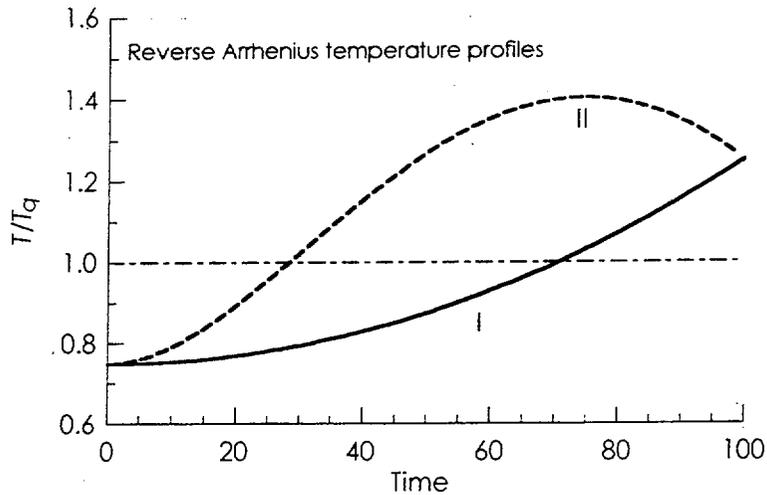


Fig. 10. Temperature profiles used for reverse-Arrhenius tests.

To assess the possible importance of this, the parallel reactions described above were explored using temperature histories that started low and progressed to very high. The profiles chosen are shown in Figure 10; the results are shown in Figures 11 and 12.

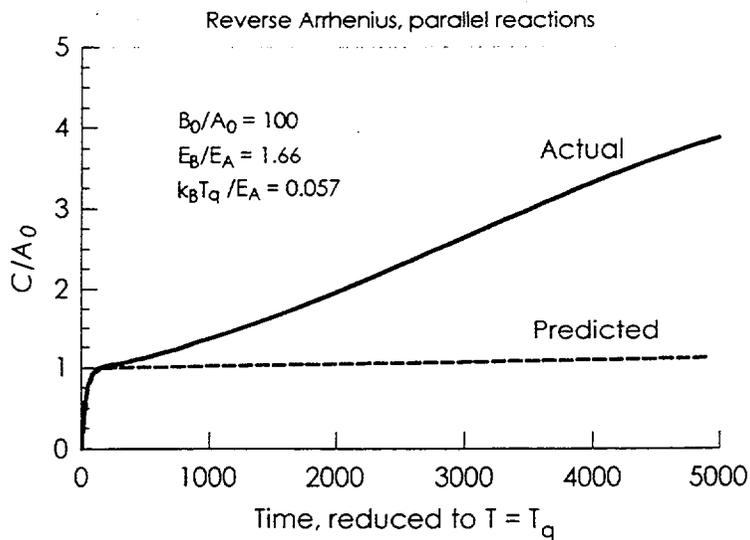
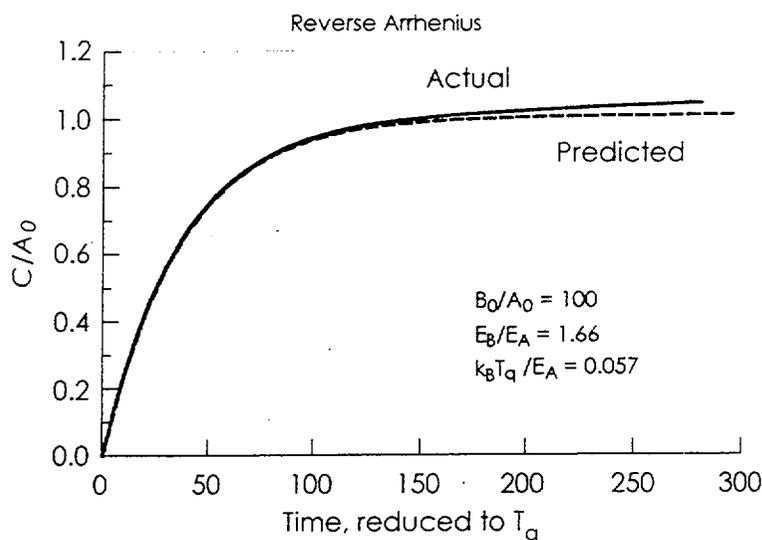


Fig. 11 A severe case of a reverse Arrhenius problem. Kinetic assumptions are the same as Figure 12, but the temperature history includes more time at high temperatures (Curve II in Figure 10) Reaction times are also long.



**Fig. 12.** Results of a more reasonable reverse Arrhenius test. Kinetic conditions are the same as for Figure 11, but the temperature excursion is not as severe. (Curve I in Figure 10).

The conditions in Figure 12 might correspond to a qualification temperature of 127 °C, and an aging temperature starting at 27 °C and rising to 227 °C, activation energies of 0.6 and 1.0 eV for A and B respectively, and initial concentrations of 0.01 and 1.0 mol/L, respectively. The result is a slight underprediction of the faster-than-expected rates at the high temperatures.

The conclusion concerning the reverse Arrhenius problem is about what one would expect; there is no problem as long as the temperature does not rise much beyond the qualification temperature. Application of the Arrhenius method to temperature spikes can underpredict degradation quite severely if the temperature excursion is high.

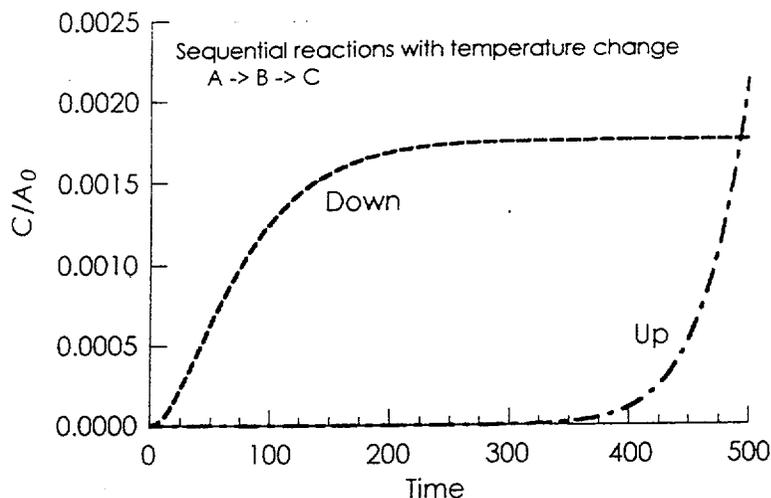
#### E. Sequential reactions and temperature changes

The purpose of this section is to explore the possibility that reactions typical of hydrocarbon oxidation can have a memory of past temperature conditions that introduces error in the Arrhenius method. The example chosen considers the transient situation where an intermediate (hydroperoxide) builds up at high temperature, leading to a faster-than-expected reaction as the temperature drops. The temperature histories picked were designed to have the same Arrhenius average temperature (or equivalent time).

The reactions assumed were:



The results of the simulations are shown in Figure 13.



**Fig. 13.** Sequential reactions. Temperature changes linearly Up or Down between 300 and 450 K, giving the same Arrhenius equivalent time for each path. ( $E_1 = 0.7$ ,  $E_2 = 0.9$ ,  $A = 1.E6$ ,  $A_0 = 1$ .)

While the evolution of the product **C** is quite different for the two temperature programs, the net result is roughly the same, with the increasing temperature overtaking the decreasing at the last moment. With the decreasing temperature, the high temperatures early on build up intermediate **B**, which then continues to pass to **C** at a high rate because of its high concentration.

Ignored in this analysis is the history that led to the two different starting temperatures in the first place.

Many more variations of the reactions and kinetic parameters are possible; however, they are likely to be similar to the simplified situations provided for illustration. The extreme cases shown were used to emphasize certain points, and should not be taken as evidence that there is a problem with the Arrhenius method for more normal conditions.

## GENERAL CONCLUSIONS

The Arrhenius relationship does seem to have the ability to predict accurately for many reaction conditions. Perhaps the easiest way to produce discrepancies is with the reverse Arrhenius case, i.e., with temperature excursions that exceed the qualification temperature by a large amount. This is illustrated in Figures 10 and 11. Adverse curvature in the Arrhenius relationship obtains with parallel reactions under rather severe assumptions concerning the individual activation energies or the relative amounts of the reactants (Figure 6). Certain literature data mimic this curvature, but most involve polymers with considerable crystallinity.

The obvious recommendation from this study is for a program aimed specifically at quantifying the magnitude of curvature in the Arrhenius plot using amorphous materials of interest to the nuclear industry. To be most informative, this program should look for the dependence of any curvature on material, aging level and characterization method. Practically, it could employ simple end-of-life test and seek to find changes in the distributions of life times with temperature.

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January 11, 1999

*OKA*  
*1/12/99*

**VIA FEDERAL EXPRESS**

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Dear Satish:

Further to my letter of November 23, 1998, to Mr. Vora, enclosed is a copy of the Nuclear Utility Group on Equipment Qualification's ("NUGEQ") Report on the "Acceptability of Arrhenius Methodology to Analyze LOCA and Post-LOCA Environments." As we note therein, this report was specifically developed to provide the NRC staff with relevant information and aid the staff in its evaluations regarding the use of the Arrhenius methodology during LOCA and post-LOCA environments. The report, prepared by the NUGEQ consultant, Strategic Technology And Resources, Inc., has been reviewed by NUGEQ group member utilities and reflects consensus technical and licensing views. However, it does not represent an "industry position" nor have there been efforts to insure the report fully represents all licensee practices.

To facilitate your review, this document is organized so as to address NRC regulatory and technical considerations, as follows:

- Section 2, **Results of NUGEQ Review**, summarizes the insights and conclusions from the NUGEQ review.
- Section 3, **Risk Significance**, indicates that the issue of whether correct accident acceleration techniques have been used is not risk significant.
- Section 4, **International Practices**, outlines EQ practices in other countries where qualification tests are limited to a two week duration and the test conditions represent some acceleration of the post-accident period.
- Section 5, **Regulatory Considerations**, overviews NRC EQ-related requirements, guidance, and generic evaluations with relevance to using Arrhenius-type analysis of LOCA test data, indicating that historically the NRC has accepted this use of Arrhenius, particularly for establishing equipment post-accident operating time (PAOT).

Mr. Satish K. Aggarwal  
January 11, 1999  
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- Section 6, **Technical Considerations**, is a broad discussion of information of relevance to using the Arrhenius methodology to analyze accident conditions. The section includes background information on the Arrhenius method and presents technical information, including models of transient accident temperatures, to address what are perceived as possible NRC concerns.

Finally, it warrants noting here that in the context of the consideration of risk significant conditions, prior work for the NRC and by NRC PRA practitioners has found that there is little additional risk reduction in extending qualification beyond 14-30 days after the accident. Indeed, the Group has previously suggested in the NRC's Marginal to Safety Program that an effort to reduce and make uniform the post accident operating times for licensees (e.g., to 14-30 days) would be justified under a risk-based analysis. Such factors would seem appropriate to consider in assessing the potential benefit to be achieved in addressing questions in this arena.

We trust this information will be of use in resolving the matters the Staff is reviewing on this topic. Please feel free to give Phil Holzman (781-729-9212) or myself (301-371-5737) a call if you have any questions.

Sincerely,



William A. Horin  
Counsel to the Nuclear Utility Group  
on Equipment Qualification

Enclosure

cc: Mr. Jitendra P. Vora (NRC)  
Mr. Jose A. Calvo (NRC)

**Acceptability of Arrhenius Methodology to Analyze  
LOCA and Post-LOCA Environments**

**NUCLEAR UTILITY GROUP ON EQUIPMENT QUALIFICATION**

January, 1998 <sup>9</sup>

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## 1. INTRODUCTION

The NRC has recently raised a question regarding the use of the Arrhenius methodology to analyze differences between equipment qualification (EQ) LOCA test profiles and licensee plant-specific profiles. It has long been recognized that licensees use the Arrhenius method and accident qualification test data to establish qualification for some test durations that do not envelope the plant-specific LOCA or MSLB temperature profiles. During an October 1997, meeting to discuss the use of Arrhenius for accident analysis, the NRC staff sought general information and outlined possible concerns [1]. The staff has stated in recent power uprate safety evaluations that they are evaluating this use of the Arrhenius methodology as a separate issue. In a recent NRC safety evaluation for power uprate at Monticello [2], the NRC draws the following conclusions regarding the use of Arrhenius for accident analysis:

- Because the use of Arrhenius for accident analysis has not been generically approved by the staff, it cannot be used without a supporting justification and technical basis.
- Arrhenius can be justified if temperatures are constant and if LOCA conditions do not cause material changes. This includes its use to determine post-accident operating times.
- Arrhenius is not generally considered an accurate method to determine degradation during transient temperature conditions.
- Using Arrhenius to justify higher required temperatures using lower test temperatures (i.e., reverse Arrhenius) is an inappropriate application of the methodology. This includes cases where the test profile falls below the plant-specific profile at non-peak temperatures for some period of time.

Because the Arrhenius model is perceived to have several theoretical and practical limitations, NRR has request that RES provide perspectives, technical bases, and guidelines to the NRR staff for evaluating licensee methods that use the Arrhenius methodology for LOCA and post-LOCA environments. The NRC has encouraged the industry to provide the staff with any relevant technical information that may help define the technical bases for using Arrhenius to analyze LOCA and post-LOCA environments.

This NUGEQ report was specifically developed to provide the NRC staff with relevant information regarding the use of the Arrhenius methodology during LOCA and post-LOCA environments. The report, prepared by the NUGEQ consultant, Strategic Technology And Resources, Inc., has been reviewed by NUGEQ group member utilities and reflects consensus technical and licensing views. This document is intended to aid the staff in its evaluations. It does not represent a "industry position" nor have there been efforts to insure the report fully represents all licensee practices.

This document is organized to facilitate NRC regulatory and technical considerations. Section 2, **Results of NUGEQ Review**, summarizes the insights and conclusions from the NUGEQ review. Section 3, **Risk Significance**, indicates that the issue of whether correct accident acceleration techniques have been used is not risk significant. Supporting this lack of risk-significance, Section 4, **International Practices**, outlines EQ practices in other countries where qualification tests are limited a two week duration and the test conditions represent some acceleration of the post-accident period. Section 5, **Regulatory Considerations**, overviews NRC EQ-related requirements, guidance, and generic evaluations with relevance to using Arrhenius-type analysis of LOCA test data. Such information includes SERs, Regulatory Guides, EQ Inspection Reports, IEEE Standards and other documents. The documents indicate that historically the NRC has accepted this use of Arrhenius, particularly for establishing equipment post-accident operating time (PAOT). Finally, Section 6, **Technical Considerations**, is a broad discussion of information of relevance to using the Arrhenius methodology to analyze accident conditions. The section includes background information on the Arrhenius method and presents technical information, including models of transient accident temperatures, to address what are perceived as possible NRC concerns.

## 2. RESULTS OF NUGEQ REVIEW

We conclude, based on a review of relevant material and additional analyses performed in support of this document, that an adequate technical basis exists to justify the application of the Arrhenius methodology for analyzing test data to establish qualification for plant specific accident conditions. A variety of factors, including risk significance, past regulatory practice, equipment design, qualification criteria (e.g., DOR or NUREQ 0588), available margins, LOCA profiles, and test duration, should be considered when establishing the acceptability of such analyses. Given the other conservatisms inherent in EQ methodologies and the relatively small uncertainties associated with using Arrhenius for accident analysis, we conclude that rationally implemented applications provide a reasonable basis to demonstrate accident qualification.

Based on the information contained in this report, the NUGEQ draws the following conclusions regarding the use of Arrhenius to analyze accident conditions.

1. Determining if correct accident acceleration techniques have been used is not risk significant. This conclusion was also reached by the NRC sponsored EQ Risk Scoping Study.
2. The NRC's professional engineering judgement, both generically and in plant-specific circumstances, has accepted the use of Arrhenius to establish post accident operating times (PAOT).
3. There is an ample technical basis supporting the use of Arrhenius to analyze accident conditions, including transient portions of the accident profile.

4. Based on first principles and supporting research results, it is reasonable to use Arrhenius to evaluate nonconstant temperature conditions, including transient portions of the accident profile.
5. The single critical factor when analyzing nonconstant conditions is determining the temperature profile of the critical component/material. For slow changing quasi-equilibrium conditions, ambient temperature is a reasonable representation of component temperature. For rapidly changing transient conditions, conservative assumptions or heat transfer analyses can be used.
6. Based on modeling and analysis of component/material temperatures during accident transients, use of the "entire accident profile" when evaluating PAOT is acceptable since there are only minor differences between these results and those based on analyses using only the post-transient period. These differences are not risk significant.
7. It is not common practice to use the Arrhenius method as the basis for establishing qualification for peak accident temperatures that are greater than qualification test conditions. Equipment heat transfer calculations (i.e., thermal lag analysis) are the recognized method to evaluate these situations.
8. It is a reasonable and appropriate application of the Arrhenius method to analyze cases where the test profile falls below the plant-specific profile for some period of time.

### 3. RISK SIGNIFICANCE

Critical to establishing the proper framework for considering this issue is recognition that EQ issues related to long-term equipment performance are not risk significant. We fully agree with the NRC-sponsored EQ Risk Scoping Study [3] conclusion that: "*This EQ issue of whether correct accident acceleration techniques have been used is not risk significant*". Any determination regarding the acceptability of using Arrhenius to analyze accident conditions must consider risk significance. Since a number of conservatisms are inherent in EQ practices and the uncertainties associated with using Arrhenius for accident analysis are relatively small, reasonable implementations provide an acceptable basis for demonstrating accident qualification.

Licensee EQ programs typically establish, for qualification purposes, a *maximum post-accident duration*, ranging from 30 days to one year or longer. This *maximum post-accident duration* is used to establish qualification for many EQ items (typically those needed for long-term core cooling and post-accident monitoring).

These licensee defined *maximum post-accident durations* have been qualitatively established based on various considerations, including prior commitments, IEEE standards, regulatory practice, and post-DBE equipment access. Often, plants with virtually identical safety-systems and accident response scenarios have significantly

different *maximum post-accident durations* (e.g., 30 days and 1 year) in their EQ programs.

