Contract No:

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy (DOE) Office of Environmental Management (EM).

SRNL-TR-2009-00187

HLW FLEXIBLE JUMPER MATERIALS COMPATIBILITY EVALUATION (U)

T. E. Skidmore

SAVANNAH RIVER NATIONAL LABORATORY
Materials Science & Technology

August 2009

Savannah River Nuclear Solutions
Savannah River Site
Aiken, SC 29808

This document was prepared in conjunction with work accomplished under
Contract No. DE-AC09-08SR22470 with the U.S. Department of Energy.

TITLE: **HLW FLEXIBLE JUMPER MATERIALS COMPATIBILITY EVALUATION (U)**

APPROVALS

______________________________ **Date:**__________

T. E. Skidmore, Author
Materials NDE & Consultation Group
SRNL/MATERIALS SCIENCE & TECHNOLOGY

______________________________ **Date:**__________

W.L. Daugherty, Technical Reviewer
Materials Applications & Process Technology
SRNL/MATERIALS SCIENCE & TECHNOLOGY

______________________________ **Date:**__________

R. L. Bickford, Manager
Materials NDE & Consultation Group
SRNL/MATERIALS SCIENCE & TECHNOLOGY

______________________________ **Date:**__________

N. C. Iyer, Manager
SRNL/MATERIALS SCIENCE & TECHNOLOGY

______________________________ **Date:**__________

M. Hubbard
SRR Engineering/Closure Project Engineering
SAVANNAH RIVER REMEDIATION

(Blank Page)

Revision Log

Document No. **SRNL-TR-2009-00187** **Rev. No.** 0

Document Title: **HLW FLEXIBLE JUMPER MATERIALS COMPATIBILITY EVALUATION (U)**

Rev. #	Page #	Description of Revision	Date
0	all	Original document	8/13/2009

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS, TRADENAMES, AND ABBREVIATIONS

Alphasyn™	modified XLPE (Goodyear Viper® hose inner tube)
ASTM	American Society for Testing of Materials
CPE	chlorinated polyethylene
CSPE	chlorosulfonated polyethylene
DBA	Design Basis Accident
DLO	Diffusion-Limited Oxidation
DOE	Department of Energy
DSC	Differential Scanning Calorimetry
EES	Equipment Engineering Section
EPDM	Ethylene-propylene diene monomer
EPR	Ethylene-propylene rubber
ESCR	Environmental Stress Cracking Resistance
FT-IR	Fourier Transform – Infrared
G value	moles of gas released per 100 eV absorbed
Gray	International unit of radiation absorbed dose, 1 gray (Gy) = 100 rad
HEU	highly enriched uranium
HDPE	high-density polyethylene
HIH	Hose-In-Hose
HLW	high-level waste
Hypalon®	DuPont chlorosulfonated polyethylene
LDPE	low-density polyethylene
LLW	Low-level waste
LOCA	loss-of-coolant accident
MS&T	Materials Science & Technology
NAHAD	National Association of Hose & Accessories Distribution
Nordel®	DuPont tradename EPDM
OIT	Oxidation Induction Time
Omegasyn™	Goodyear Viper® hose covering (EPDM)
php	parts per hundred polymer
psi	pressure, pounds per square inch
Plicord®	Goodyear tradename, water discharge hose
rad	radiation absorbed dose (1 rad = 100 ergs/gram or 0.01 Gy)
RMA	Rubber Manufacturing Association
Royalene®	Uniroyal Chemicals EPDM elastomer (Crompton Corporation)
scm	standard cubic meters
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRS	Savannah River Site
TTR	Task Technical Request
Versiflo™	Goodyear tradename, water discharge hose
Veyance	Veyance Technologies, Inc.
Viper®	Goodyear tradename, chemical transfer hose
XLPE	crosslinked polyethylene (also PEX)
XRD	X-Ray Diffraction

1.0 EXECUTIVE SUMMARY

H-Tank Farm Engineering tasked SRNL/Materials Science & Technology (MS&T) to evaluate the compatibility of Goodyear Viper® chemical transfer hose with HLW solutions. The hose is proposed as a flexible Safety Class jumper for up to six months service. SRNL/MS&T performed various tests to evaluate the effects of radiation, high pH chemistry and elevated temperature on the hose, particularly the inner liner. Test results suggest an upper dose limit of 50 Mrad for the hose. Room temperature burst pressure values at 50 Mrad are estimated at 600-800 psi, providing a safety factor of 4.0-5.3X over the anticipated operating pressure of 150 psi and a safety factor of 3.0-4.0X over the working pressure of the hose (200 psi), independent of temperature effects. Radiation effects are minimal at doses less than 10 Mrad. Doses greater than 50 Mrad may be allowed, depending on operating conditions and required safety factors, but cannot be recommended at this time. At 250 Mrad, burst pressure values are reduced to the hose working pressure. At 300 Mrad, burst pressures are below 150 psi. At a bounding continuous dose rate of 57,870 rad/hr, the 50 Mrad dose limit is reached within 1.2 months. Actual dose rates may be lower, particularly during non-transfer periods. Refined dose calculations are therefore recommended to justify longer service. This report details the tests performed and interpretation of the results. Recommendations for shelf-life/storage, component quality verification, and post-service examination are provided.

2.0 SUMMARY

SRNL/Materials Science & Technology (MS&T) was tasked by H-Tank Farm Engineering to evaluate the compatibility of Goodyear Viper® chemical transfer hose with HLW solutions. The hose is proposed as a flexible Safety Class jumper for up to 6 months service.

Based on available data, a 50 Mrad dose limit is recommended for the hose. Doses less than 10 Mrad are not significant. Room temperature burst values at 50 Mrad are estimated at 600-800 psi for a safety factor of 4.0-5.3X over the anticipated operating pressure of 150 psi and a safety factor of 3.0-4.0X over the working pressure of the hose (200 psi). Room temperature burst values at 100 Mrad are 400-450 psi, providing a 2.7-3X safety factor over the anticipated operating pressure and a 2-2.3X factor over the working pressure. Lower doses provide greater safety margin and may allow higher operating pressures or longer service periods. Higher doses may be allowed, depending on operating conditions and required safety factors. Elevated temperature will also reduce burst and working pressure values.

The 50 Mrad dose limit is significantly less than the 6-month radiation dose (250 Mrad) initially established for the hose at a bounding dose rate of 57,870 rad/hr. At 250 Mrad, burst pressure values are reduced to the working pressure (200 psi). Mechanical properties of the hose liner such as elongation are significantly reduced. At 300 Mrad, burst pressure values (140 psi) are below the service pressure. The effects of 25% NaOH exposure appear to be minor, at least within the 30-day test period. For all radiation doses, NaOH exposure slightly decreases tensile strength and increases elongation compared to samples exposed to radiation only.

Service life of the hose depends on many factors, principally the radiation dose rate. The bounding dose rate of 57,870 rad/hr is likely very conservative for most transfers. At this rate continuously, the 50 Mrad dose limit is reached within approximately 1.2 months. However, the dose during a 20-hour transfer is only 1.2 Mrad. The dose rate during periods of non-transfer may be much lower. Refined dose rate calculations are recommended to justify longer service.

Laboratory tests cannot fully duplicate all service conditions. Therefore, hose performance should be closely monitored. Post-service examination of flexible jumper components is recommended to validate conclusions in this report and to provide a better understanding of real-world performance. Several material quality verification tests are recommended for hoses and fittings prior to use. A description of these tests and acceptance criteria is provided.

The SRS shelf-life of the Viper® hose is currently established at three (3) years. Hoses should be within one year of cure date upon receipt at SRS. This is consistent with the lowest shelf-life values defined in the SRS Shelf-Life Program and other shelf-life documents for materials known to be more sensitive to aging than the polymers used in the Viper® hose construction. Post-storage examination of hose is recommended to support possible shelf life extension.

3.0 BACKGROUND

3.1 Service Conditions

Jumper piping in Liquid Waste tank farm facilities is typically fabricated from Type 304L stainless steel that has been Corrosion Evaluated (CE) per SRS Engineering Standard 05951. Jumper fabrication and balancing for crane operation involves significant time and effort for specific configurations. H-Tank Farm Engineering has proposed using the Goodyear Viper® hose as a flexible jumper for emergency, short-term transfer of HLW solutions, particularly in cases where urgent transfers are needed and stainless steel jumpers of the proper configuration are not readily available. Use of the non-metallic, composite hose is currently limited to 6 calendar months per Design Services.

The anticipated service conditions for the hose in high-level radioactive waste (HLW) service are as outlined in Task Technical Request [1]:

- High pH radioactive waste solutions (pH =13+), maximum free hydroxide ~ 25%
- Radiation dose rate: 250 Mrad over 6 months = 57, 870 rad/hr (58 krad/hr)
- SpG = 1.3+
- Viscosity = 10 cp
- Maximum pressure = 150 psig
- Maximum temperature = 200 °F (93 °C), operating temps will likely be lower

The chemistry of high-level radioactive waste solutions is very complex, with nearly all known elements present in at least some concentration. The chemistry is generally dominated by sodium hydroxide, sodium nitrate, sodium aluminate and other compounds. High pH from sodium hydroxide is expected to dominate the chemical resistance of the hose, in the absence of significant organics. No significant organics are expected, though certain compounds may be present in limited concentration.

Other waste constituents are expected to be less aggressive toward most polymers, though synergistic effects are possible. Cumulative effects from limited concentrations of organics are possible but are not expected to be significant during a 6 month service. The combined effect of radiation, temperature, mechanical stress and chemistry is unknown.

3.2 Hose Description

The Goodyear Viper® hose is constructed of a modified crosslinked polyethylene (XLPE) inner tube (Alphasyn™), reinforced with a spiral-plied synthetic fabric with double wire helix, and an abrasion-resistant Omegasyn® EPDM cover [2]. The Viper® hose is rated from -40°F to 250 °F at a working pressure of 200 psi and can be cleaned using open-end steam up to 50 psi or in a bath containing 10% NaOH solution up to 212 °F. Operating temperature limits vary with the specific chemical media.

The Viper® hose is currently used as the primary hose in an aboveground Hose-In-Hose (HIH) system transferring low-level HEU solution from H Pump Pit-6 to Tank 50 via Tank 41. The system consists of ~ 600' of hose (100' sections) connected in an aboveground trench or overhead support. A 1.5" diameter Goodyear Viper® hose is used as the primary hose inside a 4" EPDM water discharge hose (Goodyear Plicord®/Versiflo® 125) for secondary containment and leak detection (Figures 1-2).

The HIH system has been operating for nearly 4 years with no known problems. In that system, radiation levels are relatively low, with moderate temperatures and pressures during limited duration transfers. The inner hose drains back to the HPP-6 sump but may contain standing waste between batches. A small section of hose extends into Tank 41 (C3 riser) which involves a higher dose rate (660 rad/hr). This results in a dose of 23 Mrad, assuming a 4 year exposure. Actual dose depends on time installed and actual dose rates. SRNL/MS&T previously reviewed the hose for the low-level HEU application, including service life estimates and recommendations for examination [3, 4].

For the HIH system, SRNL/MS&T previously analyzed the hose to identify materials of construction. A sample of the Viper® hose was analyzed by Fourier Transform Infrared (FT-IR) spectroscopy, Figure 3. Major bands of the sample spectrum were matched to a library spectrum of low density polyethylene (LDPE). Ethylene-propylene diene monomer (EPDM) was also likely present as a minor component of the liner but difficult to detect. The outer covering was confirmed to be EPDM.

X-ray diffraction (XRD) analysis identified low density polyethylene, which has a fair amount of crystallinity. The presence of aluminum silicate, polypropylene and iron were also detected (Figure 4). The use of precipitated silica or aluminosilicate (kaolin/clay) as a filler in polyethylene and other plastics is common. It offers certain advantages to carbon black filler including superior mechanical properties, lower permeability and product color variation if desired [5]. Carbon black fillers are normally used for UV light stability or for conductivity/antistatic properties. The polypropylene detected is likely a crystalline phase in the predominately amorphous EPDM. The source of iron is unknown and may be related to the wire reinforcement.

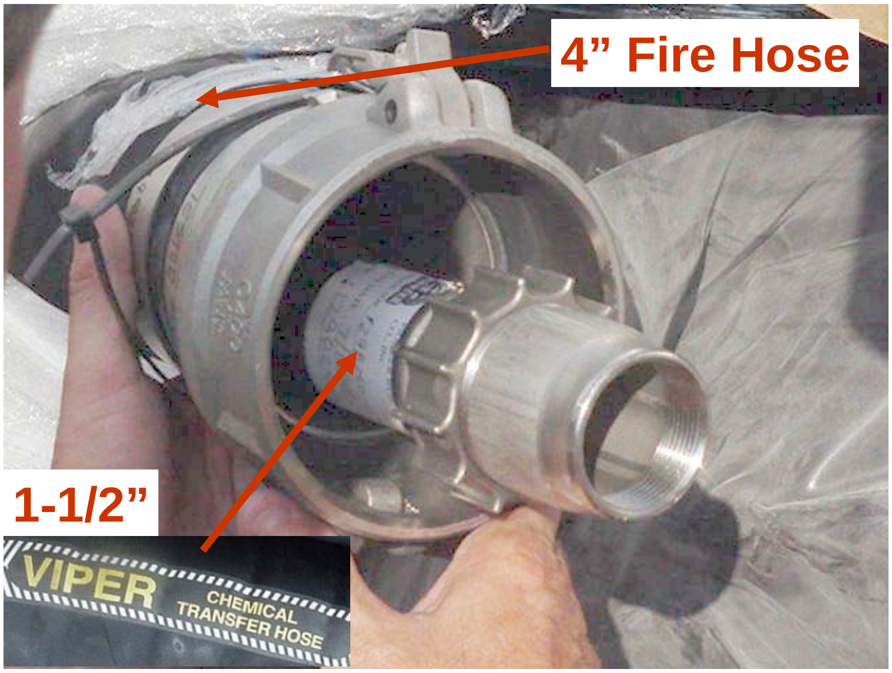


Figure 1. Low-level HEU “Hose-In-Hose” Transfer System
(1.5” Goodyear Viper® hose inside 4” Pliocord®/Versiflo™ 125 water discharge hose)

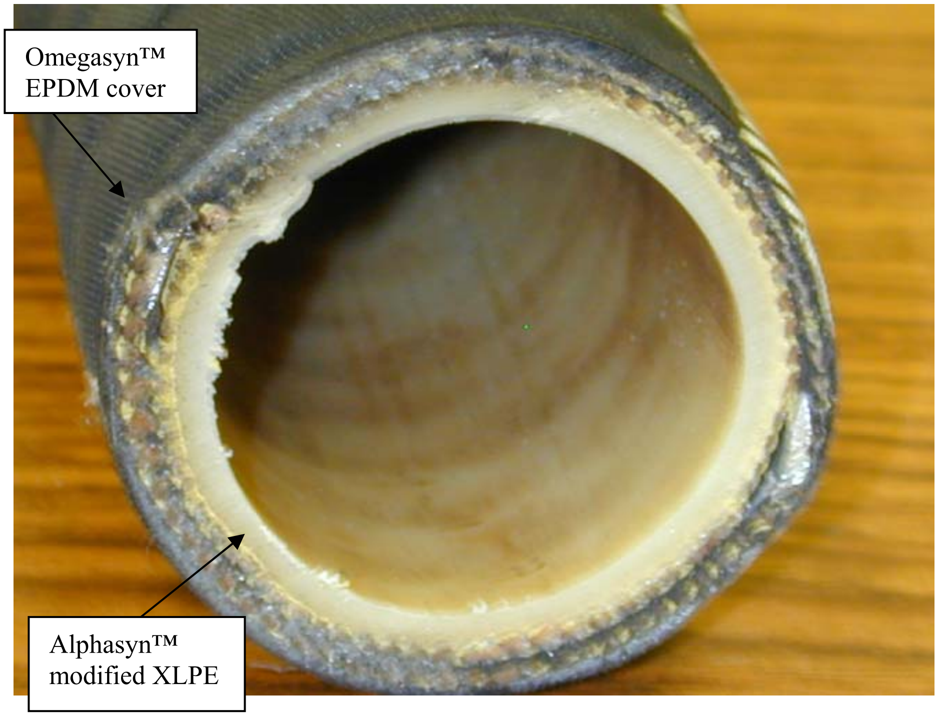


Figure 2. Cross-section of new Goodyear Viper® hose (1.5” OD)
(Modified XLPE inner tube, synthetic fiber/wire helix reinforced, EPDM cover)

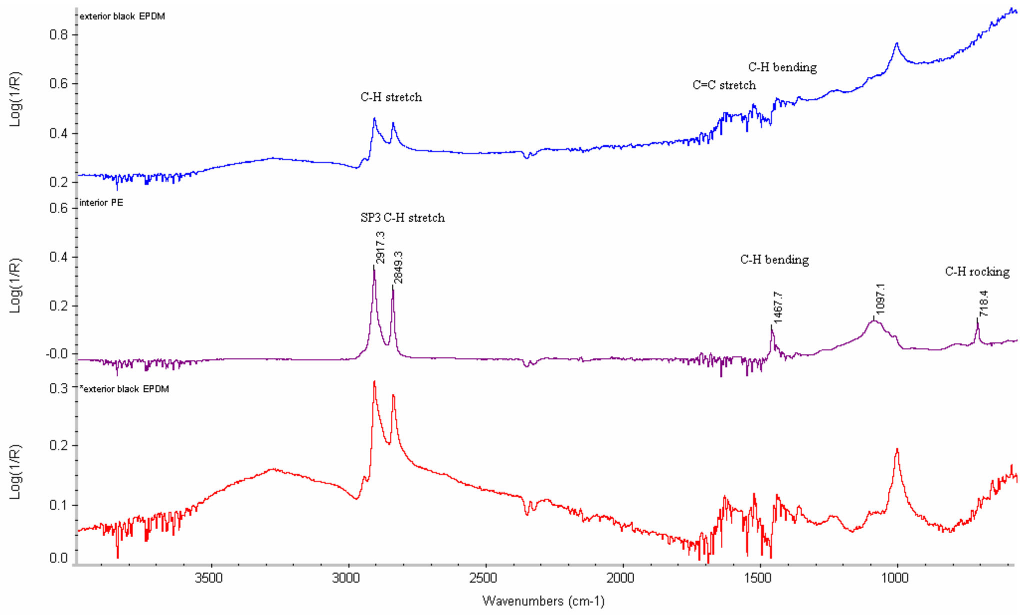


Figure 3. FT-IR spectra of modified XLPE lining and EPDM jacket of Viper® hose (top spectra for EPDM jacket with bond labels, liner filler at 1097 cm^{-1})

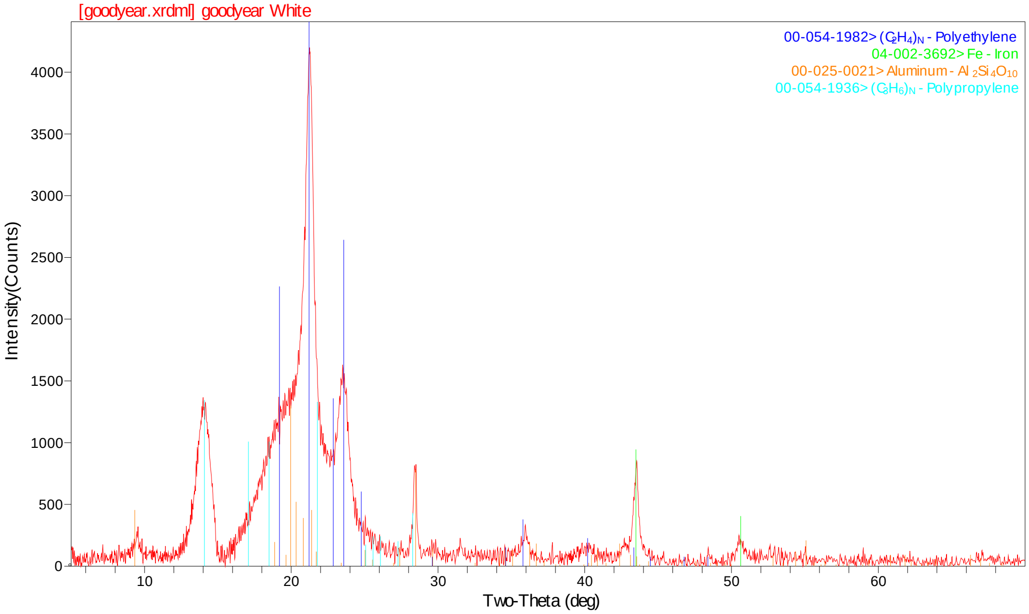


Figure 4. X-ray diffraction spectra of modified XLPE lining
(low-density polyethylene, iron, aluminosilicate, and polypropylene identified)

SRNL/MS&T found US Patent (#6440512) filed by Goodyear Tire & Rubber on 10/28/1999 for a hose construction based on an inner lining with a ternary blend of polymers comprised of 60-85% low-density polyethylene, 10-20% chlorinated polyethylene (CPE), chlorosulfonated polyethylene (CSPE) and mixtures thereof and 2-25% ethylene-propylene diene monomer (EPDM) [6]. The hose liner is peroxide-cured and may contain 5-150 php of silica reinforcing filler. Conductive carbon black fillers may be used when conveying flammable liquids.

SRNL/MS&T discussed the composition of the Alphasyn™ inner lining with Mr. Pascal Langlois, one of the patent assignees and the R&D manager of Veyance Technologies, the manufacturer of the Viper® hose for Goodyear. Veyance Technologies, now an independent company, is a former division of Goodyear Engineered Products Canada Inc. (Granford Plant). Mr. Langois confirmed that this patent covers the Viper® composition. Initial SRNL analysis did not specifically identify CPE or CSPE polymers, as a C-Cl stretch peak is expected at ~ 650-750 cm^{-1} and sulfonyl groups would be expected at ~1369 cm^{-1} and 1160 cm^{-1}.

Veyance and SRNL signed a Non-Disclosure Agreement to obtain composition and manufacturing details on the hose. Composition details are not included in this report, but the hose liner composition is generally consistent with the patent described above.

4.0 LITERATURE REVIEW

The principal polymers used in the Viper® hose composition (XLPE, EPDM and CSPE) are commonly used in instrumentation and control (I&C) cables in commercial nuclear applications. Therefore, many studies have been performed on the thermal and radiation aging behavior of these materials.

A particular aspect of polymers is that lower dose rate exposures in service can cause faster degradation than predicted from high dose rate exposures such as performed in laboratory tests or qualification protocols. This behavior is primarily attributed to diffusion-limited oxidation which is minimized during short-term exposures at very high dose rates. Therefore, highly accelerated radiation exposures may give misleading and overly optimistic results. Dose rate effects are generally less significant for short-term service or if the testing dose rate is similar to the service dose rate. Dose rate effects also tend to be reduced in inert or limited oxygen atmospheres, though this is not an absolute rule.

Fewer studies have involved combined exposure to radiation, heat, and chemicals or immersion in water, also with mechanical stress. Reasons for this likely include more extensive cost and because most nuclear cables are not usually exposed to harsh chemicals or elevated temperature during normal service, except for hot spots in the system and what might occur during a design basis accident (DBA) or loss of coolant accident (LOCA) event.

Nuclear cables with XLPE, EPR (ethylene-propylene rubber), EPDM and CSPE polymers are often qualified to radiation doses of 50-200 Mrad per IEEE standards [7, 8]. EPR is preferred over EPDM for most nuclear cables due to less sensitivity to dielectric breakdown and corona/ozone effects. Nuclear motors are often qualified to similar doses, though higher doses may be tolerated by most thermosetting resins used in motor insulation systems. Protective coatings used in primary containment for decontamination purposes are qualified to doses of 1000 Mrad, imposed at 1 Mrad/hr per ASTM D4082 [9]. Such doses are intended to account for cumulative dose expected over a typical service life (40-60 years), plus an accident scenario.

The critical property and dose to failure for a particular component can vary. The failure criterion often used for nuclear cable insulation is the dose to reduce elongation to 50% absolute or in some cases, the dose to reduce the initial elongation value by a certain percentage (e.g. 50%). Though conservative, this approach provides a margin of flexibility for aged cables, particularly in stressed or bent configurations.

The mechanical property most relevant for the Viper® hose and the failure parameter is unknown. Hoses are typically rated in terms of working pressure, which is normally based on a 4-5X safety factor reduction from burst pressure values. As the liner is the primary containment barrier, the mechanical properties of the liner likely play a significant role in tolerating expansion from thermal and pressure changes as well as accommodating bending stresses.

A summary of the more relevant studies on the degradation of XLPE, EPDM/EPR and CSPE polymers in nuclear applications is provided. CPE is less commonly used in nuclear cable insulations so it has not been widely studied.

Reference 10 gives a comprehensive summary of work done by many investigators on the environmental qualification of nuclear cables from 1975 to 1995. These are summarized here for reference, with emphasis on studies relevant to polymers used in the Viper® hose (XLPE, EPDM, CSPE).

One of the most notable examples of dose rate effects in service occurred in the SRS K-Reactor in 1976. Control cables for the #5 pump suction valve in K-Reactor were found to be severely embrittled after ~12 years exposure to a relatively low dose of 2.5 Mrad at 25 rad/hr at 43°C [11]. The polyethylene-insulated, PVC jacketed cables were initially deemed suitable for 40 years service based on high dose rate data.

Subsequent investigation by Sandia National Laboratory researchers showed that the dose to equal damage (DED) for PVC cable jacketing could vary from ~20 Mrad at 0.1 Mrad/hr to ~3 Mrad at 100 rad/hr (1 Gy/hr), Figure 5 [11, 12]. This translates to a dose rate factor of about 6X. Dose rate effects were also observed for the low-density (not cross-linked) polyethylene insulation, Figure 6. This work led to many studies on dose rate effects in polymers, particularly for cables used in the commercial nuclear industry. Even today, dose rate effects are not always recognized as a possible factor in material degradation.

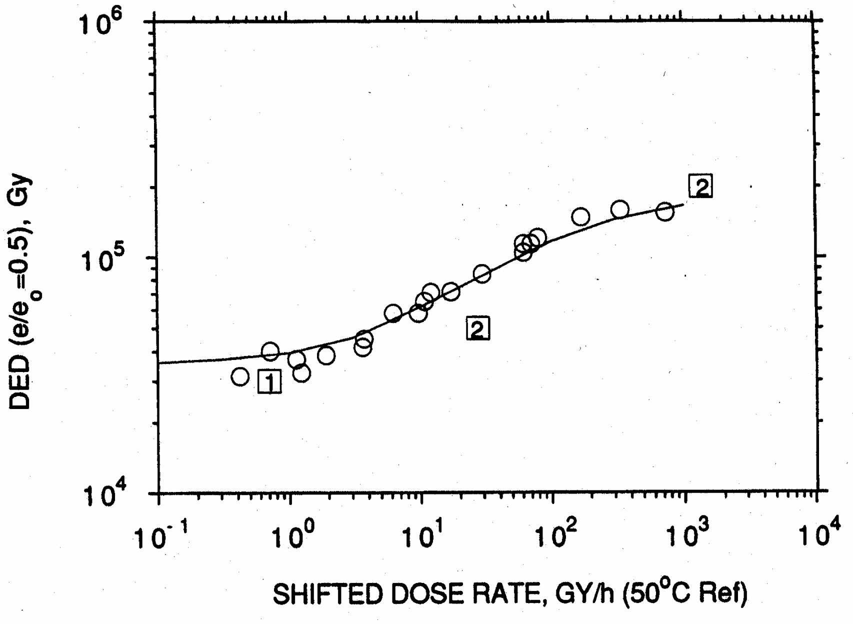


Figure 5. Dose to lose 50% elongation in PVC insulation [11].
(Data shifted by superposition to a reference temperature of 50°C, 1 Gy = 100 rad)

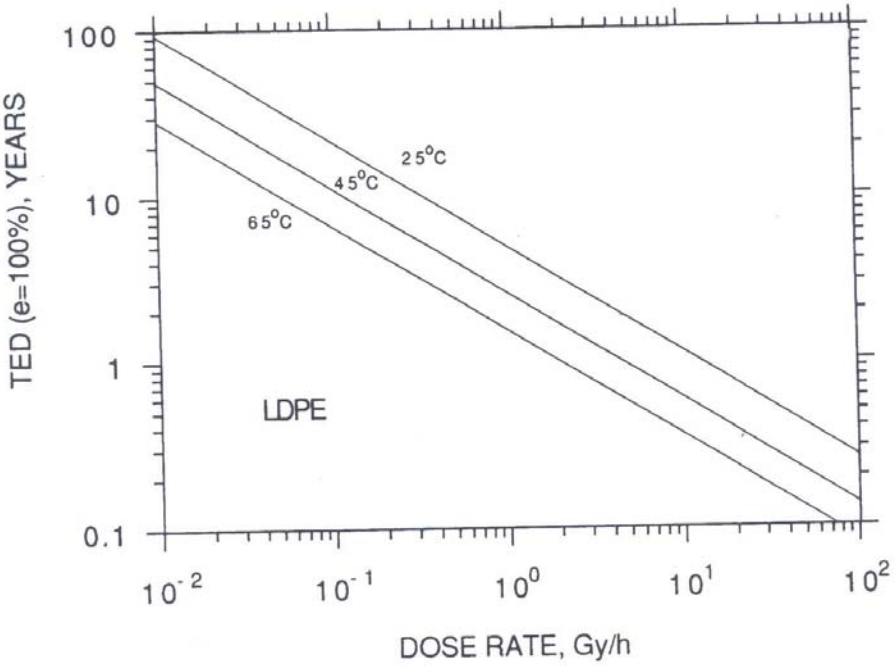


Figure 6. Time to 100% elongation, LDPE insulation (not XLPE) [12].

