

OCT 22 1980

MEMORANDUM FOR: Harold R. Denton, Director  
Office of Nuclear Reactor Regulation

FROM: Thomas E. Murley, Acting Director  
Office of Nuclear Regulatory Research

SUBJECT: PROPOSED GUIDELINES FOR REVIEW OF THE METHODOLOGY TO  
PRECONDITION OR AGE EQUIPMENT FOR DESIGN BASIS ACCIDENT  
QUALIFICATION TESTING

On September 16, 1980 we arranged for a seminar on the above subject that was well attended by your staff. The seminar was conducted by personnel from Sandia Laboratories who have been working in this field for many years, in conjunction with the nuclear weapons program, and have been under contract to NRC for the last 5 years. During that time they have been working towards developing an acceptable aging methodology that could be used to precondition test samples prior to design basis LOCA and seismic-type accident qualification testing. We plan to issue a Research Information Letter covering this subject when the work is completed. Although their work is not complete, considerable progress has been made. The seminar was an attempt to explain to your staff the data and conclusions reached thus far, prior to NRR's evaluation of the licensee qualification data that will be submitted in November.

The enclosed papers and vugraphs cover the material presented at the seminar. I have also enclosed an outline, written as a check list, that can be used by your staff in conducting its reviews.

As you know, the issue of materials aging has been a difficult one for both the NRC and industry. Considerable effort and money have been expended by industry on this issue with little noticeable progress. A contributing factor to the lack of progress has been the absence of specific regulatory guidelines or industry standards. I feel it is imperative that the NRC provide this guidance at this time and the attached outline represents our recommendation of what is both necessary and reasonable to assure proper preconditioning for LOCA and seismic-type qualification tests.

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Please feel free to call on Ronald Feit of my staff, or the Sandia personnel, for any further assistance you may need.

Original Signed by

T. E. Murley

Thomas E. Murley, Acting Director  
Office of Nuclear Regulatory Research

Enclosures:

1. Materials and papers presented at 9/16/80 seminar
2. Outline (check list)

Distribution:

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PICPSB r/f  
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(List enclosed)

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QUALIFICATION TESTING EVALUATION

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OUTLINE OF METHODOLOGY TO PRECONDITION OR AGE  
EQUIPMENT FOR DESIGN BASIS ACCIDENT QUALIFICATION TESTING

I. Identify the Required Safety Functions and Associated Equipment

For each design basis accident the safety functions that must be maintained should be defined. For each of these safety functions the associated equipment that is vulnerable to common mode, or nonrandom, failures that may be caused by the design basis accidents should be identified. These critical equipment items should then be examined and their constituent components and materials listed.

Completion of this portion of the aging program will result in a list of components and/or materials that should be preconditioned or aged and then meet some measure of performance during a design basis accident.

II. Identify the Stresses That Are Relevant to Aging

The stresses that are relevant to the component and/or material are determined by the normal external conditions such as the thermal, humidity and radiation ambient environment as well as the internal characteristics of the component. For example, the thermal stress on an instrument is a function of the ambient temperatures but may also be influenced by internal heat generated during operation.

The radiation stress is usually determined solely by the external environment and the mechanical and electrical stress is a function of the internal and operational characteristics of the component.

The stress that pollutants may cause can come from the ambient

environment but may also be generated if materials within the component or reactor outgas as a result of operation and age.

### III. Obtain Failure Mode Test Data

Failure mode tests, usually at the component level, should be conducted to stimulate failures or at least detectable degradation. The chief purpose of these tests is to detect material degradation and compatibility interactions, due to the stress environment, that can have an effect on the ability to perform the required safety function. Two types of compatibility interactions can exist: first, a distal interaction where a by-product from one species is transferred to another as a gas; and second, a proximal interaction where the degradation results from the direct physical contact of two materials. This direct physical contact can result in either a chemical or a physical process. Because of the destructive nature of failure mode testing, an iterative test procedure may be necessary after failure is noted to either reduce or retard reaction rates so that they can be better analyzed.

The failure mode tests consist of exposing the component and/or material to relatively high values of the stresses identified under item II to accelerate possible degradation reactions. In order to conduct these tests and properly interpret the results, significant measures of performance and damage should be identified that relate to the safety function which must be performed during the design basis accident. For example, where a complete component will be tested under a design basis accident condition, such as a pressure

transmitter, a measure of performance might be the ability to transmit the required pressure signal with some limit of signal degradation. However, for equipment such as electrical cable, connectors, terminal blocks, etc., that will have to be qualified for a myriad of safety functions, more general measures of acceptable performance and material damage must be established. An example of a measure of damage for electrical cable materials could be the tensile properties remaining after being subjected to the design basis accident.

With these measures of performance and damage in mind, the failure mode tests are conducted and analyzed. Although it would be desirable to conduct these tests under various combinations of stresses, they are usually conducted under "single stress" environments and, given the complications (both experimental and theoretical) in carrying out combined environmental exposures, this is usually an acceptable method.

Acceleration of stress due to a humid environment is not easily accomplished. If humidity is considered to be an important stress, then testing should be conducted at various temperatures keeping the relative humidities constant.

It would seem reasonable that most suppliers of equipment to the nuclear industry will already have conducted some failure mode testing. Also, with regard to degradation due to common environ-

mental stresses (such as humidity or thermal), it would seem that longer term failure mode tests and operating experience should have eliminated from use most of those materials that degrade readily in these environments.

The analysis of a given failure mode will typically involve a combination of visual observations, literature data, past experience, and the use of various analytical techniques. Degradation which has no direct influence on the required safety function and the measurement of performance or which results from the high over-stress environment but will not be a factor at the normal ambient stress levels, can be eliminated from further consideration.

Discoloration of a metal instrument cover would be an example of the first type of degradation that can be eliminated since it has no direct bearing on the safety function or the measure of performance. Increasing the temperature of a material above a physical transition point can lead, for instance, to a failure caused by the melting of the material. If the aging environment temperature is below this transition, this would constitute an example of the second type of failure mode that need not be considered further.

In summary, the results of this portion of the program should consist of a listing of the following:

- a. The components and/or materials degraded during the test that could affect the safety function, and
- b. The important stresses causing these degradations.

#### IV. Obtain Material Aging Data to Estimate Lifetimes, in the Reactor Environment, of Equipment Susceptible to Degradation

Using the above results, an accelerated aging program should be developed. The results of this program can then be used to preage components and/ or materials prior to their use in design basis accident qualification tests. In order to accomplish these objectives an experimental aging program must be conducted to quantify the aging of all components and/or materials under the identified degrading stress environments. This normally requires that the performance or degradation of the components and/or materials be monitored at a series of stress levels higher than the normal ambient stress.

In addition to the materials and stress levels identified in Item III, data should be obtained (or referenced) on the thermal aging of all organic materials and on the radiation aging of all organics exposed to a total dose of  $10^5$  rads or more. If existing data is utilized, it should be checked experimentally or thoroughly reviewed in terms of the guidelines set forth in this document.