Licensee and the NRC implicitly justified these time differences based on several considerations. First, there is recognition that establishing operability for the *maximum post-accident duration* is a reasonable basis to conclude that additional long term operability is available under similar or less severe post-accident conditions (e.g., qualifying for 30 days provides confidence that equipment will be available for longer periods). Secondly, equipment performance during the long-term post-accident period is not risk-significant. Accident mitigation occurs within the first few hours or days of the accident. Subsequently, plant conditions change slowly, permitting a range of accident management scenarios. Because of these accident management options, most PRAs conclude that the risk of further radiation release during subsequent periods is insignificant. From a risk perspective, operability only needs to be demonstrated for several days or possibly weeks. Demonstrating operability for longer times is not relevant to overall accident risk. This risk perspective on EQ is consistent with the NRC views presented in the *Equipment Qualification (EQ) - Risk Scoping Study* [3], which is discussed further below. Finally, many EQ programs have conservatively established the *maximum post-accident duration* as the assumed operability time for all equipment. These licensees only establish shorter equipment-specific operating times, based on accident and system analysis, in those cases where Arrhenius-based PAOT calculations cannot establish qualification for the *maximum post-accident duration*. These industry perspectives on post-accident operability are expressed in Section 6.2, *Equipment Performance Requirements*, of the EPRI EQ Reference Manual [4].

### EQ Risk Scoping Study

NUREG/CR-5313, *Equipment Qualification (EQ) - Risk Scoping Study*, January, 1989, [3] provides important risk-based insight into EQ requirements and practices. The EQ Risk Scoping Study Preface, signed by NRC Moni Day and Thomas King, states in part:

*"The study concluded that several historical EQ issues lack risk significance as a result of conservatisms embedded in NRC's EQ regulations that provide defense in depth considerations of equipment performance. . . . Therefore, this report is being published for information and for use by the industry and the NRC, as appropriate, in assessing EQ issues associated with individual plants."*

The risk-based conclusions in this Sandia report are significant since many of these "historical EQ issues" were technical questions initially raised by Sandia. A portion of the report's *Technical Summary* is titled, *Risk Significant Accident Time Durations*. Here, the document recognizes the difference between PRAs which "only model plant accident response for the first 24 to 48 hours" and EQ programs which deterministically "qualify some equipment for very long post-accident time periods (up to one year)". Importantly, it concludes, "From a PRA perspective and given NRC inspection philosophy, this EQ issue of whether correct accident acceleration techniques have been used is not risk

*significant.*" It reaches similar conclusions regarding the lack of risk significance for several other issues related to long term operability. These other issues include *simultaneous vs. sequential simulations* and *including oxygen within the qualification test chamber*. In a paper presented during an international EQ conference [SAND88-2171C], the EQ Risk Scoping Study authors make the following recommendation: "*The U.S. nuclear industry practice of specifying long duration equipment mission times during harsh accident conditions might be reduced when appropriate so that test resources focus on assuring equipment operability for the first few days of an accident exposure.*"

#### 4. INTERNATIONAL PRACTICES

We believe considerations similar to those discussed in the EPRI EQ Reference Manual and the NRC's EQ Risk Scoping Study, (i.e., lack of risk significance and reasonable conclusions regarding long-term performance), prompted other countries (e.g., France and Germany), whose EQ practices are not directly patterned after US practices, to limit their post-accident test durations.

The most severe French qualification category, "K1", applies to inside containment equipment which must function under accident conditions. The K1 qualification standard specifies qualification parameters, including aging and accident conditions. The LOCA steam simulation test duration is limited to 14 days (4 day accident and 10 day post-accident) for all devices, including long-term core cooling and accident monitoring equipment.

In Germany qualification is based on the appropriate KTA and Seimens KWU standards. For inside containment equipment the LOCA simulation test is typically limited to 24 hours with a 12 day steam or water-immersion post-accident test used to simulate long-term performance. An overview of other European qualification practices is contained in [5]. That report indicates that the UK (Sizewell B), Sweden, Spain, Finland, and Belgium accelerate the post-accident period using Arrhenius considerations. For the UK the standardized LOCA test profile lasts only 14 days. Although some thermal acceleration in the post-accident test period exists in the France, Germany, and UK standardized profiles, this does not account for variations in activation energy among the qualified equipment items.

#### 5. REGULATORY CONSIDERATIONS

This section overviews NRC EQ-related requirements, guidance, and generic evaluations with relevance to using Arrhenius-type analysis of LOCA test data. We conclude from several documents, including SERs and Regulatory Guides, that the NRC's historical professional engineering judgement has been to accept this use of Arrhenius, particularly for determining PAOT. Further support for this conclusion is provided by numerous

NRC EQ Inspection Reports of individual licensees and the general use of Arrhenius for establishing PAOT by virtually all licensees. Such practices would have been routinely available for NRC review whether or not documented in specific NRC inspection reports.

### **Regulations and NRC Guidance Documents**

The EQ rule, 10 CFR 50.49 [6], at (f)(1), specifically accepts testing under similar conditions with supporting analysis as an acceptable qualification basis. Although no specific reference to Arrhenius is made, the rule's statements of consideration (SOC) stipulate that the rule is based on the DOR Guidelines [7] and NUREG-0588 [8] and accepts qualification for existing equipment based on these documents. Both these guidance documents recognize and accept technically justified uses of accelerated aging techniques to evaluate accident conditions.

NUREG-0588, Section 2.1(3)(a) states that equipment ...*"should be qualified by test to demonstrate its operability for the time required in the environmental conditions resulting from that accident."* Section 4(4) considers Arrhenius as an acceptable method to address accelerated aging and in 4(6) stipulates that aging acceleration rates used in testing and their basis should be described and justified. Public Comment No. 87 states: *"We interpret Section 4(6) as being applicable to post-accident environmental thermal age acceleration also."* In its response the NRC states: *"For equipment that is required to function for an extended period of time in a hostile environment, post-accident environmental aging considerations may be warranted."*

DOR Guidelines, Section 5.2, Qualification by Type Testing, states: *"The time duration of the test should be at least as long as the period from the initiation of the accident until the temperature and pressure service conditions return to essentially the same levels that existed before the postulated accident. A shorter test duration may be acceptable if specific analyses are provided to demonstrate that the material involved will not experience significant accelerated thermal aging during the period not tested."* [emphasis added].

It is apparent from these regulatory documents, including the qualification standards in the DOR Guidelines and NUREG-0588, that the NRC recognized and accepted that acceleration of the post-accident period could be performed and that Arrhenius was a methodology for addressing accelerated aging conditions.

### **IEEE Standards and Applicable Regulatory Guides**

IEEE 323, *IEEE Standard for Qualifying Class 1E Equipment for Nuclear Power Generating Stations* [9], is the broad industry standard applied to the qualification of electrical equipment. The standard was initially issued in trial use form in 1971, and subsequently revised in 1974. Neither of these revisions provides explicit direction on accelerating the post-accident simulation. In the most recent revision, IEEE 323 1983, Section 7, *Simulated Test Profile*, states: *Accelerated thermal testing may be used to*

*simulate the temperature/time profile following the major temperature transients.* No additional information is provided regarding this accelerated thermal testing. Regulatory Guide 1.89, Rev. 1 [11] provides guidance on meeting the requirements of 10 CFR 50.49 and comments on the acceptability of IEEE 323-74. The guide states that equipment should be qualified for the length of time its function is required. It also recognizes the Arrhenius methodology as an acceptable method of addressing accelerated thermal aging within the limitation of state-of-the art technology. A revision to the guide has not been issued for the 1983 version of IEEE 323.

More explicit direction is provided in industry and NRC guidance on penetration assembly qualification. Two revisions of IEEE 317, *IEEE Standard for Electric Penetration Assemblies in Containment Structures for Nuclear Power Generating Stations*, [10] provide guidance on accelerating the post accident period and have been accepted by applicable revisions of NRC Regulatory Guide 1.63 [12]. IEEE 317 1983, Section 6.3.3(3)(b) states that, "*Accelerated thermal testing may be used to simulate the temperature-time profile following the major temperature transient(s) of the most severe DBE environmental conditions*". Appendix D2, *Simulation of LOCA Conditions by Accelerated Thermal-Life Testing*, provides a specific method for accelerating the time after the peak transient conditions. The method uses the Arrhenius methodology, a thermal aging based activation energy value, and the test and required accident times from the last peak transient until the end of the event. Regulatory Guide 1.63 Rev. 3 [11] describes methods acceptable to the NRC for penetration assemblies. The regulatory guide states that IEEE 317 1983, provides methods acceptable to the staff for satisfying qualification regulations, including 10 CFR 50.49, applicable to these penetration assemblies. The regulatory guide takes no exceptions to the IEEE 317 provisions applicable to accelerating the post-accident period. Similarly, although with less detail, Section 6.4.13 of IEEE 317 1976, permits accelerated testing to be used to simulate the post accident period beginning after transient peak temperatures have been achieved. Regulatory Guide 1.63 Rev. 2 [12] endorsed IEEE 317-1976, and also takes no exceptions to the provisions applicable to accelerating the post-accident period.

### **Other Industry Submittals and Applicable NRC Reviews**

Various revisions of WCAP-8587, *Methodology for Qualifying Westinghouse WRD Supplied NSSS Safety Related Electrical Equipment*, [13] specify that NSSS vendor's approach to satisfying the provisions of IEEE 323 and 10 CFR 50.49. The NRC has issued several SERs, see for example [14], on the Westinghouse EQ program which have not taken exception to the Westinghouse approach for accelerating the post-accident environment. In initial WCAP revisions, Westinghouse discussed its acceleration of the post-accident environment in WCAP-8587 Section 7 (see Figure 7-2 and notes in Revision 4, January 1981) and in Appendix B (Item 15, *Thermal Effects*, in Revision 4). In summary, Westinghouse used the Arrhenius method with either a material appropriate activation energy or a conservative value. The post accident time-temperature test conditions were defined using this method and activation energy values. Beginning with Revision 5 and included in all subsequent revisions, Appendix D, *Accelerated Thermal*

*Aging Parameters*, Section 5.0, *Post Accident Thermal Aging*, describes essentially the same approach.

In summary, Westinghouse accelerates the post-accident period after 24 hours to address long term operability (e.g., 4 - 12 months). The acceleration is based on Arrhenius analysis of times beyond 24 hours using the smallest activation energy applicable to thermally sensitive components or a generic value of 0.5 eV.<sup>1</sup> Westinghouse also notes that ambient temperatures will be used in the analysis since equipment within their scope does not experience significant heat rise (e.g., transmitters, MOVs, etc.) during this post-LOCA period. Our review of related NRC correspondence indicates this Westinghouse practice has not resulted in NRC staff exceptions or concerns. This has been confirmed in recent discussions with knowledgeable Westinghouse personnel.

### Example EQ SERs

**Shoreham:** In a SER supplement for Shoreham [15], the NRC evaluated additional LILCO information on GE 200 Series Electrical Penetrations. Under item "e" the SER discusses a previous deficiency involving inadequate analysis to demonstrate operability for the 180 day duration. The SER goes on to state: *"The applicant has now provided analysis to extend the test operability time to 180 days by equating temperature margins to time. We find this analysis to be acceptable."* LILCO used the Arrhenius methodology to equate temperature margin to time.

**Palo Verde:** In an SER supplement for the Palo Verde units [16], the NRC staff responded to licensee submittals intended to demonstrate a post-accident operating time of 182 days. The SER states: *"By letters dated May 25 and September 19, 1984, the applicant informed the staff that by using Arrhenius methodology it was able to demonstrate 182 day post-accident operability. The staff considers this item resolved"*. In its May 25th letter APS states that the 182 day operability is demonstrated, for any activation energy equal to or greater than 0.68eV, by using Arrhenius techniques to analyze the EQ-specified 16 day test profile against the predicted LOCA profile.

### Example NRC EQ Inspection Reports

Based on our knowledge of industry practices, we believe that all or virtually all licensees utilize Arrhenius to establish PAOT for some equipment items. In the 1980s and 1990s the NRC initiated team inspections of all licensees to determine if they had implemented programs to meet the requirements of 10 CFR 50.49. As part of these inspections detailed reviews of selected EQ files were performed. It was impossible to conduct reasonable reviews of these licensees' EQ files without considering this practice. Typical language in the NRC inspection reports regarding these detailed file reviews states: *"In addition to comparing plant service conditions with qualification test conditions and*

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<sup>1</sup> The Westinghouse post-accident profile decreased from approximately 200°F at 24 hours to approximately 155°F at 4 months and remained constant thereafter.

## NUGEQ - Arrhenius Methodology for Accident Analysis

*verifying the basis for these conditions, the inspectors selectively reviewed areas such as required post-accident operating time compared to the duration of time the equipment has been demonstrated to be qualified...*"[emphasis added]. Additional information in some inspection reports further confirms this aspect of the review. In several of these reports the NRC specifically discusses the use of Arrhenius for analyzing accident operating times. For example:

In an inspection report for Detroit Edison's Fermi Atomic Power Plant Unit 2 [17] the NRC indicates that although another method for extending short term accident test data into long term operability is unacceptable that: *"Extrapolation of test data using the Arrhenius methodology is considered acceptable."* In a similar report for Mississippi Power & Light Company's Grand Gulf Nuclear Station Unit 1 [18] regarding accident qualification of GE motors it states: *"The 100 day operating time was established by test and analysis (216 hours at 383 °F which is equivalent to 3000 hours at 311 °F [winding temperature])"*. Mississippi Power & Light used Arrhenius to establish this equivalency.

### **Other Documents Describing NRC Practices**

#### Equipment Qualification Inspection Course

During August, 1987, eighteen NRC staff and four INEL staff attended an EQ Seminar at Sandia. The intent was to present technical and administrative information to NRC EQ inspectors. Handouts were provided and lecturers included personnel from Sandia (e.g., Mark Jacobus) and NRC (e.g., Dick Wilson and Jeff Jacobson). The following is quoted from the handout materials.

#### Post-Accident

*The regulations generally require that equipment be qualified for the time duration that they need to function, plus margin. The staff position has been that post-accident acceleration using Arrhenius analysis is normally acceptable as long as the acceleration is not excessive (not easily defined, of course). The DOR Guidelines tend to be most permissive in that they only require qualification up until the time that the accident conditions have essentially returned to pre-accident values, and they also specifically allow thermal aging-type calculations to justify even shorter tests.*

#### Sandia Paper on NRC EQ Inspection Experience

Sandia's Mark Jacobus presented a paper [19] during a 1986 international topical meeting on EQ held in Albuquerque and sponsored by the American Nuclear Society. The paper notes that the work was supported by the NRC. Mark Jacobus has indicated that the paper was thoroughly reviewed by the NRC prior to presentation and publication. In the paper section on *Post Accident Qualification* Jacobus states:

*A second method that is used frequently by utilities is post accident acceleration using the Arrhenius technique. The implicit assumption in using this technique is that the limiting degradation mechanism is thermal aging via a first order reaction. This method has generally been accepted by inspectors for "reasonable" amounts of acceleration for the long-term steady-state conditions of the post accident environment. None of the qualification regulations deal specifically with post accident acceleration, but testing combined with analysis is considered by the regulations to be an acceptable qualification method.*

### BNL EQ Literature Review

Brookhaven National Labs (BNL) as part of the NRC cable research program recently issued a literature review and analysis on equipment qualification and cables [20]. In public meetings the NRC has stated that the BNL reports have been carefully reviewed by RES and NRR and are consistent with NRC views. Volume 2, Literature Analysis and Appendices, Section 2.4, *Dossier D: LOCA Profiles*, contains the following additional information.

*Accepted practice is the performance of qualification tests for a specific enveloping post-transient durations, with time margin, and the utilization of analysis, i.e., Arrhenius techniques, to demonstrate longer post-transient operating durations, including time margin.*

*Accepted practice has been to perform real time testing for long post-transient durations or to accelerate post-transient conditions artificially, using the Arrhenius methodology.*

## 6. TECHNICAL CONSIDERATIONS

This section addresses NRC technical concerns with using Arrhenius for accident analysis. Section 6.1 provides *General Background* information regarding the Arrhenius methodology and its application to LOCA type (e.g., steam) conditions. Section 6.2 discusses the use of Arrhenius for establishing *Post-Accident Operating Times* (PAOT) that exceed the test duration. Finally, Section 6.3 discusses the use of Arrhenius for those instances where the EQ test profile does not fully envelope the required plant profile (*EQ Profile Deficiencies*) for some short duration but substantially exceeds the plant-specific profile for other periods.

Analysis of accident conditions using the Arrhenius methodology only compares the cumulative degradation occurring as a result of different accident thermal exposures. Importantly, Arrhenius is not used to infer physical, mechanical, or electrical performance at accident temperatures beyond those occurring during the accident simulation tests. The test exposure must subject the equipment to representative

maximum temperature conditions. Thermal analysis (often termed “thermal lag analysis”) is the recognized method to justify qualification when peak test conditions are lower than plant-specific requirements. NUREG-0588, Appendix B describes an NRC accepted methodology for performing component thermal analysis to justify qualification whenever peak qualification test conditions are less than plant-specific requirements. Arrhenius cannot be used to justify peak temperatures beyond those experienced in the accident simulation test. This has often been referred to as “*reverse Arrhenius*”. As discussed further in Section 6.3, Arrhenius can be used to compare cumulative degradation from lower temperatures to higher temperatures within the temperature range simulated in the accident test.

## 6.1 Background

This section provides an overview of the Arrhenius methodology with a focused discussion on NRC concerns with its use during LOCA steam conditions. We believe these potential concerns are (1) applicability of Arrhenius during varying temperature conditions and (2) appropriate activation energy values during accident conditions. The activation energy value concerns may include appropriate values at high accident temperatures, applicability of thermal aging values during steam conditions, and possible changes in values during the accident exposure.

### 6.1.1 General Arrhenius Information

The rates of most chemical reactions increase as temperature rises. Qualitatively, this temperature effect is explained by noting that raising the temperature greatly increases the fraction of molecules with higher kinetic energies. Since higher energy molecules are more likely to react, reaction rates increase with increasing temperature.

For a particular chemical reaction and an involved molecular species A, the reaction rate during any increment of time ( $\Delta t$  or  $\delta t$ ) can be expressed as the change in the concentration of A ( $C_A$ ) with time or:

$$A_{\text{reaction rate}} = \Delta C_A(t)/\Delta t \text{ or } \delta C_A/\delta t \quad \text{Eq. 1}$$

Reaction rates vary with reactant concentrations. In the simplest case, the rate is proportional to the concentration of the reactants. The constant of proportionality is referred to as the rate constant ( $k$ ) for the reaction. Since  $k$  is a function of temperature and  $C_A$  varies with time, they can be expressed as  $k(T)$  and  $C_A(t)$ .

$$\delta C_A/\delta t = k(T) C_A(t) C_B(t) \dots C_N(t) \quad \text{Eq. 2}$$

The Swedish chemist Svandte Arrhenius around 1887 demonstrated that the log of the reaction rate was inversely proportional to temperature. According to Arrhenius, the reaction rate constant depends on the number of collisions between reactant molecules

and the kinetic energy of these molecules. Based on Arrhenius, the relationship between temperature and the reaction rate constant can be expressed as:

$$\ln k(T) = B - E_a/KT \quad \text{Eq. 3}$$

or

$$k(T) = B \exp [- E_a /KT ] \quad \text{Eq 4}$$

Where  $k(T)$  is the reaction rate,  $B$  is a constant pre-exponential factor,  $K$  is Boltzmann's constant,  $T$  is the absolute temperature, and  $E_a$  (another constant) is the Arrhenius activation energy.