Reference 13 discusses the inadequacy of margin (overdose) historically used in nuclear qualification protocols. Based on observations from the Savannah River cable and subsequent studies, the use of overdose methods and high dose rate exposures to qualify materials for decades of service was shown to be inadequate for predicting the service life of such components.

Reference 14 shows the dose to lose 50% elongation for cross-linked low-density polyethylene (LDPE) could range from 100 Mrad at a dose rate of 1 Mrad/hr to a dose of 1E+05 rad (0.1 Mrad) at a dose rate of ~ 1 krad/hr (Figure 7). These data are for a particular formulation with no antioxidants present or added. Other formulations show improved resistance. At 58 krad/hr (the Viper hose rate), this reference would predict the dose to reduce elongation 50% at ~40 Mrad.

Reference 15 evaluated the effect of dose rate on the elongation to break value after 100 Mrad at dose rates of 18 Mrad/hr and 3.6 krad/hr. The dose to reduce elongation by 50% was 95 Mrad at 18 Mrad/hrand 52.5 Mrad at 3.6 krad/hr. Corresponding doses for EPR copolymers were 70 Mrad and 33 Mrad.

Reference 16 compares the effectiveness of antioxidants in EPR and XLPE cable insulations for nuclear power plant class 1E applications. Thermal aging conditions were 125 and 135 °C for 20 and 40 days. Radiation aging was done at ~230 Gy/hr (23 krad/hr) for 20 and 40 days for total doses of 11 and 22 Mrad. The authors derived an activation energy of 1.3eV for EPDM and

XLPE and predict that 20 days at 125 °C is equivalent to ~2 years at 90 °C and 40 days at 135 °C correlates to ~11 years at 90 °C. One aspect of this study showed that the elongation retention for both EPDM and XLPE with antioxidants (all variations) was 40-50% at a dose of 0.5 MGy (50 Mrad) compared to 5-15% for materials without any antioxidants. The most effective antioxidants in the study were Agerite MA or a combination of ZMTI/Aminox.

Reference 17 compares dose rate effects for nine cable insulation materials, including five EPR, three XLPE and one silicone compound. Irradiations were performed at room temperature, with measurements taken at 5 different dose rates from 5 to 2500 Gy/hr (500 to 2.5E+05 rad/hr). Results of this study indicate that for the XLPE materials, no dose rate effects were noted for the three lowest dose rates. The ultimate stress (tensile strength) increased by about 10% over unaged values at 0.1 MGy and fell to 70-80% of unaged values at 1.0 MGy (100 Mrad). No significant dose rate effects for the EPRs were noted. A small dose rate effect was noted above 340 Gy/hr at high doses. A dose rate effect was observed for two of three XLPE materials at dose rates above 30 Gy/hr (3000 rad/hr), but no dose rate effect was observed for any XLPE below 30 Gy/hr (down to 5 Gy/hr or 500 rad/hr). Effects at lower dose rates were not evaluated. Dose rate effects in XLPE are given in Figure 8.

Reference 18 discusses procedures for monitoring oxidation thermal degradation of XLPE and EPR cable insulations. Micro-specimens of cable samples aged for about 2 years were analyzed for melting point, crystallinity, gel content, infrared carbonyl absorbance, hardness and DSC oxidation induction time. Samples were aged at 115-145 °C with no radiation exposure. This study showed the time to reach 50% absolute elongation ranged from ~50 days at ~145 °C to 242 days (XLPE) and 780 days (EPR) at 115-120 °C (Figure 9). This reference indicates that the lifetime (defined as time to reach 50% absolute elongation) increases ~5x for a 30 °C decrease in temperature. In Reference 16, the authors' activation energy predicts a "life" increase of ~36x for a similar 35 °C decrease in temperature. The reasons for this variation are unknown but there are several possible. For one, the experiments in Reference 16 involved combined radiation and thermal exposures. Reference 18 only involved thermal exposure. The characterization techniques vary and the cable insulation formulations may also differ.

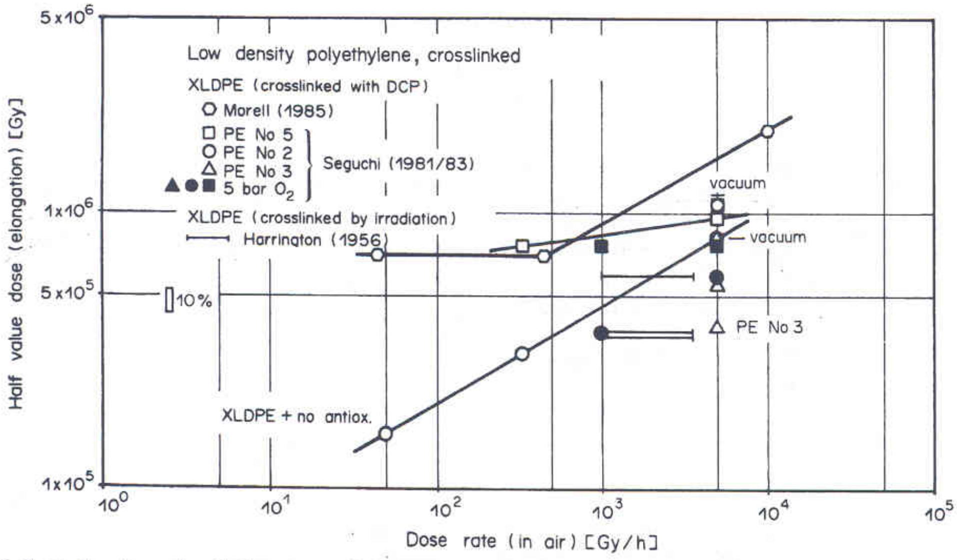


Fig. 6. Low density polyethylene, crosslinked. Sheets 1 mm thick, crosslinked with DCP: ○ No. 2: with no antioxidant; △ No. 3: with 1 phr NBC; □ No. 5: with 1 phr Irganox 1010.(31) ⊢⊣ Different types of Irrathene (Irradiation crosslinked LDPE).(32) ○ Cable insulation material of unknown composition.(33)

Figure 7. Dose rate effects in XLPE (in air) [14]

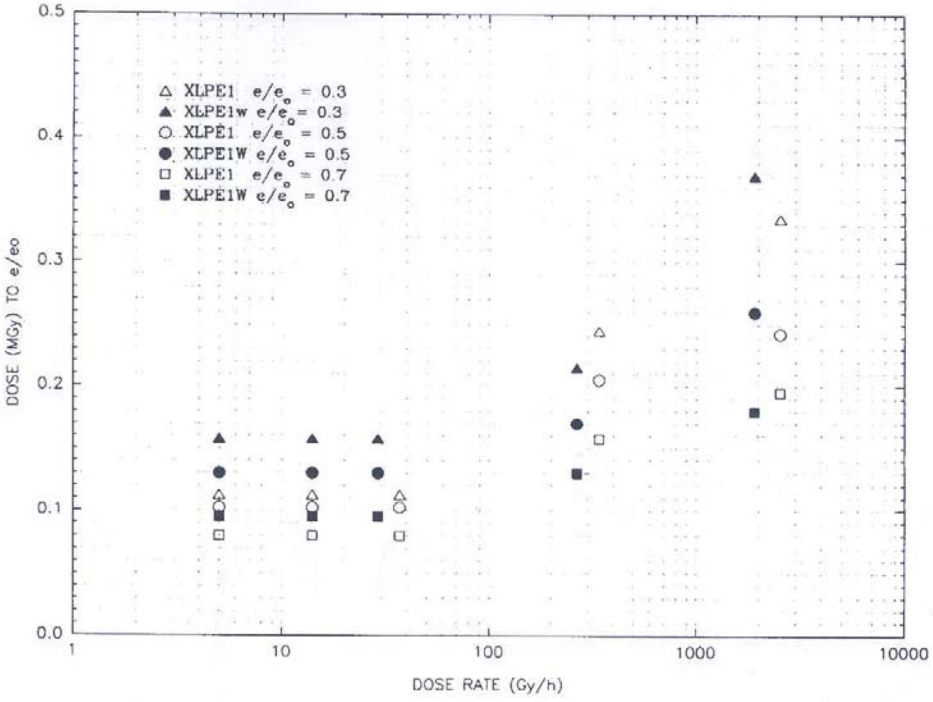


Figure 8. Dose Rate Effects in XLPE [17].

Reference 19 discusses the crosslinking of LDPE, which is mainly achieved via free radical polymerization of a peroxide or by a silanol condensation reaction of a silane modified polyethylene (Figure 10). The most common peroxide used is dicumylperoxide (DCP) which is reasonably stable at LDPE cable extrusion temperatures of 130-150 °C. This study showed that peroxide crosslinking produces a more homogeneous but weaker network whereas silane crosslinking results in a less homogeneous but stronger network. This is most likely due to the crosslinking process, with peroxide crosslinking occurring in the molten state, while silane crosslinking is carried out in the solid state after crystallization (more localized).

An interesting observation from this study is that thermal aging of XLPE (1.5% peroxide) at 90°C in oxygen showed the elongation at break remained stable at 500% for about 6 days, but then sharply dropped to around 50% absolute after only 12 days (Figure 11). This is far faster degradation than observed in other studies Reasons for this significant variation were not discussed. Exposure to pure oxygen is suspected as a contributing factor.

Reference 20 investigated the long-term performance of nuclear cables with CSPE (Hypalon®) insulations. Cables were aged in air and nitrogen at 120 °C and 200 °C. Conditions were assessed by micro-indenter and tensile tests. Some cables were not naturally aged prior to thermal aging, while some were naturally aged at 30-54 °C for nearly 25 years. Mechanical lifetime of cables was defined as the time for indenter modulus value to increase by 2X (Figure 12). Results showed Arrhenius behavior from 40-200 °C. No radiation aging was evaluated.
Reference 21 shows the effect of air vs. vacuum on the thermal stability of XLPE (high-density) crosslinked to 10 Mrad by electron beam irradiation. At 150 °C, the XLPE material was severely degraded after 1000 hours in air, with minimal degradation in vacuum. At 10 Mrad, the cross-link density of the polymer was approximately 48%. The study indicated that XLPE, normally rated for 120-130 °C service could be used to 150 °C in the absence of oxygen.

Reference 22 discusses nuclear industry lessons learned and the newly issued IEEE Std. 1205 (2000). In this document, XLPE cable insulations are described as showing “moderate” damage at 100 Mrad, but still highly functional with 60% elongation retained. The material is predicted to function for up to 60 years at 86.7 °C. EPR materials were predicted to retain 40% elongation after 50 Mrad.

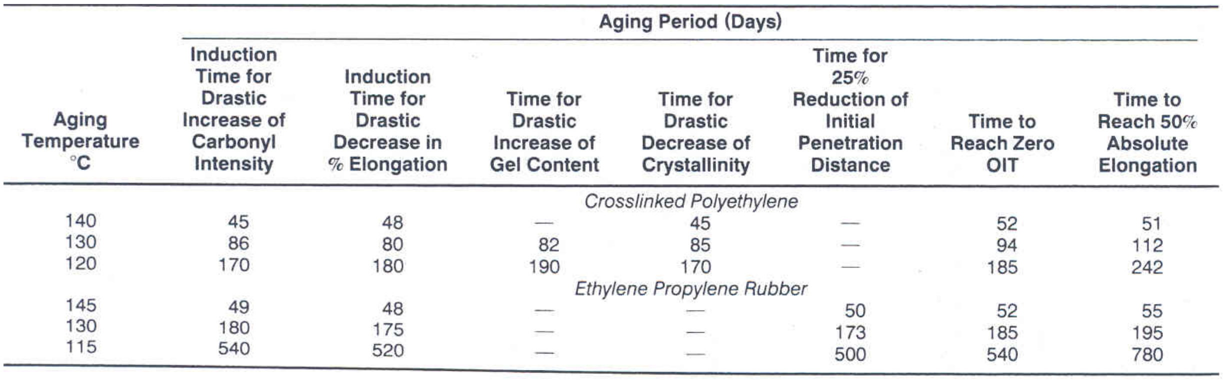
Reference 23 investigated the degradation of XLPE in water by gamma radiation. Samples were irradiated at dose rates of 6.5, 18 and 50 Gy/hr to total doses of 67-136 kGy at water temperatures of 40, 60, and 80 °C. The carbonyl index was measured via FT-IR spectroscopy with good correlation to mechanical properties. Oxygen permeability and diffusion coefficient were also measured. Degradation was least severe at 80 °C and most severe at 60 °C. Reduced degradation at the higher temperature was attributed to a lower coefficient of oxygen consumption (k), possibly due to antioxidant produced in the water by radiolysis.

Reference 24 indicates that antioxidant-free, crosslinked LDPE degrades faster (thermal oxidation) in aqueous environments than in air at the same temperature (75-92 °C) by a factor of two or more. This is contrary to the more conventional belief that oxidation rates in air are faster than in water or aqueous media (non-oxidizing). The reasons given by the authors for this observation include: extraction of low molecular weight additives by water, catalysis of free radical peroxides by transition metals in the water (copper and iron), and environmental stress cracking. XLPE samples were exposed to varying buffer solutions of different pH values from pH 3 to 10. Antioxidant-containing LDPE was shown to be more resistant to oxidation, but the same trend was observed (faster oxidation in aqueous media than air). Peroxide-cured XLPE (Union Carbide 4201) was more stabilized than straight LDPE. No radiation exposure was involved.

Reference 25 investigated the effect of co-agent on peroxide crosslinking of LDPE. Peroxide crosslinking is the most common way to produce crosslinked polyethylene (PEX or XLPE). A good diagram of various methods used to crosslink polyethylene is shown in Figure 12.

Reference 26 discusses the effects of radiochemical aging of EPDM elastomers. Films of EPR and EPDM were irradiated at 1 kGy/hr to doses between 5 and 455 kGy in an oxygen flow environment of 0.5L/min at 20 °C. Films were characterized by NMR spectroscopy, DSC and FT-IR to determine molar content, G values for oxidation products, glass transition temperatures and crystallinity. EPR films showed reduced crosslinking for doses lower than 254 kGy. Post-irradiation degradation at room temperature in the presence of light contributes to further aging.

Many other studies exist on the radiation and thermal aging of XLPE, EPR/EPDM and CSPE polymers, mostly related to nuclear cables in the absence of chemical exposure. The general consensus of the studies reviewed is that XLPE-based polymer insulations are suitable to at least 100 Mrad with moderate damage (50% retained elongation or higher). Higher doses are also possible depending on the product, formulation and failure criterion. Some nuclear cable products are qualified to doses of 200 Mrad or more. The radiation resistance of the Viper hose with modified XLPE liner is expected to show radiation resistance similar to nuclear cable insulations with similar polymers. The resistance of the blended polymer liner is likely slightly less than that of nuclear-qualified XLPE insulations but probably as high if not higher than that of EPR/EPDM or CSPE formulations.



	Aging Period (Days)						
Aging Temperature °C	Induction Time for Drastic Increase of Carbonyl Intensity	Induction Time for Drastic Decrease in % Elongation	Time for Drastic Increase of Gel Content	Time for Drastic Decrease of Crystallinity	Time for 25% Reduction of Initial Penetration Distance	Time to Reach Zero OIT	Time to Reach 50% Absolute Elongation
				Crosslinked Polyethylene			
140	45	48	—	45	—	52	51
130	86	80	82	85	—	94	112
120	170	180	190	170	—	185	242
				Ethylene Propylene Rubber			
145	49	48	—	—	50	52	55
130	180	175	—	—	173	185	195
115	540	520	—	—	500	540	780

Figure 9. Comparison of methods to characterize aging of XLPE and EPR [18]

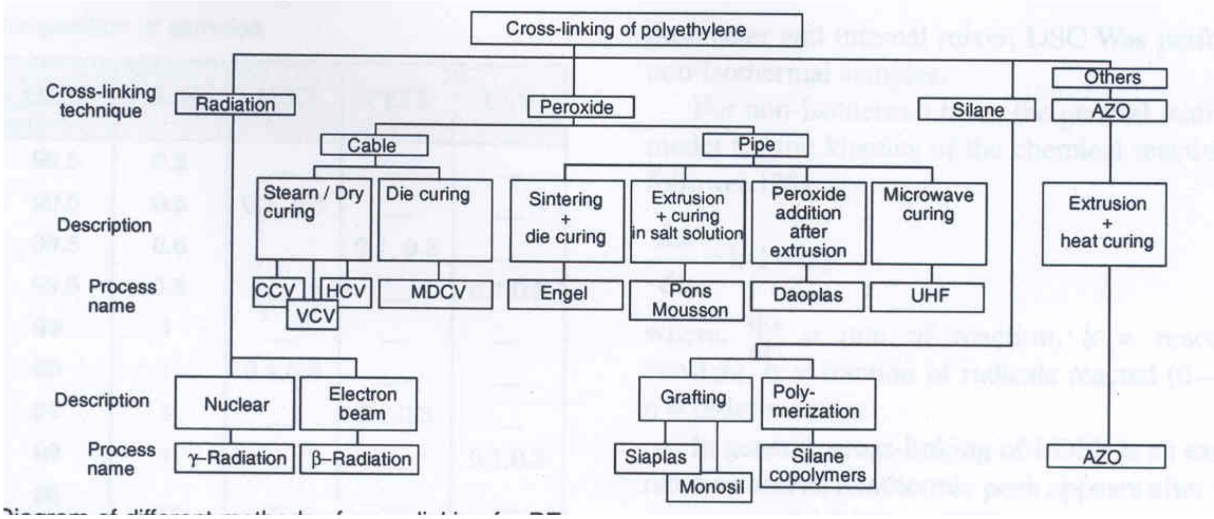


Figure 10. Methods of Cross-Linking Polyethylene [19]

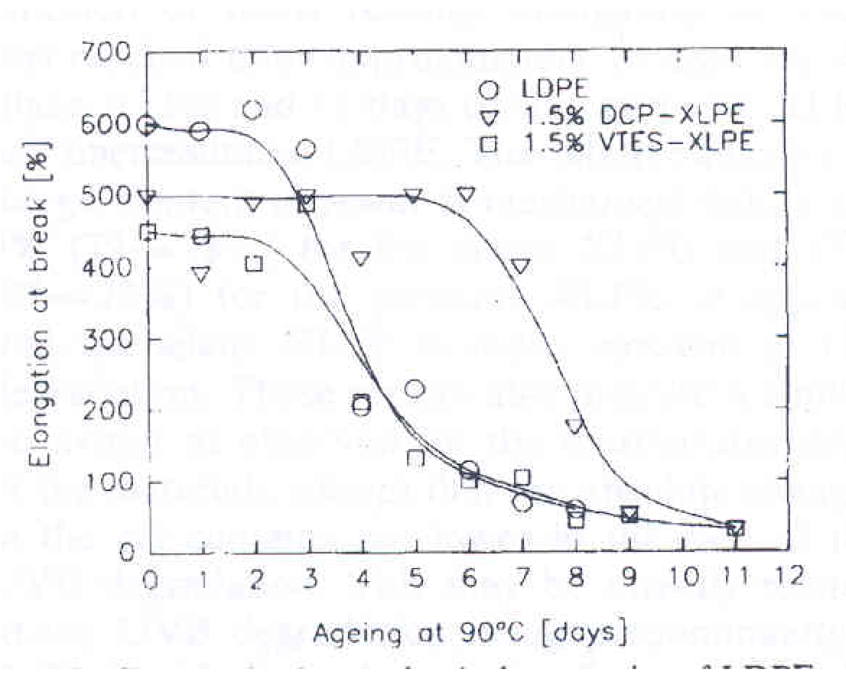


Figure 11. Thermal degradation of XLPE vs. LDPE at 90 °C [19]

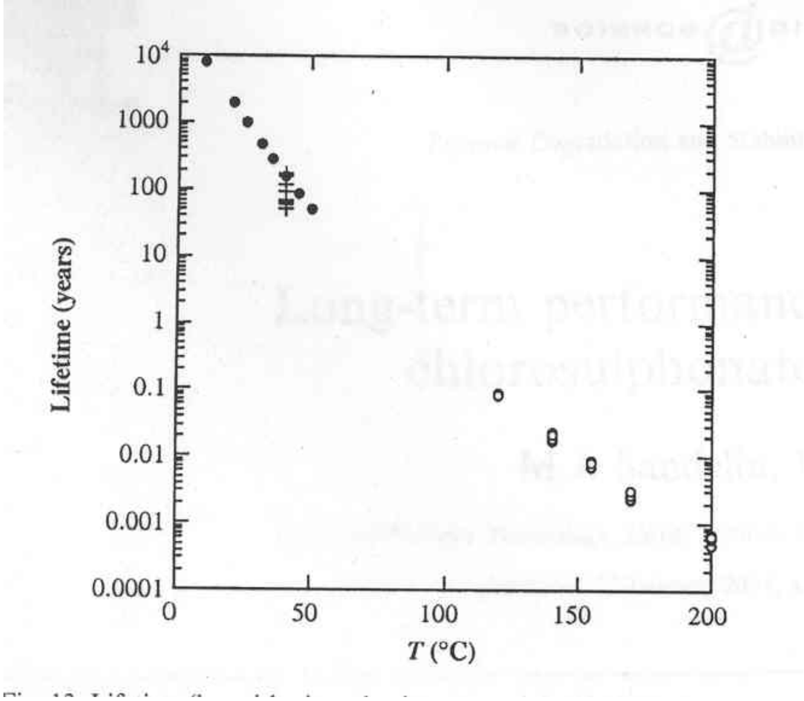


Figure 12. Service life of CSPE in air (time to reach 2X indenter modulus) [20]

Aside from heat and radiation, the Viper® hose will be subjected to HLW chemistry, which is dominated by high pH hydroxide. Literature sources indicate the main polymers used in the Viper® hose liner (XLPE, EPDM, CSPE, CPE) are all highly resistant to NaOH solutions at least at room temperature. The nylon fiber reinforcement is also resistant but this layer should never see direct fluid contact unless the inner liner is penetrated.

Several references indicate that polyethylenes are generally resistant to at least 30% NaOH up to 70°C [27-30]. Polyethylene drums are commonly used to store 50% NaOH solutions at ambient temperatures. Low-density polyethylene (LDPE) resins are more permeable than high-density versions, while high-density versions can be susceptible to environmental stress-cracking (ESC), particularly when exposed to certain chemicals such as surfactants. Crosslinked polyethylene (XLPE) resins are far more resistant to ESC. The resistance of the modified XLPE inner tube of the Viper® hose to the specific HLW chemistry is unknown. However, vendor ratings and independent data indicate that XLPE and the other polymers potentially used in the liner composition are resistant to NaOH solutions at or near the anticipated conditions. The exposure time for such ratings varies with the source.

Blending of EPDM and/or CSPE and/or EPDM polymers in the modified XLPE liner is expected to increase (or at least not reduce) the overall resistance of the inner liner to permeation, oxidation and the high pH nature of the waste. The resistance of the modified liner to certain organics such as TBP may vary depending on the type and concentration present. These effects can only be evaluated by testing in simulated waste or examining hose after extended service.

The Viper® hose is rated for "continuous" use in 50% NaOH up to 150 °F, which is below the maximum HLW solution temperature expected (200 °F) [31]. The same rating applies to the Green XLPE, Purple Flexwing® (EPDM), and Brown Flexwing® (CPE) hoses. Note that the Yellow Flexwing® hose with a Hypalon®/CSPE tube lining is rated as "B" for intermittent service in 50% NaOH at 150 °F. Such limits are likely conservative for liability reasons, but the basis for the ratings is unknown. Compatibility ratings for NaOH concentrations < 50 wt% are not provided. Each transfer is likely comparable to the allowed periodic cleaning in 10% NaOH at 212 °F, at higher hydroxide concentrations but lower temperatures.

The hose will not be exposed on a continuous basis. Approximately 36 transfers are expected in a 6 month period, or about 6 transfers per month. The duration of a given transfer is estimated at 20 hours. Therefore, the cumulative exposure time for HLW solution at elevated temperature is estimated at 720 hours, not accounting for contact during periods of non-transfer. Therefore, a 30-day exposure test is judged to reasonably simulate six months of periodic service at elevated temperature. Some residues may remain in the hose during the entire service period but at lower temperature.

In summary, many references are available that discuss the radiation, chemical and thermal resistance of the generic polymers involved in the Viper® hose construction. The combined effects of chemistry, temperature, pressure, radiation dose and dose rate are difficult to assess as no single reference addresses all factors. In addition, the liner formulation is unique. Most references available are focused on the radiation and thermal aging of nuclear cable insulations that may be exposed at varying dose rates. The effects of chemical exposure in combination with radiation are less studied for these materials due to general lack of chemical exposure in service.

The majority of references indicate that XLPE cable formulations are capable of tolerating radiation doses of up to 100-200 Mrad with reasonable retention of properties. EPR and EPDM insulations are tolerant of doses of at least 50 Mrad with some formulations and products suitable to higher doses. The modified Viper® liner is therefore likely to be less resistant to radiation than the most resistant XLPE insulations but it is likely more resistant than typical EPR/EPDM or CSPE insulations.

5.0 EXPERIMENTAL

The baseline mechanical performance of the Viper® hose was evaluated by SRNL/EES under a separate effort [32]. These tests indicate that the Goodyear Viper® hose is very robust. The SRNL/MS&T effort was focused on the compatibility of the hose with the anticipated service conditions. Compatibility testing consisted of two primary aspects: 1) chemical/thermal/radiation effects on the hose liner and 2) burst testing of irradiated hose samples

As the liner of the hose is the primary containment barrier, the properties of the liner were considered the most important. The hose reinforcement dictates mechanical robustness and bend radius. Cured dumbbell liner samples were provided by Veyance Technologies, Figure 13. Samples were cured on a 4" mandrel as used to cure actual hose sections, with a thin Teflon sheet behind the liner for mold release. The as-cured liner tube was then die-cut by the vendor into dumbbell tensile specimens meeting ASTM D638 [33]. The samples were cut in the hoop direction of the cured liner, hence the retained the curvature of the tube.

Samples were irradiated to target doses of 50, 100, 250 and 300 Mrad in the SRNL Gamma Irradiation Facility at a dose rate of ~0.4 Mrad/hr. Doses were selected to bound the anticipated doses in service during a 6 month period. A few samples were irradiated at a slightly lower rate (0.17 Mrad/hr) to evaluate the potential for dose rate effects. Samples were characterized via the following methods:

- Mechanical testing (tensile strength, elongation, modulus, hardness)
- Differential Scanning Calorimetry (DSC)
- X-Ray Diffraction (XRD)
- FT-IR spectroscopy
- FT-Raman spectroscopy
- Gel content/crystallinity/transvinylidene index

Additional tensile samples were irradiated to the same doses, then immersed in 25% NaOH at 200 °F for 30 days and similarly characterized. Immersion was performed in the 723-A Materials Laboratory using a portable recirculating chiller, a high efficiency glass condenser, stainless steel vessel and a silicone band heater (Figure 14). Uniform heating of the heavy NaOH solution on a hotplate was difficult due to poor heat transfer and lack of mixing. The chiller and heater were connected to an automatic shutoff using a calibrated thermocouple (Type K). Frequent monitoring of solution temperature indicated temperature stability of 200+/-5 °F.

Short sections (9" long) of 1" ID Viper® hose were irradiated at maximum dose rate followed by burst testing in the EES/High Pressure Lab. Due to limited space in the smaller Model 109 chamber, doses were limited to 100, 250 and 300 Mrad. Additional longer length (18") samples of 1" Viper® hose with swaged-on fittings as recommended by the hose manufacturer were irradiated in the Model 484 irradiator at ~ 8.2E+04 rad/hr for about four months. These hoses were flipped halfway during irradiation to achieve an average dose of 250 Mrad. These may be used in future tests.