##### IVa. Single Stress Environment<sup>1</sup>

Single stress degradation data should be obtained at various stress levels using performance and/or degradation parameters. Time-

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<sup>1</sup>The term "single stress" is a misnomer for non-thermal stresses since such stress cannot exist in the absence of temperature (excluding absolute zero). For convenience, however, the term "single stress" environment is generally used to refer to a stress which exists at a low enough temperature such that degradation in the thermal environment alone would not cause significant degradation for the time scale of the experiment.



stress superposition techniques should be attempted and, if validated, the form of the shift function (acceleration function) should be determined and used to extrapolate the degradation in order to predict long-term aging behavior.<sup>2</sup> As the extrapolation gets larger, the uncertainty increases because the dominant degradation reaction may change or the extrapolation may be through a stress level at which there is a physical or chemical transition. As a general rule, the extrapolation factor should not exceed the data range factor. For example, if the data extends from .1 year to 1 year, then an extrapolation beyond 10 years should not be made. Contributing elements in obtaining confidence in the extrapolation are the number and accuracy of data points obtained. For example, extrapolation based on six data points is usually more reliable than extrapolation from three data points, even though both cover the same range (assuming similar acceleration functions and uncertainties in the data).

The assumption upon which accelerated aging is based is that by raising the environmental stress level, it is possible to accelerate equally all significant reactions contributing to the material degradation. When time-stress superposition cannot be made with the data taken, the contributing reactions were not equally accelerated. For the cases where time-stress superposition cannot be made, confident predictions based on accelerated aging are not possible. However, very short-range empirical extrapolations may be made on a case-by-case basis.

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<sup>2</sup>"Predicting Life Expectancy and Simulating Age of Complex Equipment Using Accelerated Aging Techniques," K. T. Gillen and K. E. Mead, SAND 79-1561.

An important area where time-stress superposition may not work is in conjunction with radiation aging. For example, it has been found that many elastomeric materials exhibit significant radiation dose rate effects when aged in air environments.<sup>3</sup> These effects can only be determined by radiation aging tests conducted over a wide range of dose rates. The current practice is to assume that the material degradation from radiation stress is determined only by the total integrated dose and, therefore, most radiation studies are conducted at high dose rates for short time intervals. For materials that will be exposed to a total dose of  $10^5$  rads or greater, enough radiation degradation data should be obtained to determine whether or not there are significant dose-rate effects. It is suggested that radiation experiments be performed to some constant dose, utilizing two different dose rates which differ by at least two orders of magnitude, and that the highest dose rate employed in the aging experiments should not exceed 2 Mrad/hr.

#### IVb. Combined Stress Environment

When a stress environment other than temperature is significant under ambient conditions, then the possibility of synergistic interactions should be investigated by conducting experiments under the combined environment of the relevant stress plus elevated temperature.<sup>4</sup> As a minimum, an experiment should be conducted using

<sup>3</sup>K. T. Gillen and R. L. Clough, "Occurrence and Implications of Radiation Dose-Rate Effects for Material Aging Studies," in press.

<sup>4</sup>K. T. Gillen and R. L. Clough, "Radiation-Thermal Degradation of PE and PVC: Mechanism of Synergism and Dose-Rate Effects," in press.

a combination of moderately accelerated levels of the relevant stress and temperature for comparison with results of analogous experiments utilizing the two environments singly.

If significant synergistic effects are indicated, then justification for use over an extended period of time can only be made by obtaining extensive combined environment aging data.

#### V. Additional Considerations

During both the single and combined stress environment aging tests it is imperative that the atmospheric conditions be representative of those that will exist in the plant. This is particularly significant with regard to the concentration of oxygen present. For example, aging experiments conducted in a closed test container may result in oxygen depletion which would not occur under actual plant conditions. Also, aging-reaction products could accumulate in a closed test container in concentrations that may influence reaction rates or introduce new reactions.

OCCURRENCE AND IMPLICATIONS OF RADIATION  
DOSE-RATE EFFECTS FOR MATERIAL AGING STUDIES\*

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ABSTRACT

A number of commercial cable materials, including ethylene propylene rubber and crosslinked polyolefin insulations and chloroprene and chlorosulfonated polyethylene jackets have been radiation aged in air and nitrogen at radiation dose rates ranging from approximately  $10^3$  to  $10^6$  rad/hr. Material degradation was followed using ultimate tensile properties (elongation and tensile strength), swelling measurements and infrared spectroscopy. The tensile results indicate that in air environments radiation dose rate effects are important for all four materials, with more mechanical damage occurring as the dose rate is lowered. These results are interpreted as coming from a competition between crosslinking and oxidative scission in which scission becomes more important as the dose rate is lowered. The swelling results offer direct evidence in support of this interpretation. In addition the infrared results show increased carbonyl content at lower dose rates, also indicative of increased oxidation. The conclusions of this study have important implications for the qualification of elastomeric materials for nuclear applications, since they clearly indicate that the mechanism of degradation is quite different (and the amount usually more severe) under low dose rate exposures compared to the mechanism occurring under the high dose rate exposures normally utilized for simulating the natural aging.

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\*\*A U. S. DOE facility.

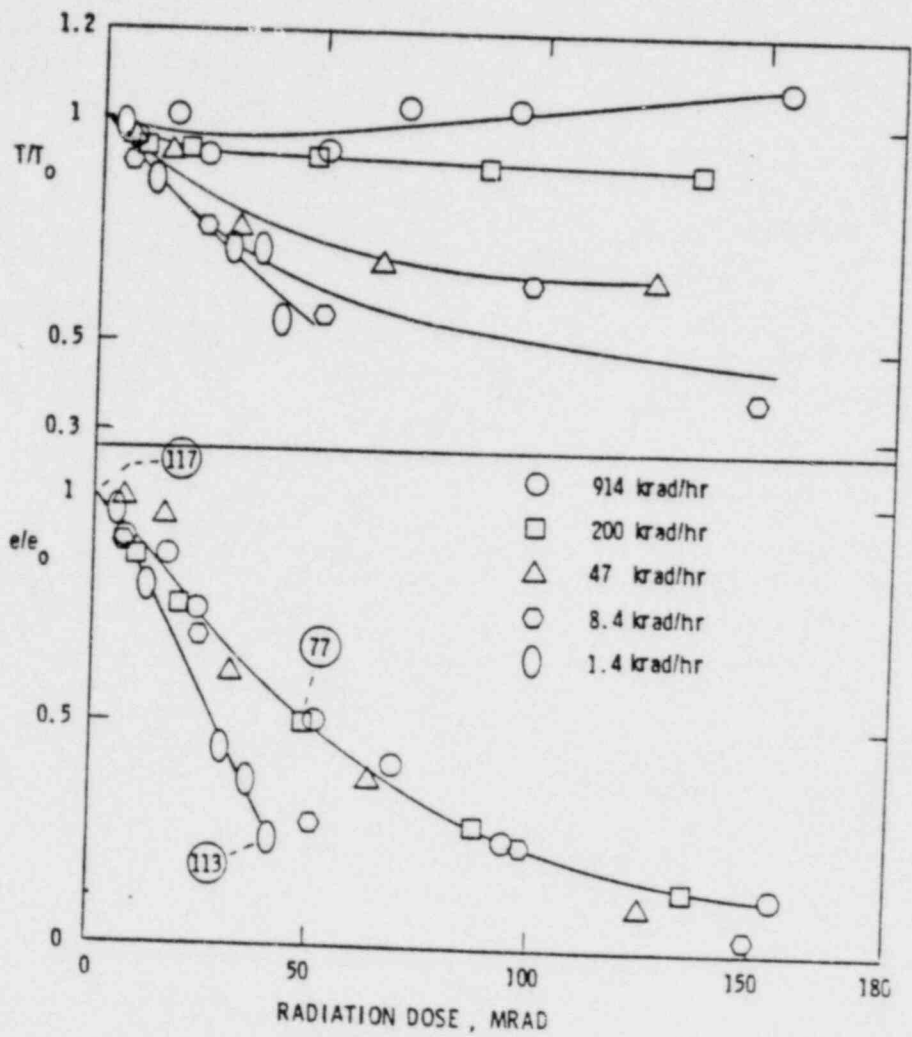


Figure 3. Aging of chloroprene rubber jacket. Explanation of figure is identical to Figure 1.