The activation energy associated with a reaction has been described as the energy required to bring the reactants to the point where they can rearrange to form products. Stable reactant molecules, before their conversion to products, pass through an unstable, higher energy intermediate species called the *activated complex*. For a single step reaction, the *activated complex* corresponds to the instant when the reactant chemical bonds are breaking and the product bonds are forming. For simple reactions  $E_a$  is conceptualized as the energy difference between the reactants and the activated complex. See Figure 1 below. These fundamental considerations can be found in most chemistry texts, for example [21].

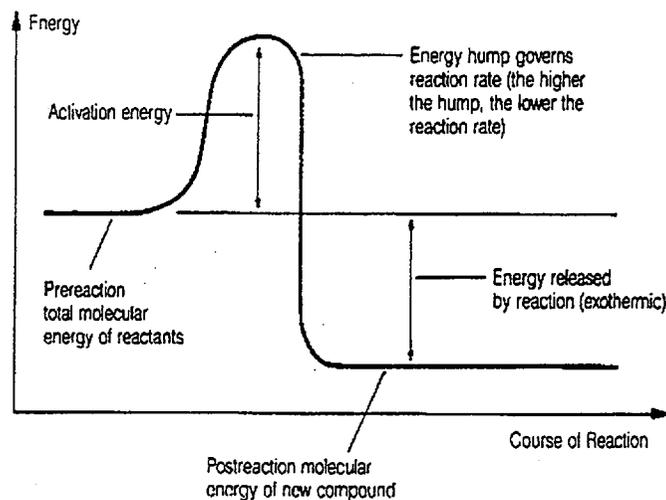


Figure 1 - Conceptual Depiction of Activation Energy [4]

Among others, Dakin at Westinghouse in the 1940's recognized that the Arrhenius equation could be used to establish a theoretical basis to explain the thermal deterioration over time of electrical insulating materials. Dakin observed that the magnitude or end point of certain physical, mechanical, or electrical properties (e.g., 50% reduction of

elongation or dielectric failure at some specified voltage) as a function of time and temperature could be described by the Arrhenius equation in the following form:

$$\ln L_1 = D \exp [ E_a /KT ] \quad \text{Eq. 5}$$

Where  $L_1$  is the time to reach the specified property endpoint (e.g., 50% relative elongation) and  $D$  is a constant. The relationship between Eq. 5 and Eq. 4 is reconciled by assuming that changes in the macroscopic property exhibiting Arrhenius behavior are directly related to concentration changes of certain critical chemical species (e.g.,  $C_A$ ) in the material.

If the material lifetime was based on a single dominant chemical species and reaction then the concentration of this species ( $C_A$ ) over time could be established by integrating the instantaneous rate equations. The concentration of this species  $C_{A1}$ , at some time  $T1$  could be expressed as:

$$C_{A1} = C_{A0} + \int_{t_0}^{t_1} \delta C_A / \delta t \, dt = C_{A0} + \int_{t_0}^{t_1} k(T) C_A(t) C_B(t) \dots C_N(t) \, dt \quad \text{Eq. 6}$$

$$= C_{A0} + \int_{t_0}^{t_1} A \exp [-E_a /RT] C_A(t) C_B(t) \dots C_N(t) \, dt \quad \text{Eq. 7}$$

Complete knowledge about the underlying kinetics and chemical species and reactions is not necessary for successful application of the Arrhenius model to material aging. The importance of the Arrhenius model to accelerated thermal aging and the correlation of time - temperature effects lies not so much in its theoretical underpinnings, but in the fact that empirical data can be correlated using this relationship. However, discussions of chemical species, critical reactions, and reaction rates offer a theoretical justification for the observed variation in macroscopic properties with time and temperature.

The deterioration of a material's property over a certain temperature range exhibits Arrhenius behavior if the various times to reach  $L$  at various temperatures yield a straight line when  $\ln(L)$  is plotted against  $1/T$ . In those cases where Arrhenius is valid, this relationship provides a powerful tool enabling higher temperature short time exposures (i.e., accelerated aging) to simulate the deterioration occurring over longer times at lower temperatures.

Since reaction rates are related to temperature, it is a convenient simplification to perform accelerated aging experiments at several constant temperatures (termed constant stress testing) to determine if the material property is exhibiting Arrhenius behavior and the associated activation energy. Numerous ASTM, IEEE, IEC and UL standards describe Arrhenius-based material testing methodologies involving several constant temperature exposures (typically three) and regression analysis to verify that the life values at these various temperatures exhibit Arrhenius behavior. Several examples follow.

Cable Insulating Materials: The activation energies for environmentally qualified cable insulating materials are typically based on several high temperature accelerated tests which establish loss of elongation information during prolonged thermal exposures. Per IEEE 383 [22], the cable qualification standard, these test results are analyzed using the statistical methods outlined in IEEE 101A [23]. Figure 2 presents the results for a typical XLPE material (Rockbestos Firewall III) [24]. In this test program numerous insulating material samples were tested at 121°C, 136°C, and 150°C. The average failure times at 60% retention of elongation were then used to establish the material's activation energy. Similarly, Figure 3 presents the aging data for a Raychem heat shrink material used on qualified electrical splices. In this case, material samples were aged at four temperatures ranging from 136°C to 175°C and the activation energy was based on 30% retention of elongation.

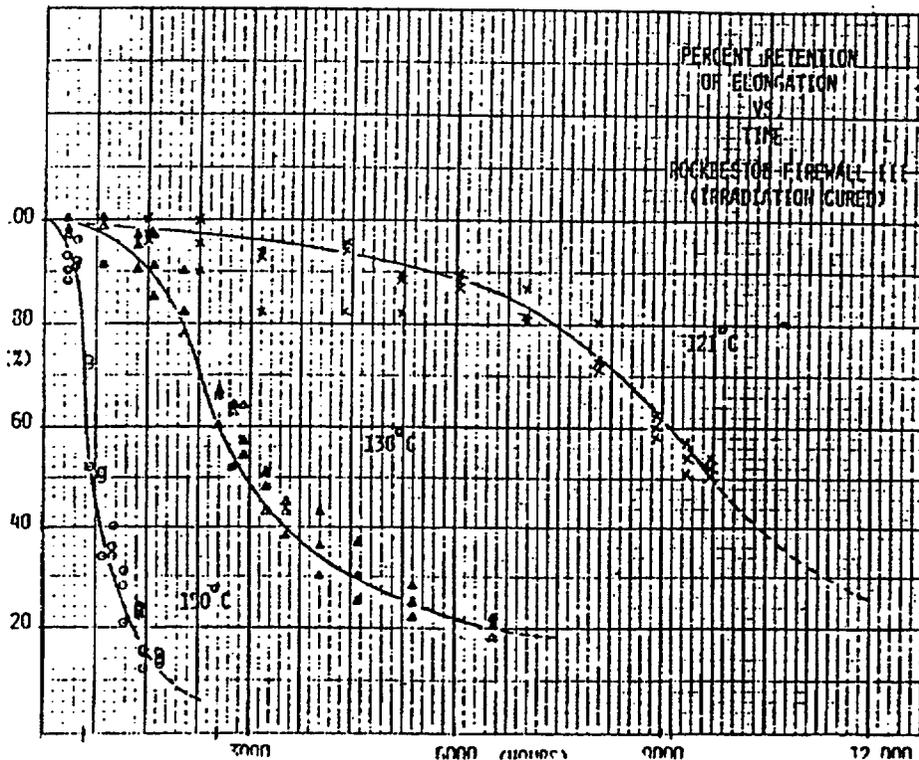


Figure 2 - Rockbestos Firewall III Accelerated Aging Test Data [24]

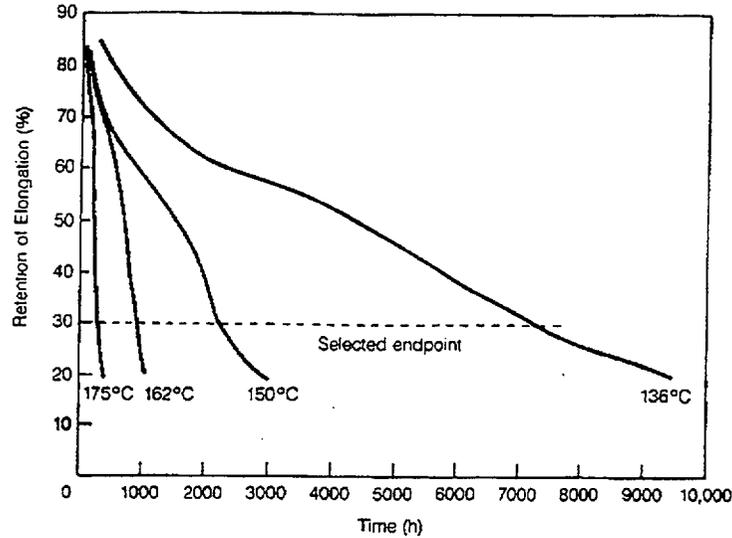


Figure 3 - Raychem heat shrink material [4]

Other Polymer Materials: Long term thermal aging data is typically available for most commercial polymer materials. The tests typically involve prolonged exposure of material samples to several high temperature conditions. Often the tests are used to establish material thermal ratings in accordance with UL standards. This test data can be used to establish material-specific activation energy values. Figures 4 and 5 present manufacturer aging data for two DuPont materials. Zytel is a Type 66 nylon with UL thermal ratings from 65°C to 125°C while Kapton is a high temperature polyimide material with a 200°C to 220°C thermal rating.

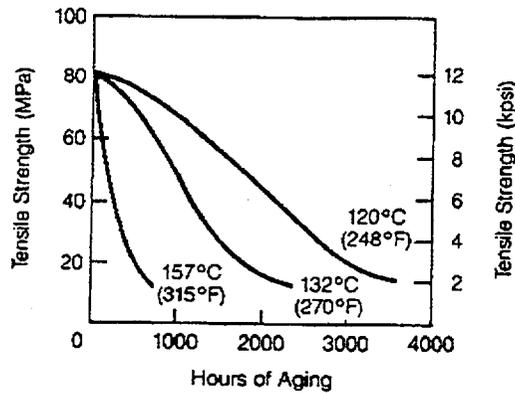


Figure 4 - Aging Data for Zytel [4]

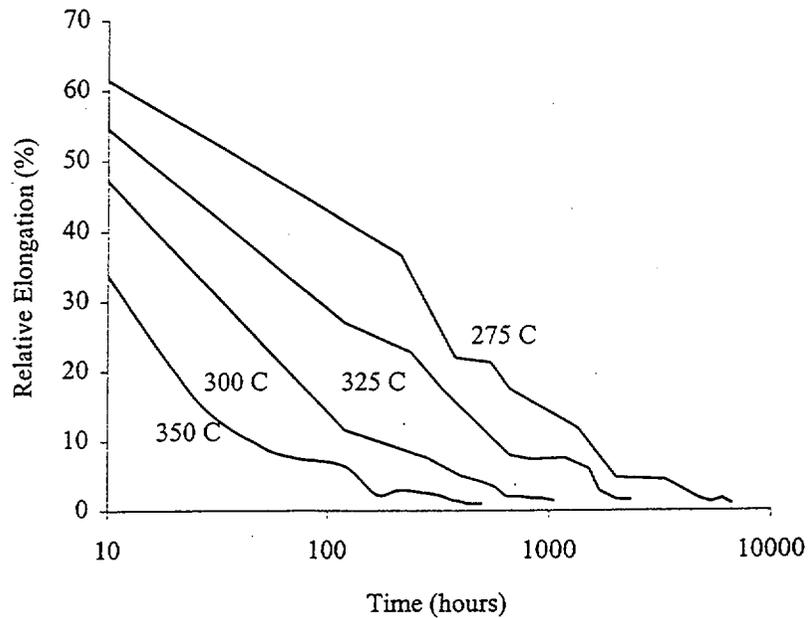


Figure 5 - Aging Data for Kapton [25]

**Motors:** The motor qualification standard, IEEE 334 [26], specifies that thermal aging conditions should be based on the methods described in IEEE 117 [27], IEEE 275 [28], and IEEE 429 [29]. These three IEEE standards establish test methods for determining the thermal aging characteristics of AC motor insulating systems and defining their thermal class. The most common motor classes for nuclear power applications are Class B (130°C), Class F (155°C), and Class H (180°C). The standards require accelerated life testing to failure of 10 insulating system samples at each of at least three temperatures. Life calculations are based on regression analysis of the average failure times at each temperature. Recommended test temperatures for Class B range from 150°C to 200°C and for Class H from 200°C to 250°C. Figure 6 presents the life curve for a Reliance insulating system. The life curve is based on tests performed at 180°C, 200°C, and 220°C.

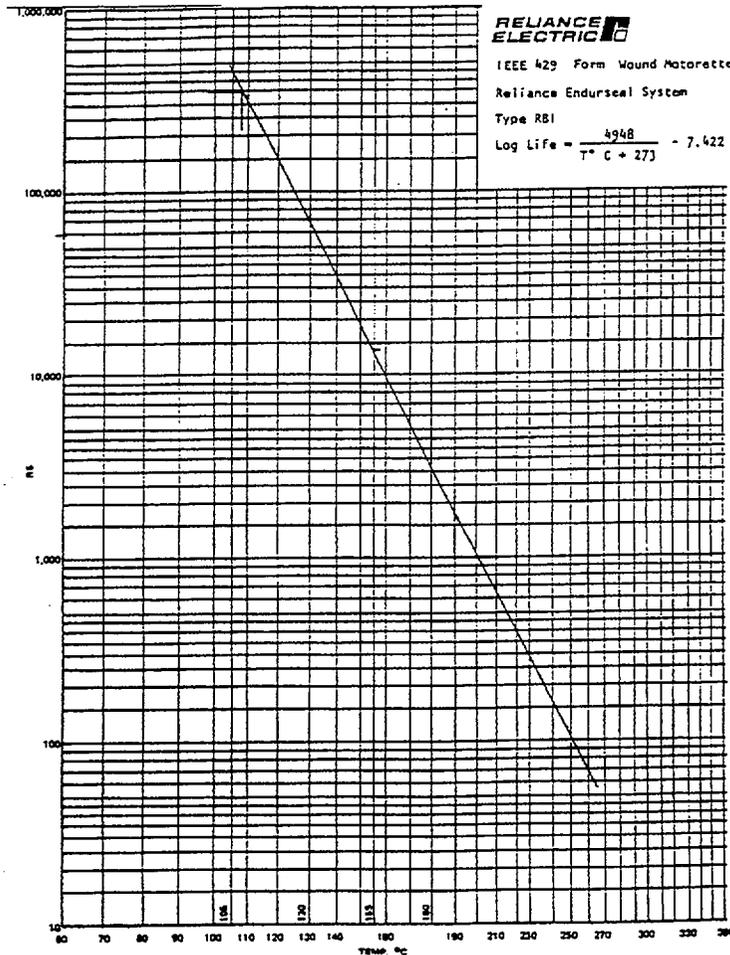


Figure 6 – Life Curve for a Typical Motor Insulating System [30]

6.1.2 Arrhenius for Varying Temperature Conditions

When the validity of the Arrhenius relationship is established for a particular material and temperature range, there are no fundamental theoretical or logical limitations to applying the model to varying temperature conditions within this temperature range. Referring to Eq. 7, a variety of time-temperature trajectories for  $C_A$  will produce the same end point condition whenever the time integrals of the instantaneous reaction rate equations result in concentration  $C_{A1}$ . In a similar manner the integration of instantaneous changes in material properties results in a final end point. Figure 7 depicts several such trajectories which could represent either a material property or a controlling molecular species concentration. Although the three thermal profiles differ, if Arrhenius is valid for the temperature range being evaluated, then the profiles will produce the same end point condition.

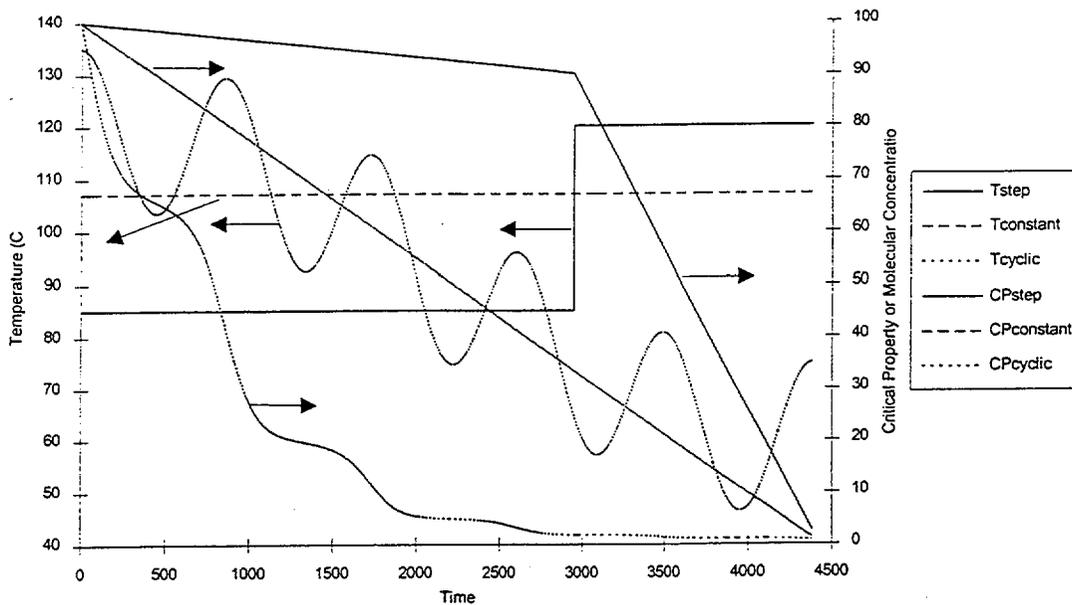


Figure 7 - Degradation Trajectories for Varying Temperatures

One practical limitation when evaluating varying temperature conditions is defining the material's thermal history. For slowly varying ambient temperature it is reasonable to assume the material is at thermal equilibrium at the ambient temperature. For rapidly changing external temperature conditions it may be difficult to define the temperature profile for certain component/material configurations. This may be particularly problematic where the component/material is somewhat insulated from the external environment. Under these conditions the material may not experience the thermal extremes for rapid cyclical ambient temperature changes. However, in cases where the material's temperature history can be reasonably characterized and other information supports Arrhenius behavior for the temperature range of interest, then the thermal history may be analyzed using Arrhenius to establish a reasonable estimate of accumulated thermal degradation.