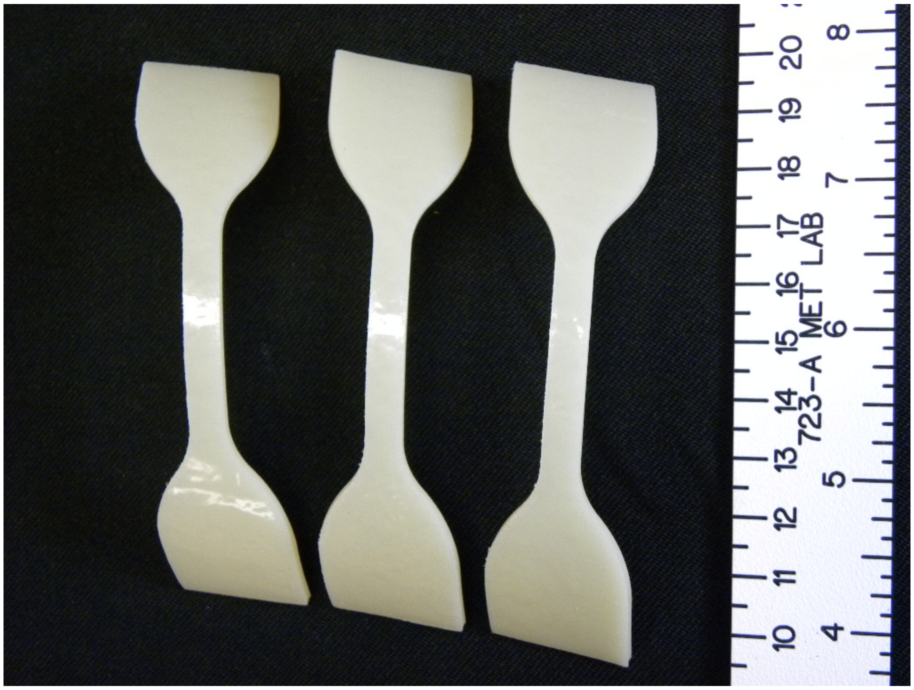


Figure 13. As-cured tensile samples of the Viper® hose liner (modified XLPE)

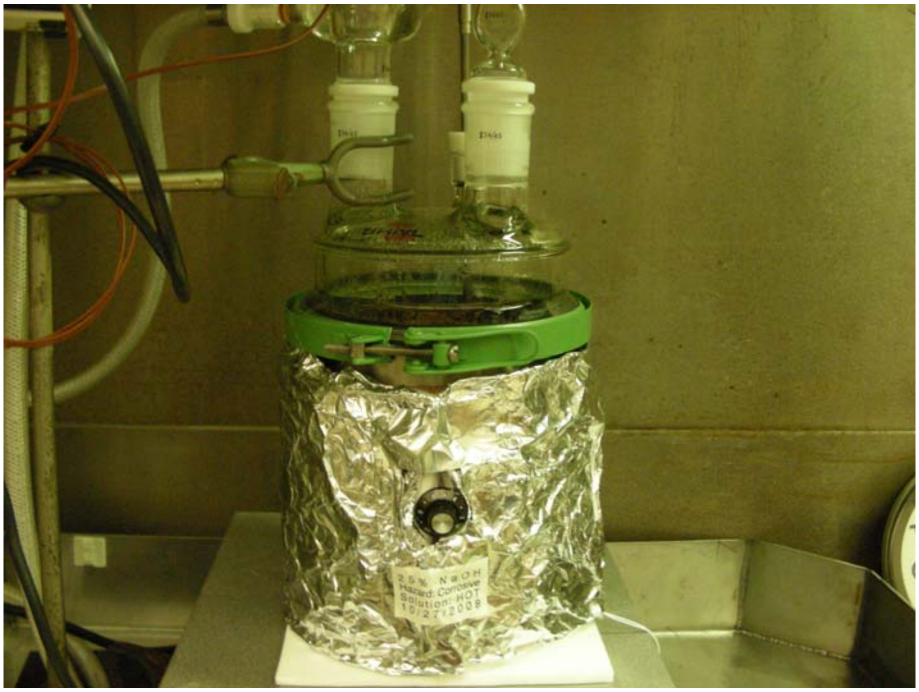


Figure 14. Chemical immersion test set-up (25% NaOH at 200 °F)

6.0 RESULTS AND OBSERVATIONS

6.1 Visual/General

Liner samples irradiated to doses of 50, 100, 250 and 300 Mrad are shown in Figures 15-19. Darkening or yellowing with radiation dose is consistent with observations in other studies. Additional darkening was observed for irradiated samples following immersion in 25% NaOH at 200 °F (Figures 20-24). This is primarily attributed to thermo-oxidation. Darkened regions at the bottom of the gage length are due to stainless steel wire used to keep samples immersed in the high density solution. No distinguishable changes in thickness were determined for the samples. Accurate measurements were difficult to obtain due to the waviness of the surface from the molding process. Weight loss solely as a function of radiation dose was not determined. In hindsight, this would have been of interest to validate gas generation estimates discussed in later sections. The degree of curvature retained by the samples from the mandrel cure did not noticeably change with radiation or chemical exposure.

Figure 15. Liner Tensile Samples Gamma-Irradiated to 50 Mrad (at 0.4 Mrad/hr)

Figure 16. Liner Tensile Samples Gamma Irradiated to 100 Mrad (at 0.4 Mrad/hr)

Figure 17. Liner Tensile Samples Gamma-Irradiated to 250 Mrad (at 0.4 Mrad/hr)

Figure 18. Liner Tensile Samples Gamma-Irradiated to 250 Mrad (lower rate)

Figure 19. Liner Tensile Samples Gamma-Irradiated to 300 Mrad

Figure 20. Liner samples after 30-day immersion (25% NaOH at 200 °F), 50 Mrad

Figure 21. Liner samples after 30-day immersion (25% NaOH at 200 °F), 100 Mrad

Figure 22. Liner samples after 30-day immersion (25% NaOH at 200 °F), 250 Mrad

Figure 23. Liner samples after 30-day immersion (25% NaOH at 200 °F), 250 Mrad (low rate)

Figure 24. Liner samples after 30-day immersion (25% NaOH at 200 °F), 300 Mrad

6.2 Mechanical Testing

Baseline tensile tests of the liner material were performed per ASTM D638 for sample type IV, using a crosshead speed of 50 +/- 10% mm/min (2 in./min). A slower crosshead speed of 5 mm/min was initially used, which produced less consistent results. Samples were cured on a mandrel and cut in the liner wrapping direction. Average baseline tensile strength and elongation values for the liner were approximately 2100 psi and 190% respectively.

Vendor production values for liner samples from a 1” hose since 2007 show an average tensile strength of 1883 psi with a standard deviation of 133.4 for 39 tests. The average vendor elongation value is 277% with a standard deviation of 23.3. SRNL tensile values are within ~1.6X the vendor’s standard deviation, with SRNL elongation values even lower.

Reasons for lower elongation values are likely due to variation in the test methods, particularly the crosshead speed. The vendor tests the liner material per ASTM D412 with a crosshead speed of 20 in./min [34]. The faster strain rate may prevent the crosslinked polyethylene structure from aligning and resisting the tension, thus allowing more elongation. There could also be some orientation of the polymer chains during the crosslinking process as cured on the mandrel but this is speculation.

Due to the observed variation in elongation values, SRNL requested Veyance to perform baseline tests of similar samples taken from both orientations at both crosshead speeds for comparison. These data are given in Table 1 below. Tensile strength and elongation values at 2 inches/min are higher in the longitudinal direction than the wrapping direction. Modulus values at 100% and 200% elongation are more similar. The results are similar at 20 inches/min, though the differences in tensile strength and elongation values between samples in the wrapping and longitudinal directions are smaller. The vendor values at 2 in./min show slightly reduced tensile strength and elongation values, but the elongation values are still higher than those measured by SRNL. Additional tests would be needed to resolve this discrepancy.

Table 1. Vendor baseline mechanical properties vs. crosshead speed and orientation

2 inches/min:	Wrap direction	Longitudinal direction	Diff%
Tensile strength, psi	1583	2049	29.4
Modulus at 100%, psi	1058	1058	0.0
Modulus at 200%, psi	1403	1384	1.4
Elongation at break,%	234	294	25.6
20 inches/min.:	Wrap direction	Longitudinal direction	Diff%
Tensile strength, psi	1867	2067	10.7
Modulus at 100%, psi	1209	1175	2.9
Modulus at 200%, psi	1517	1438	5.5
Elongation at break,%	264	302	14.4

These values are considered typical though a statistical range is unknown. Tensile test results for irradiated liner samples are given in Figure 25. The curves shown are representative of three samples per condition. Only slight variation was observed among samples at each condition.

At 50 Mrad, the tensile strength is reduced from 2100 psi to approximately 1720 psi or an 18% reduction. Elongation was reduced by 47% to 100% absolute. Assuming 190% as a starting point, the hose liner would marginally pass the 50% reduction in elongation (E/Eo=0.50) failure criterion for nuclear cables at 50 Mrad. The retained elongation (100% absolute) is significant. As SRNL elongation values are lower than the vendor-reported values, the changes expected in service may be less severe. The SRNL values are therefore conservative.

At 100 Mrad, tensile strength is reduced by 22% to 1630 psi. Elongation is reduced by 60% to 76% absolute. At this dose, the hose liner does not pass the 50% elongation reduction criterion, but it does pass the 50% absolute elongation criterion. At 250 Mrad, tensile strength is reduced by about 50% to around 1120 psi, with elongation reduced by about 90% to ~20% absolute. At 300 Mrad, the tensile strength is reduced by 55% to around 1000 psi, with elongation reduced by about 93% to ~14.3% absolute.

Results for irradiated samples after 30-day immersion in 25% NaOH at 200 °F are given in Figure 26. In practically all cases, NaOH exposure following irradiation appears to slightly reduce tensile strength and increase elongation. The effect is more pronounced at 50 Mrad. A possible cause is that different degradation mechanisms (crosslinking vs. chain scission) could be competing. Chain scission of crosslinks already present from the curing process could occur at some threshold dose, with increased crosslinking at higher doses. Notably, the elongation value of samples exposed to both 250 and 300 Mrad plus immersion in 25% NaOH is approximately 33%.

Though a significant reduction, a 33% absolute elongation value is still reasonable. These results indicate that NaOH exposure is not significantly detrimental or does not result in liner embrittlement, at least within the test period. The observed behavior may be more dependent on time at temperature in immersion, rather than the high pH environment. Elevated temperature exposure may anneal at least some damage done by ionizing radiation, providing some additional protection. One way to evaluate this aspect in future tests would be to immerse irradiated and non-irradiated samples in water at 200 °F for a control. Longer immersion tests may also be needed.

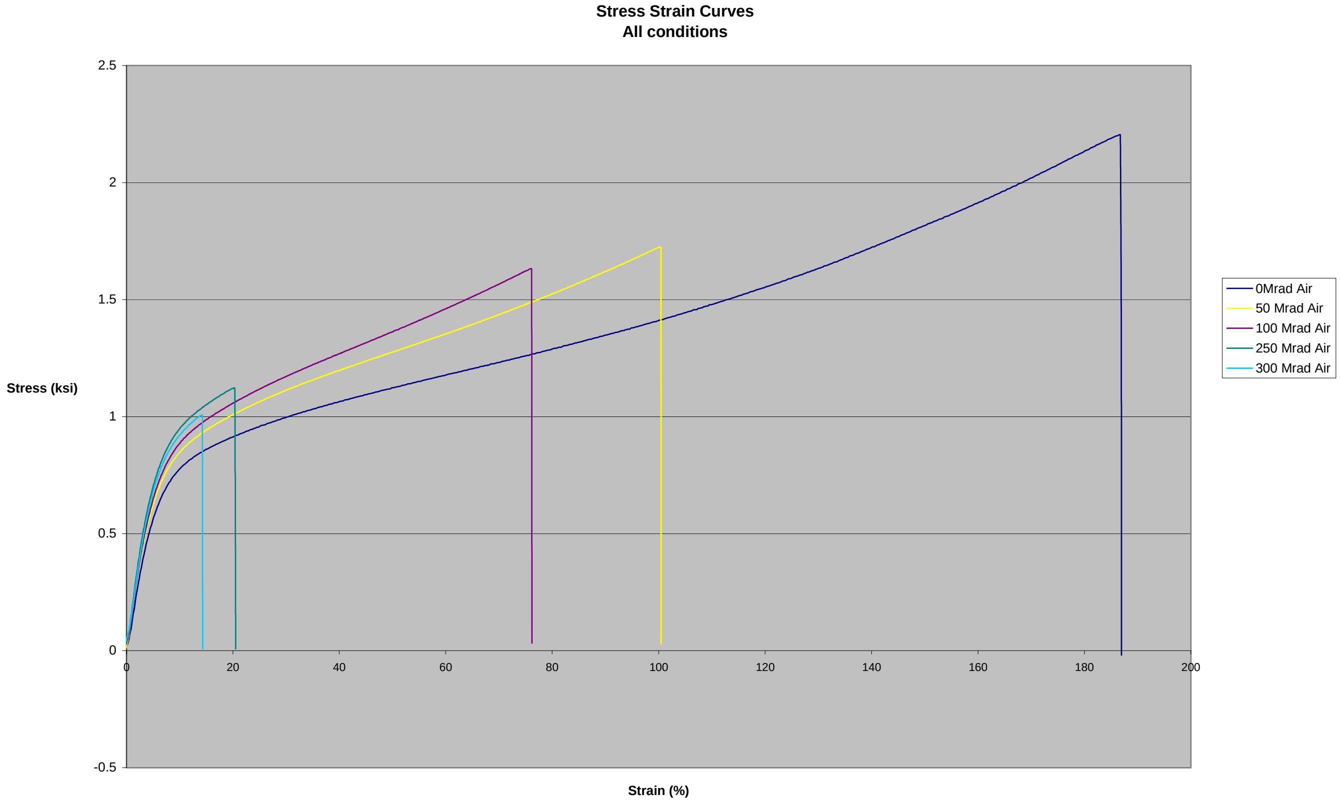


Figure 25. Stress-strain data for irradiated liner samples

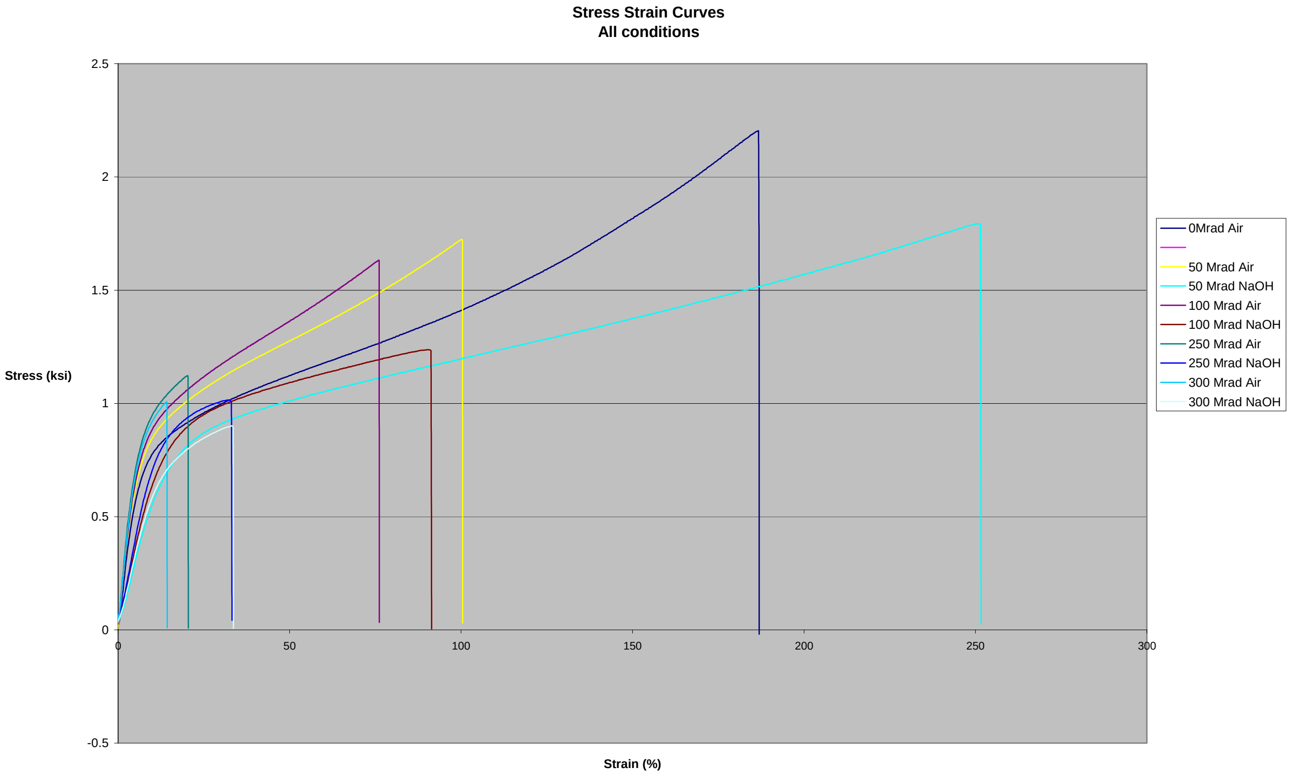


Figure 26. Combined stress-strain data for all samples (radiation only, radiation + 25% NaOH)

6.3 X-Ray Diffraction

X-ray diffraction (XRD) analysis was performed on the liner samples after irradiation to evaluate radiation effects on crystallinity of the polymer. Baseline, non-irradiated spectrum for the liner is given in Figure 27. Various scales of the spectra for irradiated samples are given in Figures 28-30. As expected, the crystallinity of the polymer liner increases with dose, though the relative increase is minor.

Subtracting out the instrument background from the spectra gives the total area under the XLPE curve. Fitting a profile under the XLPE background subtracted peak and dividing into the total times 100 provides an estimate of the percent crystallinity. Using this method, the estimated % crystallinity values are 27% (0 Mrad), 29% (50 Mrad), 31% (100 Mrad), 32% (250 Mrad) and 33% (300 Mrad) respectively. The relationship between crystallinity and changes in mechanical properties for this material is unknown.

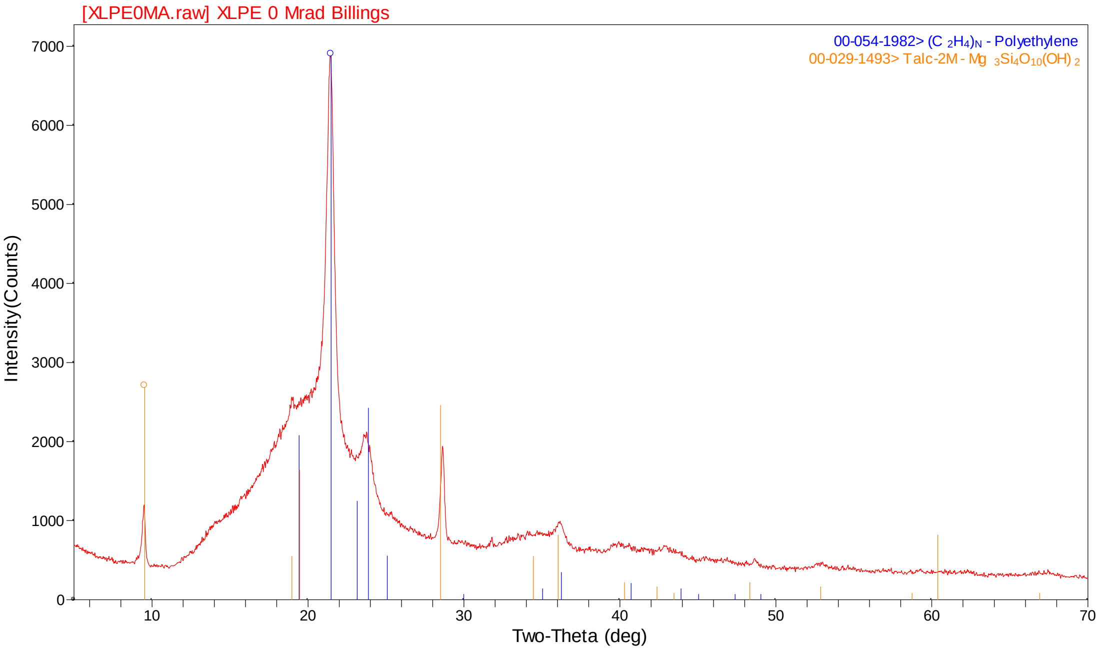


Figure 27. Baseline (0 Mrad) XRD spectra for the modified XLPE liner

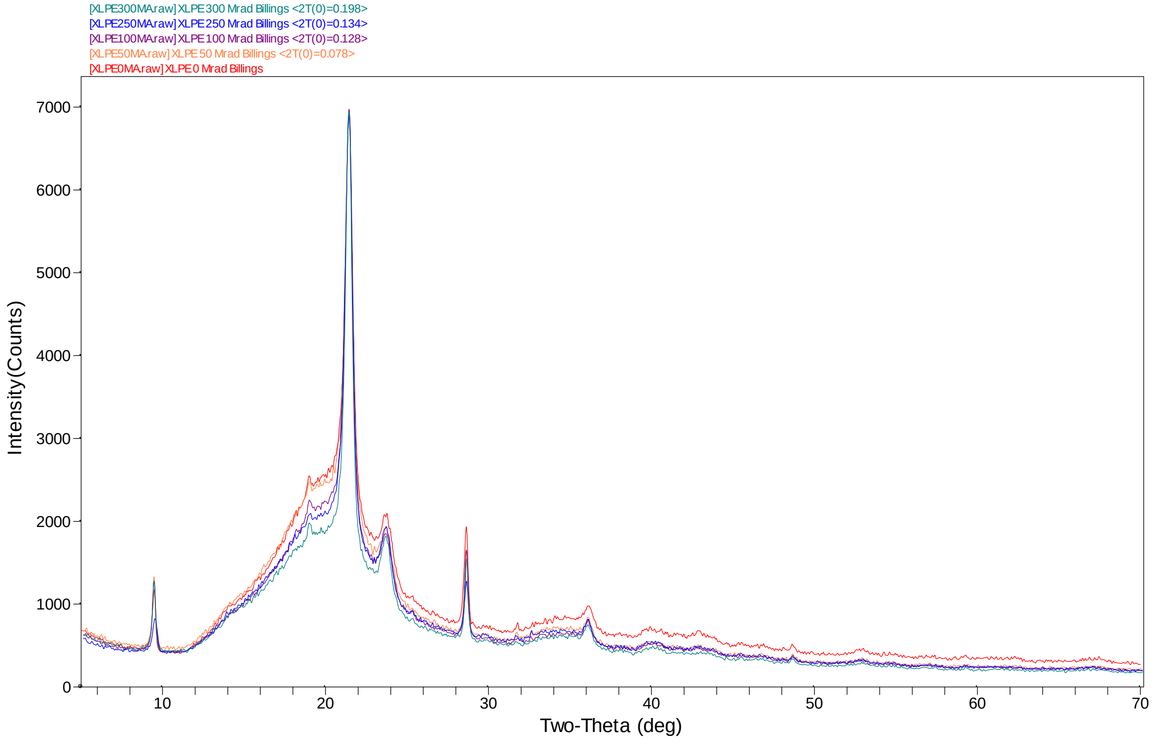


Figure 28. XRD spectra for baseline and irradiated modified XLPE liner samples

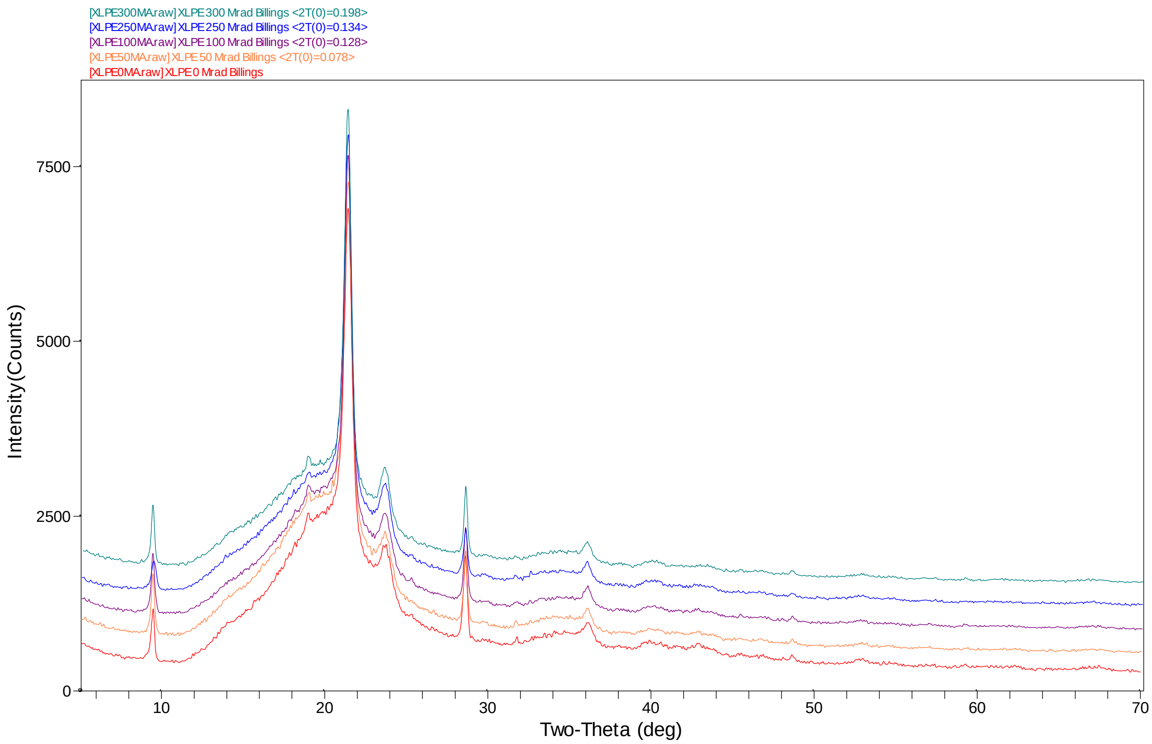


Figure 29. XRD spectra for baseline and irradiated modified XLPE liner samples

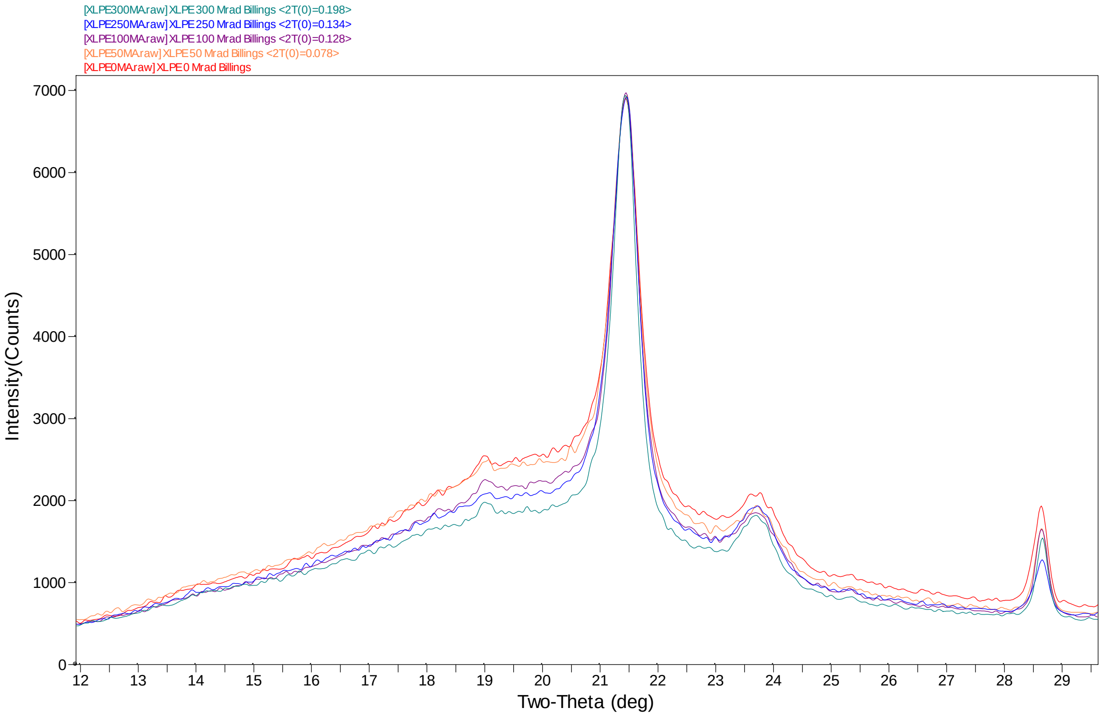


Figure 30. XRD spectra for baseline and irradiated modified XLPE liner samples (narrow band)

6.4 FT-IR Spectroscopy

The liner samples were analyzed by Fourier Transform Infrared (FT-IR) spectroscopy to determine radiation effects on the polymer backbone. The most identifiable difference between the spectra was the increase in the carbonyl band with increasing dose. All carbonyl compounds absorb in the range of 1665-1760 cm^{-1} due to the stretching vibration of the C=O bond. FT-IR spectra are shown in Figures 31a-c. The various peaks at different wavenumbers (cm^{-1}) represent different aspects of the modified XLPE polymer. Peaks at 720-730 cm^{-1} indicate C-H rocking, characteristic of polyethylene.

Peaks at 1460 cm^{-1} indicate C-H scissioning with peaks at 1715 cm^{-1} typical of carbonyl stretching. Peaks at 2850 and 2920 cm^{-1} indicate C-H stretching, with peaks at 3400 cm^{-1} typical of O-H stretching. FT-IR analysis did not conclusively identify CPE or CSPE polymers, as a C-Cl stretch peak is expected at ~ 650-750 cm^{-1} and sulfonyl groups are expected at ~1369 cm^{-1} and 1160 cm^{-1}. C-Cl peaks are possibly indicated at ~700 cm^{-1}. The vendor has stated that the Viper® liner does not typically contain CSPE though CSPE polymer is allowed in the patent identified for the Viper® hose construction.