## INTRODUCTION

In nuclear applications a variety of polymeric materials receive radiation exposure at relatively low dose rates (typically less than  $10^3$  rad/hr) for long periods of time (up to 40 years). In order to make estimates of the long-term degradation occurring in a material, it becomes necessary to carry out accelerated aging studies. These are normally accomplished by raising the radiation dose rate to the order of  $10^6$  rad/hr with the assumption that the amount of degradation will depend only on the integrated radiation dose. On this basis extensive studies have been carried out. Results from such studies are often summarized in compilations,<sup>1,2</sup> which indicate, for typical polymeric materials, the total allowable radiation dose before significant material damage occurs. On the other hand it has been reported by several workers that in air environments, certain polymeric materials can show significant dose rate effects,<sup>3,4</sup> including materials (e.g., polypropylene, polyethylene, and polyvinylchloride) whose low dose rate radiation resistance may therefore be misjudged<sup>1,2</sup> using data generated at high dose rates.

Recently Kuriyama, et al.<sup>5</sup> studied the dose rate effect (for the range of  $10^4$  rad/hr to  $5 \times 10^5$  rad/hr) on the mechanical and electrical properties of representative insulation and jacketing materials and found strong dose rate effects for crosslinked polyethylene, some evidence of a different type of dose rate effect for an ethylene propylene rubber and little evidence for dose rate effects in chloroprene rubber and chlorosulfonated polyethylene.

We have been interested for some time in determining the importance of dose rate effects for polymeric materials used in nuclear applications. In particular we have been following the degradation of commercial cable insulation and jacketing materials in room temperature radiation environments using dose rates ranging over 3 orders of magnitude, from approximately  $10^3$  rad/hr to  $10^6$  rad/hr. The effect of humidity on the aging (dry air vs. 70% relative humidity air) is also being monitored. Preliminary results reported earlier<sup>6</sup> indicated that dose rate effects were present for a crosslinked polyolefin insulation material and an ethylene propylene rubber insulation material and that no effect of humidity on room temperature radiation aging was apparent. Sufficient data has now been accumulated from the low dose rate experiments to indicate that dose rate effects are present for every material which we have studied and must therefore be considered before extrapolating high dose rate accelerated simulations to low dose rate ambient conditions. Here we highlight some of the relevant data.

## EXPERIMENTAL

### Materials

The materials for this study were carefully stripped before aging from modern Class IE (qualified for nuclear power plant safety

applications) low-voltage electrical cables obtained from a number of manufacturers. Table I gives the material abbreviations used in this paper, a description of the materials, their nominal wall thickness and unaged tensile properties.

TABLE I

Abbreviation	Material	Nominal Wall Thickness, mm	Tensile Elongation %	Tensile Strength (MPa)
CLPO	Fire retardant crosslinked polyolefin insulation	0.8	240	15
EPR	Ethylene propylene rubber insulation	1.0	420	8
CSPE	Chlorosulfonated polyethylene jacket	1.4	300	25
CP	Chloroprene rubber jacket	1.5	185	11

The two insulation materials were aged as tubes; rectangular samples approximately 5.5 mm wide by 150 mm long were cut from the jacket materials for use in the aging experiments.

#### Radiation Exposures

The radiation aging was carried out 1) at the Naval Research Laboratories facility,<sup>7</sup> modified such that continuous air flow was supplied to the aging chambers and 2) at Sandia's dedicated radiation aging facility.<sup>8</sup> The latter facility has been upgraded such that dose rates up to 1 Mrad/hr are now available. Radiation dose rates at NRL were obtained from the extensive mapping data generated by NRL personnel. Dose rates at the Sandia facility were obtained using a Victoreen Model 550 Radocon III Integration/Rate Electrometer and thermoluminescent CaF<sub>2</sub> wafers; agreement between the two methods was excellent.

#### Tensile Tests

Tensile testing was accomplished with an Instron Testing Machine Model 1020. Samples were gripped using pneumatic jaws with an air pressure of approximately  $3 \times 10^5$  Pa. Initial jaw separation was 50 mm and samples were strained at 125 mm/min; the strain was monitored with an Instron electrical tape extensometer clamped to the sample.

#### Infrared Spectra

Spectra were obtained on KBr pellets made from polymer samples that had been ground at -196°C. A Nicolet Model 7199 FTIR spectrometer was employed.

#### Swelling Measurements

Samples with an initial weight ranging from 0.3 - 1.0 g were extracted in 50°C THF in a Soxhlet extractor for 24 hrs. After quickly

removing excess solvent from the surface and capping the samples in a bottle to retard evaporation of solvent, the samples were weighed, yielding  $W_s$ ; they were then dried in a vacuum oven and weighed again, yielding  $W_d$ . The weight swelling ratio (WSR) was then calculated as

$$WSR = \frac{W_s - W_d}{W_d}$$

#### RESULTS AND DISCUSSION

Figures 1-4 summarize the results to date of the extensive ambient temperature radiation aging experiments on the 4 materials described earlier. The tensile strength after aging divided by the tensile strength before aging ( $T/T_0$ ) and the tensile elongation after aging divided by the tensile elongation before aging ( $e/e_0$ ) are plotted against the total integrated radiation dose at the various indicated radiation dose rates. The crosses represent data for experiments run in a nitrogen environment; the remaining experiments were run in flowing air environments. Each data point represents an average of between 4 and 8 tensile tests.

It is apparent from Figs. 1-4 that dose rate effects exist for all 4 materials. In every case as the radiation dose rate in air is lowered, the tensile strength results shift to lower values for a constant value of the total radiation dose. The overall degradation mechanism for polymers in an oxygen-radiation environment is quite complex, but in general is pictured as a competition between crosslinking and scission processes.<sup>3,4</sup> Since crosslinking usually increases tensile strength values and scission usually leads to a decrease in tensile strength, the tensile strength results from Figs. 1-4 can be interpreted as evidence that scission becomes more important relative to crosslinking as the radiation dose rate is lowered. The tensile strength results for moderate dose rate aging in a nitrogen atmosphere for CLPO and EPR shift to higher values compared to the high dose rate results in air. This implies that oxygen is implicated in the dose rate effects, and hence that the scission is associated with oxidation. Fig. 5 shows the carbonyl region ( $\lambda \sim 1710 \text{ cm}^{-1}$ ) of the infrared spectra of 1) unaged EPR, 2) EPR aged in air at 1.2 Mrad/hr to a total dose of 95 Mrad, and 3) EPR aged in air at 9 krad/hr to a total dose of 108 Mrad. The much larger carbonyl peak produced under low dose rate conditions is consistent with the expected increase in the extent of the oxidative reaction.