Sandia for DOE performed an Arrhenius analysis of annual and daily temperature cycles to determine their effect on the temperature used during accelerated aging experiments. The results are contained in [31]. Obviously, the Sandia researchers recognized that Arrhenius could be applied to varying temperature conditions. Sandia's analysis concluded that cyclical temperature variations result in an "effective" temperature that was always higher than the mean (average) temperature. This "effective" temperature will vary with activation energy. Sandia concluded that accelerated aging test conditions should be based on this "effective" temperature rather than average temperature. Figure 8 from the report presents typical results for annual temperature variations of 15°C, several daily variations, and several mean temperatures for a range of activation energies ( $\Delta E$ ). In the figure  $\Delta T_{(eff. - mean)}^{\circ}C$  is the value which is added to the mean temperature to establish the "effective" temperature.

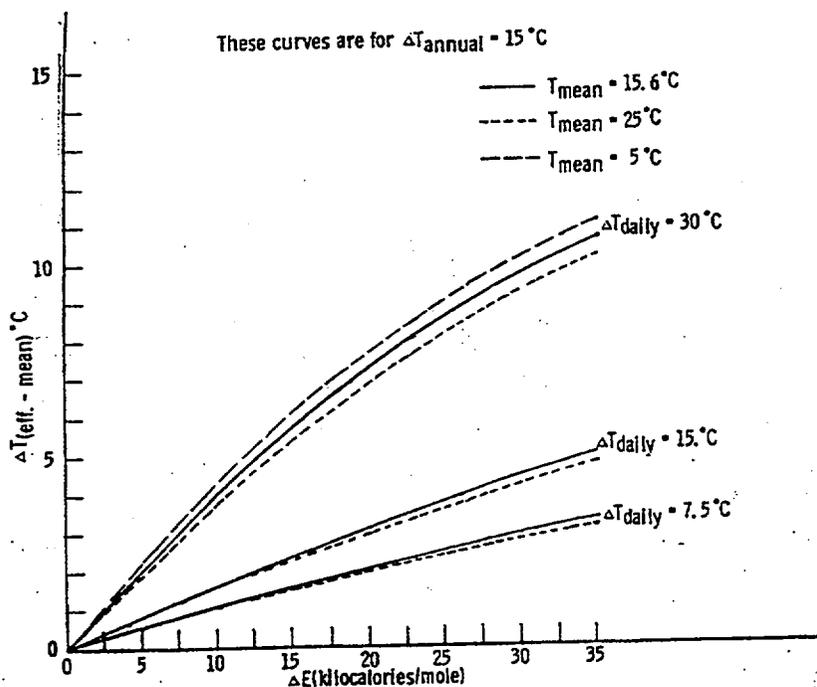


Figure 8 - Effective Temperature for Daily and Annual Temperature Cycles [31]

In summary, there are no theoretical or logical bases which limit the use of Arrhenius to constant temperature conditions. The Arrhenius relationship may be used to analyze the cumulative impact of varying temperature on the thermal degradation of any material properties exhibiting Arrhenius behavior. For slowly changing conditions (quasi-equilibrium) ambient temperature is a reasonable representation of material temperature. For more rapidly changing (i.e., transient) conditions ambient temperature may not represent component/material temperatures and analytical errors may be introduced. The significance of using ambient temperatures during transients is evaluated in Section 6.2.3.

**6.1.3 Activation Energy at Accident Conditions:** The NRC may be concerned that the activation energy values used for accelerated thermal aging may be inappropriate at the higher temperatures encountered during LOCA transients (e.g., 250°F to 400°F). Concerns may include possible variations in activation energy at these high temperatures and extrapolation through material phase transition regions.

Most industrial (non-nuclear) efforts to accelerate thermal degradation are focused on predicting long term conditions with short term testing. By their very nature these efforts use data from tests with durations ranging from weeks to a year, or more, to extrapolate long term performance. Most questions regarding the accuracy of these extrapolations involve the amount of extrapolation and associated statistical uncertainties, morphological changes (e.g., amorphous vs. semicrystalline) and changes in the dominant thermally-activated degradation reaction. None of these concerns should exist when

Arrhenius is applied to accident conditions since accident temperatures are typically within the temperature range used in the accelerated aging experiments used to define material activation energy values. See, for example, the test temperatures used in Figures 2 through 6. These test temperatures are representative of the temperatures occurring during most LOCA qualification tests. The LOCA test temperatures typically range from peak values of 300°F - 400°F (150°C - 200°C) down to post-transient values of 200°F - 250°F (100°C - 121°C).

According to DuPont Literature, thermal aging experiments for Kapton, a polyimide and one of the most thermally-resistant polymers, are performed at 250°C - 450°C [32]. Comparatively, aging experiments for Neoprene, a chloroprene and one of the least thermally-resistant elastomers used in nuclear applications, are typically performed at 90°C - 150°C [33]. The aging experiments for other polymers generally fall between these two ranges. Since the test temperatures for these and other materials span the temperatures encountered during accident simulations, Arrhenius analysis of accident temperatures involves either data interpolated or minor extrapolation. Consequently, concerns associated with large accelerations and data extrapolations do not exist when analyzing accident temperatures. In summary, there is strong evidence that the activation energy values used for thermal aging are appropriate at typical accident temperatures.

*6.1.4 Changing Activation Energy:* The NRC has expressed concerns with the potential for activation energy changes during the accident exposure. This apparently includes a concern about potential material phase changes.

Historically, in the context of accelerated aging, concerns about phase transitions have focused on data extrapolations across phase transition boundaries. For thermoplastics, melt temperature defines the boundary between solid and liquid phases. For some crosslinked elastomeric-type materials, the crystalline melt temperature is often cited as the boundary between regions with potentially different thermal age relationships. As noted above in 6.1.3, interpolations or minor extrapolations are involved when applying thermal aging activation energy values at accident temperatures. This minimizes the potential for and significance of data extrapolations across phase transition boundaries.

The NRC may also be concerned that activation energy values change during the accident exposure as a result of cumulative degradation. This is analogous to changes in activation energy resulting from differences in the end point criterion (e.g., activation energy values may differ at 60% and 5% retention-of-elongation). Accident analyses using Arrhenius could be nonconservative if a material's activation energy value significantly decreases with increasing levels of degradation.

Sandia's Ken Gillen, among others, has argued that Arrhenius is most justified when the thermal degradation curves at various temperatures can be superposed (i.e., shifted in time) using a constant shift value (i.e., activation energy) [34, 35]. See for example Figure 9. For those material properties exhibiting Arrhenius behavior (e.g., elongation-

at-break) it is most common to find reasonable time-temperature superposition of the degradation curves using a representative activation energy value. A review of traditional aging test elongation data for several materials suggests that activation energy values sometimes change slightly based on degradation level. These variations may be based on experimental uncertainties or variations in the relationship between the macroscopic properties and thermal deterioration. Whatever the mechanism, in those cases where the activation values changed they tended to increase rather than decrease with increasing degradation level. For example, the activation energy values associated with the Raychem WCSF material depicted in Figure 3 progressively increase from 1.28 eV at 50% elongation to 1.34 eV at 20% elongation. Since such activation energy changes are in the conservative direction, it suggests there should not be a concern about material activation energies at the latter stages of the accident exposure being significantly lower than pre-accident values.

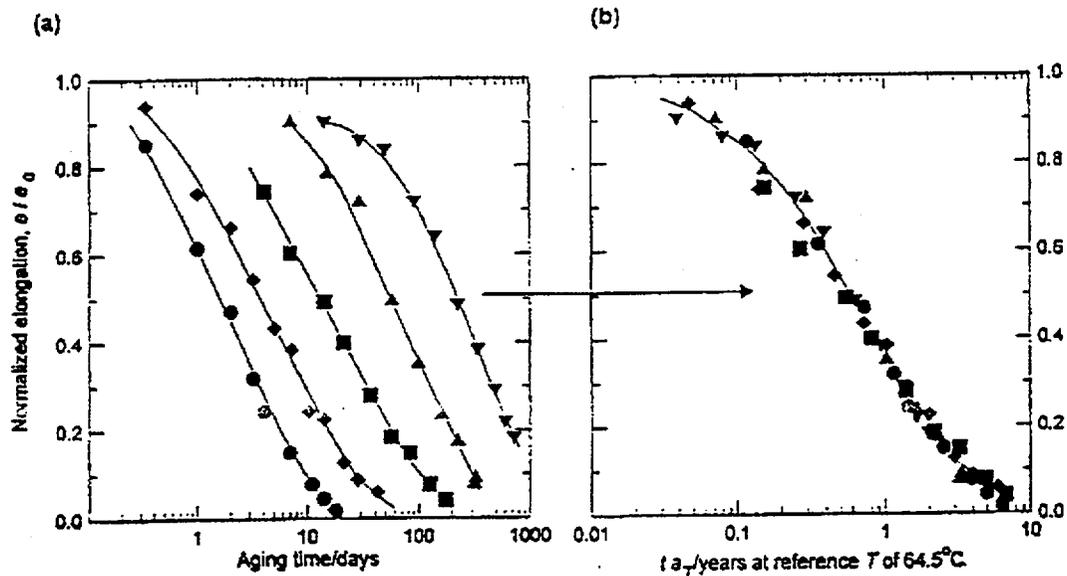


Fig. 2 (a) Normalized ultimate tensile elongation (the ultimate tensile elongation  $e$  divided by the unaged ultimate tensile elongation  $e_0$ ) results for a nitrile rubber as a function of time at 125°C (●), 111°C (◆), 95°C (■), 80°C (▲) and 64.5°C (▼). (b) Empirical time-temperature superposition of the data from (a) using a reference temperature of 64.5°C (associated values of the shift factors  $a_T$  are shown as triangles in Fig. 3). This figure is based on a modified version of work previously published in Ref. 25.

Figure 9 - Superposition of Elongation Data [35]

**6.1.5 Activation Energy During Steam Conditions:** There have been questions regarding the applicability of thermal aging-based activation energies to steam or high humidity environments. Thermal aging activation energy values are generally based on dry air tests but during accident simulations the devices are exposed to high humidity, steam conditions.

Many types of qualified devices are sealed to prevent steam intrusion into sensitive internals. These devices include most instrument detectors (e.g., electronic transmitters, RTDs, accelerometers, instrument switches, transducers, and RTDs), limit switches, certain MOVs (Rotorque), and some solenoid operated valves (SOVs). For devices such

as these whose internals remain isolated from the steam environment, thermal aging based activation energy values have direct applicability.

The remaining devices with organic components exposed to steam conditions include cables, certain motors, most motorized valve actuators (MOVs), some SOVs, terminal blocks and many types of terminations (splices and connectors). Since the materials used in these devices are selected to be hydrolytically stable, degradation rates under high humidity steam and dry air conditions are not expected to differ significantly. Little data are available to directly correlate high humidity/steam and dry air degradation for most materials. However, available information indicates it is reasonable to use thermal aging based activation energy values when performing Arrhenius analysis of accident conditions. The follow discussion of three research reports provides supporting information.

NUREG/CR-2763 [36]: During the research reported in NUREG/CR-2763 Sandia studied the possible use of air oven tests as a screening tool to determine performance during LOCA steam conditions. Sandia compared the elongation values for numerous cable materials after two simulated accident exposures. The first was a 96 hour, 145°C thermal aging oven exposure. The second was a 96 hour, 145°C steam exposure in a LOCA test chamber. Material test samples included both unaged and preaged materials. The post-test results extracted from the NUREG are presented in Table 1.<sup>2</sup> Based on this data Sandia concluded that the "air oven" and "LOCA steam" test results correlated well.

SAND92-1404C [37]: This Sandia paper is a collaboration between two Sandia researchers in fire safety and equipment qualification. They compare the cable thermal damageability data developed during the fire test program and the equipment qualification test program and conclude that a direct correlation exists between the program results. The fire safety program tests involved exposure of unaged and aged cables to the high temperature hot air conditions encountered in locations shielded from the direct effects of a fire. As part of the EQ program, samples previously aged to the equivalent of 20 years and then exposed to a LOCA simulation where subsequently exposed to high temperature superheated steam conditions. Sandia concludes for the two evaluated cable styles (Neoprene jacketed, XLPE insulated and Hypalon jacketed, EPR insulated) that the damage threshold for the two exposures (i.e., hot air and superheated steam) correlated quite well and the principal damage mechanism involved thermal degradation.

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<sup>2</sup> The same data are presented as Table 5.10 in NUREG/CR-6384, the Brookhaven National Labs summary of EQ Literature.

Table 1  
Sandia Comparison of Air Oven and LOCA Steam Derived Elongation Values

Material	Preaging	relative elongation (%)	
		Air Oven	LOCA Steam
EPR	Unaged	77	89
	24 hrs. - 21 Mrad & 44°C	49	38
	50.5 hrs. - 45 Mrad & 44°C	12	17
	958 hrs. - 23 Mrad & 26°C	14	12
CLPE	Unaged	65	68
	50.5 hrs. - 45 Mrad & 44°C	5	42
	622 hrs. - 14 Mrad & 26°C	56	53
CLPO	Unaged	79	98
	24 hrs. - 21 Mrad & 44°C	33	70
Tefzel	Unaged	92	102
	958 hrs. - 23 Mrad & 26°C	0	4
Silicone	Unaged	93	96
	24 hrs. - 21 Mrad & 44°C	24	38
	958 hrs. - 23 Mrad & 26°C	17	36
	50.5 hrs. - 45 Mrad & 44°C	24	49
	958 hrs. - 23 Mrad & 26°C	26	72
CSPE	Unaged	40	74
	24 hrs. - 21 Mrad & 44°C	27	61
	50.5 hrs. - 45 Mrad & 44°C	19	48
	958 hrs. - 23 Mrad & 26°C	15	58
PVC	Unaged	57	53
	24 hrs. - 21 Mrad & 44°C	18	9
	958 hrs. - 23 Mrad & 26°C	4	3
CP	Unaged	1	5
	24 hrs. - 21 Mrad & 44°C	1	3

JAERI-M88-178 [38]: This report summarizes the results of Japanese Atomic Energy Research Institute (JAERI) research on cable qualification methodologies. In one series of experiments typical cable materials, some pre-irradiated to 150 Mrad, were exposed to saturated steam conditions for 11 days at 120°C, 140°C, or 160°C to determine the effect of different saturated steam conditions on material degradation. Samples were periodically removed from the test chambers and subjected to mechanical, electrical, and weight change tests. Some of the steam tests included air; others did not. Figures 10 through 12, extracted from the report, present representative elongation, electrical and weight change results for three materials irradiated to 150 Mrad prior to the steam exposures. For these EPR (EPR3), Hypalon (CSM1), and silicone (SIR1) materials,

several observations can be made. First, the relative degradation for the steam exposures with and without air are not significantly different.<sup>3</sup> Secondly, the degradation curves have a similar shape to air oven aging elongation degradation curves often used to establish the activation energy for cable materials. See, for example, Figures 2 and 3. Thirdly, if the 120°C and 140°C, 264 hour values in these figures are shifted using Arrhenius and typical thermal aging-based activation energies (1.0 - 1.3 eV), they reasonably correlate with the 140°C and 160°C results. In all three figures, the 120°C and 140°C, 264 hour values shifted to 160°C have been superimposed as solid rectangles.<sup>4</sup> The 120°C, 264 hour values shifted to 140°C have been superimposed as hollow rectangles on the three figures. Although significant experimental uncertainties can exist and shifting of all parameters for all materials should not be expected even under oven aging conditions, this information supports a conclusion that Arrhenius analysis of steam testing data using thermally-based activation energy values is justified. This is consistent with the guidance of IEEE 317-83 which recommends using thermal aging-based values when performing PAOT calculations.

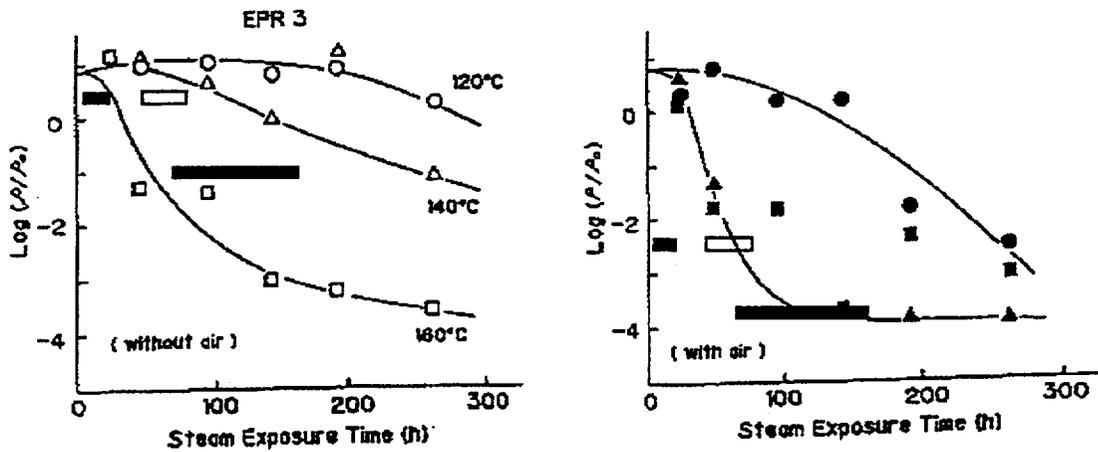


Fig.178 Effect of steam temperature on volume resistivity of EPR3 (1.5MGy at 10KGy/h) under simulated LOCA environment.

Figure 10 - JAERI EPR3 (EPR) Test Results

<sup>3</sup> This is not true for all material properties. Sandia, among others, has observed differences in certain physical properties as a result of LOCA simulations with and without air. In the EQ Risk Scoping Study, Sandia concluded that this was not a risk significant qualification concern.

<sup>4</sup> The rectangles' length reflect shift variations for the activation energy range (1 - 1.3 eV). Their width has no numerical basis (for presentation purposes only).