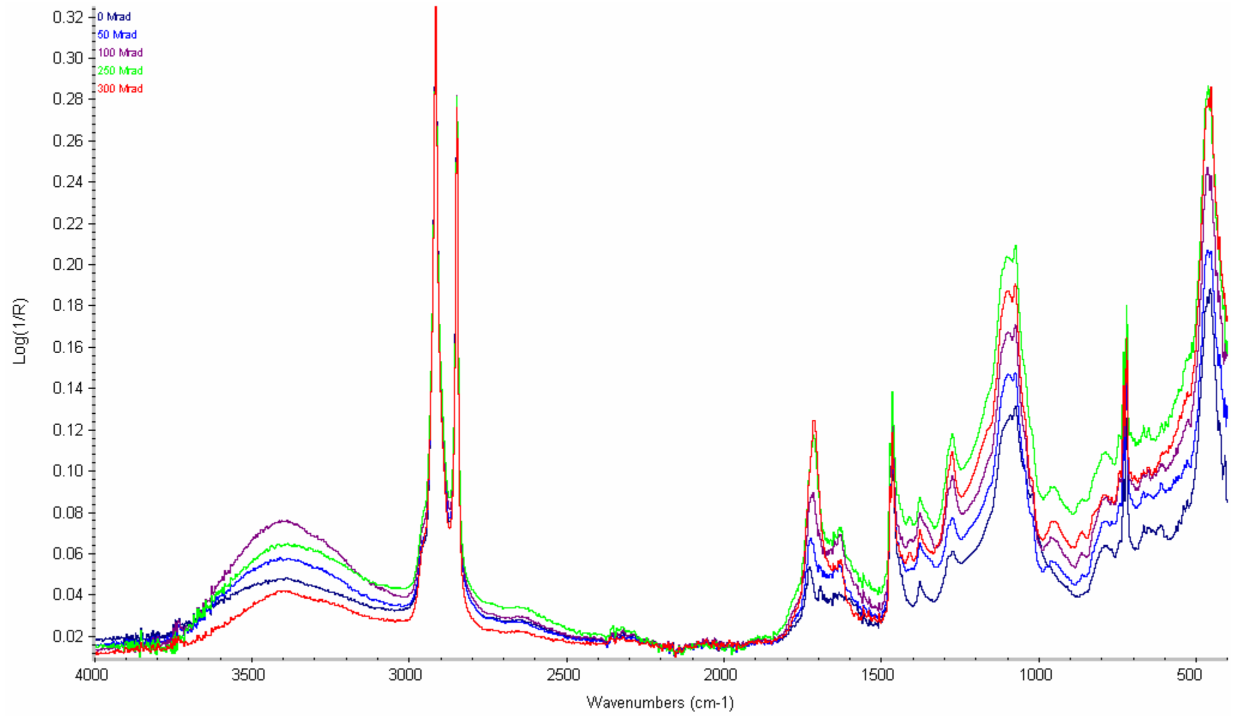


Figure 31a. FT-IR spectra for baseline and irradiated XLPE liner

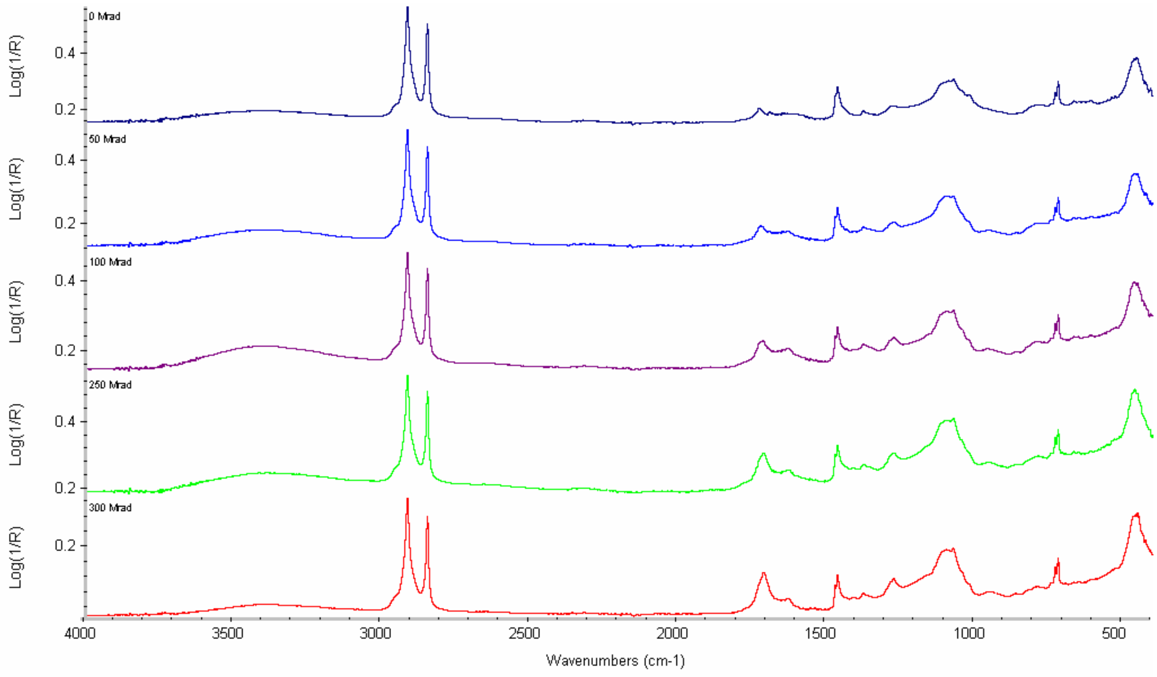


Figure 31b. FT-IR spectra for baseline and irradiated XLPE liner (separated before overlay)

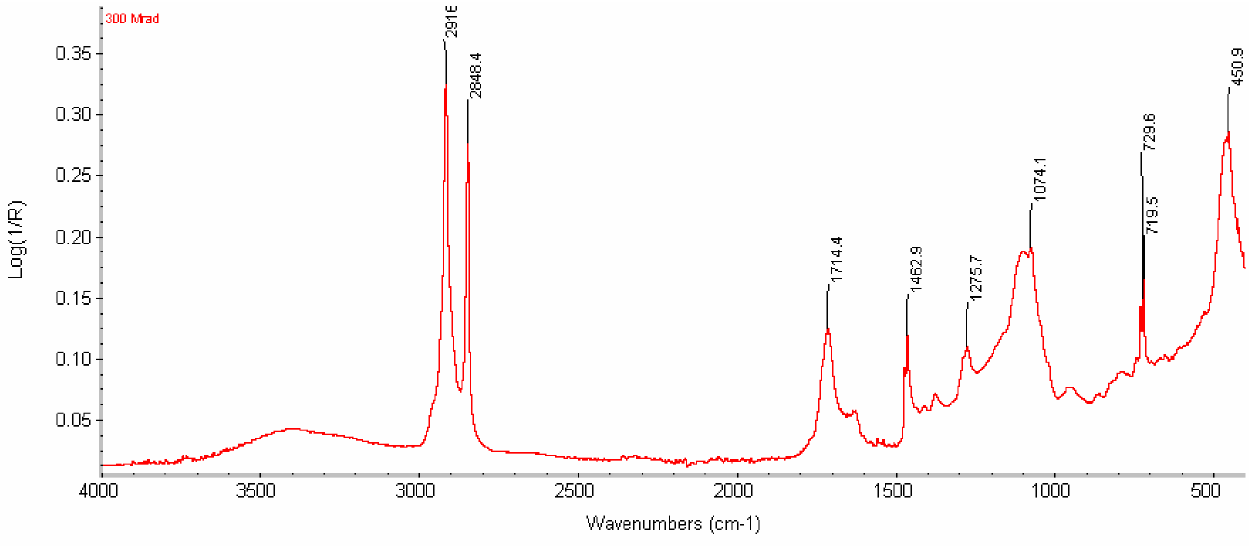


Figure 31c. FT-IR spectra for irradiated XLPE liner (300 Mrad, with peaks labeled)

6.5 FT-Raman Spectroscopy

A Kaiser Optics FT-Raman spectrometer using holographic technology for wavelength dispersion was used to shine a 1mm diameter 785 nm laser on the sample. The integration time was two seconds and 40 scans were combined. An observation is that the laser was weak (7 years old) such that the scattering process is noisy hiding the peak from the polar groups.

Raman spectra of XLPE after irradiation and exposure to 25% NaOH solution are in Figure 32. The spectra are very similar. However, the ratio of carbon-carbon stretch to hydrogenated carbon shows a minimum with applied radiation (Figure 33). The early part of the minimum could be due to re-hydrogenation and the latter part of the minimum could be due to carbonization of the polymer. Such behavior could occur if the degradation mechanism (chain scission vs. crosslinking) changes at some threshold dose. The last spectrum was obtained from a small surface chip of the XLPE sample irradiated at 300 Mrad. Ionized carboxylates are represented at 1550 cm^{-1}. This band is not visible in the thicker sample, likely because the laser penetration samples material below the surface that was not affected by radiation to the same extent. Figure 34 shows the increase in aromatic content vs. dose.

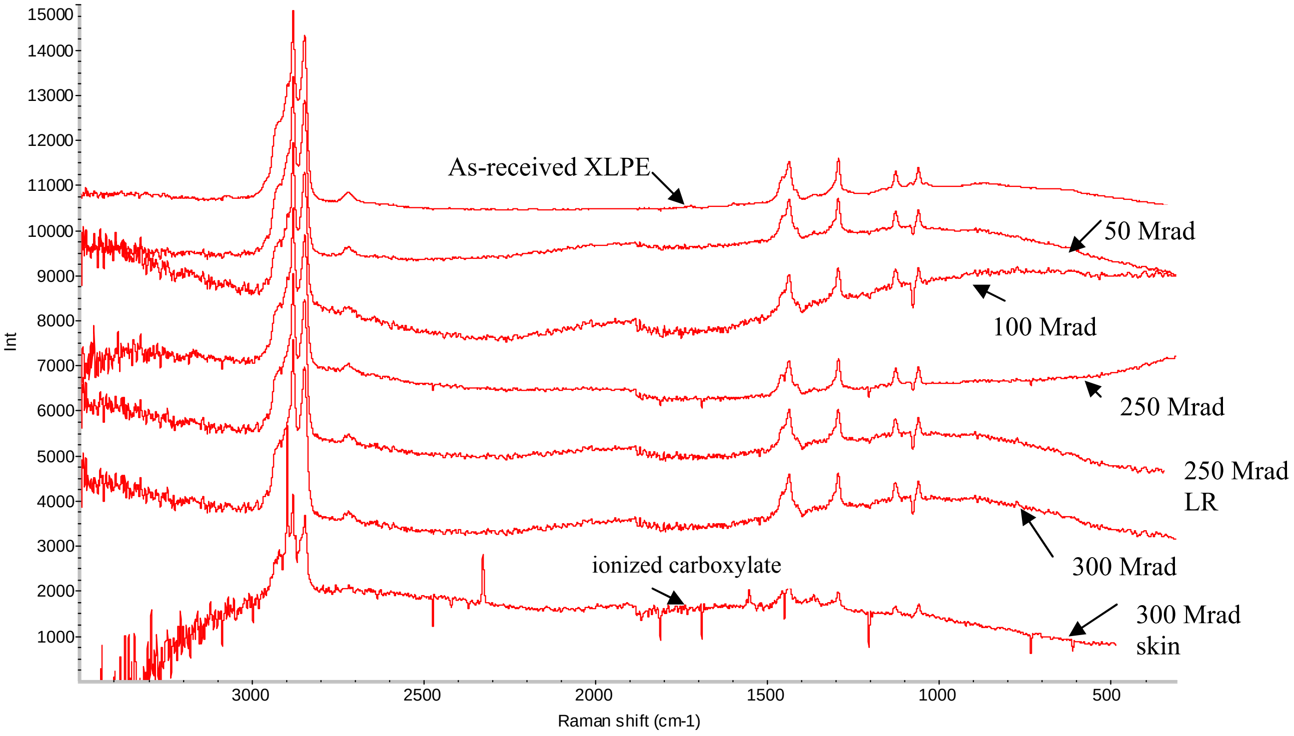


Figure 32. Raman spectra for XLPE after exposure to radiation and 50% NaOH at 200 °F

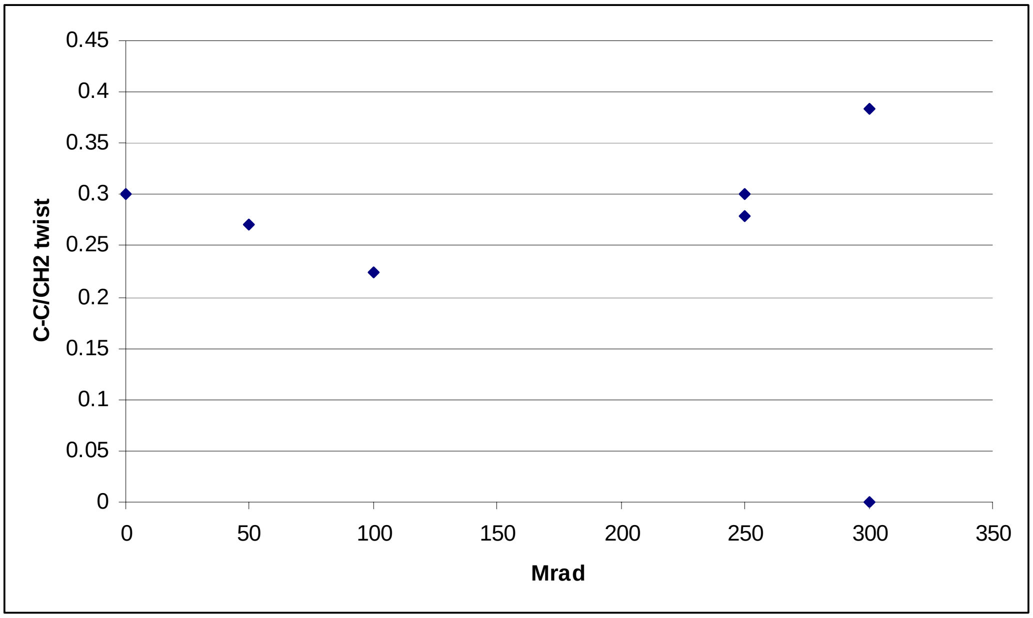


Figure 33. The ratio of the backbone stretch to hydrogenated carbon vs. radiation

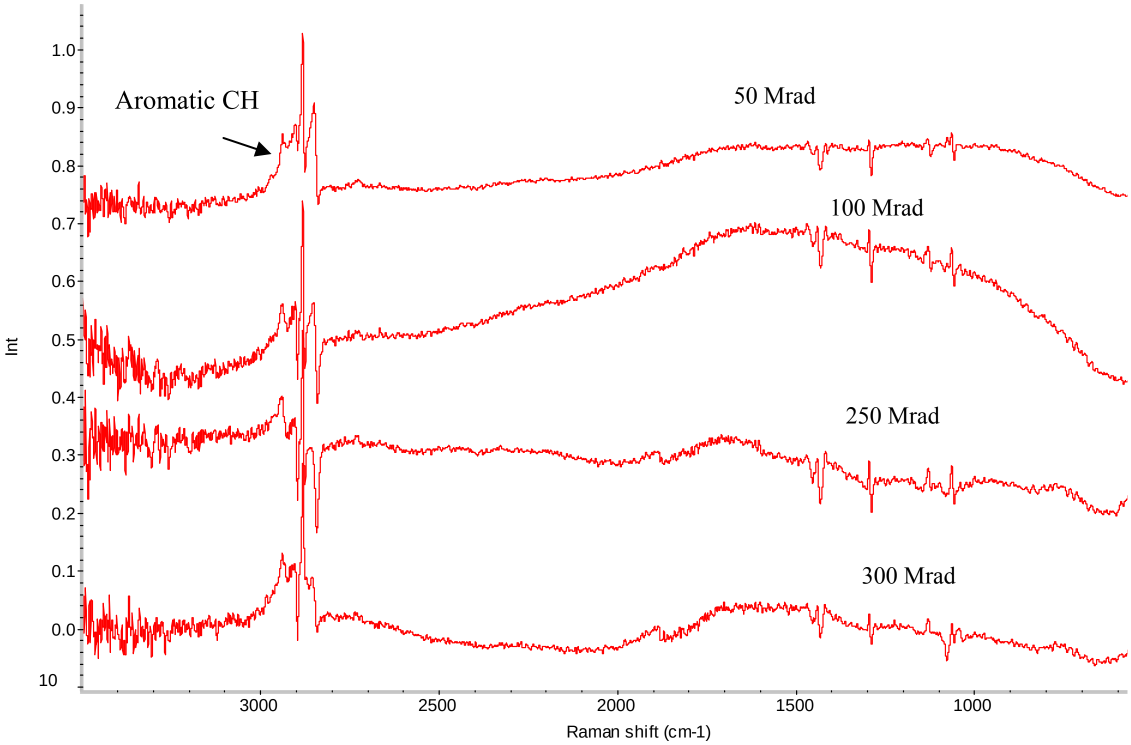


Figure 34. Increase in the polymer aromatic (carbonaceous) content vs. radiation

6.6 Differential Scanning Calorimetry

A series of XLPE samples that were exposed to 50, 100, 250, and 300 Mrad of gamma irradiation in the presence of NaOH were tested using a TA Instruments DSC. The DSC samples were taken from the shoulder portion of the tensile samples. Similar samples were taken from samples after irradiation in air only.

DSC samples of nominally 10 mg were cut from the shoulder of the tensile samples. These samples have been subjected to a modest amount of deformation which may promote different thermal responses. An argon purge of 30 scm for a few minutes was used to protect the cell.

Three typical curve geometries were observed for the XLPE irradiated / NaOH exposed samples. These characteristic curves are shown in Figures 35a-c for the 250 Mrad samples at both the high and low dose rates. Figure 35a exhibits the single large endothermic peak at about 105 °C for the higher dose rate, Figure 35b exhibits a diffuse peak at 81 °C with a well defined peak at 101 °C for the same sample as Figure 35a and Figure 35c exhibits a double endothermic trough with peaks at 89 and 103 °C for the 250 Mrad sample exposed at a lower dose rate. The presence or absence of the dual peak was not consistent from sample to sample on the first heating. The lower temperature endothermic peak was consistently missing from samples that had been reheated.

The dual peak may be attributed to the radiation/chemical/thermal exposure (one or more mechanisms), mechanical damage, or a combination of many factors. Only single peaks were observed from the previous samples exposed to air during irradiation. Table 2 is a compilation of the data from this series of DSC runs and the previous series showing the peak locations and integrated energies. Note that all peaks indicated are endothermic.

The twin peaks for the irradiated / exposed materials are somewhat inconsistent, with several samples exhibiting the dual peaks and others not. There are at least two possible reasons for the observed behavior. The test articles are nominally 10 mg samples cut from the shoulders of tensile samples. These samples have been irradiated and exposed to NaOH, thus this exposure could be the reason for this response. A second possible reason, is that the samples are from the shoulders and they exhibit some mechanical damage. Interestingly, the dual peak converges to a single peak on reheating. The single peak is consistent with the virgin material, so dual peaks appear to indicate a reversible material change. Figure 36 shows the heat and reheat profiles of two samples.

Note the similarity of the curves for the reheated samples with some variations. Since the dual peak disappears when reheating, it is postulated that some or all of the damage (if degradation) was annealed out. If the peaks were due to additional cross-linking, reheating would not have such an effect. It may be true that in service at elevated temperature, at least some degradation by ionizing radiation may be annealed. The amount of damage annealed in service is difficult to determine as it will occur at a different rate than observed in laboratory exposures.

A single sample from each of the irradiated samples in NaOH is shown in Figure 37. Sample data from replicate samples are shown in Figure 38. These samples do not show identical behavior, but are included for completeness.

Table 2. Reaction Temperatures and Total Energy

File	Sample ID	Peak 1 (°C)	Total Energy (J/g)	Peak 2 (°C)
XLP0MA3	XLPE Baseline	96	45	NA
XLPMA4	XLPE Baseline Reheat XLP0MA	96	49	
X50NA	XLPE 50Mrad NaOH	87	58	103
XLPE50MA	XLPE 50 Mrad Air	98	63	Shoulder
X100NA	XLPE 100 Mrad NaOH	89	54	102
XLP100MA	XLPE 100 Mrad Air	98	61	Shoulder
X250NA	XLPE 250 Mrad NaOH	82	62	99
X250NA2	XLPE 250 Mrad NaOH dup 1	105	37	NA
X250NA3	XLPE 250 Mrad NaOH reheat X250NA2	100	46	NA
X250NA4	XLPE 250 Mrad NaOH dup 2	81	44	101
X250NALR	XLPE 250 Mrad Low dose rate NaOH	89	54	103
X250NAL2	XLPE 250 Mrad LDR dup 1	93	43	107
X250NAL3	XLPE 250 Mrad LDR reheat of X250NAL2	101	39	NA
XLP250MA	XLPE 250 Mrad Air	98	65	NA
X300NA	XLPE 300 Mrad NaOH	90	51	103
X300NA2	XLPE 300 Mrad NaOH Dup 1	94	32	105
XL300MA	XLPE 300 Mrad Air	99	65	NA

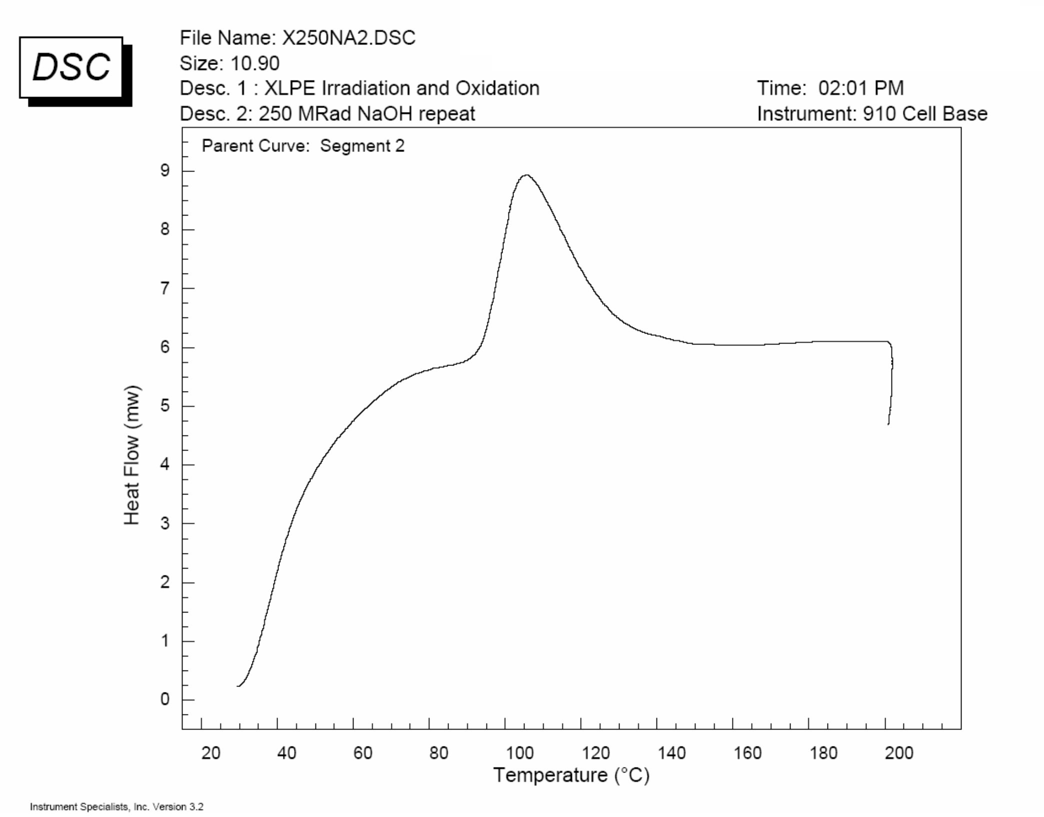


Figure 35a. XLPE irradiated to 250 Mrad at the nominal rate. Note single peak.

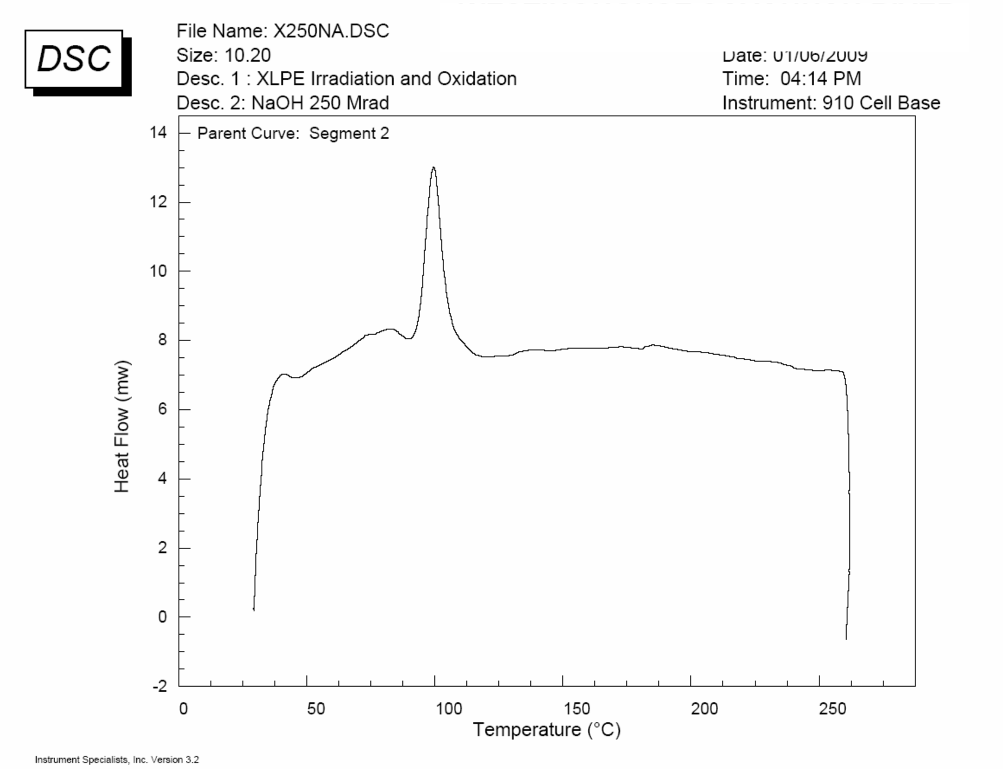


Figure 35b. XLPE irradiated to 250 Mrad at the nominal rate. Poorly defined peak at 80°C.

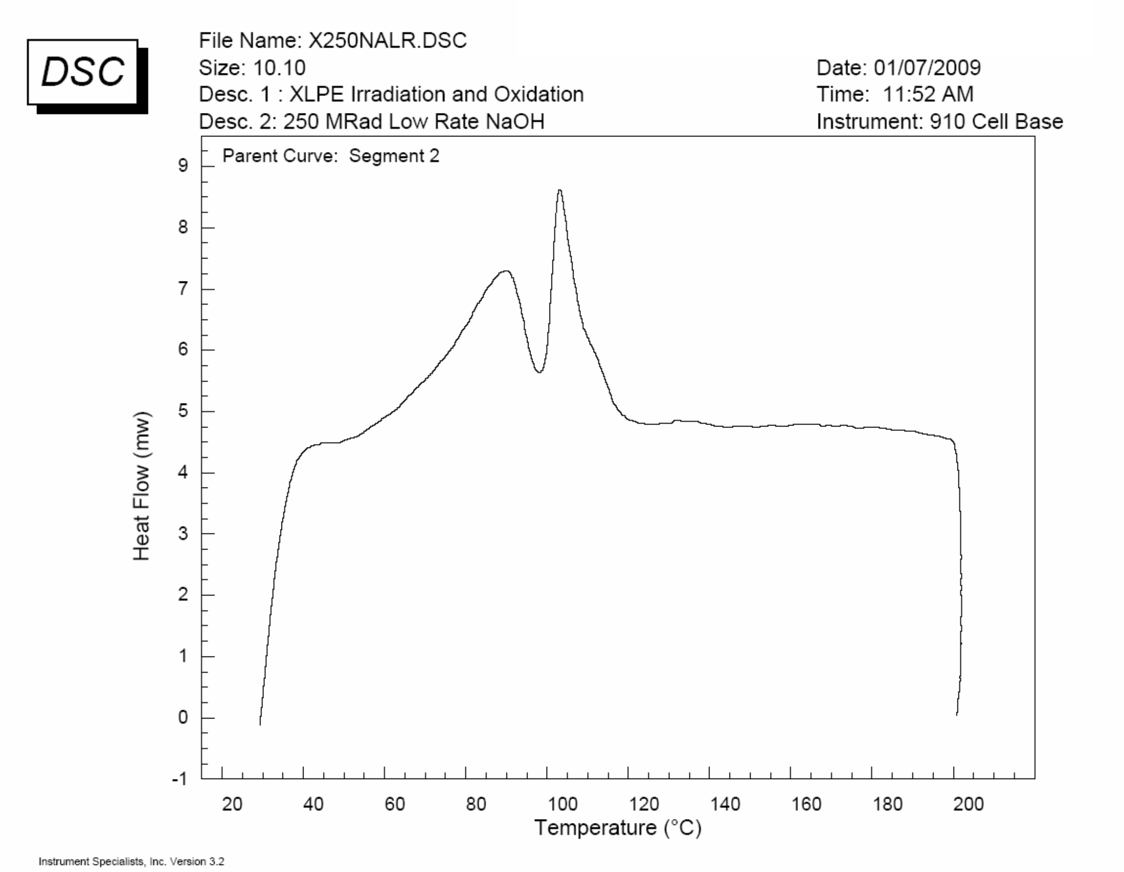


Figure 35c. XLPE irradiated to 250 Mrad at a “low” rate, note well defined dual peaks.

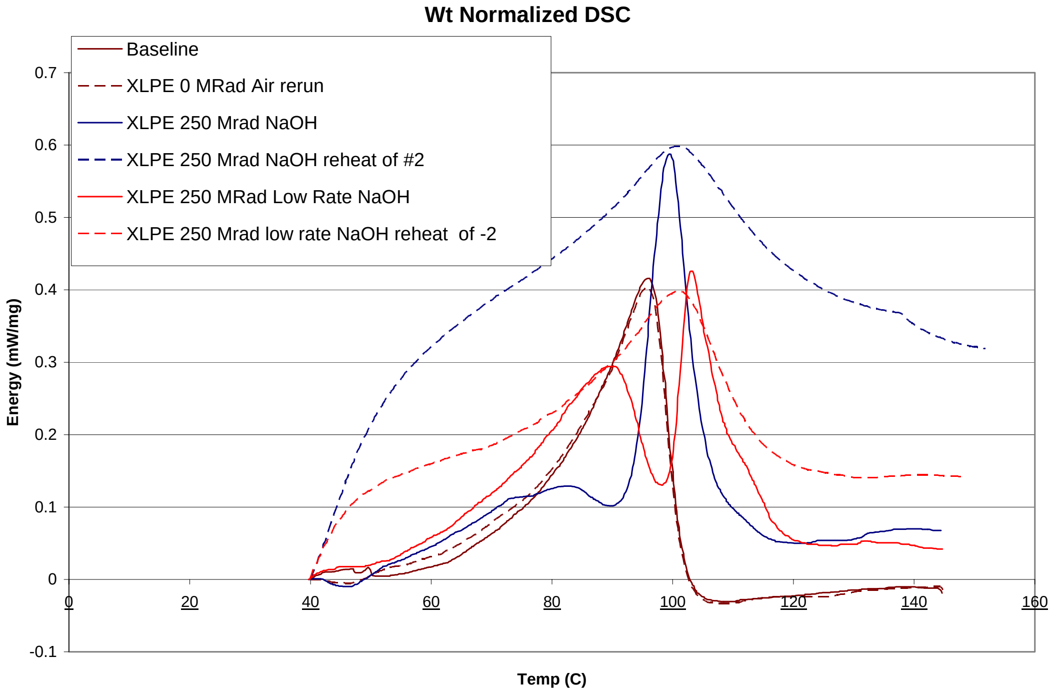


Figure 36. Heat and reheat profiles for baseline, 250 Mrad and 250 Mrad low dose rate samples.