Although the elongation results for EPR (Fig. 2) imply dose rate effects for the whole dose rate range investigated, clear  $e/e_0$  dose rate effects for the other three materials become apparent only at the lowest dose rates. The relative lack of sensitivity of elongation to the changing competition between crosslinking and scission is due to the fact that both phenomena tend to lower this parameter, leading in general to a rather complicated dependence on dose rate. In CLPO for



example, degradation dominated by crosslinking appears to lead to a faster initial rate of decrease in the elongation only to be followed later in the degradation by a smaller rate of decrease. Eventually at dose rates where scission becomes sufficiently important, the rate of degradation in the elongation begins to accelerate for all 4 materials.

Solubility determinations and swelling techniques are two other excellent methods of assessing the relative importance of crosslinking and scission. Since the 4 materials studied represent commercial formulations whose exact constituents and constituent proportions are unknown, the numbers obtained in our measurements represent the solubility and percentage swell of the commercial filled material rather than the polymeric component. Some representative results from the swelling experiments are shown in Figs. 1-4, where the circled numbers represent the weight swelling ratios corresponding to the indicated experimental conditions. For example in CLPO, unaged material swells 56%, material aged in air at 220 krad/hr to a total dose of 96 Mrad swells 34% and material aged in air at 9 krad/hr to a total dose of 119 Mrad swells 78%. The swelling data shown in Figs. 1-4 is typical of the swelling (and solubility) data generated to date and again indicates that crosslinking dominates scission at high dose rates but scission becomes more important relative to crosslinking as the dose rate in air is lowered. The results from these techniques therefore offer confirmatory evidence for our interpretation that the changing competition between crosslinking and scission leads to the observed dose rate effects for the 4 materials.

A number of possible explanations for the above dose rate effects exist. One possible mechanism involves oxidative degradation limited by the rate of breakdown of hydroperoxides which are relatively stable at room temperature, but will break down over long periods of time, yielding free radical precursors to oxidative degradation. Clough and Gillen<sup>9</sup> found evidence that this mechanism contributes to substantial dose rate effects in polyvinyl chloride and low density polyethylene. One piece of evidence came from thermal treatments of samples which were previously irradiated at room temperature. The relatively rapid degradation which occurred during the thermal treatment and the fact that the degradation could be blocked by chemically removing the hydroperoxides implicated hydroperoxide breakdown as important to the observed dose rate effects. Similar sequential experiments run on the 4 present materials did not lead to rapid deterioration during the thermal portion of the exposure; we therefore conclude that hydroperoxide breakdown is not a major cause of the present dose rate effects.

A second plausible explanation involves oxidative degradation limited by the rate of oxygen diffusion into the polymer, a mechanism invoked by Kuriyama, et al.,<sup>5</sup> to explain their crosslinked polyethylene results. We are currently carrying out experiments to assess the

importance of diffusion effects for our materials.

The results of this study indicate that dose rate effects exist for CLPO, EPR, CSPR and CP, four commonly used cable insulation and jacketing materials. We also find evidence of important dose rate effects in polyvinyl chloride cable jacketing material and in low density polyethylene cable insulation material.<sup>9</sup> These results have important implications for the use of such materials for nuclear applications, since they clearly indicate that the mechanism of degradation is often quite different (and the amount usually more severe) under the low dose rate exposures characteristic of actual aging conditions compared to the mechanism occurring under the high dose rate exposures normally utilized for aging simulations. Material aging data generated at high dose rates<sup>1,2</sup> must therefore be treated cautiously if a low dose rate application is intended.

#### ACKNOWLEDGEMENT

The authors would like to express their thanks to Lee Johnson and Frank Campbell of the Naval Research Laboratories for the use of their radiation facility and for their assistance in a number of the aging exposures. We are also grateful to Dave Haaland for obtaining the FTIR spectra.

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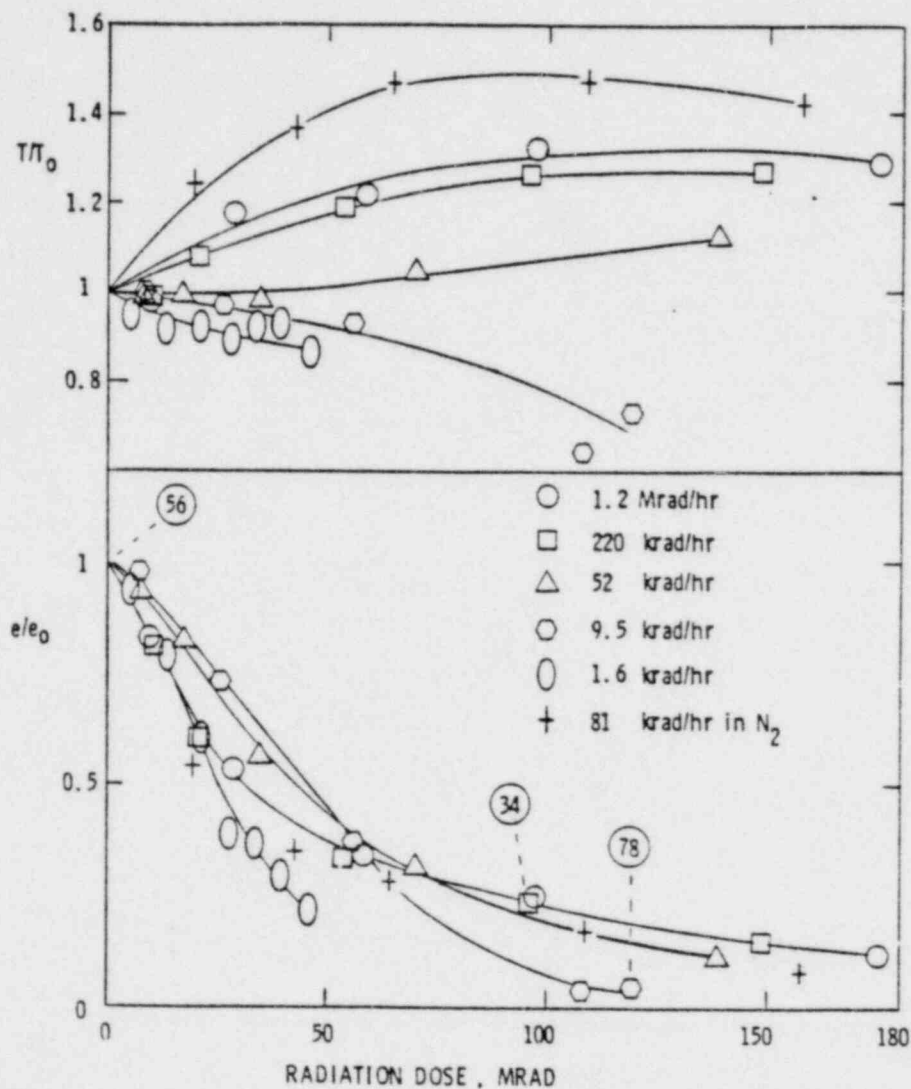


Figure 1. Aging of crosslinked polyolefin insulation. The tensile strength after aging divided by the tensile strength before aging ( $T/T_0$ ) and the tensile elongation after aging divided by the tensile elongation before aging ( $e/e_0$ ) plotted against the total integrated radiation dose at the various indicated dose rates. The circled numbers refer to the weight swelling ratios corresponding to the indicated experimental conditions.