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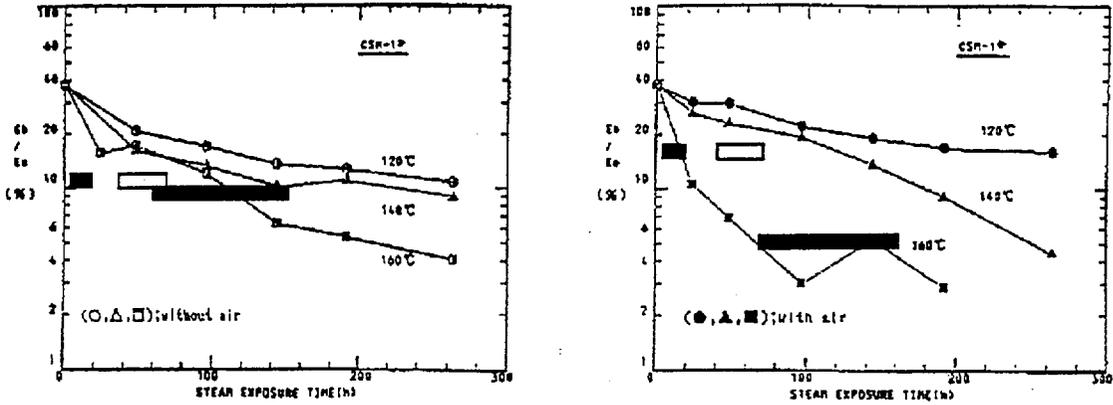


Fig.160 Effect of steam temperature on mechanical properties of CSK1 (1.5MGy at 10KGy/h) under simulated LOCA environment.

Figure 11 - JAERI CSM1 (Hypalon) Test Results

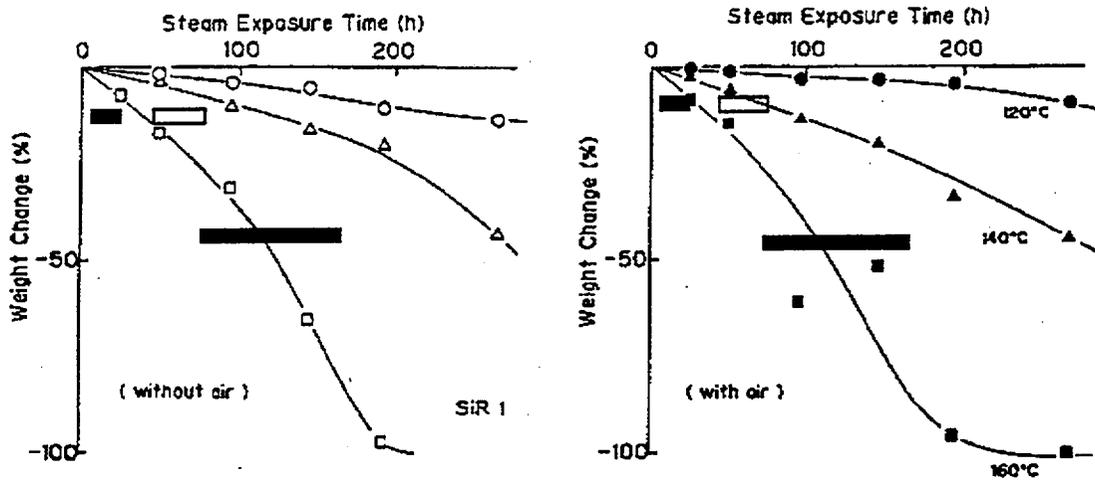


Fig.192 Effect of steam temperature on water sorption of SIR1 (1.5MGy at 10KGy/h) under simulated LOCA environment.

Figure 12 - JAERI SIR1 (Silicone) Test Results

## 6.2 Post-Accident Operating Time

This section addresses the use of Arrhenius to establish post-accident operating times (PAOT) that are longer than the duration of the EQ test. For example, a utility may use Arrhenius analysis of a 30 day LOCA test to establish operability for a 180 day required operating time. In order for this PAOT analysis to be applied, LOCA test profile temperatures must exceed the required plant-specific temperatures for some extended period of time during the accident simulation. Typically, only the steady-state, post-transient portions of the test and plant-specific profiles are analyzed. However, other methods have been used. The potential issues related to the use of Arrhenius for PAOT calculations are: (1) significance of other degradation mechanisms, (2) self-heating considerations, and (3) use of the initial transient period.

*Degradation equivalency analysis* is a term commonly used in the industry to describe the use of Arrhenius to evaluate the relative cumulative degradation from two thermal profiles. Typically one of the profiles is the qualification test profile and the other is the plant-specific required profile. The methodology involves using Arrhenius and an appropriate activation energy value, typically the same value used to calculate qualified life, to calculate cumulative degradation times at some baseline temperature (e.g., 100°C) for both thermal profiles. Since closed form integral solutions are not available, licensees typically divide each of the temperature profiles into a number of discrete time intervals, conservatively assume a constant temperature during each interval, shift the interval durations using Arrhenius to the baseline temperature, and sum the shifted durations over the entire profile. More severe thermal degradation occurs for the profile with the longer duration at the baseline temperature.

A variety of acceptable methods have been implemented by licensees for using *degradation equivalency analysis* to establish PAOT durations. The most common approach is to use only the post-transient portions of the accident test and plant-specific profiles in the analysis. Using the temperatures during these relatively stable post-transient periods simplifies the analysis and eliminates the need to consider transient temperature effects and other considerations that otherwise might complicate the analysis if the transient portions were included. However, PAOT calculations which have considered the entire plant-specific and test profiles have been performed. These results have been accepted when they demonstrate adequate margin between the required and calculated operating. As discussed in Section 6.2.3, analyses were performed to determine the significance of including the transient portion of the profiles in PAOT calculations. The results indicate that degradation equivalency analysis errors for typical equipment and profile conditions are generally less than 10% and should not exceed 15% for limiting equipment and profile conditions. This error magnitude is considered insignificant, given the margins and conservatism inherent in the qualification process and the lack of risk significance for long-term operability.

*6.2.1 Other Degradation Mechanisms:* It has been suggested that significant degradation mechanisms, other than thermal, may occur during long-term steam/humidity exposures and are not explicitly considered when using the Arrhenius methodology. Other degradation mechanisms, if they exist, during sequential-type, steam test simulations, are either pressure-related or moisture-related. Both are discussed in this section. Based on the information presented below, it is concluded that such mechanisms are not significant during the post-transient period. Potential failures, if any, due to these mechanisms should be exhibited during the initial portions of accident tests and their long term effects, if any, are considered to be secondary in importance to thermally-induced degradation. As discussed below, such effects are accelerated in the post-accident period by increasing accident simulation temperatures. This further supports the use of Arrhenius as a method to analyze post accident operating times.

Pressure-related degradation mechanisms involve either crushing of enclosures or leakage/diffusion of the external environment through seals or gaskets. The ability of enclosures to tolerate differential pressures is established during the high temperature, high pressure transient conditions. Since pressure during the post-transient period is significantly lower than during the accident transients, physical failures related to pressure do not occur during the post-transient period. Similarly, adverse leakage effects, if any, would become evident during the higher pressure transient period. Importantly, EQ testing experience indicates that pressure-related failures do not typically occur during the post-transient period. Finally, we note that during the post-transient period test chambers are typically maintained at saturation pressure and temperature. Since saturation pressure is exponentially related to temperature, leakage and other mechanisms that are proportional to differential pressure would be accelerated by the higher pressure conditions. Figure 13 illustrates the saturation pressure-temperature relationship when plotted in Arrhenius form (i.e., log of pressure vs. the inverse of absolute temperature). This indicates that cumulative pressure-related degradation, if any, is accelerated in Arrhenius fashion if the degradation is proportional to pressure. Moisture diffusion through polymers is proportional to the partial pressure differential across the polymer [39]. Similarly, compressible fluid (e.g., steam and air) leakage around seals/gaskets or through cracks is typically proportional to differential pressure [40]. Both these mechanisms would be accelerated by higher saturated steam temperatures. In summary, we conclude that pressure alone is not a significant degradation mechanism during the post-transient period. However, pressure-related degradation mechanisms, if any, would be accelerated by increasing temperature, since saturated conditions are typically maintained during the post-transient test phase.

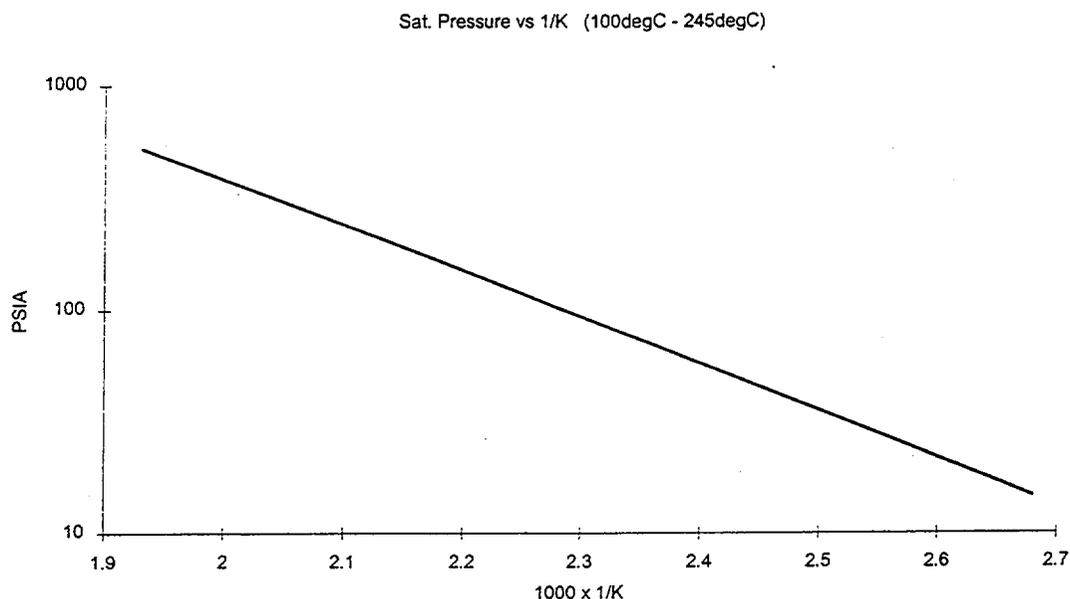


Figure 13 - Saturation Pressure vs. Inverse Absolute Temperature

Moisture-related effects potentially include *corrosion*, *polymer hydrolysis* (i.e., chemical degradation due to moisture exposure), or *combined moisture/electrical degradation* (e.g., wetting of terminal block surfaces or insulation cracks combined with electrical tracking). *Corrosion and hydrolysis* are not typically mechanisms involved in LOCA test failures since equipment manufacturers select materials that are resistant to these forms of degradation. For example, critical polymers used in EQ equipment (e.g., XLPE, EPR, silicone, epoxy, phenolic, melamine) are hydrolytically stable.

Regarding *corrosion and hydrolysis*, both are chemical reactions accelerated by temperature. These mechanisms are often amenable to Arrhenius analysis provided other important factors, such as relative humidity, remain constant. Sandia in [34], illustrates that the hydrolytic degradation of a polyurethane potting material is properly described by Arrhenius if the analysis considers relative humidity conditions.<sup>5</sup> Figure 14 from [34] is the Arrhenius plot. The resulting activation energy, 21 kcal/mole (0.91 eV), is similar to published oven thermal aging values for polyurethane.<sup>6</sup> Although hydrolysis of materials used in EQ equipment is not considered a significant degradation mechanism during LOCA simulations, this example illustrates that such a mechanism, if present, would be accelerated by the higher temperature.

<sup>5</sup> Because of their hydrolytic instability most urethane compounds are not used in EQ equipment applications.

<sup>6</sup> See for example, EPRI EQ Reference Manual Table A7.1, Summary of Activation Energy Ranges.

Corrosion involves oxidation-reduction reactions whose rates are temperature dependent and increase with temperature in Arrhenius-like fashion. Like hydrolysis, corrosion is not considered a significant degradation mechanism during accident simulations since metals (other than protective enclosure) are either protected from exposure to the steam environment or selected to be non-corrosive under accident conditions. In summary, we conclude that *corrosion and hydrolysis* are not significant degradation mechanisms during the post-transient period. However, such mechanisms would be accelerated by the increasing saturation temperatures during the post-transient test phase.

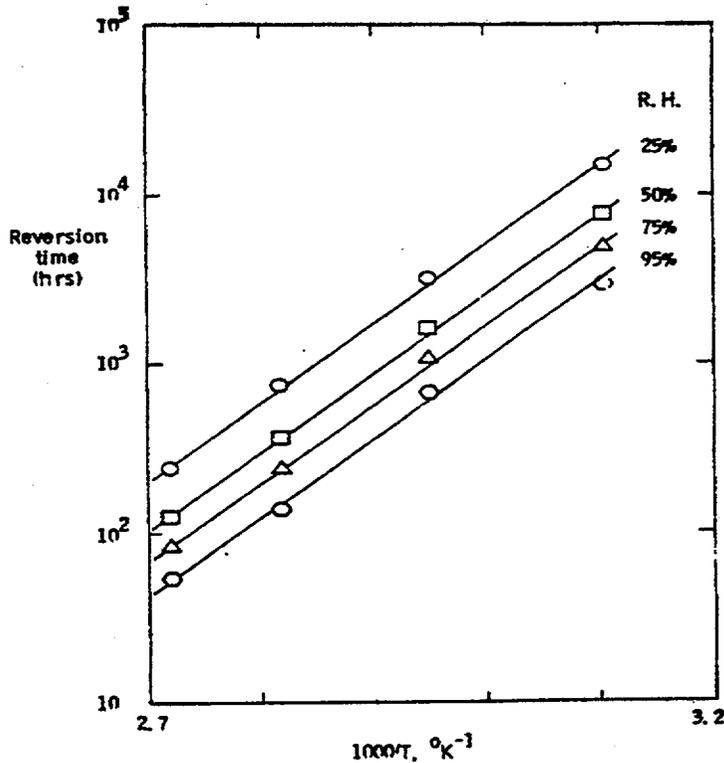


Figure 14 - Polyurethane Arrhenius Plot at Varying Relative Humidity

The last mechanism, *combined moisture/electrical degradation*, is also not considered significant during extended operation in the post-transient period since it is accelerated by more severe, shorter duration tests. Degradation effects either manifest themselves during the initial accident transient or are accelerated by increasing temperature during the post-transient test phase. Potential *combined moisture/electrical degradation* effects can be conceptually divided into those affecting *bulk insulating* properties, for devices such as cables, and those affecting *surface insulating* devices, such as terminal blocks.

For cables, splices, and similar electrical insulators whose performance is based on bulk insulating properties, moisture can affect performance in two ways, moisture penetration and physical damage. Moisture penetration into the insulation layers may produce degradation in certain bulk electrical characteristics (e.g., decreasing insulation resistance). Moisture/steam penetration is driven by temperature, pressure, and material

permeation characteristics. Polymer permeation values follow an Arrhenius relationship with temperature. As previously noted, saturation pressure also exhibits an Arrhenius-like temperature relationship. Because of both these temperature effects, elastomers become saturated with moisture during the high temperature, high pressure, transient portions of accident test profiles. Additional moisture permeation into these polymers is not expected during the lower temperature, lower pressure, post-transient period unless the materials experience physical damage (e.g., splitting or cracking). Such physical damage, if any, would be due to mechanisms (such as embrittlement or moisture-induced swelling) which are accelerated by high temperature, high pressure conditions during the test exposure. Consequently, *combined moisture/electrical degradation* effects on bulk insulating properties are exhibited during the more severe portions of the LOCA test and are not considered significant during the post-transient period. However, such effects are accelerated by higher saturation test temperatures during the post-transient period.

The second *combined moisture/electrical degradation* mechanism group involves devices with electrical insulating surfaces (e.g., terminal blocks). Surface moisture in combination with voltage can generate surface leakage currents and tracking which can lead to progressive surface degradation and, ultimately, failure. Sandia in [41] and [42] demonstrated that terminal block leakage currents have a significant temperature dependence (i.e., increasing with temperature) under saturated steam conditions. Consequently, surface degradation due to leakage currents is accelerated by higher temperatures. NUREG/CR-1682 [42] suggested this behavior can be described by Arrhenius. Figure 15 from the NUREG plots failure probability vs. the inverse of absolute temperature.

Sandia in [41] observed that equipment residual heat during cooldown can keep the insulating surface slightly above saturation which minimizes tracking due to surface moisture. This beneficial effect, should be more effective during progressively decreasing accident conditions than during qualification tests which typically employ several constant temperature plateaus connected by rapid temperature transitions.

In summary *combined moisture/electrical degradation* effects are accelerated by higher temperature conditions and are adequately simulated by more severe, shorter duration tests.

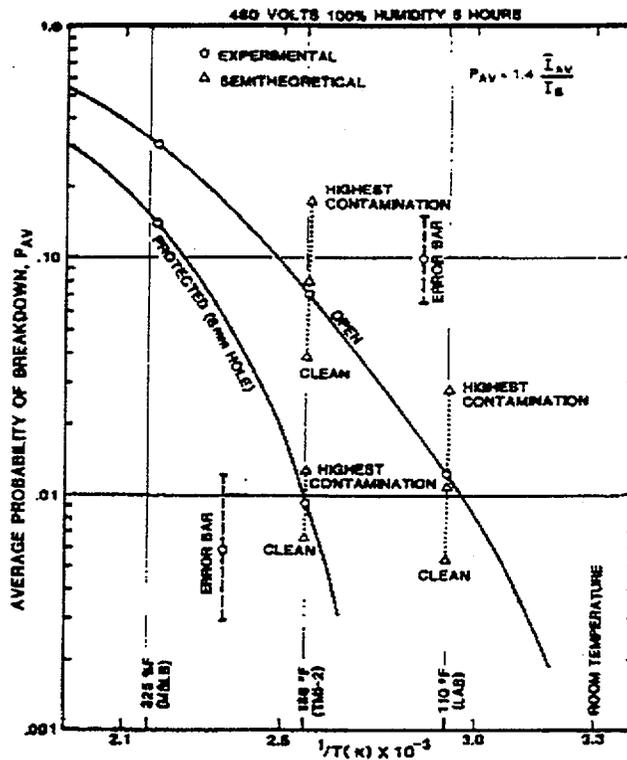


Figure 15 - Terminal Block Leakage Current vs. Steam Temperature [42]

**6.2.2 Self-Heating Effects:** When performing PAOT calculations self-heating effects must be considered. It is common licensee practice to consider such effects. For devices with little or no self-heating, device and ambient temperatures should be similar during the prolonged post-transient LOCA period. Consequently, Arrhenius PAOT analysis is easily performed using the test and plant-specific profiles. For continuously energized devices, self-heating effects are considered by performing the Arrhenius analysis using device temperatures (i.e., ambient + self heating) rather than profile temperatures. Alternatively, in cases where the test specimen was adequately energized/loaded during the LOCA simulation, analysis based on profile temperatures is justified.