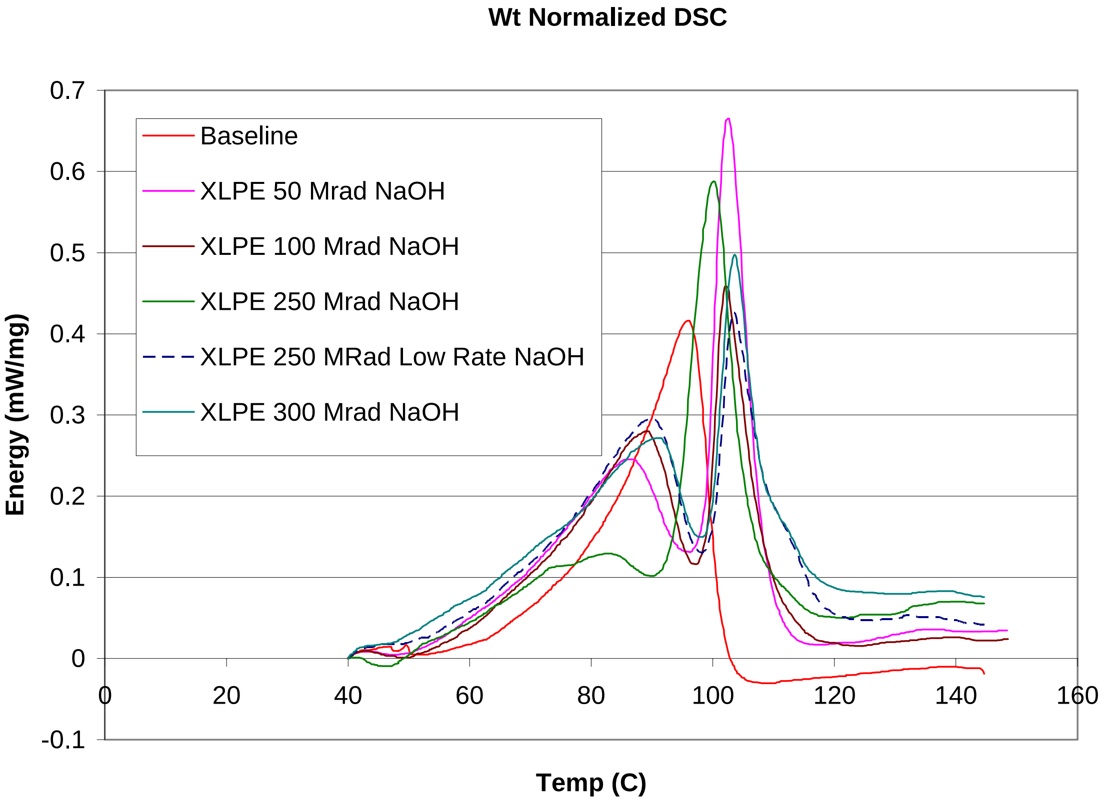


Figure 37. Typical results from single samples for the NaOH irradiation exposure.

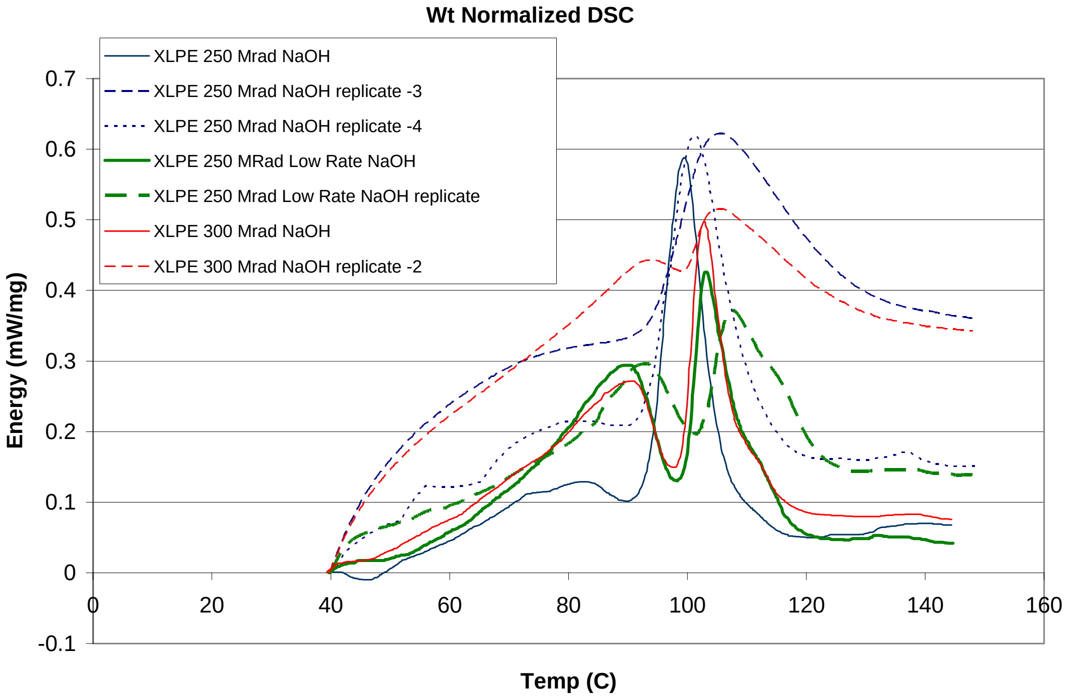


Figure 38. Irradiated samples with NaOH exposure that had replicate samples run.

6.7 Burst/Leak Testing

Baseline and irradiated sections of 1” ID Goodyear Viper® hose (9” long) were burst tested in the EES/High Pressure Laboratory. ASTM D380 and the RMA Hose Handbook require a minimum length of 18 inches for burst tests [35, 36]. However, such lengths cannot be easily irradiated to a uniform dose. Due to limited gamma chamber space and because higher doses were initially considered more important, samples were only irradiated to doses of 100, 250 and 300 Mrad.

The 1” diameter hose has the same working pressure rating (200 psi) as 3” ID hose. The smaller hoses were tested using Dixon stem #RMS-11 (stainless steel) and #156 Boss clamps (plated iron), similar to EES tests on larger hoses. Stainless steel clamps were not used for the smaller sizes as the clamps themselves were not being qualified.

Initial tests showed that torque values (21 ft-lbs) for the smaller bolts were insufficient for burst testing. This style of clamp is not typically recommended by the hose manufacturer due to lack of uniform compression. Higher strength bolts were considered but cracking of the clamps was likely, as observed in EES tests. A few baseline tests were performed at increasing torque values to see if valid burst values could be obtained. At 35 ft-lbs, the hoses could be burst tested, with some bolt deformation.

Room temperature burst pressure values for baseline and irradiated hoses are in Figure 39. Sample photographs and test reports are in Appendix I. Baseline values ranged from 850-1400 psi, with an average of 1214 psi. The hose manufacturer quotes a theoretical burst pressure of 1080 psi, providing a ~5X safety factor over the working pressure rating (200 psi). Per Veyance representatives, the 1080 psi value is a theoretical calculation based on fabric strength and number of plies, not an average burst value. Hoses are normally tested per ASTM D380 with a pressure rate of 1000 psi/min and a sample length of 18” between fittings.

Vendor burst test results from 187 samples of similar 1” hose give an average of 1309 psi with a standard deviation of 91.3 psi. Using a 3σ rule, the lowest acceptable burst pressure is 1309 - (3 x 91.3) = 1035 psi. The single baseline burst test performed by SRNL/EES on the 3” ID hose (3 foot length) failed at 1100 psi, with failure near the stainless steel clamp. These values are similar to the 1080 psi theoretical value.

The average burst pressure of five 1” ID baseline samples (1214 psi) is only slightly less than one standard deviation below the 1309 psi average value quoted above, or 1218 psi. The cause for the lower 850 psi value is unknown. If the 850 psi test value is dropped, the baseline average burst pressure is increased to 1305 psi, very close to the 1309 psi value. Additional tests would be needed to establish a better statistical basis.

Per the manufacturer, there can be a lot of variation in burst tests on short samples due to coupling/hose interaction. This is likely less of an issue for the wire and fabric-reinforced Viper® hose but the short hose section may not allow proper fiber alignment of reinforcement fabric when hose is pressurized, resulting in more variation in the burst value.

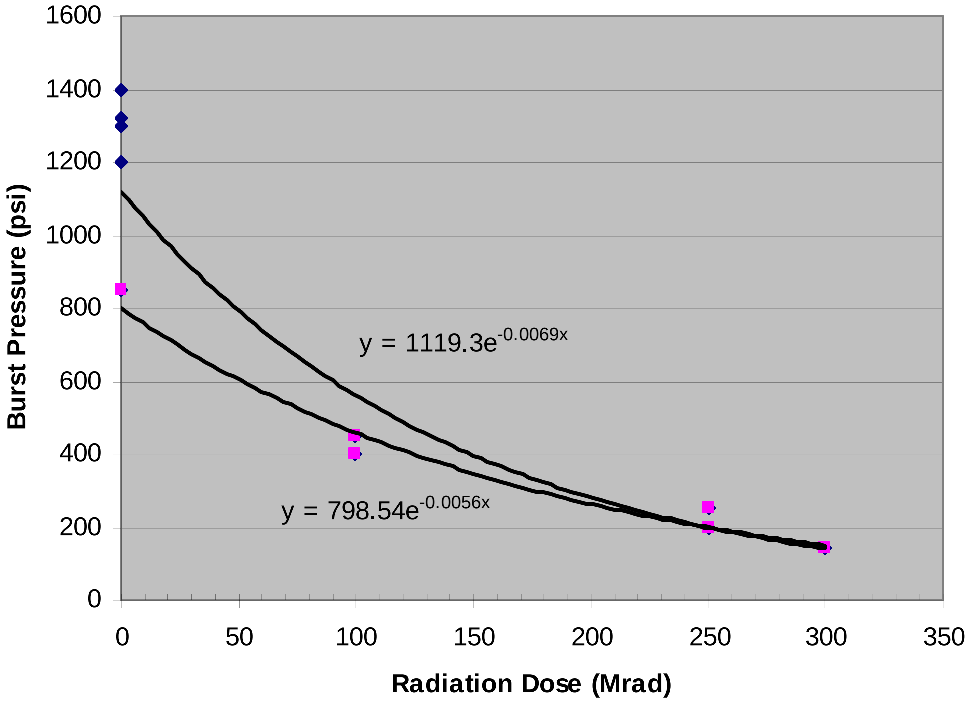


Figure 39. Burst Pressure (psi) vs. Radiation Dose (Mrad)
(top curve is exponential fit including all data, bottom curve is exponential fit from 850 psi only)

To evaluate possible end or length effects, three longer baseline sections of 1" Viper hose (18" length total, 9" free between fittings) were burst tested. These sections were obtained from the local Viper® hose supplier (Lewis-Goetz) with swaged-on MPT fittings (1000 psi rated) as recommended by the hose manufacturer. Results are given in Appendix I.

The swaged-on fittings provide more uniform compression and a 5X safety factor, but did not allow for hose rupture. The leakage pressure values were all greater than 1000 psi (1240, 1150, 1230 for an average of 1207 psi). This is very close to the 1214 psi burst pressure average for the 5 shorter baseline samples but less than the average value (1305 psi) if the single 850 psi value is dropped. Actual burst values for the longer hoses are therefore unknown. However, these results indicate that the shorter lengths do not significantly influence burst test results, at least compared to results for 18" samples.

Burst pressures at doses less than 100 Mrad were not determined. The estimated burst pressure in Figure 39 at 50 Mrad is approximately 600-800 psi, using an exponential fit approach. These values provide a 3.5-4X safety factor over the working pressure rating and a 4.7-5.3X safety factor over the anticipated operating pressure. Actual values may be higher if there is a threshold dose below which radiation has no measureable effect on burst pressure. Alternatively, the values at 50 Mrad could be closer to the 100 Mrad values. The worst case is that the burst pressure at 50 Mrad is the same at 100 Mrad. Therefore, additional tests at 10-50 Mrad are recommended. Several 18" long samples were irradiated to ~250 Mrad over ~4 months in the variable dose rate chamber. These can also be tested if needed.

It must be noted that the burst tests of irradiated hoses were performed at room temperature. NAHAD guidelines recommend that hose working pressure be reduced by 30% if operating between 150 and 225 °F. The combined effect of temperature and radiation should therefore be considered in flexible jumper design. The estimated room temperature burst pressure at 50 Mrad is approximately equal to the burst pressure obtained by EES at 200 °F, without radiation damage.

6.8 Vendor Laboratory Tests

Samples of irradiated hose liner were submitted to an independent laboratory (Cambridge Polymer Group, Inc.) that specializes in characterization of polyethylene for medical industry and implant applications. The following tests were performed. These parameters were considered important to determine, particularly the degree of crosslinking and oxidation induction time. The laboratory test report is given in Appendix II.

The following analytical tests were performed:

- ASTM D2765 (gel content) [37]
- ASTM F2214 (swell ratio, crosslink density) [38]
- ASTM F2381 (transvinylidene yield) [39]
- ASTM F2102 (oxidation index) [40]
- ASTM D3895 (oxidation induction time, OIT) [41]

Sample 10785-1 is a baseline as-cured sample, with samples 10785-2 through 10785-5 irradiated to doses of 50, 100, 250 and 300 Mrad, respectively. The ASTM D2675 result (extract%) is an indication of the degree of crosslinking of the material, with the extract percentage being the amount of polymer that can be dissolved in a specific solvent at certain conditions. The crosslinked fraction that cannot be dissolved is the extract.

The range of cross-linking for cross-linked polyethylene (PEX) tubing is 65-89% per ASTM F876-93 [42], when tested in accordance with ASTM D2765, Method B. Depending on the process used, ASTM F876 requires the following minimum percentage crosslinking values: 70 % by peroxides, 65 % by Azo compounds, 65 % by electron beam, or 65 % by silane compounds.

Cross-linking improves thermal stability and chemical resistance, but excessive cross-linking can result in embrittlement. These results would indicate that the as-cured liner is approximately 77% crosslinked (70.4 to 83.8%). Additional samples would be needed to establish a better statistical basis.

The extract % increases with slight radiation dose of 50 Mrad (35.6%), decreases at 100 Mrad (27%) but then increases again to 32.6% and 32.0% at 250 Mrad and 300 Mrad, respectively. The reason for the reduced value at 100 Mrad is unknown. Additional tests would be needed to confirm this is not a test anomaly or variation among samples, but there could also be competing degradation mechanisms (crosslinking vs. chain scission) at this dose range. The average values are reduced but there is some overlap in the data, so the variation is not considered significant.

Variation in other parameters is more significant (swell ratio, crosslink density per ASTM F2214), though changes in the oxidation induction time are not significant. The dose levels involved in this study are much higher than normally used for medical implant sterilization (typically <10 Mrad). These tests are also primarily used on UHMWPE not XLPE polymer.

6.9 Gas Generation

During radiolysis, polymers absorb a portion of the energy which produces changes in the polymer structure. This may result in chain scission, crosslinking, ejection of low molecular weight fractions and generation of gases.

The specific amount and type(s) of gas liberated depends on several factors, including the base polymer type, specific formulation, additives/curing agents, total dose, radiation type, dose rate and presence of oxygen. Gas generation is usually of less concern for well-ventilated systems or open environments, while closed systems require more scrutiny. Some gases liberated may be toxic, corrosive or flammable, while others may be relatively benign.

An excellent discussion of radiolytic gas generation for polymers comes from Reference 43. Gas generation rates are usually expressed in terms of G-values, which represent the number of molecules of gas liberated per 100 electron volts (eV) of energy absorbed by a material. G-values may vary with the type of radiation absorbed due to the linear energy transfer (LET) effect. For example, alpha radiation has a high LET value so much energy is imparted to the material. However, alpha particles are easily stopped within the first 1-2 mils of most materials.

The bounding G-value for the polymers in the hose is polyethylene, with a $G(H_2)$ value of 4.0 and a G(flammable gas) value of 4.1 due to slight methane (CH_4) formation. Ethylene-propylene and EPDM elastomers are expected to show behavior bounded by that of polyethylene. The only polymer listed in this reference with a higher G(flammable) value is polyoxymethylene (POM, acetal) with a value of 5.6. This polymer (commonly known as Delrin®) is not used in the hose.

Polymers containing chlorine such as PVC tend to liberate HCl gas rather than hydrogen. Such polymers are sometimes stabilized to reduce the catalytic effect of HCl generated by thermal degradation or radiolysis. The amount of CPE or CSPE in the hose liner formulation is possibly 10-20 wt%. Therefore, some HCl gas could be liberated from the hose liner during irradiation. HCl gas is not flammable and would be neutralized by the high pH HLW chemistry if internally released. If HCl gas is externally released and if it condenses, corrosion of components could occur. However, the proportional amount of HCl possibly generated is much less than that of hydrogen due to the limited amount of chlorinated polymer present, lower G values and decreased permeability through the hose due to larger molecule size.

SRNL/MS&T consulted SRNL/Actinide Technology (J. Laurinat) for an estimate of gas generation rates for the Viper® hose at a bounding dose of 100 Mrad. The vendor's estimated "composite" hose density value of the polymers in a 1" ID Viper hose is 1.18 g/cc, based on weight of the hose per length without the wire helix.

Assuming a total dose of 50 Mrad, a composite hose density of 1.18 g/cm^3, a hose thickness of 0.3 inches (3.6" OD-3"ID) and a G (flammable gas) value of 4.1, the estimated gas generation rate at room temperature is given as:

> (50 Mrad) x (1E6 rad/Mrad) x (0.01 J/kg/rad) x (0.001 kg/g) / (1.602E-13 J/Mev) * (1E4 (100 ev/Mev)) * (G, 4.1 molecule/100 ev) / (Avogadro No., 6.022E23 molecule/mole) * (R, 82.057 cm^3 atm/mole/K) * (T, 298 K) / (P, 1.0 atm) * (density, 1.18 g/cm^3) * (hose thickness, 0.3 in.) * (2.54 cm/in) =
>
> = 4.67 cm^3 per cm^2 of hose at 0.3" thickness with a density of 1.18 g/cc

This value assumes atmospheric pressure, a uniform dose through thickness and no attenuation of gamma radiation. To determine the amount of gas generated from the hose per unit length, the total surface area of the exposed hose is needed. For a 20' length of 3" ID hose, the surface area of the exposed liner is estimated at 2π(1.5 in)(20 feet)(12 in/ft)(2.54 cm/in.)^2 = 14, 586 cm^2.

Multiplying the surface area by the gas generation rate per area gives 68, 116 cm^3 or ~ 68 L flammable gas evolved per 20 foot length of 3" ID hose at 50 Mrad absorbed at room temperature. This translates to a gas generation rate of about 1.36L of flammable gas per Mrad for a 20 foot length of hose, or 0.068L per Mrad per linear foot.

As the hose can be changed out between transfers, the only time duration of real concern is a single transfer. Assuming a bounding dose rate of 57,870 rad/hr and transfer duration of 20 hours, the dose per transfer is estimated at only 1.2 Mrad. This results in approximately 1.63L of flammable gas generated per transfer for a 20 foot length of 3" ID hose or about 0.082L gas per transfer per foot.

The hose will be subjected to elevated temperature during transfers so the effect of temperature on gas generation is considered. The relationship between rate constants at two different temperatures is given as:

> ln (k2/k1) = (E_a/R) [(T2-T1)/(T2*T1)] with Ea as the activation energy and R the gas constant.

Assuming a bounding activation energy of 0.6 kcal/g-mole for H_2 formation, the gas constant as 1.99 cal/K-mole and a maximum service temperature of 93 °C (366K), the ratio of the G (flammable gas) value at 93 °C to the G (flammable) value at 25 °C (298K) is calculated as:

> G (93 °C)/G(25 °C) = exp {(600/1.99) [(366-298)/(366*298)]} = exp (0.1883) = 1.21

This translates to an ~ 21% increase in the room temperature G value (4.1) to 4.96 at 93 °C. This increases the gas generation rate to 4.67 x 4.96/4.1= 5.7 cm^3 per cm^2 of exposed hose. Therefore, the flammable gas generation rate at 93 °C could be as high as (0.082/4.1)*4.96 = 0.0992L gas (or about 0.1L) per 20-hour transfer per foot of 3" ID hose.

The actual gas generation rate during service is unknown but will likely be much lower if lower radiation dose rates apply. A formal calculation is recommended for safety analysis. Formal calculations should consider the total gas air volume inside the hose to show if a flammable mixture can be created, conservatively assuming that all gas is released internally.

The proportion of inward vs. outward diffusion of flammable gas is unknown. The proportion is likely more sensitive to the permeability of the inner vs. outer layer of the hose than to the internal hose pressure. The relative gas permeability of the liner compared to the outer layers is unknown.

If the outer layer is impermeable or far less permeable than the liner, the radiolytically generated gas will remain inside the hose unless it is swept out by purging. If the outer layer is very permeable, then roughly half the gas should diffuse inward into the hose and half should diffuse outward. This assumes that the effective partial pressure of radiolytically generated gas is significantly greater than the partial pressure of the gas inside the hose. For safety analysis, both cases (100% internal and external) should be considered.

6.10 Static Charge

Non-metallic hoses are known to have the potential for developing static charge due to friction during transfer of internal media. This behavior is of less concern for transfer of aqueous, non-flammable liquids as compared to flammable liquids or particulate solids such as in material handling or sandblasting.

The specific tendency of the Viper® hose to develop static charge is unknown. Per the manufacturer, neither the liner nor the EPDM cover contains antistatic additives and the hose construction does not include a grounding wire. Compounds with conductive carbon blacks can be used to dissipate static charge. Achieving an electrically continuous hose assembly is possible via grounding the helix wire.

Aqueous HLW salt solutions are not expected to pose a problem as they are conductive and non-flammable. A possible case of static charge being a problem would be the ignition of flammable gas liberated from the polymer hose due to radiolysis. External release of radiolytically-generated gas into an open atmosphere inside a diversion box would be quickly diluted and tend to rise due to low density. The hydrogen concentration at the point of ignition would have to be above the lower flammability limit (LFL, 4 wt%) and below the upper flammability limit (UFL, 75%) to ignite. The region of flammability would be very limited and would disperse quickly, particularly with ventilation. The risk of static charge development and ignition of flammable gas generated due to radiolysis is considered low. However, additional review may be needed.

To minimize this concern, the end user may request the hose incorporate a tube and/or cover compound that can dissipate static electricity and prevent any build-up. An example of this is aircraft refueling hose. API 1529 standard specifies that the cover of such hose must provide an electrical resistance between 1e3 and 1e6 ohms/meter of hose [44]. Other applications may require the hose assembly to be electrically continuous, i.e. that the helix wire or grounding wires (usually copper) be bonded to the fittings which will themselves be connected to a grounded pipeline. These options should be discussed with Goodyear and Veyance representatives. Changes to the liner formulation for antistatic purposes are not expected to significantly affect radiation and chemical stability, but the impact has not been determined.

6.11 Shelf Life

The shelf life of the Goodyear Viper® hose has not been established by the hose manufacturer. The shelf life of age-sensitive materials is generally more dependent on storage conditions than time alone. Shelf-life is defined as the time a material or component can be stored without impacting functionality, which implies that properties are not changed from initial fabrication or are within acceptable limits.

Several industry documents address the shelf life of age-sensitive materials. These include:

- SAE AS1933 Rev.A (2004-06**),** Age Controls for Hose Containing Age-Sensitive Elastomeric Material [45]. Per Section 3.2, the age limit at acceptance by the user procuring activity for a final vehicle or component is 32 quarters or 8 years. A 12 quarter (3 year) limit is imposed on hose coming directly from the manufacturer. Per section 4.1, hose and hose assemblies that contain age-sensitive elastomeric materials shall be protected from circulating air, sunlight, fuel, oil, water, dust, and ozone. The storage temperature limit in this document is 125 °F.

- EPRI NP-6608, "Shelf Life of Elastomeric Components" [46]: This document concluded that with proper storage, shelf life for elastomer seals could be extended to 32 years with proper storage. The authors concluded that the age values in MIL-HDBK-695C, were very conservative in many cases, particularly for silicone and fluoroelastomer materials.

- SAE ARP5316 REV. B, Storage of Elastomer Seals and Seal Assemblies Which Include an Elastomer Element Prior to Hardware Assembly [47]: This document addresses the general requirements for storage of elastomeric seals and seal assemblies which include an elastomeric element prior to the seal being assembled into hardware components. ARP5316 requires storage temperatures between 59 °F and 100 °F, except when higher temperatures are caused by temporary climate changes and articles shall be stored away from direct sources of heat and direct sunlight. The 100 °F temperature limit is more restrictive than SRS Level A or B storage, which allows temperatures up to 140 °F.

- MIL-HDBK-695D, w/Change 2, May 2005, DOD Handbook, Rubber Products: Recommended Shelf Life [48]: This often-referenced handbook establishes shelf-life guidelines for elastomeric products, principally those described by Government specifications and standards or by nationally recognized technical society specifications and standards. The minimum shelf-life value for any age-sensitive polymer in this reference is three (3) years. A storage temperature limit is not identified.

- SAE J1273, Recommended Practices for Hydraulic Hose Assemblies, February 2009 [49]: This document specifically covers hydraulic hose, which may be constructed of various polymers. The shelf-life in this document is forty quarters (10 years) from date of manufacture if stored per ISO 2230. Hose assemblies that pass visual inspection and proof test shall not be stored more than 2 years.

In all of the shelf-life documents reviewed, no shelf-life values less than three (3) years are indicated for the polymers used in the Viper® hose construction. Even elastomers known to be sensitive to aging such as natural rubber and nitrile rubber are typically given shelf-life values of 3-5 years. Lower values may be imposed for critical components such as glovebox gloves. EPDM and CSPE elastomers generally fall in the 5 to 10 year category, with EPDM, Viton®/FKM fluoroelastomers and silicone elastomers listed in the "unlimited" category per SAE ARP5316 REV. B. XLPE and CPE polymers are not specifically addressed in these documents, mainly because they are not traditional elastomers.

The SRS shelf-life program establishes a 10-year shelf life for CSPE and EPDM elastomers based on MIL-HDBK-695D values. Fuel, Oil and Hydraulic Hoses for automotive and diesel applications are given a 3-year shelf life, with Level B storage required.

The RMA Hose Handbook (IP-2) outlines several aspects of storage for consideration. A key aspect identified in this document is that the ideal temperature for the storage of rubber products ranges from 50°F to 70° F (10°C to 21°C) with a maximum limit of 100°F (38°C). This is less than allowable under current Level A or B storage at SRS.

Based on the above discussion, the SRS shelf-life of the Goodyear Viper® hose is currently recommended at three (3) years. This is likely conservative but history with the hose is limited and the application is critical. Hoses should be within one year of cure date upon receipt at SRS. This is consistent with the minimum 3-year shelf-life value allowed in other age-control documents and the SRS shelf-life program, even for materials known to be more sensitive to aging than the polymers used in the Viper® hose. At the end of shelf life, hoses should be examined for evidence of degradation to possibly justify shelf life extension if needed.

The storage requirements of the hose manufacturer should be followed. Unless otherwise specified, hoses should be stored in a Level A storage facility, with temperatures ideally between 50 and 70 °F and no greater than 100 °F. The relative humidity of the atmosphere in storage should be less than 75% RH. Hoses should be stored away from sources of heat, ozone, direct sunlight, ionizing radiation, chemicals and other harmful environmental factors. Hoses should be inspected for signs of damage or degradation upon receipt and prior to use.

Per the hose manufacturer, the 5 digit code printed on the hose at regular spacing indicates when the branding tape was purchased. The code allows the plant to likely determine when the specific hose was built to within a month or possibly a week. This is common practice for commercial hose not requiring tight tracking of cure dates. The vendor can also apply serial numbers to indicate exactly when the hose was built at additional cost. This process is used for military hose and is recommended for the Safety Class jumper application.

6.12 Quality Verification Tests

The quality and consistency of the Viper® hose is expected to be excellent. However, the safety and radiological aspects of this application must be considered, not only in terms of material degradation but for assessing risk and consequences of failure.

The hose and proposed clamps are off-the-shelf components. The clamps mechanically qualified by the fitting supplier and by SRNL/EES are not normally recommended by the hose manufacturer for this hose style. Swaged-on fittings are normally recommended with ratings to 1000 psi. These provide more uniform compression of the wire-reinforced hose but are more expensive and less practical for field installation. It is noted that the Dixon RBU35 clamps used in both EES and MS&T tests held higher pressure than the swaged-on fittings, allowing valid burst tests. However, the clamps have to be manually torqued and the bolts are bent due to the stresses involved.

The following hose/fitting quality verification and post-assembly tests are recommended. Additional requirements may be imposed. Some tests can be performed on a lot or percentage basis, while others should be performed 100% as indicated. Certain tests should be performed upon receipt, with others performed prior to and/or after jumper assembly.