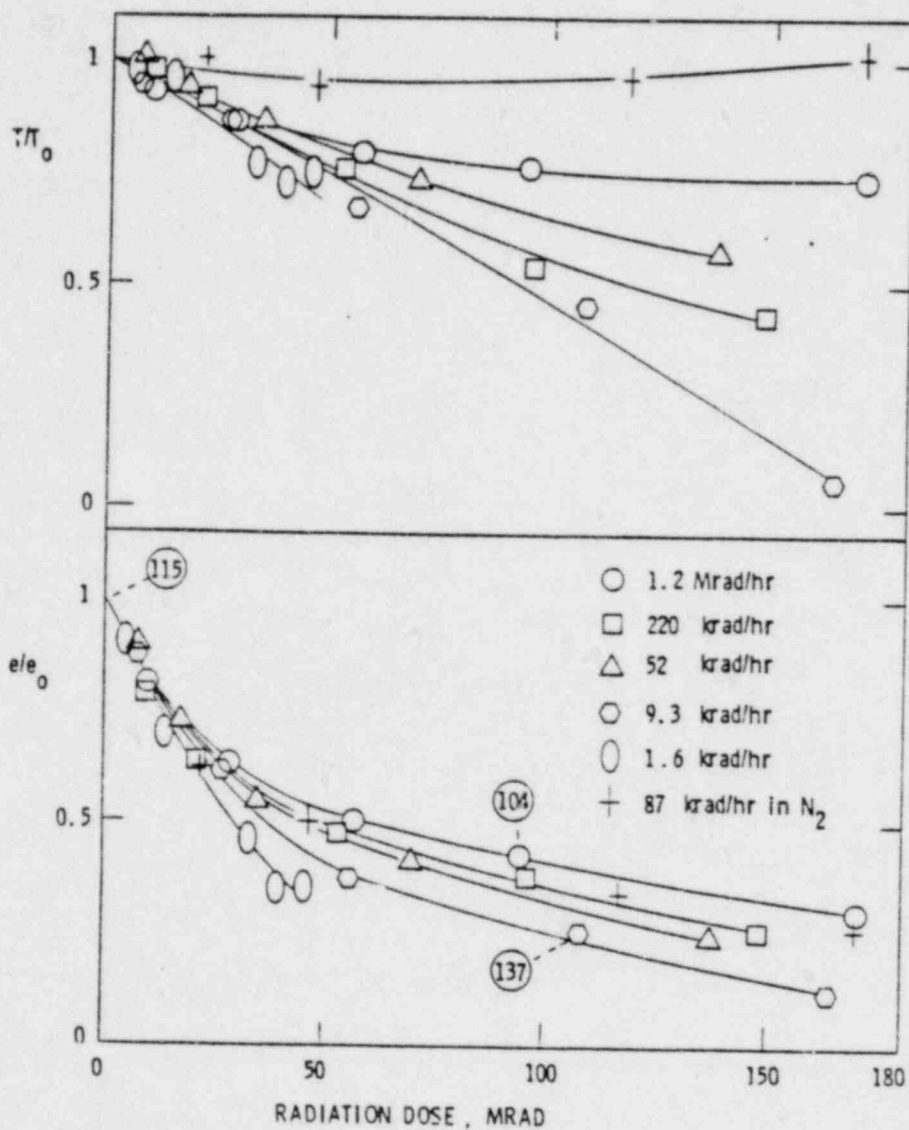


Figure 2. Aging of ethylene propylene rubber insulation. Explanation of figure is identical to Figure 1.

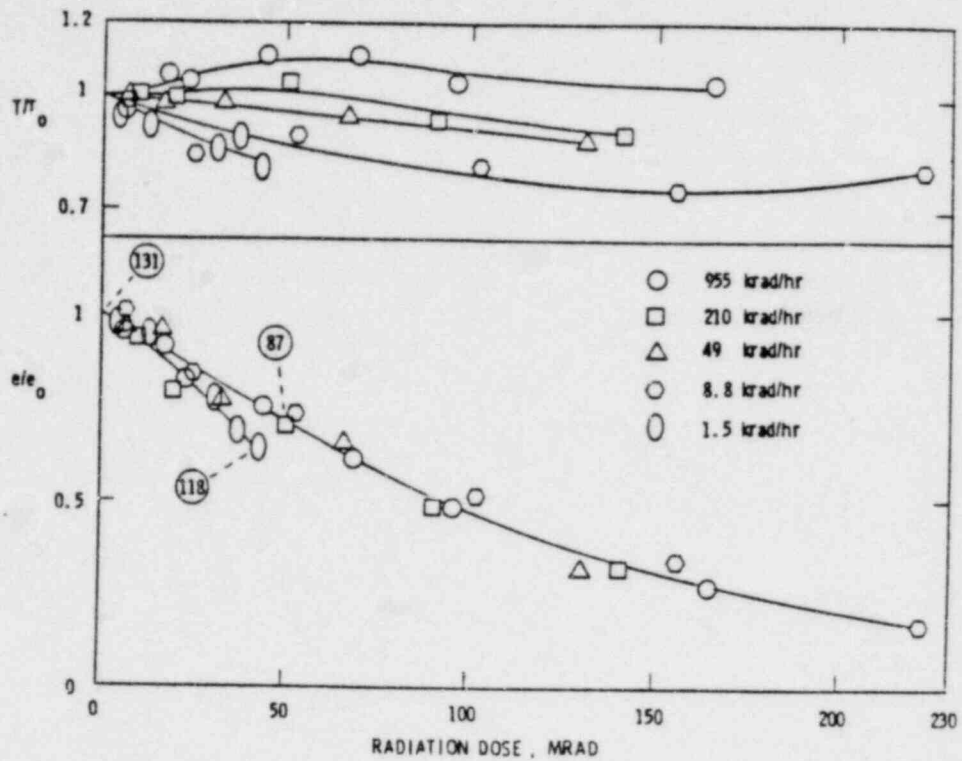


Figure 4. Aging of chlorosulfonated polyethylene jacket. Explanation of figure is identical to Figure 1.



Figure 5. Infrared spectra of ethylene propylene rubber insulation. Curve 1 - unaged material. Curve 2 - aged in air at 1.2 Mrad/hr. Curve 3 - aged in air at 9.3 krad/hr.

RADIATION-THERMAL DEGRADATION OF PE AND PVC:  
MECHANISM OF SYNERGISM AND DOSE RATE EFFECTS\*

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ABSTRACT

Polyethylene insulation and polyvinyl chloride jacketing materials that had been in use in a nuclear application were recently found to be substantially deteriorated. The damage had occurred under conditions where both the total estimated dose (about 2 Mrad) and the operating temperatures (about 42°C maximum) seemed relatively moderate. These results prompted us to initiate a program to study polyvinyl chloride and polyethylene degradation under conditions of combined  $\gamma$ -radiation and elevated temperature environments. A number of interesting aging effects were observed, including a striking synergism between radiation and temperature, and strong dose-rate dependent effects which occur over a wide range of dose rates. The aging effects are explained in terms of a chain branching degradation mechanism involving thermally induced breakdown of peroxides which are formed in reactions initiated by the radiation. Evidence for this mechanism is derived from infrared spectra, from sequential radiation-elevated temperature experiments including experiments under inert atmosphere, from Arrhenius calculations, and from a new technique involving treatment of intact samples with  $\text{PH}_3$  for chemical reduction of peroxides. The results of our studies call into question earlier work which presented data purportedly indicating "tolerable radiation doses" for a variety of polymers, and which was intended to serve as a general guide for materials selection and life expectancy estimation under radiation conditions.