**6.2.3 Transient Analysis Considerations:** Arrhenius analysis of the transient portion of the accident simulation and plant-specific profiles are technically justified if uncertainties when estimating component/material temperatures during rapidly changing ambient temperatures are adequately considered. Due to thermal lag, device surface and internal temperatures will differ from ambient temperatures during transient conditions. Consequently, analysis errors can be introduced if ambient temperatures are used in lieu of component/material temperatures during Arrhenius analysis of the transient. Based on the test data and model results discussed below, such errors are relatively insignificant. In summary, transient temperature data from various steam tests with different devices, including large motors and containment penetrations, indicate that most devices will achieve thermal equilibrium with the test environment within a relatively short time.

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Even for the more limiting profiles and devices the time to equilibrium should be less than 3 hours. For the vast majority of devices and profiles equilibrium should occur much faster (within 30 to 60 minutes). Simulations indicate that degradation equivalency analysis errors for typical equipment and profile conditions are typically less than 10% and should not exceed 15% for limiting equipment and profile conditions. This error magnitude is considered insignificant, given the margins and conservatism inherent in the qualification process and the lack of risk significance for long-term operability.

Although device surface and internal temperatures will differ from ambient temperatures during transient conditions, critical component/material temperatures are not normally measured during accident qualification tests. Heat transfer calculations (i.e., thermal lag analysis) can be performed but are often difficult to accurately implement due to a variety of heat transfer modes and mechanisms (e.g., conduction, forced and natural convection, condensing) and complex device geometry. Analysis complexities include differences in superheat and saturated steam heat transfer rates.

Several factors suggest that Arrhenius analysis using transient ambient temperatures in lieu of device/material temperatures may not introduce significant errors. First, since most devices heat up rather quickly to saturation temperature during the initial transient steam conditions, it is reasonable to assume that component temperatures approach equilibrium ambient temperature after a relatively short time period. Secondly, any Arrhenius analysis errors occurring during transient heat-up (when component/material temperatures are less than ambient) may be compensated by complementary errors during transient cooldown (when component/material temperatures are greater than ambient).

Most qualification and research accident tests have not monitored device temperatures. However, some data are available demonstrating rapid equipment heat-up rates to saturation temperature. Figures 16, 17, 18 and 20 present data from several tests.

Figure 16 presents data extracted from [43]. The report describes a Limitorque test involving superheated steam conditions that were used to verify analytical models for predicting component thermal response under HELB conditions. Test Chamber, Limit Switch Compartment Housing, Motor Stator, and Limit Switch Surface temperatures were monitored by thermocouples. Also presented are Test Chamber Pressure and Estimated Saturation Temperature based on chamber pressure. The figure demonstrates rapid heat-up of the MOV components to saturation temperature in less than 300 seconds. Even the temperature of the relatively large stator winding inside the motor housing is at saturation temperature by this time. We note that Limit Switch Surface thermocouple temperature remains slightly suppressed during the initial period due to accumulation of subcooled condensate on the switch thermocouple. This erroneous reading rapidly recovers to saturation temperature when the condensate is removed during the depressurization at 250 seconds. The Limit Switch Compartment Housing temperature slowly departs from saturation temperature at approximately 180 seconds. This graphically illustrates the slower heat transfer mechanism occurring in the superheat temperature region. Even with this slower heat transfer, it appears that compartment

housing temperature would reach the 400°F superheat temperature within 10 - 15 minutes if this test chamber temperature had been maintained.

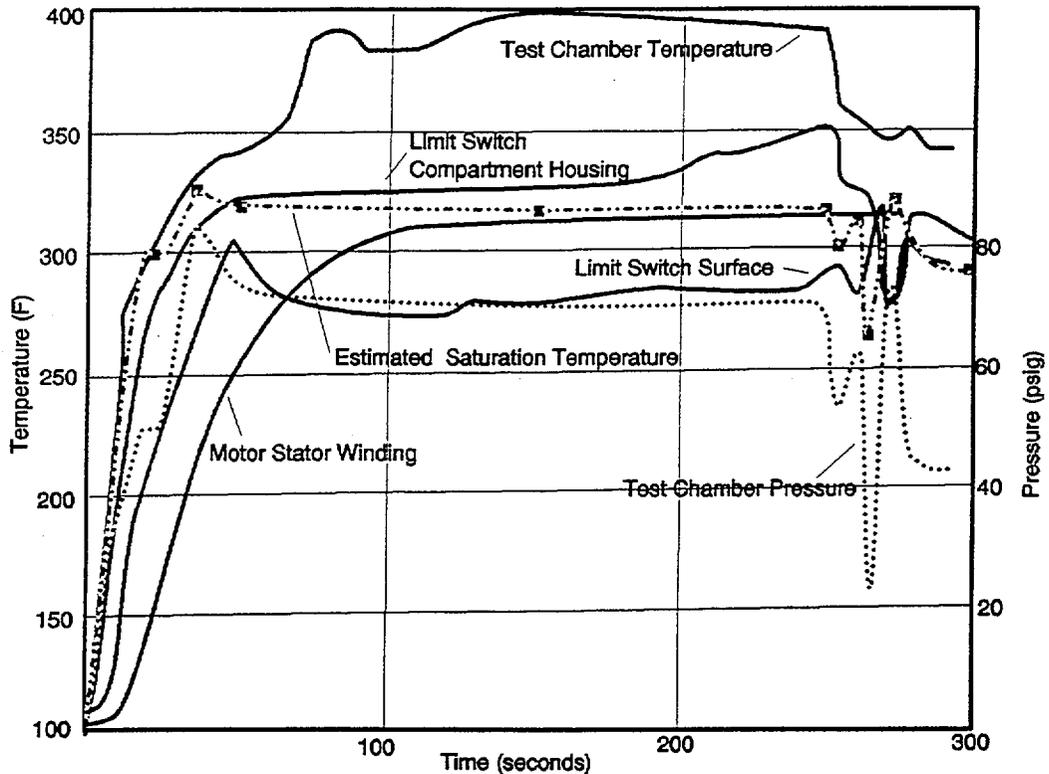


Figure 16 - Limitorque MOV Component Thermal Response

LOCA qualification testing of a 300HP, totally-enclosed AC motor is described in a Franklin Institute Research Laboratories test for General Electric [44]. Figure 17 presents the temperatures for three of the five 45 psig/280°F, 30 minute transients that were part of the accident simulation. Test chamber, motor winding, and upper and lower bearing temperatures were monitored by thermocouples. The monitored temperatures demonstrate the rapid thermal response of the winding and bearings. The winding and bearing temperature changes were affected by changing load conditions during the simulation transients. However, it appears that maximum component temperatures were achieved within the 30 minute transient. Conservatively, the windings and bearings on this massive, enclosed motor would have been at equilibrium within 1 hour.<sup>7</sup>

<sup>7</sup>

A typical 300 HP totally-enclosed motor weighs in excess of 2000 lbs.

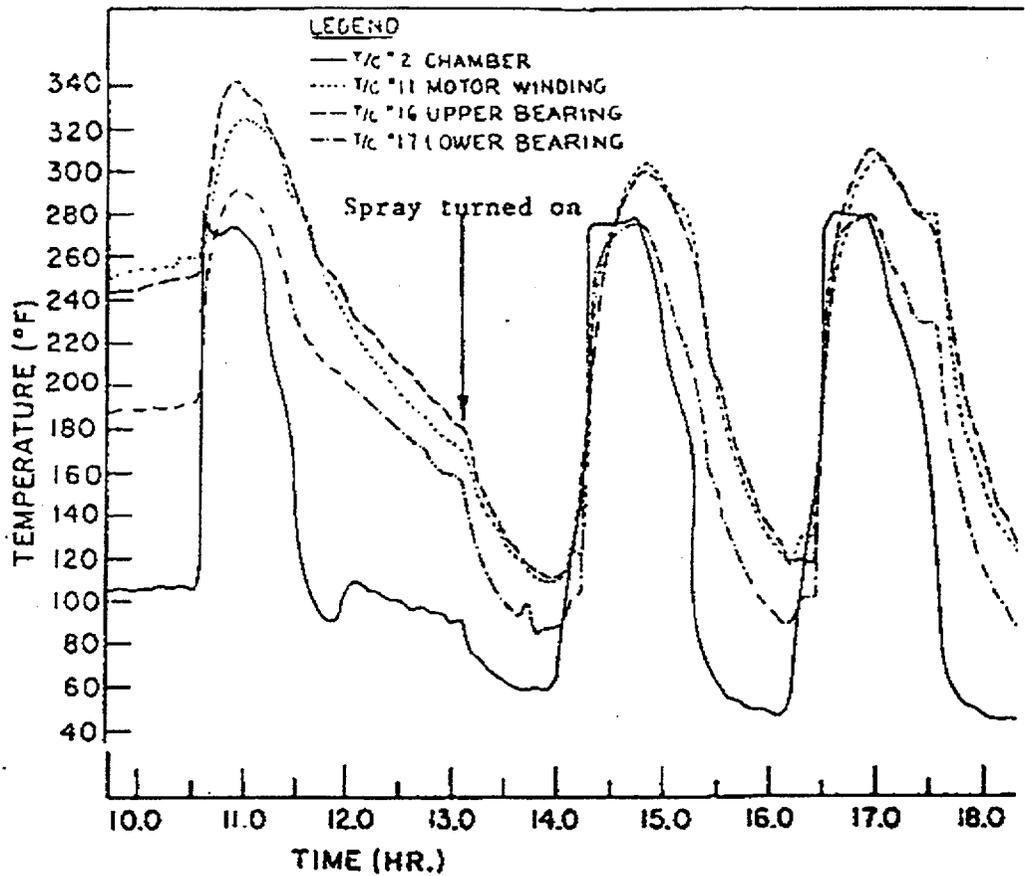


Figure 17 - GE 300 HP Motor Test Temperatures

Similar data are available from a recently completed Sandia connector and terminal block test program [45]. NUREG/CR-6412 describes LOCA testing of terminal blocks and connectors. Sandia has made available raw data for the test chamber and two terminal block (TB) enclosure thermocouples. Figure 18 presents temperature plots for average chamber temperature and the two TB enclosure air space temperatures (BoxTC1 and BoxTC2) during the initial portions of the accident simulation. Again, rapid heat-up to saturation conditions occurs within 10 minutes while roughly 2 - 3 hours are necessary to reach internal equilibrium at peak superheat temperatures. This illustrates the slower temperature changes in the superheat region. The air space temperature should be a reasonable approximation of device temperatures since both would achieve rapid heat-up to saturation conditions and conductive heat transfer from the enclosure to internally mounted devices would become significant when devices are in the superheat region.

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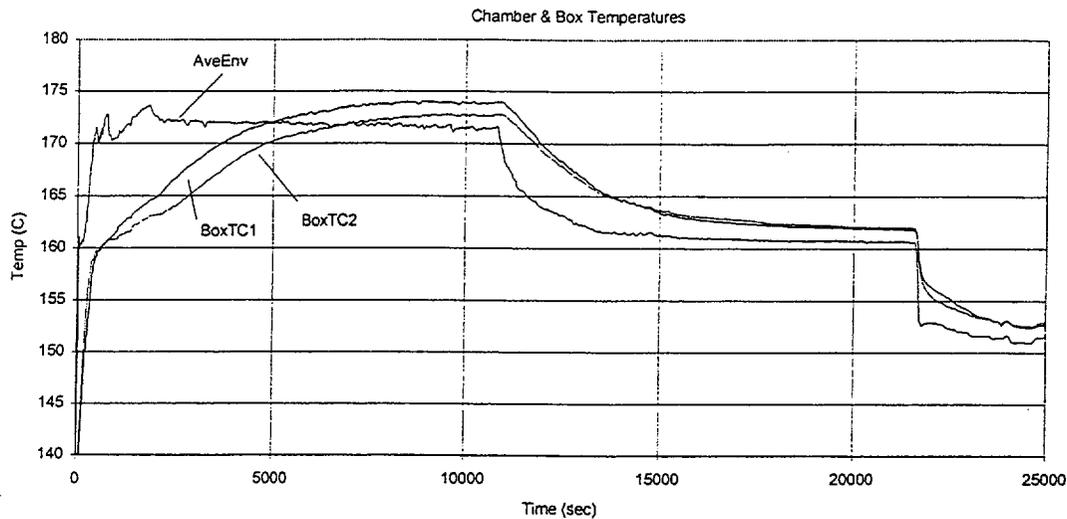


Figure 18 - Sandia Enclosure Thermal Response Data

Additional transient device temperature information during accident tests is available in [46]. The report includes data from testing of a Conax containment penetration design under severe accident conditions that included pressures ranging from 70 - 120 psig, an initial temperature of 550°F, and a prolonged peak temperature of 700°F. Figure 19 illustrates the test chamber and Conax test specimen arrangement. The penetration internals (over 8.5 ft. in length) and termination box were exposed to the accident simulation. The figure identifies the locations (A through K) of 11 thermocouples that were attached to penetration module #4. The temperature data are presented in Figure 20. Except for locations J and K which are outside the steam environment, all the thermocouples reached saturation temperature (~315°F) within 15 minutes (0.0104 days = 0.0312 - 0.0208 days). Subsequent temperature changes among the TCs reflect their relative isolation from the superheated condition. Stable, peak superheat temperatures are achieved within 3 - 4 hours. This severe accident testing contains extreme superheat conditions (over 350°F of superheat) that are not typical of design basis LOCA or MSLB conditions. Since the extreme superheat extends the time for reaching equilibrium temperatures, it is reasonable to assume 3 hours as a conservative upper time limit to reach equilibrium for typical LOCAs and MSLBs for virtually all inside containment equipment.

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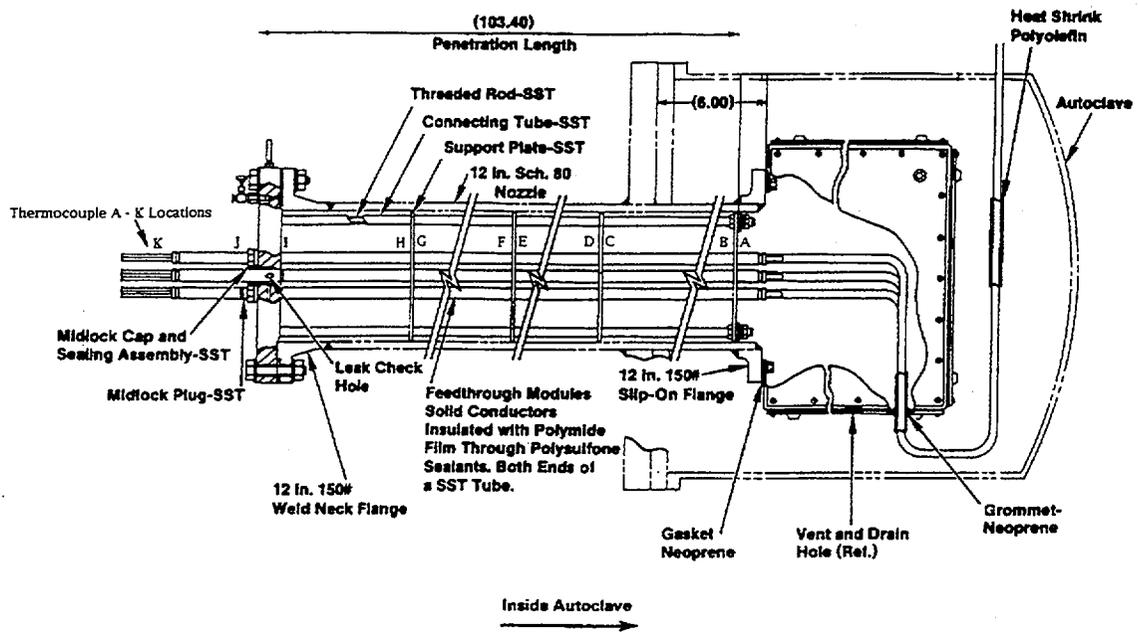
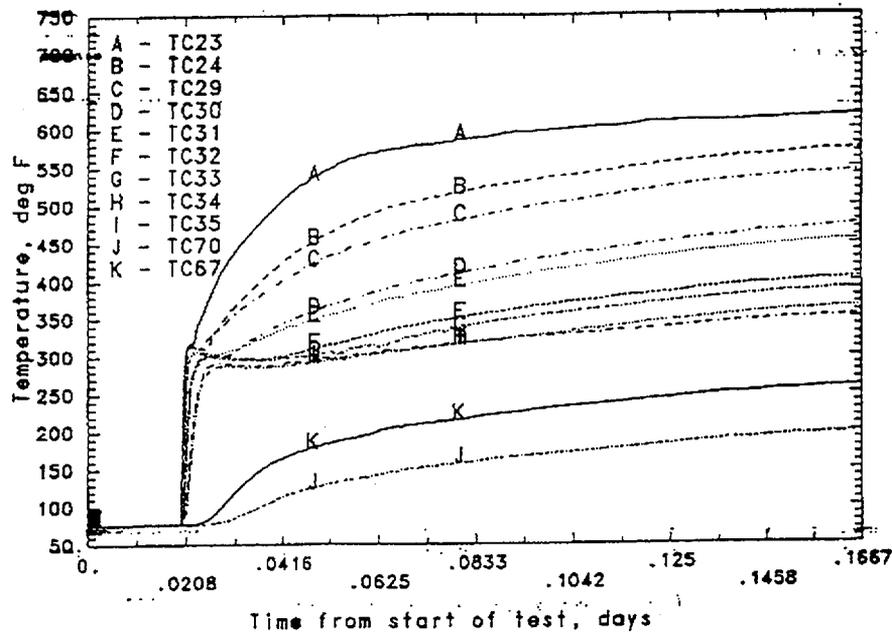
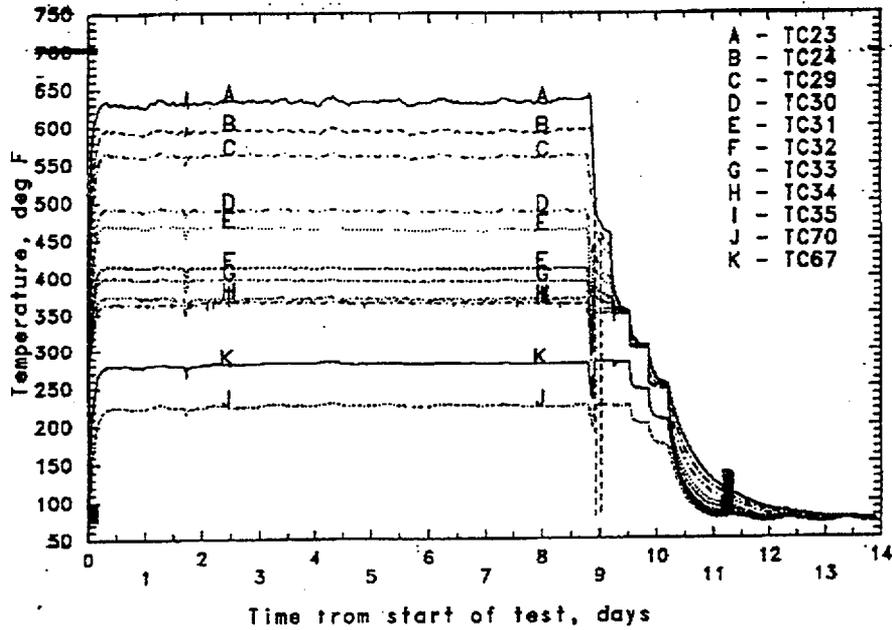


Figure 6-1 Conax EPA Design

Figure 19 - Chamber and Conax EPA Arrangement [46]



(a) First 4 Hours of SAC Test



(b) 10 day SAC Test and Cool-down  
Figure 6-21 Temperature Profile Along Module #4

Figure 20 - Temperature Data for Module No. 4 [46]

These four tests provide important data which can be used to qualitatively characterize the thermal response of devices/materials during transient portions of the accident. The data indicate a very rapid rise in device temperature up to saturation temperature during the initial transient. Within 30 minutes virtually all device temperatures should be at or near saturation temperature. Subsequent heat-up into the superheat region may require substantially longer times that vary based on the amount of superheat, device arrangement/geometry, and velocity of the superheated gas (i.e., forced convective heat transfer). However, the data suggest that stable conditions should exist within a few hours for a wide range of devices.