- 100% visual examination of hose surfaces for damage (cuts, tears, etc.) Hoses should be rejected if damage exposes fiber reinforcement. Hoses may be cut to remove localized damaged sections. Hoses should show no signs of aging/embrittlement.
- All hoses should be marked with cure date or otherwise coded. Hoses should be within 1 year of cure date upon receipt and within 3 years of the cure date prior to use.
- Liner hardness shall be Shore Durometer 90 +/-5A. Hardness should be verified upon receipt and 30 days prior to use. Hardness measurement should be taken away from wire reinforcement.
- Visual inspection of clamps/bolts (defects, cracks, damage other than minor surface dings from handling, part numbers, bolt head markings)
- Alloy verification of clamps/bolts (per ASTM F593, Group 1) [50]
- Tensile strength testing of bolts meeting ASTM F593C, Condition CW
- Each length of hose to be used should be qualified by performing burst tests per ASTM D380 or RMA Handbook IP-2 with clamps proposed for service. Multiple lengths may be qualified from a single set of tests if from the same production run. Minimum burst pressure should be 1000 psi or as otherwise designated by Design Authority. A minimum of three tests should be performed with the safety factor based on the lowest test value.
- Post-assembly: Pressurize a full length assembly to 1.5-2X the working pressure (or operating pressure per Design Authority) and hold for the anticipated duration of one transfer. Note: This duration is longer than specified by ASTM D380 (1 min). The proof pressure shall not exceed 50 % of the specified minimum bursting strength.
- Dye-penetrant testing of clamps before and after proof-testing to identify cracks

7.0 CONCLUSIONS AND RECOMMENDATIONS

7.1 Based on available data, a maximum dose limit of 50 Mrad is suggested for the Goodyear Viper® hose. Higher doses may be acceptable depending on the required safety factor, service conditions expected and with increased operating history. A more conservative limit of 10 Mrad minimizes concern over radiation effects.

7.2 Burst values at 50 Mrad are estimated at 600-800 psi, providing a 3-4X safety factor over the working pressure (200 psi) and a 4.0-5.3X safety factor over the operating pressure (150 psi), independent of temperature. At 100 Mrad, burst values were approximately 2.0-2.3X the working pressure and 2.7-3X the operating pressure. Burst values at 250 Mrad are approximately equal to the working pressure. Burst values at 300 Mrad are below the anticipated service pressure.

7.3 NAHAD guidelines recommend that hose working pressure be reduced by 30% if operating between 150 and 225 °F. Goodyear representatives confirm this applies to the Viper® hose, though this is not readily indicated in Goodyear literature. This reduces the working pressure from 200 psi to 140 psi, slightly less than the anticipated service pressure. Alternatively, a 30% reduction of normal burst pressure (1000 psi) gives a burst pressure of 700 psi. This is similar to the room temperature burst pressure estimated at 50 Mrad and the burst values obtained by EES at 200 °F, in absence of radiation.

7.4 Burst tests at doses < 100 Mrad were not initially performed due to focus on higher target doses and limited irradiation chamber space. Additional tests at 10-50 Mrad are therefore recommended for completeness. These tests can be performed quickly as the irradiation doses are lower. Some samples should be heated during testing to determine combined radiation/temperature effects. Several 18” long hoses irradiated to 250 Mrad are also available for future testing.

7.5 At a bounding continuous dose rate of 57, 870 rad/hr, a 50 Mrad dose will be reached in ~ 1.2 months. For a 20-hour transfer, the dose per transfer is 1.2 Mrad. The bounding dose rate is likely conservative for most HLW transfers but refined dose rate calculations are recommended to extend service life. Calculations should account for lower dose rates during non-transfer periods if possible.

7.6 SRNL tests indicate the Viper® hose liner loses approximately 46% of initial elongation (100% absolute retained) at 50 Mrad and 60% of initial elongation (75% absolute retained) at 100 Mrad in air. Approximately 90% of initial elongation (20% absolute retained) is lost at 250 Mrad and 93% is lost at 300 Mrad (15% absolute retained). The minimum properties of the liner required are unknown. At least 10-15% elongation is needed to accommodate linear growth due to heat and pressure factors. Additional elongation is likely needed to accommodate bending or dynamic conditions.

7.7 Exposure to 25% NaOH at 200 °F did not embrittle the hose liner, at least within the 30-day test period. In most cases, chemical exposure at elevated temperature slightly decreased tensile strength but increased elongation. The behavior is more pronounced at 50 Mrad, with elongation increasing from 100% to 250%, higher than the baseline elongation value. The mechanism for this behavior is not well understood. There may be an annealing phenomenon at this particular dose or some other mechanism. Additional tests at 50 Mrad and lower doses are recommended to better understand this behavior.

7.8 Laboratory testing cannot fully duplicate all service conditions. Therefore, hose performance in service should be closely monitored. Post-service examination and laboratory testing is recommended. Such data are needed to validate conclusions in this report and may be useful for future applications.

7.9 The SRS shelf-life of the Viper® hose is currently recommended at 3 years. The hose should be within 1 year of cure date upon receipt. Unless otherwise instructed by the hose manufacturer, hoses should be stored in a Level A storage facility with temperatures less than 100 °F. Hoses should be protected from sources of heat, ozone, ultraviolet light (including indoor lighting), ionizing radiation, chemicals and other harmful factors. Hoses should be procured with serial numbers printed on the brand tape to identify exact cure date for Safety Class applications. Hoses can be examined at the end of shelf-life to evaluate the potential for shelf-life extension.

7.10 Polymers evolve gases during radiolysis. For the principal polymers in the Viper® hose construction, the primary gas generated is hydrogen with some methane. Preliminary estimates indicate ~0.1L of flammable gas per linear foot of 3” hose could be generated per 20-hour transfer. The impact of flammable gas generation internal and external to the hose during a given transfer is believed to be minimal but should be further evaluated. Formal gas generation and flammability calculations are recommended.

7.11 Non-metallic hoses can develop static charge. This behavior is of less concern for aqueous, non-flammable, conductive liquids such as HLW salt solutions as compared to flammable, non-conductive liquids or dry particulate solids. The standard Viper® hose does not contain antistatic additives or grounding wire. The risk of static charge development in combination with flammable gas generation should be evaluated. Based on anticipated operating conditions, the risk is considered very low.

8.0 ACKNOWLEDGEMENTS

The author acknowledges the contributions of the following individuals to this report:

Ken Billings, Jean-Guy Vaillancourt and Pascal Langois (Veyance Technologies), Chris Beam and Gregg Creech (SRNL Gamma Irradiation Facility), Glenn Chapman (MS&T/tensile testing), Paul Korinko (MS&T/DSC analysis), Lin Thacker, Bridget Miller and Tony Curtis (MS&T/chemical resistance testing), Wayne Good, Doug Holiday (EES High Pressure Lab - burst testing), Tom White (ADS/FT-IR spectroscopy), David Missimer (ADS/X-ray diffraction), Fernando Fondeur (ADS/Raman spectroscopy), Steven Spiegelburg and Gregory Neal (Cambridge Polymer Group), James Laurinat (E&CP/Actinide Programs, gas generation estimates), Brett Mikell (Lewis-Goetz).

9.0 REFERENCES

[1] Task Technical Request, HLE-TTR-2008-26SRNL Material Qualification for HLW Safety Class Flexible Jumper

[2] Goodyear Industrial Hose Viper® hose data sheet, www.goodyearindustrialproducts.com

[3] WSRC-TR-2004-00471, LLW Aboveground Transfer Hose Service Compatibility Review, T.E. Skidmore, September 2004.

[4] WSRC-TR-2007-00161, SERVICE LIFE EVALUATION OF THE HEU HOSE-IN-HOSE TRANSFER SYSTEM (U), T. E. Skidmore, May 2007.

[5] “Interactions of Clay Minerals with Organic Polymers, Some Practical Applications”, B.K.G. Theng, *Clays and Clay Minerals*, 1970.

[6] U.S. Patent# 6440512, “Hose construction containing ternary blend of polymers”, issued August 27, 2002.

[7] IEEE 323, IEEE Standard for Qualifying Class 1E Equipment for Nuclear Power Generating Stations

[8] IEEE384, IEEE Standard for Qualifying Class 1E Electric Cables and Field Splices for Nuclear Power Generating Stations

[9] ASTM D4082– 02, Standard Test Method for Effects of Gamma Radiation on Coatings for Use in Light-Water Nuclear Power Plants

[10] NUREG/CR-6384, Literature Review of Environmental Qualification of Safety-Related Nuclear Cables, April 1996.

[11] NUREG/CR-2877, SAND81-2613, Investigation of Cable Deterioration in the Containment Building of the Savannah River Nuclear Reactor, K. T. Gillen, R. L. Clough, L. H. Jones.

[12] Combined Environment Aging Effects: Radaition Thermal Degradation of Polyvinylchloride and Polyethylene, R.L. Clough, K.T. Gillen, Journal of Polymer Science, Vol.19, 2041-2051.

[13] "Inadequacy of Margin in Qualification Tests", R.L. Clough, K.T. Gillen, SAND83-2085C.

[14] The Radiation Induced Degradation of Polymers, H. Wilski, Radiation Physical Chemistry, Vol. 29, No.1, 1987.

[15] "The effects of radiation on the mechanical properties of polymers used as electrical cable insulation and Jacketing materials", D.I. Johnson, Harwell Laboratory, U.K., AERE R 13286.

[16] "Comparison of Antioxidants for Combined Radaition and Thermal Aging and Superposition of Radiation and Thermal Aging for EPR and XLPE, A.B. Reynolds, P.A. Wlodkowski, Radiation Physical Chemistry, Vol. 38, No.6, 1991.

[17] "Dose Rate Effects on the Radiation-Induced Oxidation of Electric Cable used in Nuclear Power Plants", A.B. Reynolds, R.M.Bell, M.N. Bryson, T.E. Doyle, M.B. Hall, L.R. Mason, L. Quintric, P.L. Terwilliger, Radiation Physical Chemistry, Vol. 45, No.1, 1995.

[18] "Assessment of Oxidative Thermal Degradation of Crosslinked Polyethylene and Ethylene Propylene Rubber Cable Insulation", K. Ananakumaran, D.J. Stonkus, Polymer Engineering & Science, 1992, Vol. 32, No.18.

[19] "Characterization and Degradation Studies of Peroxide and Silane-Crosslinked Polyethylene, M. Celina, G.A. George, Polymer Degradation and Stability, 48, 1995 (297-312).

[20] "Long-Term Performance of Cables Based on Chlorosulfonated Polyethylene", M.J. Sandelin, U.W. Gedde, *Polymer Degradation and Stability*, Vol.86, 2004 (331-338).

[21] "Thermal Degradation of Crosslinked High Density Polyethylene", S.O. Han, D.W. Lee, O.H. Han, Polymer Degradation and Stability, 63 (1999), 237-243.

[22] "Updated Aging Assessment Approach and Use with Electric Cable Insulation", D. A. Horvath, R.P. Colaianni, Nuclear Technology, Vol. 143, August 2003.

[23] "Degradation of Crosslinked Polyethylene In Water by Gamma-Irradiation", T. Matsui, T. Takano, S. Takayama, M. Ito, I. Narisawa, Radiation Physics and Chemistry, Vol. 63 (2002) 193-200.

[24] "The Kinetics of Polyolefin Oxidation in Aqueous Media", J.L. Henry, A.L. Ruaya, A. Garton, Journal of Polymer Science: Part A, Vol.30, 1693-1703, 1992

[25] "The Effect of Co-Agent on the Peroxide Cross-linking of LDPE", I. Ghasemi, J. Morshedian, Iranian Polymer Journal, 12 (2), 2003, 119-125.

[26] "Radiochemical Ageing of EPDM Elastomers – 2. Identification and Quantification of Chemical Changes in EPDM and EPR films γ-irradiated under oxygen atmosphere

[27] Corrosion Resistance Tables, P.A. Schweitzer, 1995, Marcel Dekker.

[28] PDL Handbook Series, Chemical Resistance, Vol. 1 – Thermoplastics, 2nd Edition, 1994.

[29] Handbook of Plastics, Elastomers and Composites, C.A.Harper, 2nd Edition, 1992.

[30] Compass Corrosion Guide II, Compass Publications, 1983, 2nd Edition.

[31] Goodyear Chemical Resistance Ratings, Industrial Hose Catalog, #98-130.

[32] SRNL-L1300-2008-00041, Structural Testing of Hose and Fittings for HLW Flexible Jumper, R.L. Minichan, December 2008.

[33] ASTM D638-08, Standard Test Method for Tensile Properties of Plastics

[34] ASTM D412-06a, Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers-Tension

[35] ASTM D380 – 94 (Reapproved 2006), Standard Test Methods for Rubber Hose

[36] RMA Hose Handbook, IP-2, Seventh Edition, 2003

[37] ASTM D 2765-01 (Reapproved 2006), Standard Test Methods for Determination of Gel Content and Swell Ratio of Crosslinked Ethylene Plastics

[38] ASTM F 2214-02 (Reapproved 2008), Standard Test Method for *In Situ* Determination of Network Parameters of Crosslinked Ultra High Molecular Weight Polyethylene (UHMWPE)

[39] ASTM F 2381 – 04, Standard Test Method for Evaluating Trans-Vinylene Yield in Irradiated Ultra-High-Molecular-Weight Polyethylene Fabricated Forms Intended for Surgical Implants by Infrared Spectroscopy

[40] ASTM F 2102 – 06, Standard Guide for Evaluating the Extent of Oxidation in Ultra-High-Molecular-Weight Polyethylene Fabricated Forms Intended for Surgical Implants

[41] ASTM D 3895 – 07, Standard Test Method for Oxidative-Induction Time of Polyolefins by Differential Scanning Calorimetry

[42] ASTM F876-08b, Standard Specification for Crosslinked Polyethylene (PEX) Tubing

[43] CH-TRU Payload Appendices Rev. 2, February 2009, APPENDIX 3.1
RADIOLYTIC G VALUES FOR WASTE MATERIALS

[44] API 1529, AVIATION FUELLING HOSE AND HOSE ASSEMBLIES, 6th Ed, May 2005

[45] SAE AS1933, Rev. A, Age Controls for Hose Containing Age-Sensitive Elastomeric Material

[46] EPRI NP-6608, "Shelf Life of Elastomeric Components"

[47] SAE ARP 5316, Rev.B, Storage of Elastomer Seals and Seal Assemblies Which Include an Elastomer Element Prior to Hardware Assembly

[48] MIL-HDBK-695D, RUBBER PRODUCTS: RECOMMENDED SHELF LIFE

[49] SAE J1273, SURFACE VEHICLE RECOMMENDED PRACTICE, FEB2009
Recommended Practices for Hydraulic Hose Assemblies

[50] ASTM F593-02 (Reapproved 2008), Standard Specification for Stainless Steel Bolts, Hex Cap Screws, and Studs

Appendix I – Burst Test Results

11.11.2008 10:32

Figure 40. Baseline 1” ID Viper® hose section for burst testing

11.12.2008 10:49

Figure 41. Baseline sample A (failure at 850 psi)

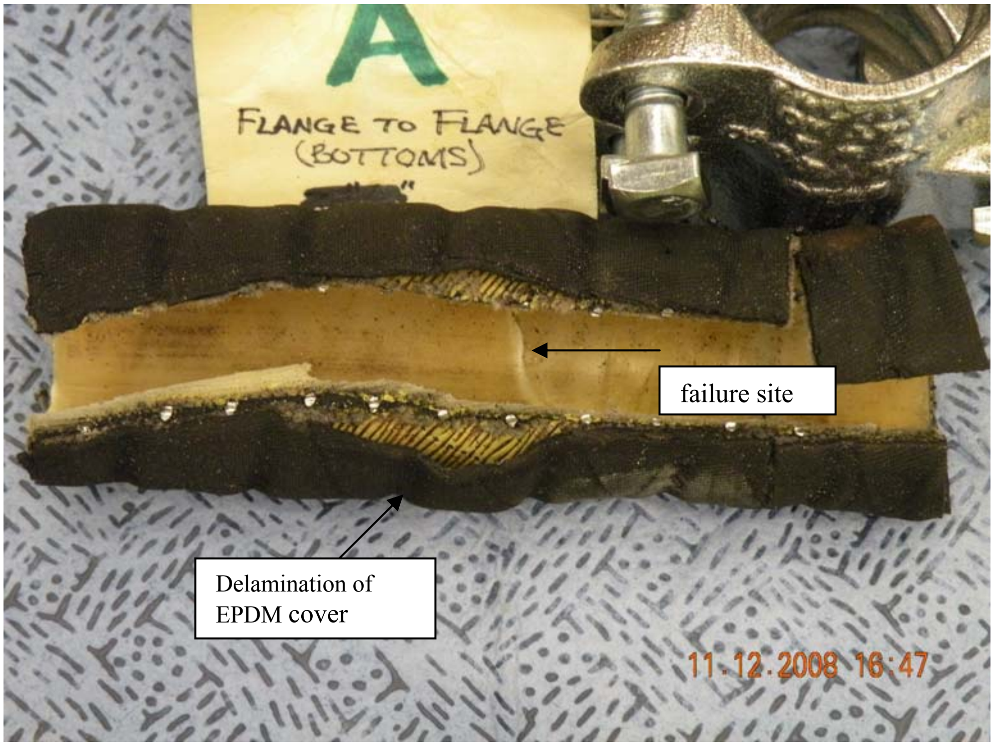


Figure 42. Post-failure examination of baseline sample A

Figure 43. Baseline sample B

Figure 44. Baseline sample B, failure at 1200 psi (near fitting)

Figure 45. Post-failure examination of baseline sample B

Figure 46. Baseline sample C (prior to test)

Figure 47. Baseline sample C, failure at 1400 psi (bubble retained in delaminated cover)

Figure 48. Post-failure examination, baseline sample C

Figure 49. Baseline sample D (pre-test)

Figure 50. Baseline sample D, failure at 1300 psi (bubble retained after testing)

Figure 51. Baseline sample D, cover rupture

Figure 52. Post-failure examination, baseline sample D

Figure 53. Baseline sample E, pre-test

Figure 54. Baseline sample E, failure at 1320 psi (small bubble retained)

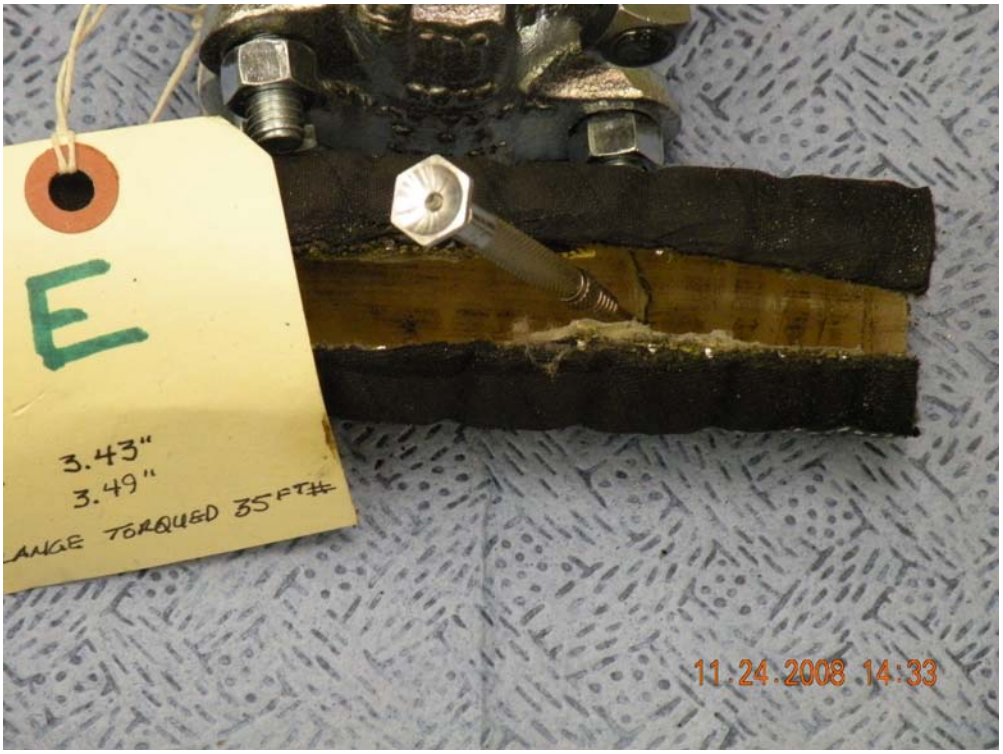


Figure 55. Post-failure examination, baseline sample E

Figure 56. Sample A1 (irradiated to 100 Mrad) – pre-test

Figure 57. Sample A1 (100 Mrad), failure at 450 psi

Figure 58. Post-failure examination, sample A1 (100 Mrad), exterior

Figure 59. Post-failure examination, sample A1 (100 Mrad), interior

Figure 60. Sample A2 (irradiated to 100 Mrad), pre-test

Figure 61. Sample A2 (100 Mrad), failure at 400 psi

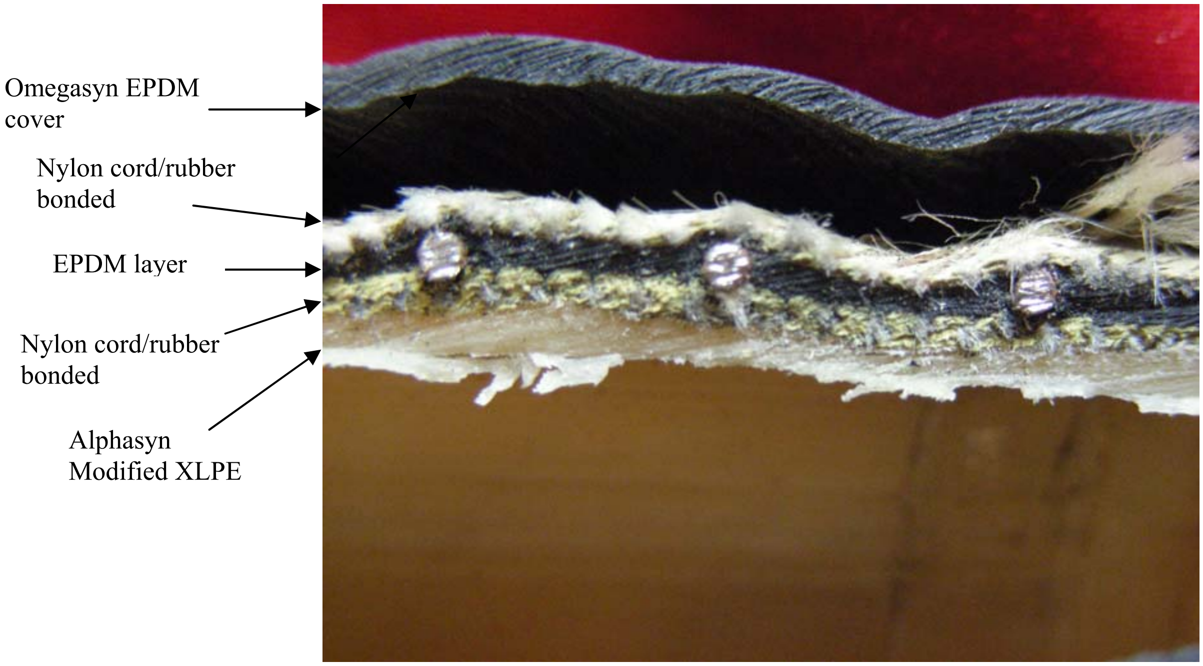


Figure 62. Post-failure examination, cross-section of sample A2 (100 Mrad, 400 psi burst)

Figure 63. Sample B1 (250 Mrad), pre-test

Figure 64. Sample B1 (250 Mrad), failure at 200 psi (dual bubbles formed)

Figure 65. Sample B2 (irradiated to 250 Mrad), pre-test

Figure 66. Sample B2 (250 Mrad), failure at 250 psi

Figure 67. Sample C1 (irradiated to 300 Mrad), pre-test

Figure 68. Sample C1 (300 Mrad), failure at 140 psi (minor bubble retained)

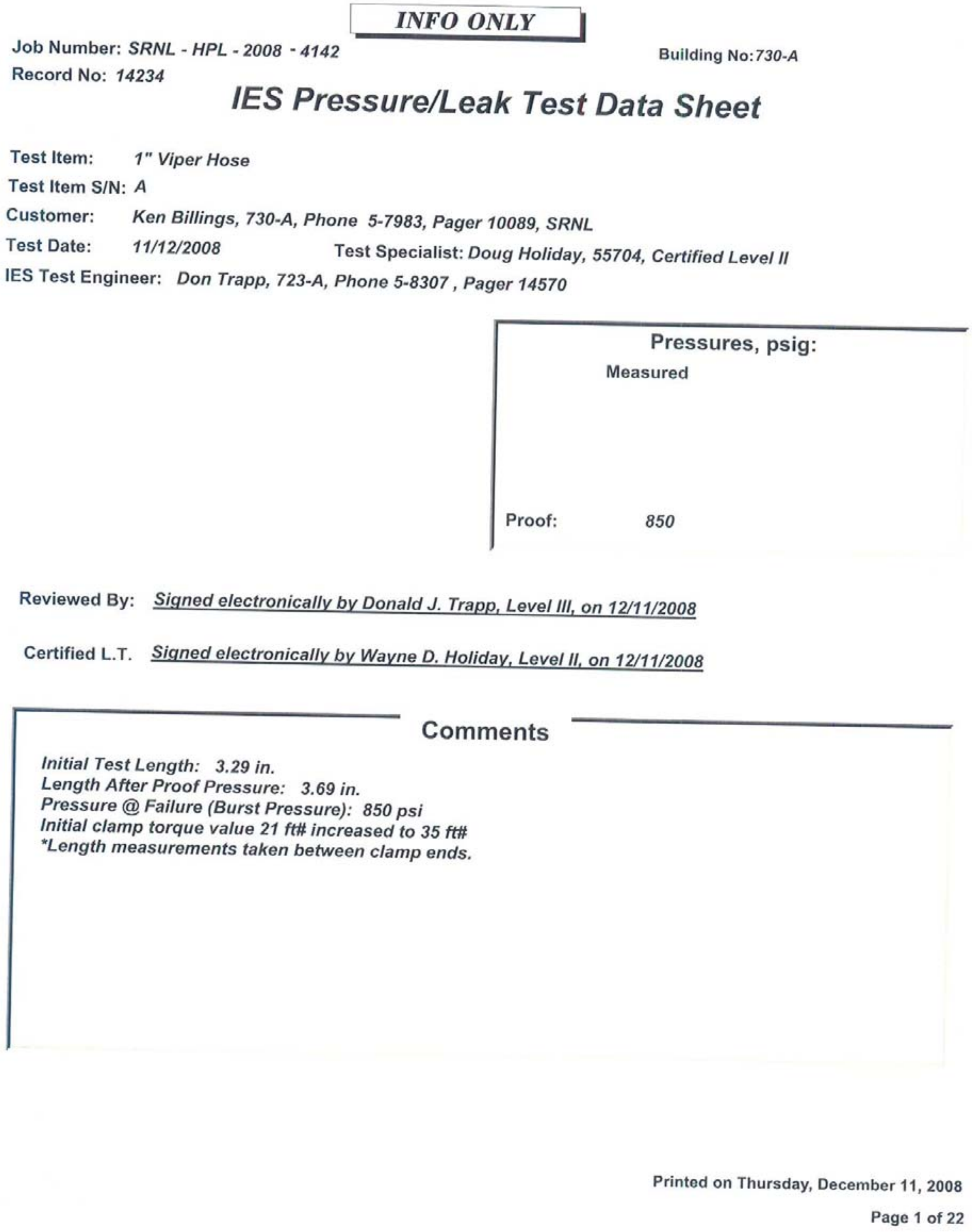
Figure 69. Sample C2 (300 Mrad), pre-test

Figure 70. Sample C2, failure at 140 psi (minor bubble)

Figure 71. Longer-length (18") baseline hose samples, with swaged-on fittings

Figures 72a-c. 18 inch baseline samples (leakage at swaged-on fittings > 1000 psi)

Appendix II – Hose Burst Test Reports



INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*
Building No: *730-A*
Record No: *14234*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose*
Test Item S/N: *A*
Customer: *Ken Billings, 730-A, Phone 5-7983, Pager 10089, SRNL*
Test Date: *11/12/2008*
Test Specialist: *Doug Holiday, 55704, Certified Level II*
IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:

	Measured
Proof:	850

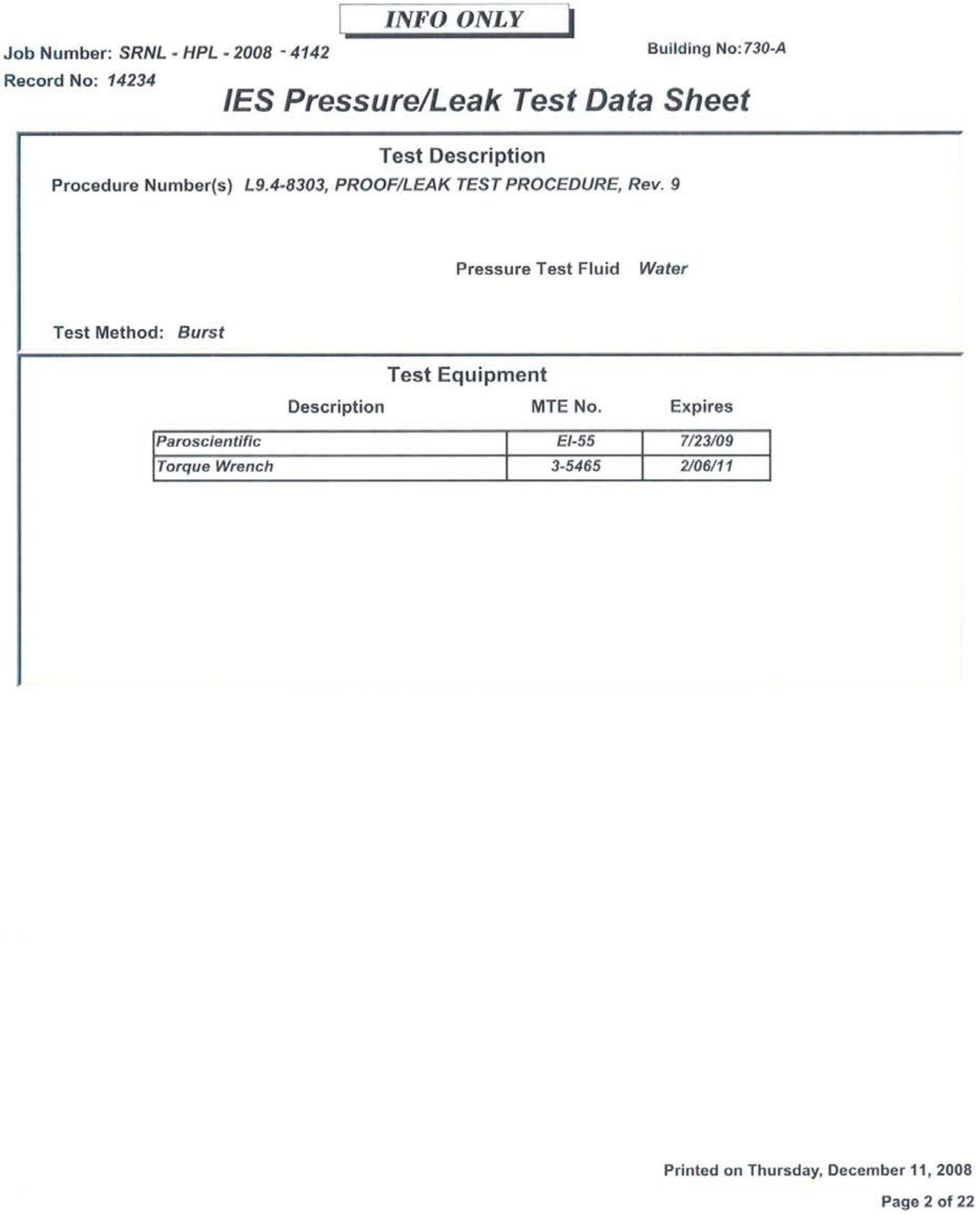
Reviewed By: Signed electronically by Donald J. Trapp, Level III, on 12/11/2008

Certified L.T. Signed electronically by Wayne D. Holiday, Level II, on 12/11/2008

Comments

Initial Test Length: 3.29 in.
Length After Proof Pressure: 3.69 in.
Pressure @ Failure (Burst Pressure): 850 psi
Initial clamp torque value 21 ft# increased to 35 ft#
**Length measurements taken between clamp ends.*

Printed on Thursday, December 11, 2008
Page 1 of 22



INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*

Building No: *730-A*

Record No: *14234*

IES Pressure/Leak Test Data Sheet

Test Description

Procedure Number(s) *L9.4-8303, PROOF/LEAK TEST PROCEDURE, Rev. 9*

Pressure Test Fluid *Water*

Test Method: *Burst*

Test Equipment

Description	MTE No.	Expires
Paroscientific	*EI-55*	*7/23/09*
Torque Wrench	*3-5465*	*2/06/11*

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*

Building No: *730-A*

Record No: *14235*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose*

Test Item S/N: *B*

Customer: *Ken Billings, 730-A, Phone 5-7983, Pager 10089, SRNL*

Test Date: *11/12/2008*

Test Specialist: *Doug Holiday, 55704, Certified Level II*

IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:

	Measured
Proof:	1200

Reviewed By: *Signed electronically by Donald J. Trapp, Level III, on 12/11/2008*

Certified L.T. *Signed electronically by Wayne D. Holiday, Level II, on 12/11/2008*

Comments

Initial Test Length: 3.52 in.
Length After Proof Pressure: 3.73 in.
Pressure @ Failure (Burst Pressure): 1200 psi
**Length measurements taken between clamp ends.*

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142* **Building No:** *730-A*

Record No: *14235*

IES Pressure/Leak Test Data Sheet

Test Description

Procedure Number(s) *L9.4-8303, PROOF/LEAK TEST PROCEDURE, Rev. 9*

Pressure Test Fluid *Water*

Test Method: *Burst*

Test Equipment

Description	MTE No.	Expires
Paroscientific	*EI-55*	*7/23/09*
Torque Wrench	*3-5465*	*2/06/11*

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142* Building No: *730-A*

Record No: *14238*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose*

Test Item S/N: *C*

Customer: *Ken Billings, 730-A, Phone 5-7983, Pager 10089, SRNL*

Test Date: *11/17/2008* Test Specialist: *Doug Holiday, 55704, Certified Level II*

IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:

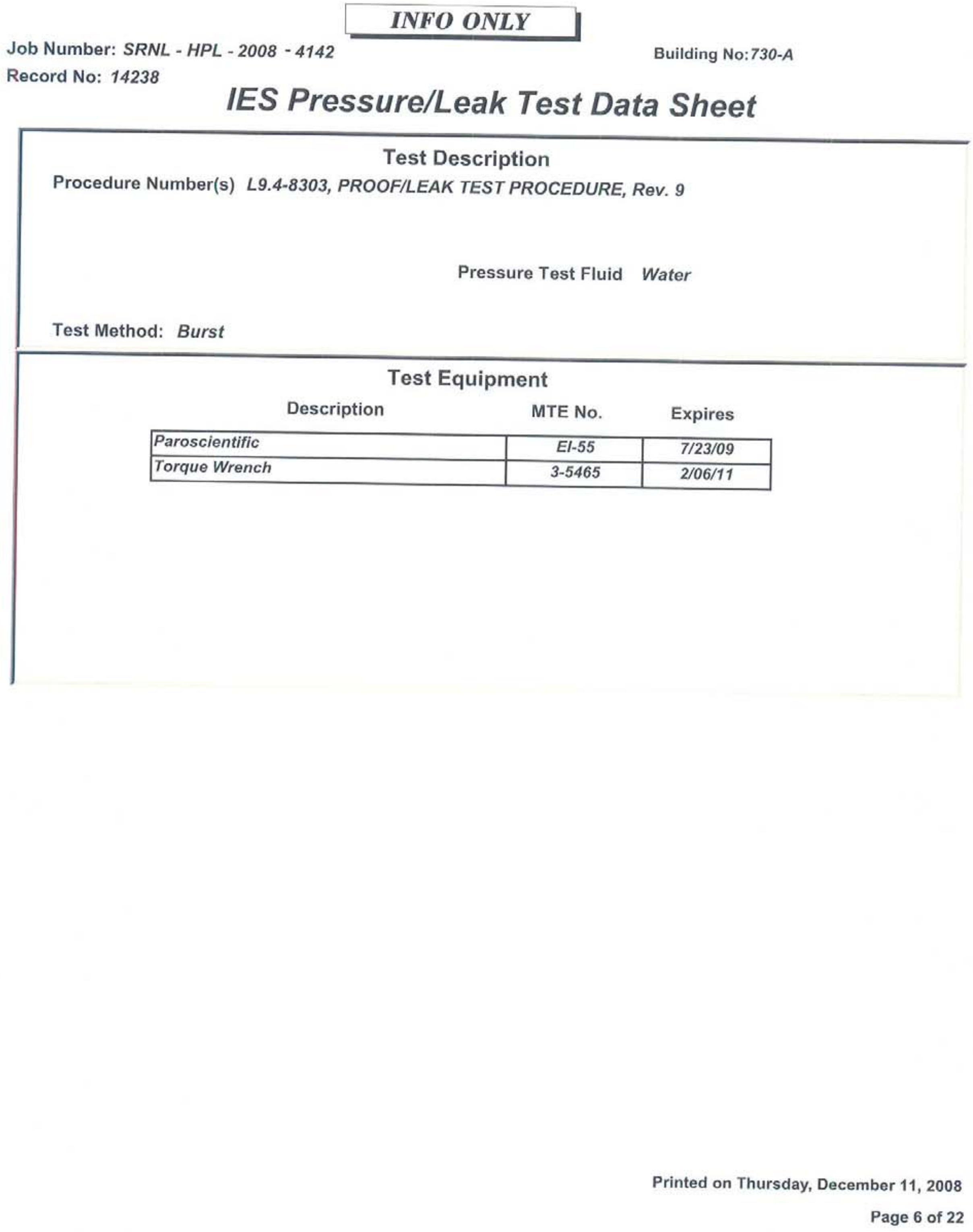
	Measured
Proof:	*1400*

Reviewed By: *Signed electronically by Donald J. Trapp, Level III, on 12/11/2008*

Certified L.T. *Signed electronically by Wayne D. Holiday, Level II, on 12/11/2008*

Comments

Initial Test Length: 3.39 in.
Length After Proof Pressure: 3.68 in.
Pressure @ Failure (Burst Pressure): 1400 psi
Clamp Torque Value: 35 ft#
**Length measurements taken between clamp ends.*



INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142* **Building No:** *730-A*

Record No: *14238*

IES Pressure/Leak Test Data Sheet

Test Description

Procedure Number(s) *L9.4-8303, PROOF/LEAK TEST PROCEDURE, Rev. 9*

Pressure Test Fluid *Water*

Test Method: *Burst*

Test Equipment

Description	MTE No.	Expires
Paroscientific	*EI-55*	*7/23/09*
Torque Wrench	*3-5465*	*2/06/11*

Printed on Thursday, December 11, 2008

Page 6 of 22

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142* **Building No:** *730-A*
Record No: *14239*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose*
Test Item S/N: *D*
Customer: *Ken Billings, 730-A, Phone 5-7983, Pager 10089, SRNL*
Test Date: *11/17/2008* **Test Specialist:** *Doug Holiday, 55704, Certified Level II*
IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:	
	Measured
Proof:	*1300*

Reviewed By: *Signed electronically by Donald J. Trapp, Level III, on 12/11/2008*

Certified L.T. *Signed electronically by Wayne D. Holiday, Level II, on 12/11/2008*

Comments

Initial Test Length: 3.59 in.
Length After Proof Pressure: 3.77 in.
Pressure @ Failure (Burst Pressure): 1300 psi
Clamp Torque Value: 35 ft#
**Length measurements taken between clamp ends.*

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142* Building No: *730-A*

Record No: *14239*

IES Pressure/Leak Test Data Sheet

Test Description

Procedure Number(s) *L9.4-8303, PROOF/LEAK TEST PROCEDURE, Rev. 9*

Pressure Test Fluid *Water*

Test Method: *Burst*

Test Equipment

Description	MTE No.	Expires
Paroscientific	*EI-55*	*7/23/09*
Torque Wrench	*3-5465*	*2/06/11*

Printed on Thursday, December 11, 2008

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142* Building No: *730-A*

Record No: *14240*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose*

Test Item S/N: *E*

Customer: *Ken Billings, 730-A, Phone 5-7983, Pager 10089, SRNL*

Test Date: *11/20/2008* Test Specialist: *Doug Holiday, 55704, Certified Level II*

IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:

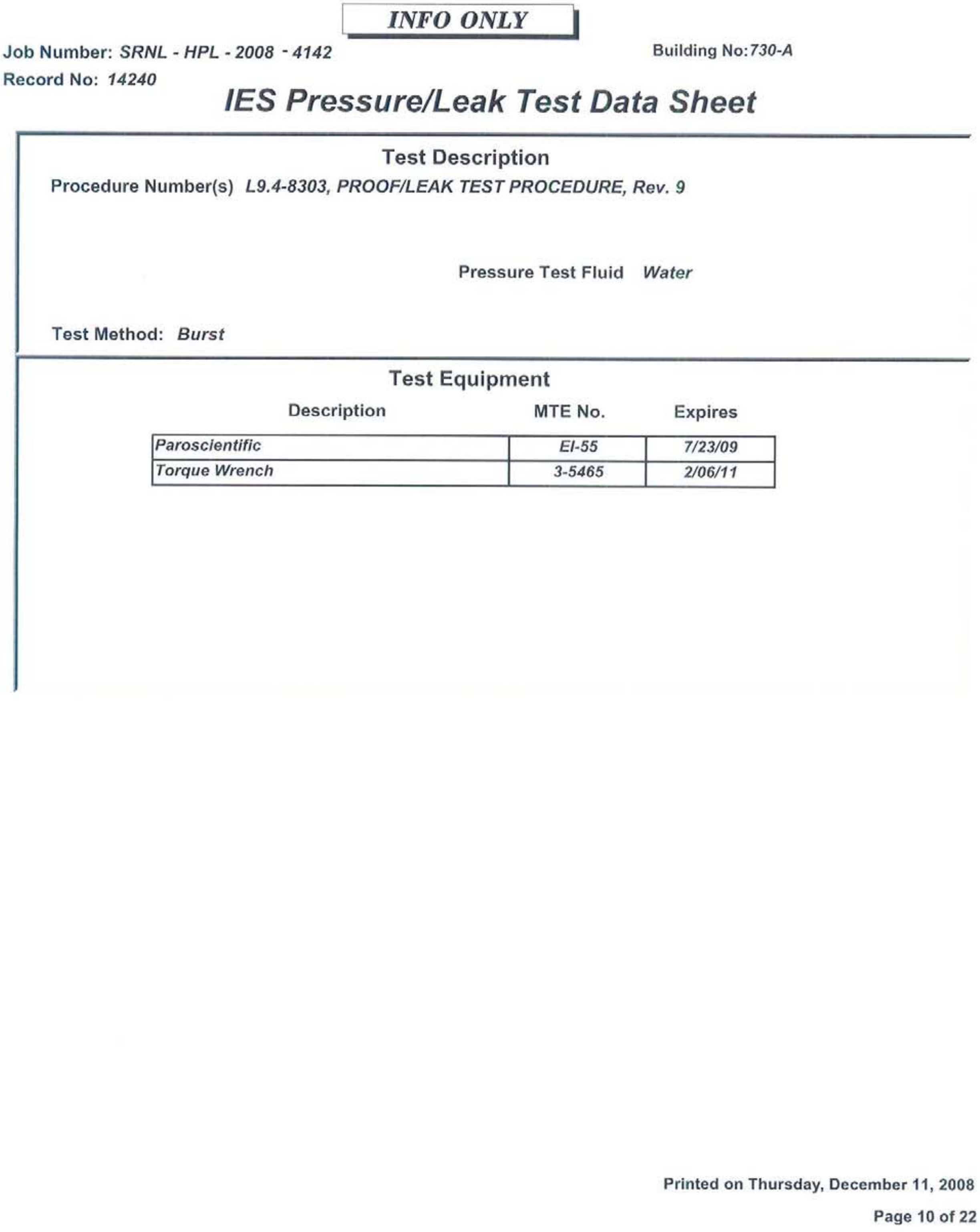
	Measured
Proof:	*1320*

Reviewed By: *Signed electronically by Donald J. Trapp, Level III, on 12/11/2008*

Certified L.T. *Signed electronically by Wayne D. Holiday, Level II, on 12/11/2008*

Comments

Initial Test Length: 3.43 in.
Length After Proof Pressure: 3.49 in.
Pressure @ Failure (Burst Pressure): 1320 psi
Clamp Torque Value: 35 ft#
**Length measurements taken between clamp ends.*



INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*

Building No: *730-A*

Record No: *14240*

IES Pressure/Leak Test Data Sheet

Test Description

Procedure Number(s) *L9.4-8303, PROOF/LEAK TEST PROCEDURE, Rev. 9*

Pressure Test Fluid *Water*

Test Method: *Burst*

Test Equipment

Description	MTE No.	Expires
Paroscientific	*EI-55*	*7/23/09*
Torque Wrench	*3-5465*	*2/06/11*

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142* Building No: *730-A*

Record No: *14241*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose*

Test Item S/N: *A1*

Customer: *Ken Billings, 730-A, Phone 5-7983, Pager 10089, SRNL*

Test Date: *12/1/2008* Test Specialist: *Doug Holiday, 55704, Certified Level II*

IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:

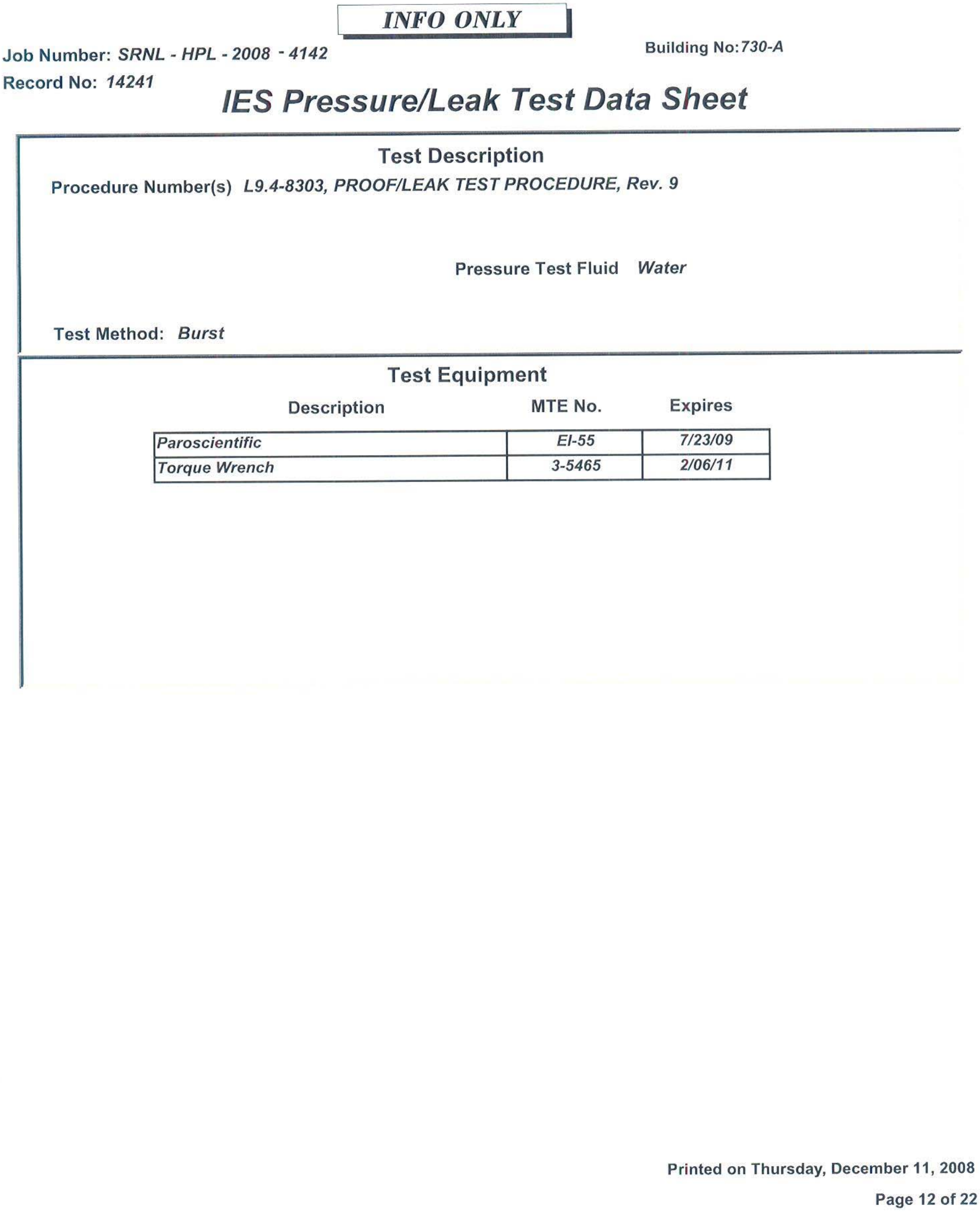
	Measured
Proof:	*450*

Reviewed By: *Signed electronically by Donald J. Trapp, Level III, on 12/11/2008*

Certified L.T. *Signed electronically by Wayne D. Holiday, Level II, on 12/11/2008*

Comments

Initial Test Length: 3.64 in.
Length After Proof Pressure: 3.74 in.
Pressure @ Failure (Burst Pressure): 450 psi
Clamp Torque Value: 35 ft#
**Length measurements taken between clamp ends.*



INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*

Building No: *730-A*

Record No: *14241*

IES Pressure/Leak Test Data Sheet

Test Description

Procedure Number(s) *L9.4-8303, PROOF/LEAK TEST PROCEDURE, Rev. 9*

Pressure Test Fluid *Water*

Test Method: *Burst*

Test Equipment

Description	MTE No.	Expires
Paroscientific	*EI-55*	*7/23/09*
Torque Wrench	*3-5465*	*2/06/11*

Printed on Thursday, December 11, 2008

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142* **Building No:** *730-A*

Record No: *14243*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose*

Test Item S/N: *A2*

Customer: *Ken Billings, 730-A, Phone 5-7983, Pager 10089, SRNL*

Test Date: *12/1/2008* **Test Specialist:** *Doug Holiday, 55704, Certified Level II*

IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:

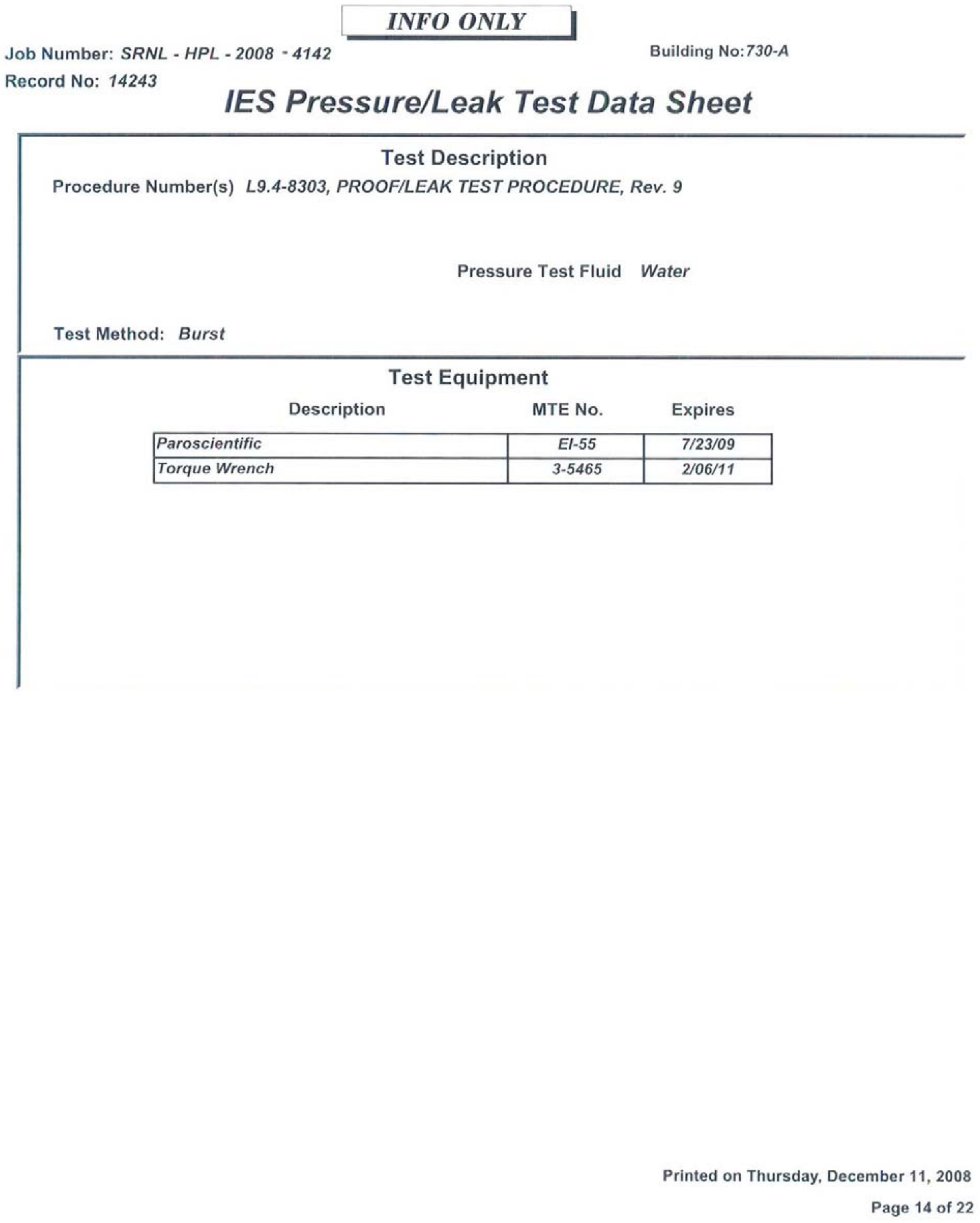
	Measured
Proof:	*400*

Reviewed By: *Signed electronically by Donald J. Trapp, Level III, on 12/11/2008*

Certified L.T. *Signed electronically by Wayne D. Holiday, Level II, on 12/11/2008*

Comments

Initial Test Length: 3.60 in.
Length After Proof Pressure: 3.68 in.
Pressure @ Failure (Burst Pressure): 400 psi
Clamp Torque Value: 35 ft#
**Length measurements taken between clamp ends.*



INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*

Building No: *730-A*

Record No: *14243*

IES Pressure/Leak Test Data Sheet

Test Description

Procedure Number(s) *L9.4-8303, PROOF/LEAK TEST PROCEDURE, Rev. 9*

Pressure Test Fluid *Water*

Test Method: *Burst*

Test Equipment

Description	MTE No.	Expires
Paroscientific	*EI-55*	*7/23/09*
Torque Wrench	*3-5465*	*2/06/11*

Printed on Thursday, December 11, 2008

Page 14 of 22

INFO ONLY

Job Number: SRNL - HPL - 2008 - 4142
Building No: 730-A
Record No: 14244

IES Pressure/Leak Test Data Sheet

Test Item: 1" Viper Hose
Test Item S/N: B1
Customer: Ken Billings, 730-A, Phone 5-7983, Pager 10089, SRNL
Test Date: 12/2/2008 Test Specialist: Doug Holiday, 55704, Certified Level II
IES Test Engineer: Don Trapp, 723-A, Phone 5-8307 , Pager 14570

Pressures, psig:

	Measured
Proof:	200

Reviewed By: Signed electronically by Donald J. Trapp, Level III, on 12/11/2008

Certified L.T. Signed electronically by Wayne D. Holiday, Level II, on 12/11/2008

Comments

Initial Test Length: 3.76 in.
Length After Proof Pressure:
Pressure @ Failure (Burst Pressure): 200 psi
Clamp Torque Value: 35 ft#
**Length measurements taken between clamp ends.*

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*

Building No: *730-A*

Record No: *14244*

IES Pressure/Leak Test Data Sheet

Test Description

Procedure Number(s) *L9.4-8303, PROOF/LEAK TEST PROCEDURE, Rev. 9*

Pressure Test Fluid *Water*

Test Method: *Burst*

Test Equipment

Description	MTE No.	Expires
Paroscientific	*EI-55*	*7/23/09*
Torque Wrench	*3-5465*	*2/06/11*

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*

Building No: *730-A*

Record No: *14245*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose*

Test Item S/N: *B2*

Customer: *Ken Billings, 730-A, Phone 5-7983, Pager 10089, SRNL*

Test Date: *12/2/2008*

Test Specialist: *Doug Holiday, 55704, Certified Level II*

IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:

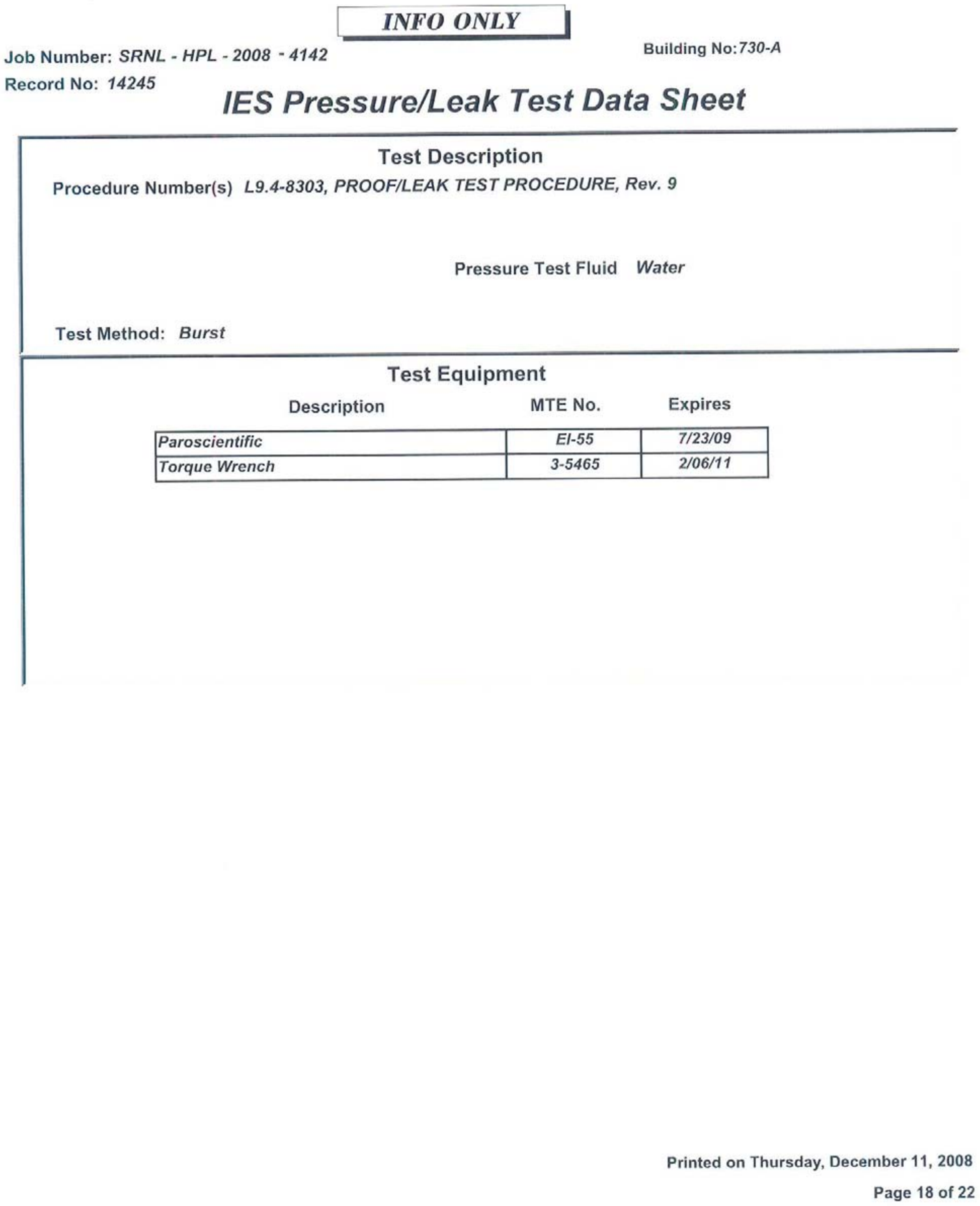
	Measured
Proof:	*250*

Reviewed By: *Signed electronically by Donald J. Trapp, Level III, on 12/11/2008*