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\*\*A U. S. DOE facility.

## INTRODUCTION

Lengths of cabling material which had been in service in a nuclear application for a period of 12 yr<sup>1</sup> were recently examined and found to exhibit substantial deterioration. This cabling consisted of polyethylene (PE) insulation having a thin nylon sleeve, with an outer jacket of polyvinyl chloride (PVC). In certain areas, the polyethylene was visibly embrittled; it readily cracked and fell off the wire when subjected to bending. Adjacent areas along the same cable exhibited no apparent damage and were found by tensile tests to possess good mechanical properties (elongation about 500%). Tensile tests revealed that for areas of the cable showing strong PE embrittlement, the PVC jacketing also showed decreased elongation (as low as 170%, compared with 300% for undamaged areas). Dosimetry mapping revealed a correlation between damaged areas of the cable, and areas of elevated radiation intensity within the application environment. However, the maximum dose rate experienced was estimated to be about 20 rad/hr, giving a total 12 yr integrated dose of about 2 Mrad. The ambient temperature was estimated to be about 42°C maximum. The extent of damage incurred by the cable was rather surprising in light of industry guidelines which suggest only minor effects at this level of total absorbed dose.

The discovery of the damaged cabling prompted us to undertake an investigation of the radiation-thermal aging behavior of these materials. Radiation experiments were performed on PE insulation and carbon black filled PVC jacketing similar in formulation to the degraded materials from the nuclear applications. Samples were irradiated using a Co-60 facility which is capable of delivering a range of dose rates and which has provision for temperature regulation. The air atmosphere surrounding the samples was continuously replenished during irradiation.

## RESULTS

Tensile elongation data for PE samples aged in environments of: 1) room temperature radiation (5 krad/hr, 25°C), 2) elevated temperature radiation (5 krad/hr, 80°C) and 3) elevated temperature in the absence of radiation (80°C) are presented in Fig. 1. It is seen that the combined effect of radiation and elevated temperature results in dramatically enhanced degradation compared with elevated temperature alone or radiation at room temperature. The joint effect of  $\gamma$ -radiation and elevated temperature was also found to occur when the two environments were applied in a sequential fashion, but only when the experiments were performed in the order: radiation at room temperature followed by elevated temperature. This rapid thermal degradation of preirradiated samples is illustrated in Fig. 1 and Table I. The apparent strong synergism observed with PE was also seen to occur with PVC, when similar aging experiments were performed (see Fig. 2 and Table I).

A further interesting aging behavior was found when radiation experiments were carried out at 60°C but at a variety of different dose rates. Tensile elongation data from these experiments, performed with PVC, are plotted in Fig. 3 as a function of total absorbed dose. The results demonstrate the existence of a strong dose-rate dependent degradation effect. PE behaves similarly.

The aging behaviors of the PE and PVC can be understood in terms of a peroxide-mediated oxidative degradation mechanism.  $\gamma$ -Irradiation of the polymers results in bond cleavage giving free radicals, which, in the presence of oxygen, react by a chain mechanism to form oxidation products that include hydroperoxides.<sup>2-4</sup> The hydroperoxides are thermally labile; breakdown yields more free radicals which can initiate new chain reactions with O<sub>2</sub> to give further oxidation including formation of more hydroperoxides. The radical steps set in motion during the course of the reactions include pathways which lead to polymer chain scission and crosslinking. Evidence for formation and subsequent breakdown of hydroperoxides in the thermo-oxidative degradation of PE has been cited before.<sup>5-7</sup>

Several lines of evidence supporting the importance of such a peroxide-mediated oxidative degradation mechanism are outlined below. Infrared spectra obtained on polyethylene samples from our combined radiation-elevated temperature environment experiments showed a correlation between deterioration in mechanical properties and the formation and growth of strong peaks in the carbonyl region ( $\lambda_{\text{max}}, \nu$  1710 cm<sup>-1</sup>). Spectra obtained at intervals along the cable from the nuclear application showed that embrittled regions exhibited strong carbonyl absorption bands essentially identical to those obtained in the laboratory aging experiments; in contrast, undamaged portions of the cable showed no carbonyl absorption. Representative IR spectra are given in Fig. 4. The close match obtained between the carbonyl bands of samples from our aging experiments and the carbonyl bands of the degraded cable under investigation provides evidence that the aging mechanism in the laboratory experiments parallels that in the use environment.

Further confirmation of the importance of oxygen to the degradation came from experiments performed in the simultaneous environment of radiation and elevated temperature, but under an inert atmosphere of N<sub>2</sub>; here, the degradation was found to be completely blocked. For the sequential experiments, an oxidative degradation mechanism involving substantial amounts of thermally-induced peroxide breakdown, as described earlier, would require the participation of O<sub>2</sub> in both the radiation step and the thermal step. To test this, inert atmosphere sequential aging experiments were performed as follows: 1) irradiation at room temperature in N<sub>2</sub> followed by elevated temperature treatment in air; 2) irradiation at room temperature in air followed by elevated



temperature treatment in  $N_2$ . In both cases the mechanical degradation was found to be blocked, in contrast to the rapid deterioration resulting when the sequential experiment is performed with an air environment throughout (see Table I). Thus in the case of the first inert atmosphere sequential experiment, the lack of  $O_2$  in the radiation environment prevented the radicals generated by the radiation from inducing oxidative chain reactions, and hence from forming any peroxides. In the second inert atmosphere sequential experiment, the lack of  $O_2$  during the elevated temperature treatment prevented the radicals generated by thermal breakdown of previously formed peroxides from inducing further oxidative chain reactions. In either case, radicals generated in the absence of available  $O_2$  largely disappear by recombination and disproportionation reactions.

To provide further evidence for the role of peroxides in the degradation effects observed, a chemical technique was developed. This technique is based on an analytical solution chemistry method in which hydroperoxides are reduced to alcohols by treatment with triphenylphosphine.<sup>8</sup> In our experiments, we treated intact polymer specimens with gaseous  $PH_3$  for 24 hr. The  $PH_3$  diffuses into the polymer to react with existing peroxide sites. Unreacted  $PH_3$  is then allowed to diffuse out of the sample. Sequential aging experiments were performed in which polymer samples were  $\gamma$ -irradiated at  $25^\circ C$ , treated with  $PH_3$ , then exposed to an elevated temperature. The results (Table II) show that the thermally-induced mechanical degradation was blocked, in contrast to the result for samples identically aged except for omission of the  $PH_3$  treatment. Additionally, infrared analysis of the samples that were irradiated and then treated with  $PH_3$  showed that subsequent thermal treatment resulted in no change in the carbonyl absorption, whereas strong carbonyl growth was observed during thermal treatment of samples similarly irradiated but not treated with  $PH_3$ .