We have conducted a supplementary analysis of the NUREG/CR-6412 data to help quantify the error associated with using ambient temperatures during transient conditions. Degradation equivalency analysis using a base temperature of 100°C was performed for the average ambient temperature (AveEnv) and average terminal box temperature (AveBox). The average box temperature was reduced by less than 2°C to compensate for slight ohmic self-heating effects for the terminal blocks within the enclosure. Figure 21 illustrates these average temperatures during the initial test transients which terminate at 10 hours. Using these profiles degradation equivalency analyses were performed. Figure 22 presents the analysis results for two activation energy values (0.9 and 1.3 eV). The 0.9 values have been multiplied by 4 for presentation purposes. After approximately 36,000 sec. (10 hours) the difference between the AveEnv and AveBox cumulative times at 100°C is less than 10%. The cumulative time ratios of AveBox to AveEnv are 0.92 (3.26e3/3.53e3) for 1.3 eV and 0.95 (5.28e2/5.55e2) for 0.9 eV. Since environment and box temperatures should be equal for the remainder of the test, the cumulative time differences constant but become a smaller percentage of the total cumulative time. The cumulative time error at test completion (240 hours) is 6% for 1.3 eV and 2.5% for 0.9 eV.

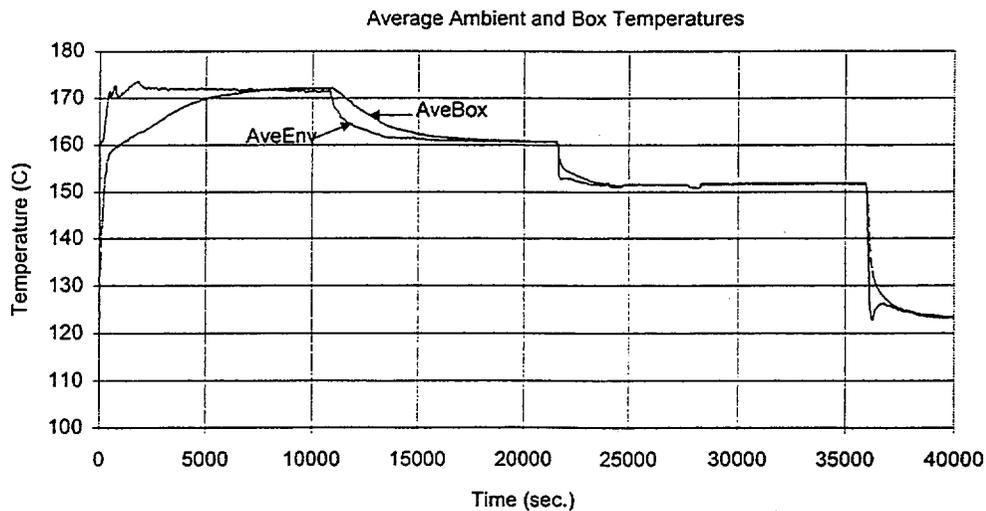


Figure 21 – Average Temperatures During Sandia Test

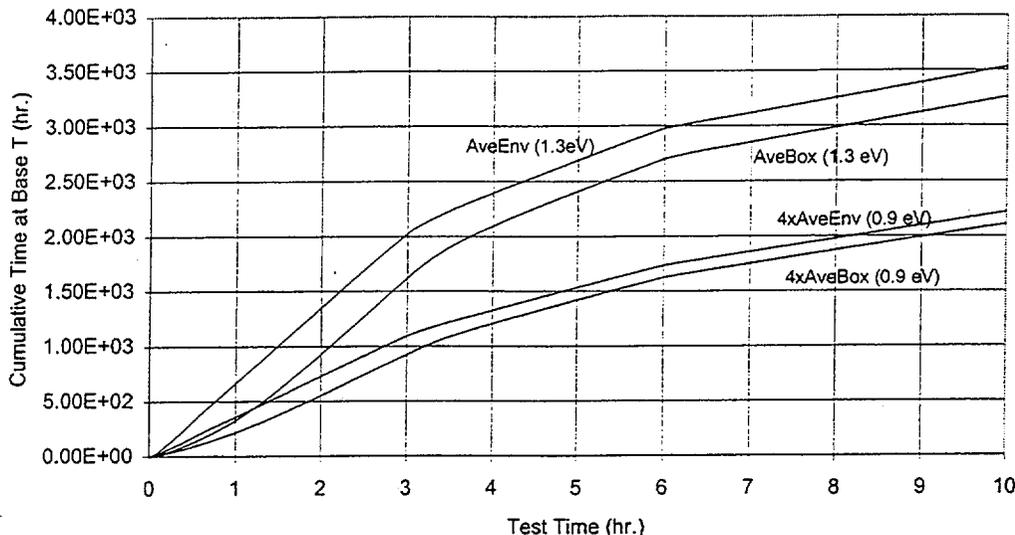


Figure 22 - Cumulative Times For Average Temperatures

Using a similar methodology, a simplified Excel model was developed to analyze hypothetical component/material temperatures using the NUREG/CR-6412 test profile. The model simulates thermal lag effects by assuming that device temperatures can be simulated using simple thermal lag time constants ( $\tau = 1/16, 1/8, 1/4,$  and  $1/2$  hour) to determine the relative significance of using ambient temperature instead of device/material temperatures in degradation equivalency calculations. Since it requires approximately 5 time constants for temperatures to reach near equilibrium conditions, near equilibrium for the  $1/2$  hour thermal lag is achieved within 2.5 hours.<sup>8</sup> This thermal lag simplification does not account for variations in heatup rates occurring in the saturation and superheat regions but it is adequate for our purposes. Figure 23 presents the computed temperatures during the initial 10 hours. Comparing this and Figure 21 suggests that the 0.25 curve is most representative of measured box internal temperatures. Since the 0.5 hr. curve achieves equilibrium within 3 hours, this should be considered as a conservative upper limit for inside containment equipment.

<sup>8</sup> After 1 time constant, device temperature would reach 63% of the differential temperature forcing function. After 5 time constants, the temperature would be within 99% of the differential temperature.

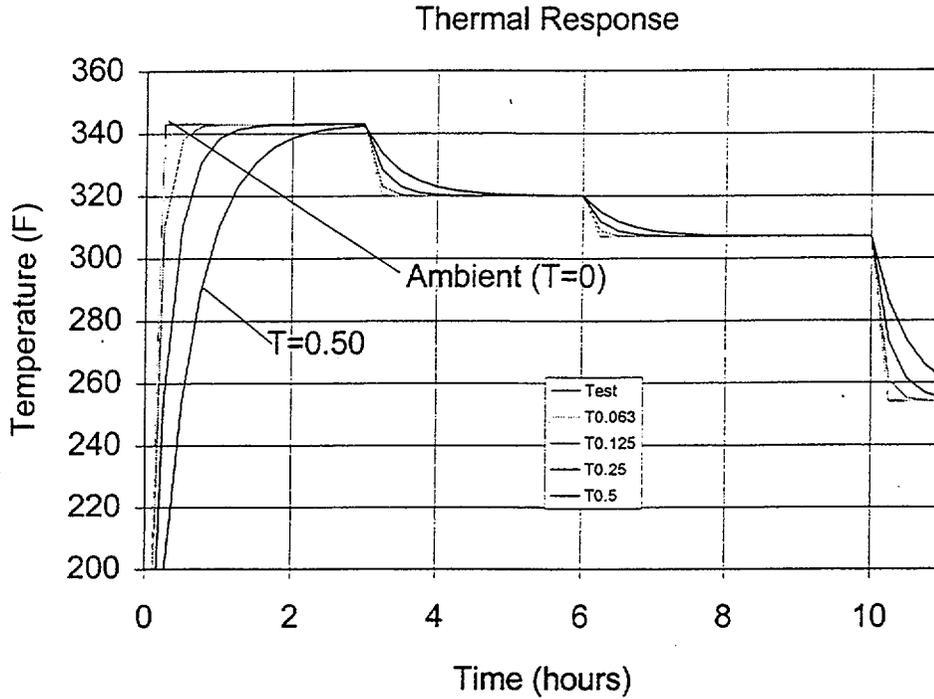


Figure 23 - Model Temperatures: NUREG/CR-6412 Profile (initial 10 hours)

Using the thermal model data, degradation equivalency analysis was performed for each time constant using 0.9eV and 1.3eV. Figure 24 illustrates the results for the 0.9eV case and Figure 25 for the 1.3eV case. As expected, the figures indicate that cumulative times at the end of the test transient (10 hours) decrease with increasing thermal lag. This demonstrates that degradation equivalency analysis based on ambient temperature overestimates material degradation during the transient period. However, the relative error decreases when cumulative times for the entire profile (240 hours) are calculated. Table 2 summarizes the cumulative times (CTime) and the relative time errors occurring when the ambient profile is used in lieu of the appropriate time constant profile. Except for the 0.5 hour, 1.3 eV case, all the cumulative time errors at 240 hours are less than 10%. The limiting 0.5 hour, 1.3 eV case has a cumulative time error of only 13%.

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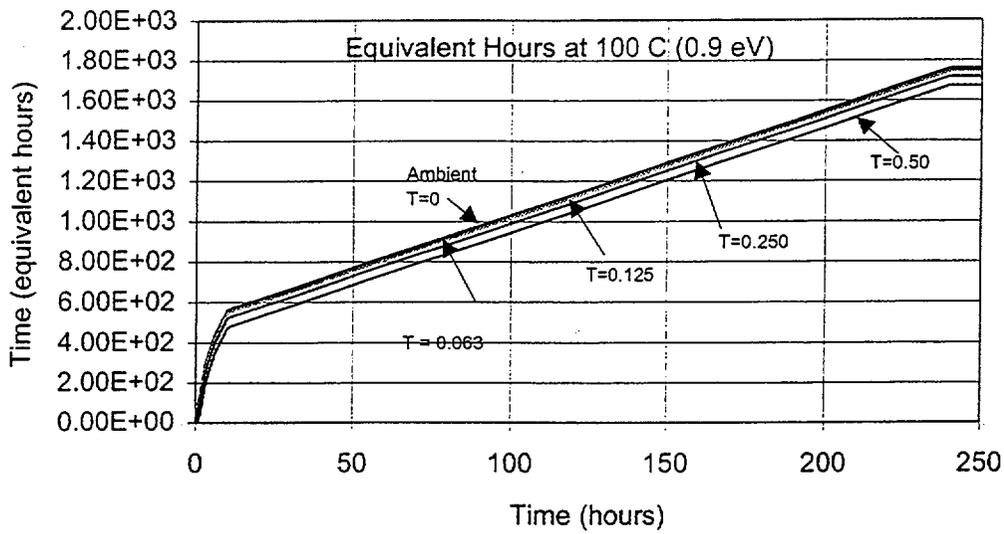


Figure 24 - Cumulative Times and Ratios: 100°C Base Temp. - 0.9eV

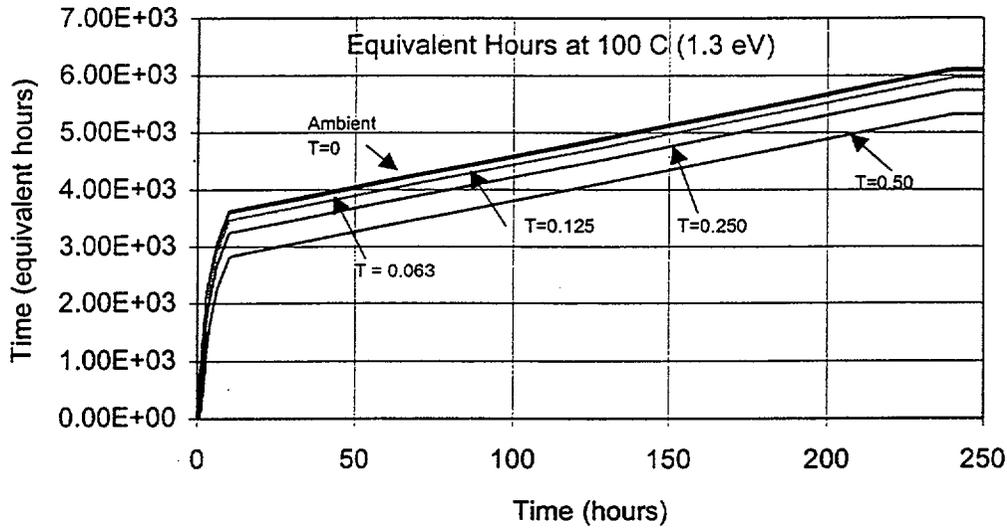


Figure 25 - Cumulative Times and Ratios: 100°C Base Temp. - 1.3eV

**Table 2**  
**Simulation Cumulative Time Results**

Time Constant ( $\tau$ )	eV	CTime* @ 10 hours	CTime error*	CTime @ 240 hours	CTime error*
0 (Ambient)	0.9	5.64e2	N/A	1.76e3	N/A
0.063	0.9	5.61e2	0.5%	1.76e3	~0%
0.125	0.9	5.47e2	3%	1.74e3	1.1%
0.250	0.9	5.21e2	7.6%	1.72e3	2.3%
0.500	0.9	4.72e2	16.3%	1.67e3	5%
0 (Ambient)	1.3	3.63e3	N/A	6.11e3	N/A
0.063	1.3	3.59e3	1%	6.08e3	0.5%
0.125	1.3	3.46e3	5%	5.95e3	2.6%
0.250	1.3	3.24e3	10.7%	5.73e3	6.2%
0.500	1.3	2.81e3	21.7%	5.32e3	12.9%

\*CTime denotes cumulative time and CTime error is the error occurring when the ambient profile is used in lieu of the applicable time constant profile.

Several generic observations can be made based on these simulations:

1. Cumulative time errors become more significant as activation energy values increase. This is expected since higher activation energy values will increase the significance of higher temperatures.
2. Changes in base temperature have no impact on the cumulative time errors.
3. The errors become less significant when total cumulative time is calculated for the entire profile. In our example, the 10 hour cumulative times represents roughly 30% to 60% of the total cumulative times at 10 days. For qualification tests with 30 day durations, the transient cumulative time would represent a smaller percentage of the total cumulative time and the cumulative errors would become less significant.
4. For devices whose thermal response can be characterized by the 0.0125 hr. or smaller time constants (equilibrium would be achieved within roughly 30 minutes), rapid heatup to ambient conditions will result in very small degradation equivalency analysis errors (i.e., < 2% - 3%). This would include transients with little superheat and smaller devices directly exposed to the test environment.

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5. For devices whose thermal response can be characterized by the 0.250 hr. or smaller time constants (equilibrium would be achieved within roughly 1 - 1.25 hours) rapid heatup to ambient conditions will result in insignificant degradation equivalency analysis errors (i.e., < 10%).
6. The limiting case analysis, using a 0.5 hr. time constant (i.e., equilibrium within 2 - 2.5 hours) and a 1.3 eV, results in a relatively small error (< 13%) that should not adversely effect qualification conclusions.

The preceding evaluations have not considered the significance of a plant-specific profile on the calculational errors. Several simulations were performed which included a second less severe profile to simulate a plant-specific requirement. If the transient portion of both the test and plant-specific profiles are identical, then the net transient error effect is zero. If the plant-specific profile peak conditions are substantially less severe than the test profile, the errors are slightly less than those in Table 2 but the differences are relatively insignificant. The most limiting case (i.e., maximum error) involves a plant-specific transient under saturated conditions (i.e., rapid device/material equilibrium at ambient temperature) and a qualification test with significant superheat. In this limiting case the net error would be similar to but would not exceed the errors presented in Table 2.

An additional factor minimizing the risk significance of these relatively small time errors is the common licensee practice of defining a single inside containment EQ profile that envelops both LOCA and HELB events. For example, a typical BWR EQ profile used by licensees includes an initial transient of 340°F for 3 hours followed by 320°F for 3 hours.<sup>9</sup> This temperature transient is intended to envelop the worst case conditions resulting from recirculation line LOCAs and a spectrum of MSLBs. Figures 26 and 27 from [4] depicts typical LOCA and MSLB temperature conditions that are enveloped by the 340°F/320°F composite profile. When composite profiles contain such enveloping transient conditions, the resulting degradation equivalency calculation contains additional conservatism that more than compensates for the relatively minor errors associated with using the ambient temperature conditions.

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<sup>9</sup> This BWR profile is also cited in numerous IEEE standards, including IEEE 323-1974, NUREG-0588, and Regulatory Guide 1.890, Rev. 1.