Further sequential experiments were performed in which samples were irradiated at  $25^\circ C$ , and then thermally aged at several temperatures ( $60^\circ C$ ,  $70^\circ C$ , and  $78^\circ C$  in the case of PE;  $70^\circ C$ ,  $78^\circ C$  and  $90^\circ C$  in the case of PVC). An Arrhenius plot made to estimate the activation energy of the thermally-induced degradation step gave  $E_a = 16 \pm 3$  kcal/mole for PE, and  $E_a = 23 \pm 3$  kcal/mole for PVC. These numbers correspond well with activation energies for bimolecular decomposition of hydroperoxides in solution (which largely range between 15 and 26 kcal/mole,<sup>9,10</sup> and are comparable to values for the thermo-oxidative degradation of polymers at low temperatures.<sup>11,12</sup> The data are not consistent with activation energies for oxygen diffusion in polymers ( $E_a \sim 10$  kcal/mole)<sup>13</sup>.

#### DISCUSSION

The increased production of radicals due to time dependent thermal breakdown of peroxides accounts for the aging behaviors

observed in both our laboratory experiments and under the conditions of the nuclear application. The mechanism is variously manifested as an apparent radiation-elevated temperature synergism, as an ordering effect in sequential aging experiments, and as a dose rate effect. (The latter result from the fact that at progressively lower dose rates, the material simply has a longer time period over which the thermally-induced breakdown can occur.) Thus, the degradation of the cable material which had experienced only 2 Mrad at 42°C during its 12 yr service life could be viewed in terms of either of two empirical terminologies: 1) an apparent "synergistic interaction" involving a moderate radiation dose in combination with a moderately elevated temperature during a long time period, or 2) a "dose rate effect."

The occurrence of the aging effects described above is quite significant for understanding and predicting material lifetimes in radiation environments. Comprehensive studies made in the past have often tended to overlook the type of aging phenomena described here. For example, CERN has generated extensive radiation aging data during the past decade for a wide variety of polymers; this data was compiled and published as a "Selection Guide to Organic Materials for Nuclear Engineering."<sup>14,15</sup> The data in this publication indicate that radiation effects on mechanical properties of PVC and PE should be virtually nonexistent for the 2 Mrad dose received by the degraded cable under investigation by us. The report<sup>14</sup> further presents a Table of "Radiation Stabilities" at temperatures of "> 75°C" in which no major effects of combined radiation and elevated temperature are indicated for PVC or PE. The reason for the discrepancies between the CERN results and the damage actually found in the nuclear environment is clear in light of Fig. 3, since we observe very large dose rate effects over the range of 4 krad/hr to 950 krad/hr. The dose rate in the nuclear application environment (20 rad/hr) is two orders of magnitude below the lowest dose rate of Fig. 3, whereas all aging tests performed by CERN were apparently done at 10 Mrad/hr, an order of magnitude higher than the highest dose rate shown in Fig. 3. At such high dose rates, radiation-thermal synergisms and/or dose rate effects were simply never observed. Clearly, for materials such as PVC and PE where the time dependent peroxide breakdown can play a major role in the degradation mechanism, the total "tolerable dose" for a given material will be critically dependent upon the environmental temperature and the time period over which the dose is administered. For such materials, radiation degradation predictions arrived at from high dose rate experiments are meaningful only at the same dose rate employed in the test; generalized statements about a material's "tolerable dose" are meaningless.

Experimental observations made during the past three decades on radiation experiments performed under N<sub>2</sub> or vacuum have led to a

general conclusion (often cited in review articles)<sup>16,17</sup> that dose rate effects are not important under inert atmosphere. Clearly this conclusion is not valid for radiation experiments in the presence of O<sub>2</sub>. The evidence gathered in the present study indicates that a predominant cause of the observed dose rate effects for PE and PVC results from the peroxide breakdown mechanism. Other effects which have been discussed elsewhere (e.g., oxygen diffusion)<sup>18</sup> also could play some contributing role here. Whether peroxide breakdown and/or oxygen diffusion become important factors in determining the degradation rate will depend, in the general case, on the material type, the specimen geometry, and the particular environmental conditions involved.

Two additional consequences of peroxide breakdown which relate to material lifetimes and to aging predictions, are worth mentioning. First, the buildup of peroxides at moderate temperatures means it is possible that a polymeric material could be aged into a condition of low apparent damage, yet be preconditioned to a state of susceptibility to rapid degradation in the event of an increase in ambient temperature. Second, the strong ordering effect in the sequential aging experiments is of practical consequences for aging studies since sequential aging experiments have been used in the past in an effort to replicate usage environments having both radiation and elevated temperature;<sup>19</sup> such tests have often been designed without regard to ordering.

#### EXPERIMENTAL

Radiation dosimetry was performed using a Victoreen Model 550 Radocon IYI Integration/Rate Electrometer. The resulting dose rates were verified by the thermoluminescence method using CaF<sub>2</sub> wafers. Tensile elongation tests were performed using an Instron Model 1020. Fourier Transform Infrared spectra were obtained on KBr pellets made from polymer samples that had been ground at -196°C. A Nicolet Model 7199 FTIR spectrometer was employed. For inert atmosphere experiments, samples were held under vacuum for 24 hr, then sealed under N<sub>2</sub>. Treatment of samples with PH<sub>3</sub> was carried out at ambient temperature at 200 psi in a Parr Bomb for a period of 24 hr. Samples were left standing 3 days in air prior to elevated temperature treatment.

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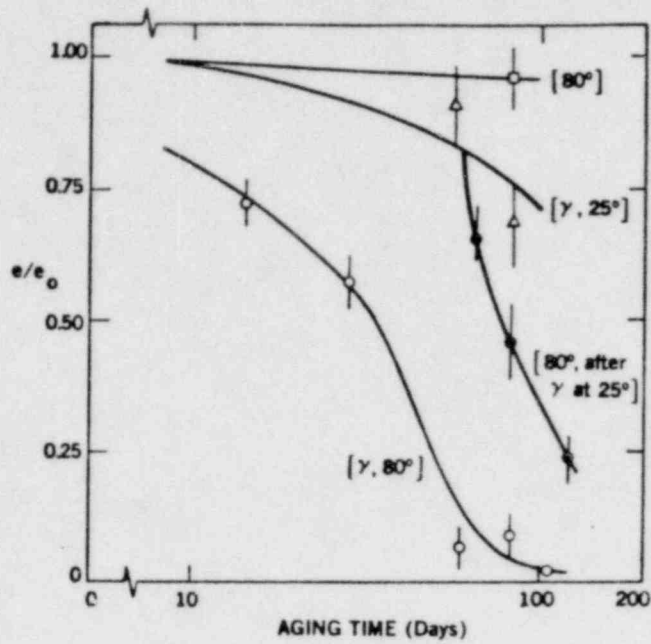


Figure 1. Aging of PE in various environments. Ultimate tensile elongation divided by initial (unaged) elongation is plotted versus aging time.