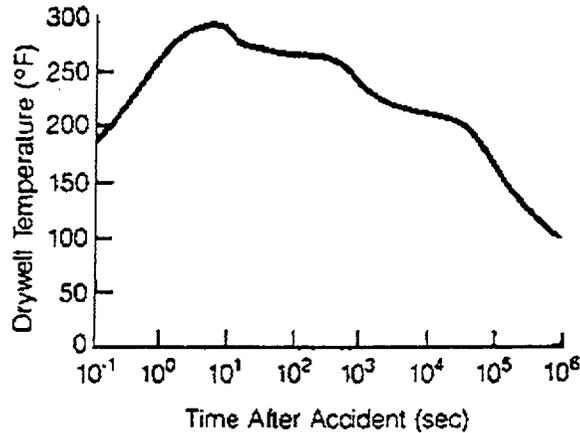


Figure 26 - Typical Mark I BWR DBA LOCA Temperature Profile [4]

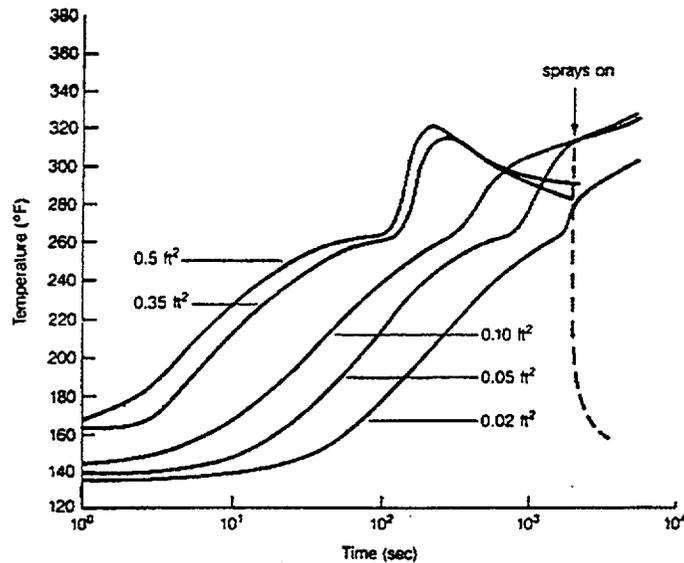


Figure 27 - Typical Mark I BWR Steam Line Break Profiles [4]

In summary, transient response thermal data from various steam tests with different types of devices, including motors and containment penetrations, demonstrate rapid device heat-up during the initial transient. The data also demonstrate the significance of saturated and superheat conditions on the component/material thermal response. The tests indicate that most devices will achieve thermal equilibrium with the test environment within a short period of time. Based on this information the limiting time to equilibrium should be less than 3 hours for most devices and profiles. For the vast majority of devices equilibrium would occur much faster (e.g., within 1 hour). Simulations based on the NUREG/CR-6412 temperature data indicate that transient errors for the limiting equipment and profile conditions would not exceed 15% based on Arrhenius-equivalent analysis of the entire profile. For the vast majority of devices the

error should be substantially less than 10%. Most PAOT calculations which use the entire test profile would contain sufficient margin to resolve this relatively minor error. These margins could be evaluated on a case-by-case basis. However, given the margins and conservatisms inherent in the qualification process and the lack of risk significance for long-term operability, such case-by-case evaluations are unwarranted.

### 6.3 EQ Profile Deficiencies

A second use for Arrhenius analysis of LOCA profiles involves instances where the test temperature profile does not fully envelope the required temperature profile during some intermediate portion of the test. Typically, except for this relatively short period of time, the temperatures during other portions of the EQ test are much more severe than the plant-specific accident profile. In most cases, engineering judgment concludes that the test profile adequately demonstrates qualification based on the overall severity of the test profile, performance demonstrated during the test, and equipment/plant-specific considerations. However, licensees have used Arrhenius analysis to provide an additional quantitative basis supporting this conclusion. The Arrhenius analysis provides a convenient method for demonstrating that the test profile is conservative (i.e., thermally more degrading) when compared to the plant-specific profile. In recent discussions with at least one licensee [2] the NRC staff has been reluctant to accept this use of Arrhenius. NRC issues related to this Arrhenius application are using lower temperature data to justify higher temperatures and using Arrhenius to analyze the higher temperature transient conditions.

The most common situation involving this Arrhenius application exists for certain PWR profiles during cooldown from the initial LOCA transient. For some plants a second, smaller, less severe thermal excursion occurs. For others the initial cooldown rate may be slower than the cooldown rate during a qualification test. In both cases, a period of time, ranging from roughly 2 to 35 hours, can exist when the test temperature profile is lower than the plant-specific profile. In most situations this profile deficiency occurs several hours after LOCA initiation. Temperature differences between the profiles vary during this time frame with maximum differences typically ranging from 10°F - 35°F. Typical profile temperatures during this time frame are in the range of 250°F - 150°F.

*6.3.1 Using Lower Temperature Data to Justify Higher Temperatures:* We maintain that it is an appropriate application of Arrhenius to compare the cumulative degradation from some lower temperature, longer time condition to a higher temperature, shorter time condition. As previously discussed, Arrhenius cannot be applied to predict material characteristics (e.g., insulation resistance) at temperatures beyond those being simulated. This limitation, often termed "reverse Arrhenius", is appropriate since testing at lower temperatures may not reveal failure mechanisms (e.g., melting or physical weakening, phase transitions, lower insulation resistance, thermal expansion) at higher temperatures when such mechanisms are related to temperature and not cumulative degradation. Therefore, a licensee must first establish that the peak test temperature profile envelopes

the peak plant-specific temperature profile. Alternatively, thermal lag analysis may be used to justify differences in the peak temperatures.

Once qualification has been established to these higher temperatures, then Arrhenius may be used to demonstrate that the cumulative thermal degradation over applicable portions of the profiles is more severe for the test profile. This includes the use of lower temperature test data. Such an application of Arrhenius should not be considered "reverse Arrhenius" since the lower temperature data are not being used to establish performance at temperatures beyond those simulated by the test.

Several additional observations strengthen the technical basis for this Arrhenius application. First, as demonstrated in Section 6.1.3, the use of Arrhenius to analyze accident profiles only involves interpolation or minor extrapolation of experimental test information since the aging experiments are conducted at temperatures that are similar to accident temperatures. This adequately resolves concerns associated with statistical uncertainty and material changes within the temperature range of concern. Similarly here, lower test temperatures are time shifted by relatively modest amounts to compensate for the 10°F - 35°F test deficiency during a relatively short portion of the test exposure. Secondly, these time shifts result in accelerations that are substantially smaller than those used to accelerate thermal degradation as part of the accelerated thermal aging portion of an equipment qualification test program. Third, qualification test thermal aging simulations typically subject test specimens to prolonged exposures at temperatures that are higher than those associated with this type of profile deficiency. As a result, acceptable performance during the thermal aging test provides additional support for equipment adequacy during these modest accident profile deficiencies.

*6.3.2 Transient Conditions:* Section 6.2.3 contains extensive information supporting the use of Arrhenius to analyze the transient portion of accident profiles. The information and conclusions presented there apply equally here. In summary, based on evaluations of existing test information and supplemental simulations, the use of ambient temperatures instead of component/material temperatures during transient conditions introduces a relatively modest error in the degradation equivalency calculation. This error is dependent on specific equipment and profile considerations but should be well within the margin typically available in these analyses. These margins could be evaluated on a case-by-case basis. However, given the margins and conservatisms inherent in the qualification process and the lack of risk significance for long-term operability, such case-by-case evaluations are unnecessary.

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## Review of Report Prepared by the Nuclear Utility Group on Equipment Qualification. (NUGEQ).

Montgomery T. Shaw

March 1, 1999

(Submitted as partial fulfillment of Tasks 1-5)

### INTRODUCTION

The document covered by this review carries the title "Acceptability of Arrhenius Methodology to Analyze LOCA and Post-LOCA Environments" and is credited to the NUGEQ. The report is dated January 1998, although this had been corrected to January 1999 on the copy I received.

The report covers a vast amount of information, and it clearly would be a monumental task to check on every aspect. Thus the objectives of this review were to focus on the substantive scientific arguments in favor of the Arrhenius extrapolation method. This was done by focusing on the equations, tables and figures. Three questions were asked: (1) is the information presented reliable, (2) is the information relevant to cable aging and (3) is the use of the information in the NUGEC report reasonable.

My general impression of this well-written document is that it covers most of the important topics as far as the available information allows. The question of technical justification for using old qualification tests for new temperature profiles is still not answered in that quantitative changes in the probabilities of unpredicted material failures are not provided. However, I agree with the general premise of the report that the justification for up-rating involves substantially the use of previously accepted methods, both good and bad.

### POINT-BY-POINT COMMENTS

Equations 1-4 discuss basic chemical kinetics and the temperature dependence of the rate constant. While this information is correct, its relevance to cable aging could be less-than-perfect, as aging in polymers involves important physical processes (e.g., diffusion, vaporization and crystallization of components) as well as chemical processes.

Figure 1 does represent the reaction pathway of an activated process, but the same remarks concerning relevance apply.

Eq. 5 is an important empirical application of the Arrhenius theory, and supposes that there is a relationship between the extent of a chemical reaction and a chosen physical property of the material. Using the Arrhenius theory to justify this equation is considered a stretch, and Eq. 5 must stand on its own merits until the tie between chemical and mechanical states is more firmly established. The oxidation uptake experiments of Wise

et al. (1995) is a good example of the type of research that could establish this tie. Other efforts to establish the chemical state of degraded elastomer have been made, but most have been successful only after extensive reaction.

Eq. 6 and 7 show how the rate could be integrated, but no attempt is made to separate variables or invoke mass balances. These equations really add very little; indeed, the authors drop the issue and turn quickly to the empirical. My interpretation of all this is that they wish to point out that the conversion can be predicted even though the temperature is changing, which also implies that a given chemical state can be achieved by many different  $T(t)$  paths. For the simple reaction depicted, this is correct. For series reactions, it is not obvious that different paths can lead to the same chemical state. For physical aging, or combinations of physical and chemical aging, path dependence is expected. For parallel reactions, path independence is generally not true, but my recent investigation of this question shows that it is substantially true even for parallel reactions of different activation energy and subjected to reasonable temperature excursions.

Figure 2 shows an aging test of a cable material at three temperatures. The entire property decay curve is given, based on roughly 30 observations per temperature. This looks like very thorough work. Figures 3-5 show similar information, but there are no data. All of these graphs should have used a log time scale to assess a very important point—the possible independence of time scaling on the degree of degradation. Time scaling is more general than Arrhenius; i.e., the time shift factors could follow any relationship, including the Arrhenius, WLF, Vogel-Fulcher, etc.. If the proper function for the time shift is the Arrhenius equation, then the reported activation energy would be independent of the end-point chosen. With parallel reaction routes, this is not expected, but the deviation appears to be slight. Empirically, the dependence has been reported to be large; for example, the activation energy for EPR changes from 1.28 to 1.05 eV if the end-of-life criterion is changed from 20% to 40 % loss of elongation [Carfagno and Gibson (1980)]. It should be noted that these numbers were from different studies.

Figure 6 is typical schematic life curve. No data points are evident, so there is no possibility to test for curvature or determine the error associated with extrapolation. Thus this figure is illustrative only and contributes little to the argument.

Figure 7 is a schematic showing possible  $T(t)$  paths. The discussion of this centers on the fact that the arithmetic average temperature will predict too little degradation. Figure 8 shows the corrections from a Sandia report. Presumably this figure is a plot of the well-known relationship for the Arrhenius-average temperature,  $T_{eq}$ , given by

$$T_{eq} = \frac{-E_q / k_B}{\ln \left[ \frac{t}{\int_0^t \exp[-E_q / k_B T(t')] dt'} \right]}, \quad (1)$$

where  $E_q$  is the activation energy measured under qualification conditions,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $t$  is the time over which the

average is taken. The derivation of this equation is simple; every time increment is expanded or contracted according to its current temperature relative to  $T_{eq}$ , and the sum of these is set equal to  $t$ . This equation is comparable in all respects to finding the “equivalent time” at a chosen reference temperature (discussed in Figures 24 and 25). Thus if two temperature histories need to be compared, there are two equivalent routes: (1) chose a reference temperature  $T_0$  (the value is arbitrary) and convert the time increments along both paths to the equivalent time at the reference temperature using

$$t_{eq} = \int_0^t \exp \left[ -\frac{E_a}{k_B} \left( \frac{1}{T(t')} - \frac{1}{T_0} \right) \right] dt' \quad (2)$$

or (2) calculate the equivalent temperatures of the two paths using Eq. 1. Again, these two are completely equivalent and are merely rearrangements of the same equation. The equivalent temperature may have a slight advantage in that no reference temperature need be chosen, which could reduce confusion.

Fig. 9 addresses again the possibility that the activation energy is independent of the degree of degradation. Superposability of the elongation data suggests such independence, at least for this material (nitrile rubber). Clearly, more extensive investigations of this type are needed, covering a variety of materials and with carefully measured property decay curves. The reason this is important is that the results could provide a basis for condition monitoring, wherein slight degradation is used to predict the expected aging at longer times. In the discussion of this figure, the authors claim that Figure 3 of the report shows that the activation energy of Raychem WCSF increases as the degradation increases. Although Figure 3 doesn't support this claim, it is the logical direction as the easy degradation pathways will be used first. It is also commonly observed in thermogravimetric analysis of the pyrolysis of polymers [Cooney et al. (1984)]. The NUGEQ authors states that this trend is conservative, which relies heavily on the compensation principle. Answers to this question await investigation of aging along nonisothermal paths.

Table 1 presents results that are invoked by the author to support the hypothesis that the degradation of materials in steam is indistinguishable from that in air ovens. The data indeed appear to support this contention, although the elongation is presented as “relative elongation” with no footnote designating the basis, which could be different for the two environments. The reporting of relative rather than actual property values is an unfortunate practice that buries important information.

Figures 10-12 compare degradation in steam using atmospheres that include or exclude oxygen. To simulate LOCA conditions, the temperatures were high. The NUGEQ authors use this information to point out that steam is not a factor in spite of the clear difference between the property decay curves of Hypalon at 160 °C in Figure 11, and the fact that oxygen (air) concentration, and not steam, was the factor in this experiment.

Figure 13 shows the vapor pressure of water and its Arrhenius form is used to argue that steam degradation is likely to be Arrhenius in form also. Aside from the fact that vapor pressure is not Arrhenius, but follows more closely the relationship

$$\ln P = a - \frac{b}{T + c} \quad (3)$$

there is little to support the concept of “pressure-related degradation.” If water takes part in the degradation reaction, then this reaction could increase in rate because of (1) the higher concentration of water in the polymer at higher temperatures, if the sample is in equilibrium with the saturated steam and (2) the higher temperature. Pressure itself often slows reactions in condensed states because activated complexes tend to require more volume. Point 1 is an empirical observation for many polymers, although it is not obvious from examination of the fugacity balance for the case when water is below the boiling point. Then:

$$\begin{aligned} f^v &= f^L \\ f^v &\approx yP = P^{sat} \\ f^L &\approx \gamma x P^{sat} \\ x &= 1/\gamma \end{aligned} \quad (4)$$

The concentration  $x$  thus depends inversely on the activity coefficient  $\gamma$ , which is mainly a function of temperature and concentration. The vapor pressure  $P^{sat}$  cancels out if the humidity is 100%. For hydrocarbon polymers, the activity coefficients are generally very high, giving low solubilities. If the relative humidity is low, then the amount of water in the polymer will indeed track the partial pressure of water in the air according to Henry’s law. The volume fraction  $v$  dissolved in the polymer can be approximated by the expression [Flory (1953)]:

$$v \approx R_H / \exp(1 + \chi) \quad (5)$$

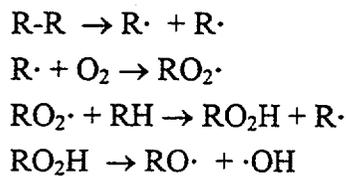
where  $R_H$  is the fractional relative humidity and is the Flory-Huggins interaction parameter. Numbers for the latter are not readily available for water; a value of 4.4 [Gündüz and Dincer (1980)] for water in polystyrene might be considered typical of hydrocarbon polymers. If the fractional relative humidity is always 1., it can again be seen that the concentration of water in the polymer is independent of vapor pressure. However,  $\chi$  often decreases with temperature, leading to an increase of dissolved water with temperature. The reason that vapor pressure is superficially absent is that as temperature increases, the activity of water *both* in the polymer and the atmosphere increase, and the net effect is zero except for the influence temperature has on the interaction of water with the polymer.

The discussion of Figure 14 is important. The NUGEQ authors use the Arrhenius behavior of polyurethane degradation in steam as an indicator that the Arrhenius method

is applicable. This appears to be a reasonable procedure if the relative humidities under qualification and accident conditions are the same. The conclusion that hydrolysis is not a significant degradation mechanism does not follow from the evidence presented. Also, polyurethanes are not commonly used in nuclear applications. Thus this data does not seem relevant to the discussion. The statement that steam has no influence on silicones should be made with some caution; Crine et al. (1986) report water reversion of silicone to form silanol. Also mechanisms of enhanced oxidative degradation of polyethylene in the presence of water have been proposed by Garton and Henry (1990).

Figure 15 shows non-Arrhenius, but conservative, behavior of breakdown probability (cumulative probability over a fixed period of time?). Although the data are a bit sparse, this work tends to support the NUGEQ authors' contention that tests at lower temperatures would safely predict the behavior at higher temperatures.

Figures 16-25 and Table 2 concern the effects temperature transients. The analysis appears to be reasonable with no surprises. To some extent, however, the question is not what the temperature is, but what influence, if any, a temperature derivative has on the rate of actual aging reactions vs. that predicted from isothermal data. In other words, given identical Arrhenius-average temperatures, is a temperature drop more serious than a temperature rise? The reason this could be the case lies with the series of reactions typical of hydrocarbon oxidation. In particular, a drop from high temperatures may leave a reservoir of hydroperoxide that will keep the rates of limiting reactions high because of concentration effects as oppose to changes in the rate constant. To be specific, consider the reaction sequence:



The last reaction is often a slow one of this sequence, implying that the hydroperoxide could be built up by rapid initiation sequences at high temperature. This would lead to high-than-expected rates of subsequent steps at the lower temperatures until the reservoir of hydroperoxide reached its new steady state. Modeling of this problem will be covered in a subsequent report.

The remainder of the report concerns "reverse Arrhenius," i.e., the prediction of performance at high temperatures using results at low temperatures. The discussion appears to be accurate. The possibility of first-order transitions above the qualification temperature was mentioned, and certainly all materials should be tested for such. The error associated with extrapolation through the first-order transition in polyethylene can be very large [Howard (1973)]. An unusual case of a negative activation energy in XLPE at high temperatures (175 -200 °C) has been reported by Ezrin and Seymour (1988). This may have due to the lose of an oxidation initiator by volatilization.

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