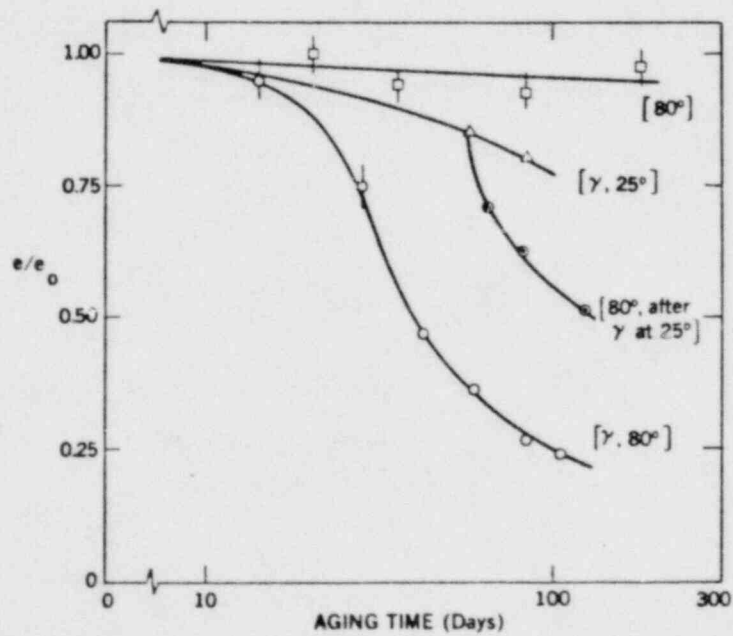


Figure 2. Aging of PVC in various environments. Ultimate tensile elongation divided by initial (unaged) elongation is plotted versus aging time.

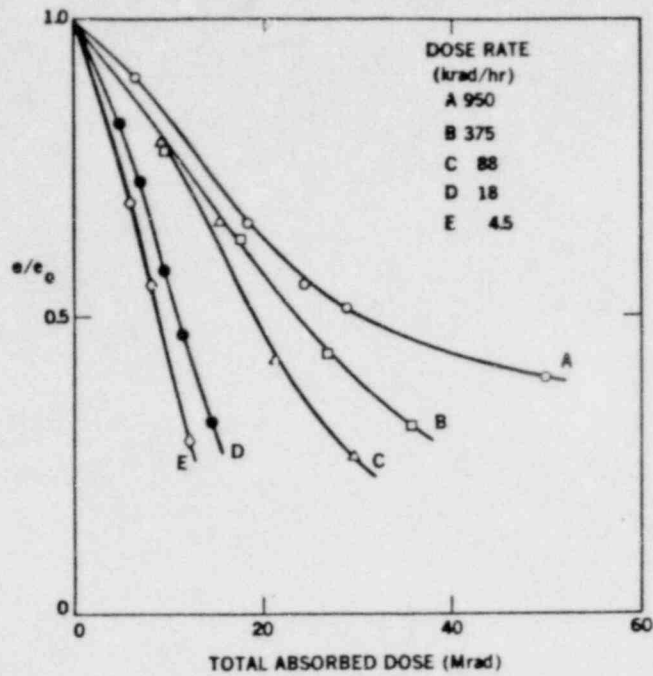


Figure 3. Aging of PVC at 60°C at a series of radiation dose rates. Ultimate tensile elongation divided by initial (unaged) elongation is plotted versus total absorbed radiation dosage.

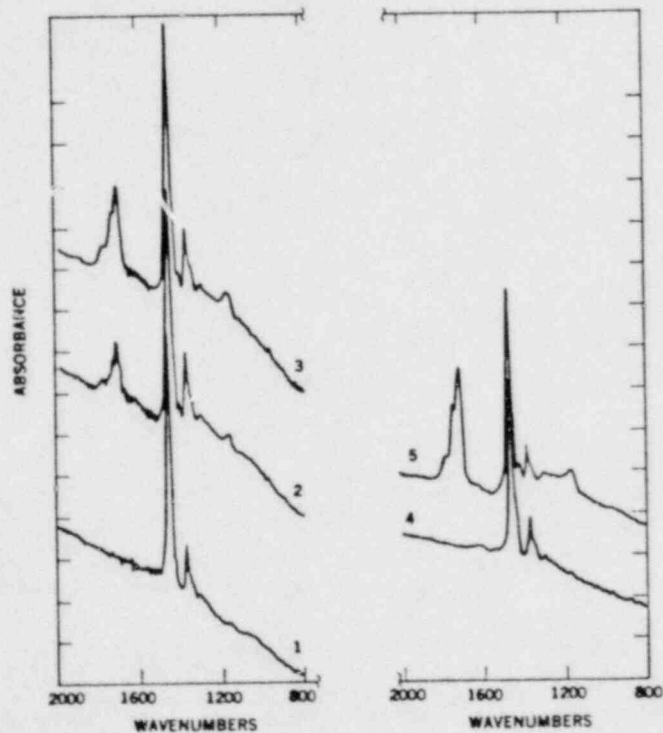


Figure 4. FTIR spectra of PE insulation from laboratory aging studies and from the cable section which had been in the nuclear environment for 12 yrs: 1) unaged sample ( $e/e_0 = 1.0$ ); 2) sample aged at 42 krad/hr, 90°C to a total dose of 7.1 Mrad ( $e/e_0 = .43$ ); 3) sample aged at 42 krad/hr, 90°C to a total dose of 17.9 Mrad ( $e/e_0 = .16$ ); 4) section of cable from nuclear application which did not show mechanical damage ( $e = 502\%$ ); 5) section of cable from nuclear application which was highly embrittled ( $e \sim 0\%$ ).

TABLE I

Sequential Aging Experiments: Tensile Elongation Data

EXPERIMENT*	$\frac{e}{e_0}^{**}$	
	PVC	PE
Unaged Material	1.0 $\pm$ 0.05	1.0 $\pm$ 0.1
$\gamma$ ; no subsequent T	0.80 $\pm$ 0.04	0.68 $\pm$ 0.09
T (in air); $\gamma$ (in air)	0.68 $\pm$ 0.04	0.72 $\pm$ 0.07
$\gamma$ (in air); T (in air)	0.32 $\pm$ 0.02	0.17 $\pm$ 0.04
$\gamma$ (in N <sub>2</sub> ); T (in air)	1.02 $\pm$ 0.05	1.01 $\pm$ 0.1
$\gamma$ (in air); T (in N <sub>2</sub> )	0.83 $\pm$ 0.04	0.81 $\pm$ 0.08

\*  $\gamma$  = gamma radiation - 5 krad/hr (for PE), 4.4 krad/hr (for PVC), at 25°C for 83 days

T = thermal exposure of 80°C for 83 days

\*\* Ultimate tensile elongation divided by initial elongation.  
 $e_0 = 310\%$  for PVC;  $e_0 = 540\%$  for PE

TABLE II

Sequential Experiments With and Without PH<sub>3</sub>: Tensile Elongation Data

EXPERIMENT*	$\frac{e}{e_0}^{**}$	
	PVC	PE
Unaged Material	1.0 $\pm$ 0.05	1.0 $\pm$ 0.1
$\gamma$	0.74 $\pm$ 0.04	0.71 $\pm$ 0.08
$\gamma$ ; T	0.38 $\pm$ 0.03	0.03 $\pm$ 0.03
$\gamma$ ; PH <sub>3</sub> ; T	0.74 $\pm$ 0.04	0.75 $\pm$ 0.08

\*  $\gamma$  = gamma radiation - 5 krad/hr (for PE), 4.4 krad/hr (for PVC) at 25°C for 96 days in air

T = thermal exposure of 80°C for 25 days in air

PH<sub>3</sub> =  $1.4 \times 10^6$  Pa (200 psi) of PH<sub>3</sub> at 25°C for 1 day

\*\* Ultimate tensile elongation divided by initial elongation.  
 $e_0 = 310\%$  for PVC;  $e_0 = 540\%$  for PE