Certified L.T. *Signed electronically by Wayne D. Holiday, Level II, on 12/11/2008*

Comments

Initial Test Length: 3.66 in.
Length After Proof Pressure: Failed 12 min. into proof test
Pressure @ Failure (Burst Pressure): 250 psi
Clamp Torque Value: 35 ft#
**Length measurements taken between clamp ends.*



INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*

Building No: *730-A*

Record No: *14245*

IES Pressure/Leak Test Data Sheet

Test Description

Procedure Number(s) *L9.4-8303, PROOF/LEAK TEST PROCEDURE, Rev. 9*

Pressure Test Fluid *Water*

Test Method: *Burst*

Test Equipment

Description	MTE No.	Expires
Paroscientific	*EI-55*	*7/23/09*
Torque Wrench	*3-5465*	*2/06/11*

Printed on Thursday, December 11, 2008

Page 18 of 22

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*

Building No: *730-A*

Record No: *14246*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose*

Test Item S/N: *C1*

Customer: *Ken Billings, 730-A, Phone 5-7983, Pager 10089, SRNL*

Test Date: *12/4/2008*

Test Specialist: *Doug Holiday, 55704, Certified Level II*

IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:

	Measured
Proof:	*140*

Reviewed By: *Signed electronically by Donald J. Trapp, Level III, on 12/11/2008*

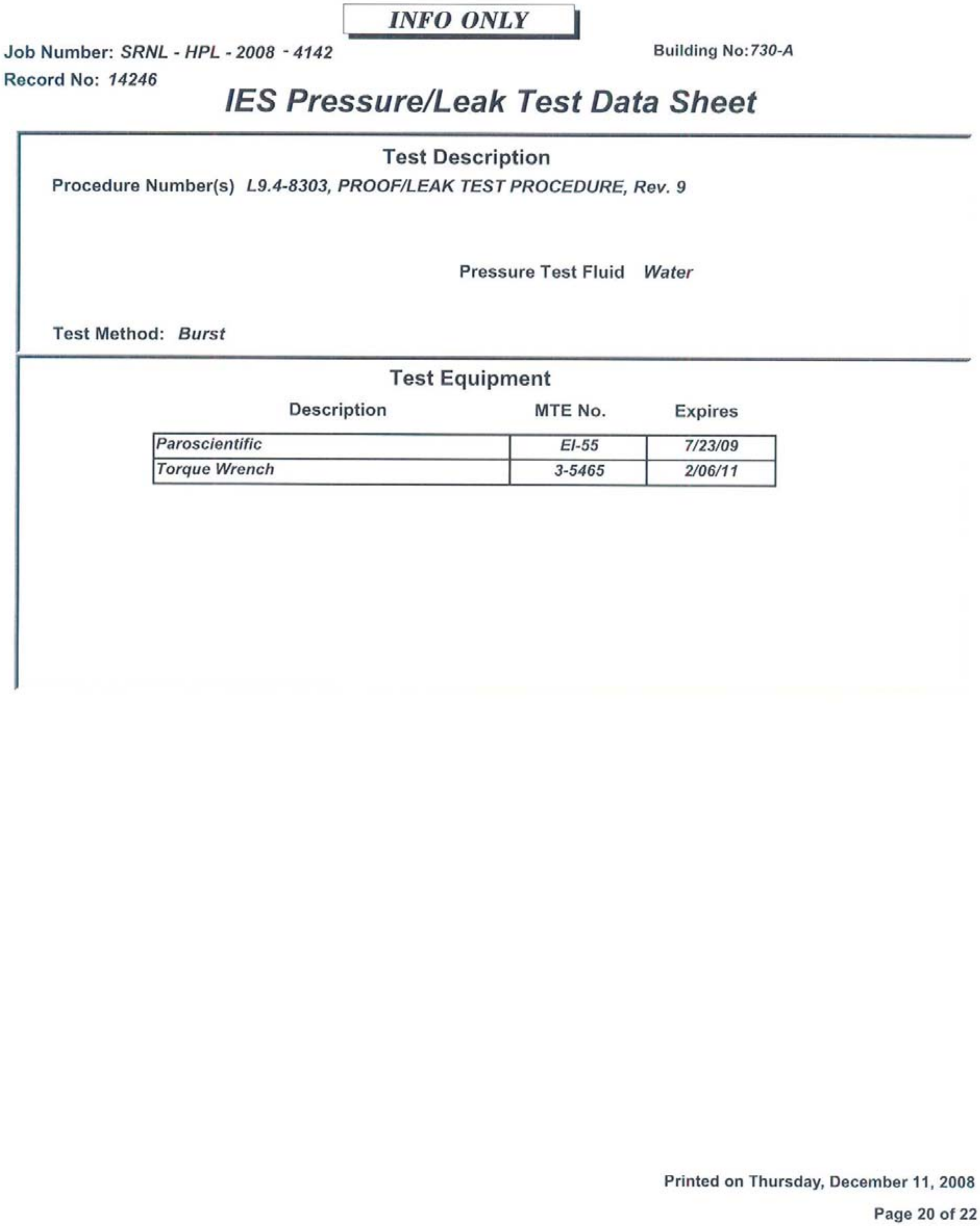
Certified L.T. *Signed electronically by Wayne D. Holiday, Level II, on 12/11/2008*

Comments

Initial Test Length: 3.53 in.
Length After Proof Pressure: Failed prior to proof pressure
Pressure @ Failure (Burst Pressure): 140 psi
Clamp Torque Value: 35 ft#
**Length measurements taken between clamp ends.*

Printed on Thursday, December 11, 2008

Page 19 of 22



INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142* **Building No:** *730-A*

Record No: *14246*

IES Pressure/Leak Test Data Sheet

Test Description

Procedure Number(s) *L9.4-8303, PROOF/LEAK TEST PROCEDURE, Rev. 9*

Pressure Test Fluid *Water*

Test Method: *Burst*

Test Equipment

Description	MTE No.	Expires
Paroscientific	*EI-55*	*7/23/09*
Torque Wrench	*3-5465*	*2/06/11*

Printed on Thursday, December 11, 2008

Page 20 of 22

INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*
Building No: *730-A*
Record No: *14247*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose*
Test Item S/N: *C2*
Customer: *Ken Billings, 730-A, Phone 5-7983, Pager 10089, SRNL*
Test Date: *12/4/2008*
Test Specialist: *Doug Holiday, 55704, Certified Level II*
IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

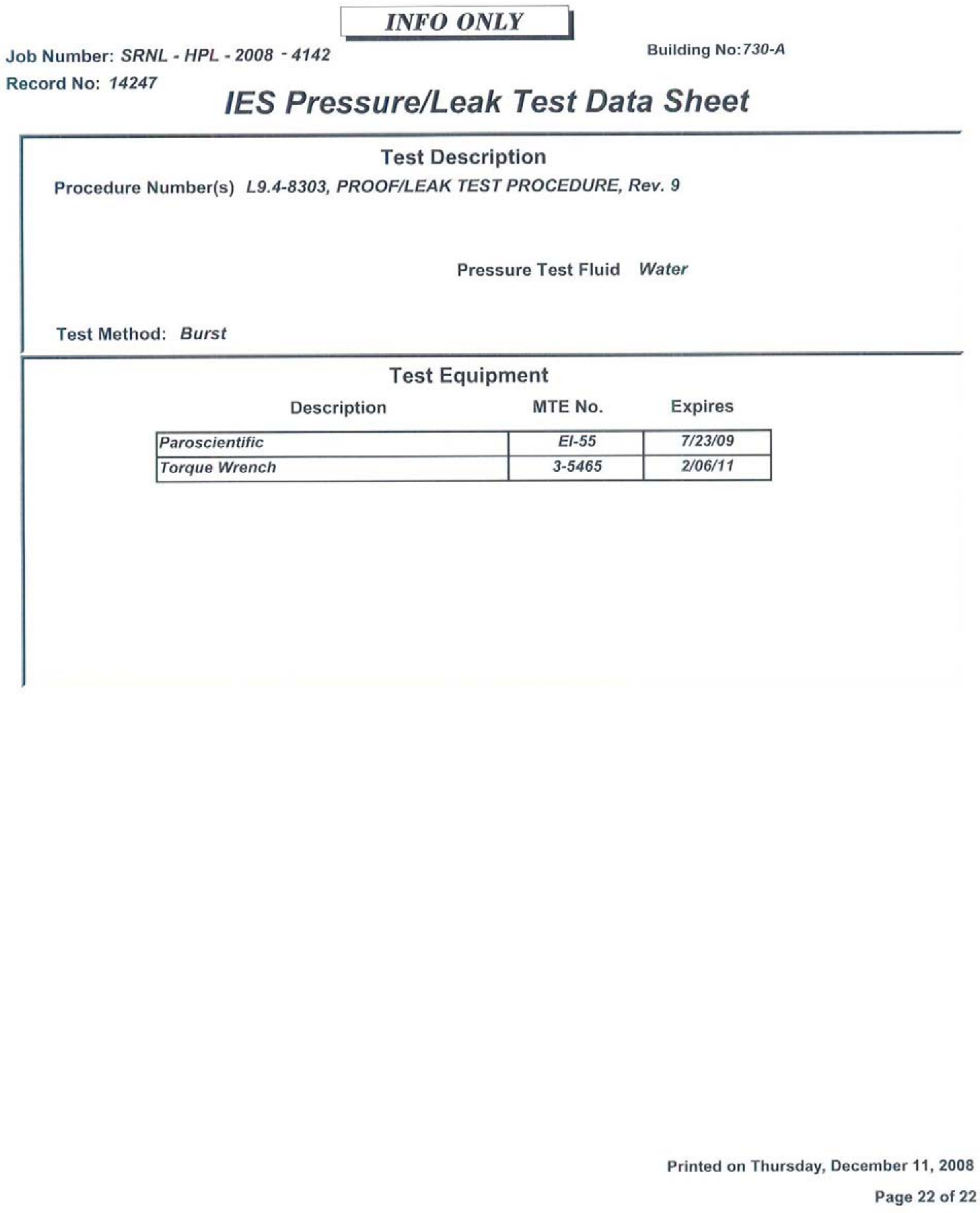
	Pressures, psig:
	Measured
Proof:	*140*

Reviewed By: *Signed electronically by Donald J. Trapp, Level III, on 12/11/2008*

Certified L.T. *Signed electronically by Wayne D. Holiday, Level II, on 12/11/2008*

Comments

Initial Test Length: 3.63 in.
Length After Proof Pressure: Failed prior to proof pressure
Pressure @ Failure (Burst Pressure): 140 psi
Clamp Torque Value: 35 ft#
**Length measurements taken between clamp ends.*



INFO ONLY

Job Number: *SRNL - HPL - 2008 - 4142*

Building No: *730-A*

Record No: *14247*

IES Pressure/Leak Test Data Sheet

Test Description

Procedure Number(s) *L9.4-8303, PROOF/LEAK TEST PROCEDURE, Rev. 9*

Pressure Test Fluid *Water*

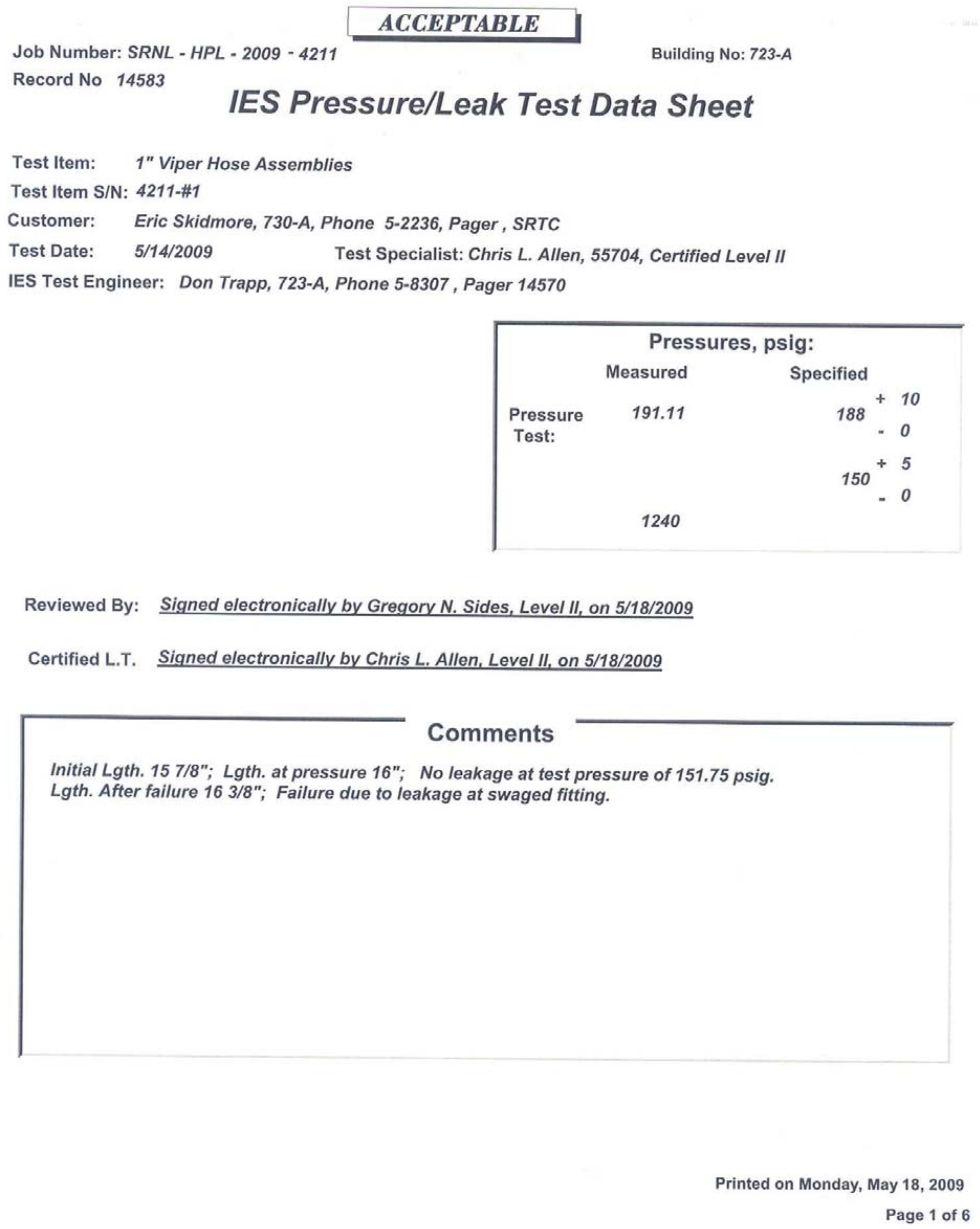
Test Method: *Burst*

Test Equipment

Description	MTE No.	Expires
Paroscientific	*EI-55*	*7/23/09*
Torque Wrench	*3-5465*	*2/06/11*

Printed on Thursday, December 11, 2008

Page 22 of 22



ACCEPTABLE

Job Number: *SRNL - HPL - 2009 - 4211* **Building No:** *723-A*

Record No *14583*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose Assemblies*

Test Item S/N: *4211-#1*

Customer: *Eric Skidmore, 730-A, Phone 5-2236, Pager , SRTC*

Test Date: *5/14/2009* **Test Specialist:** *Chris L. Allen, 55704, Certified Level II*

IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:

	Measured	Specified	
Pressure Test:	191.11	188	+ 10 - 0
		150	+ 5 - 0
	1240		

Reviewed By: Signed electronically by Gregory N. Sides, Level II, on 5/18/2009

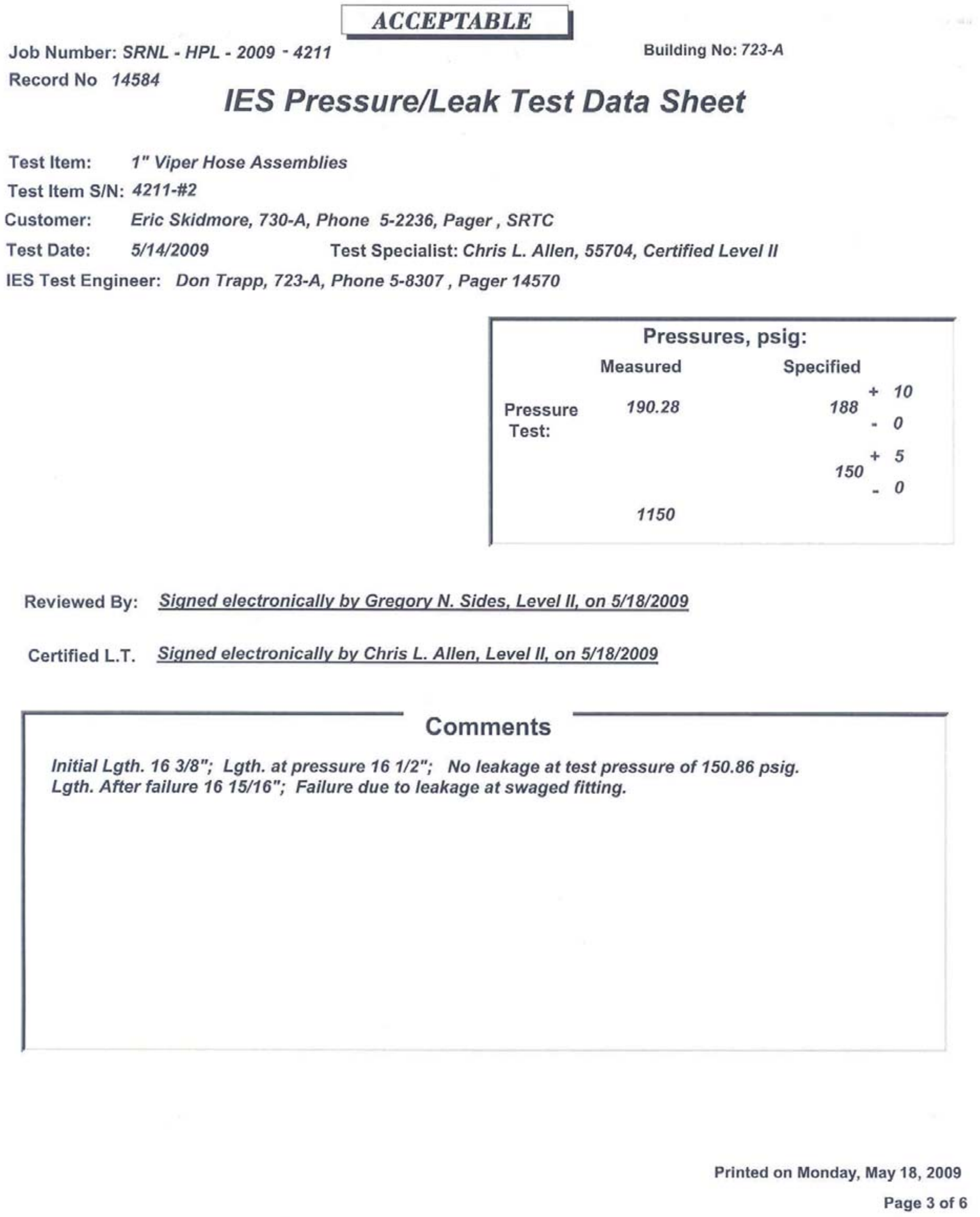
Certified L.T. Signed electronically by Chris L. Allen, Level II, on 5/18/2009

Comments

Initial Lgth. 15 7/8"; Lgth. at pressure 16"; No leakage at test pressure of 151.75 psig.
Lgth. After failure 16 3/8"; Failure due to leakage at swaged fitting.

Printed on Monday, May 18, 2009

Page 1 of 6



ACCEPTABLE

Job Number: *SRNL - HPL - 2009 - 4211*
Building No: *723-A*
Record No *14584*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose Assemblies*
Test Item S/N: *4211-#2*
Customer: *Eric Skidmore, 730-A, Phone 5-2236, Pager , SRTC*
Test Date: *5/14/2009* Test Specialist: *Chris L. Allen, 55704, Certified Level II*
IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:

	Measured	Specified	
Pressure Test:	*190.28*	*188*	*+ 10* *- 0*
		150	*+ 5* *- 0*
	1150		

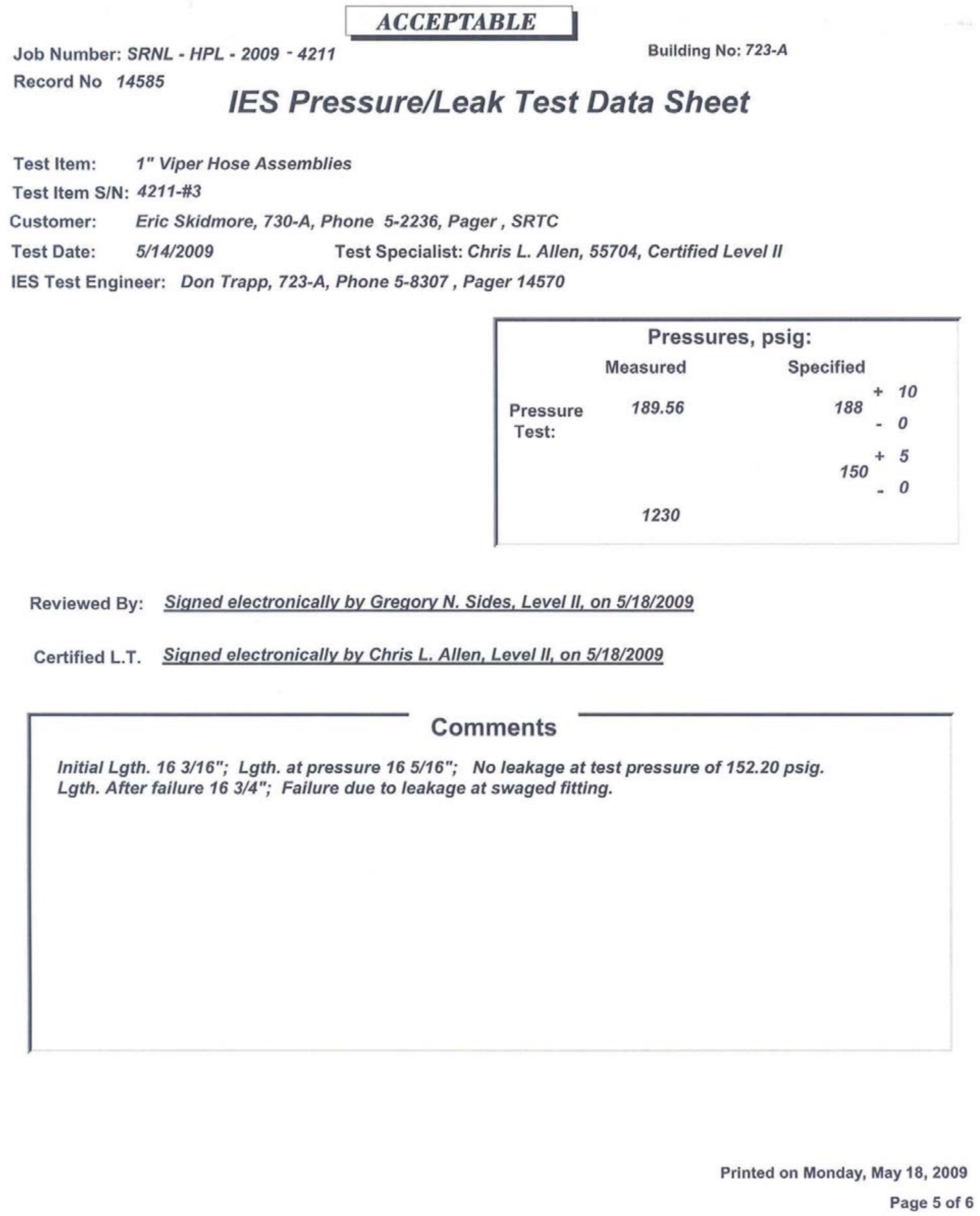
Reviewed By: *Signed electronically by Gregory N. Sides, Level II, on 5/18/2009*

Certified L.T. *Signed electronically by Chris L. Allen, Level II, on 5/18/2009*

Comments

Initial Lgth. 16 3/8"; Lgth. at pressure 16 1/2"; No leakage at test pressure of 150.86 psig.
Lgth. After failure 16 15/16"; Failure due to leakage at swaged fitting.

Printed on Monday, May 18, 2009
Page 3 of 6



ACCEPTABLE

Job Number: *SRNL - HPL - 2009 - 4211*
Building No: *723-A*
Record No *14585*

IES Pressure/Leak Test Data Sheet

Test Item: *1" Viper Hose Assemblies*
Test Item S/N: *4211-#3*
Customer: *Eric Skidmore, 730-A, Phone 5-2236, Pager , SRTC*
Test Date: *5/14/2009* **Test Specialist:** *Chris L. Allen, 55704, Certified Level II*
IES Test Engineer: *Don Trapp, 723-A, Phone 5-8307 , Pager 14570*

Pressures, psig:

	Measured	Specified	
Pressure Test:	*189.56*	*188*	+ *10* - *0*
		150	+ *5* - *0*
	1230		

Reviewed By: *Signed electronically by Gregory N. Sides, Level II, on 5/18/2009*

Certified L.T. *Signed electronically by Chris L. Allen, Level II, on 5/18/2009*

Comments

Initial Lgth. 16 3/16"; Lgth. at pressure 16 5/16"; No leakage at test pressure of 152.20 psig.
Lgth. After failure 16 3/4"; Failure due to leakage at swaged fitting.

Appendix III – Vendor Laboratory Reports

Cambridge Polymer Group, INC.
Consultation, Testing, and Instrumentation for Polymeric Materials

Tuesday, December 16, 2008

To: Eric Skidmore
Savannah River National Laboratory.

Re: Characterization of XLPE Tensile Specimens.

Project Manager:	Neal
Project Scientist:	Neal
Report Written by:	Neal
Report prepared on:	December 15, 2008
Report Reviewed by:	Spiegelberg

Samples:

CPG Sample #	Client Sample Identification
10785-1	Baseline press-cured no radiation
10785-2	50 Mrad gamma
10785-3	100 Mrad gamma
10785-4	250 Mrad gamma
10785-5	300 Mrad gamma

Equipment: TA Instruments Q1000 Differential Scanning Calorimeter, Cambridge Polymer Group SRT-3™, Bio-Rad Excalibur FTIR (FTS3000 w/UMA-500 microscope attachment), VWR Circulating Oil Bath, VWR Vacuum Oven (model 1410).

1 Summary

Test	D2675		F2214		F2381	F2102		D3895
Sample	Swell Ratio	Extract %	Swell Ratio	Crosslink Density [mol/dm^3]	TVI	SOI	BOI	OIT [minutes]
10785-1	4.4±0.4	22.9±6.7	3.97±0.38	0.13±0.02	0.009±0.004	5.20	5.31	0.18
10785-2	4.9±1.0	35.6±8.1	4.72±0.34	0.09±0.01	0.017±0.008	4.46	4.45	0.20
10785-3	4.2±0.3	27.0±2.8	5.47±0.51	0.07±0.01	0.047±0.006	4.11	4.09	0.20
10785-4	2.7±0.1	32.6±1.9	2.11±0.09	0.49±0.06	0.094±0.008	3.51	3.57	0.19
10785-5	2.5±0.1	32.0±1.2	1.56±0.08	1.39±0.37	0.110±0.007	3.25	3.26	0.18

2 Experimental

2.1 ASTM D2765-01 Sol-Gel Content

The test specimens were analyzed by a procedure similar to ASTM D2765 (Method C), which allows for measurement of the gel content (crosslinked content), and soluble content of a sample. Sections were taken from the enclosed samples and weighed on a precision balance (AND GR202, 0.01 mg resolution). Each specimen was placed in a 200ml sample jar, and fully immersed in o-xylene containing 0.1 wt.% Irganox. The jars containing the solvent and specimen were maintained at 110°C in the circulating oil bath shown in Figure 1 for 24 hours. After the required swelling period, the specimens were removed from their jars, blown with compressed air, and then placed in pre-weighed glass vials. The vials were sealed and placed in a dessicator to cool, and then re-weighed to quantify the swollen mass (polymer plus solvent). The specimens were then dried in a vacuum oven heated at 100°C for 24 hours, and re-weighed to determine the amount of remaining solids (gel fraction). Comparison of the swollen sample mass with the dried sample mass allows calculation of the swell ratio. Three specimens were tested for each sample provided.

Figure 1: Circulating oil bath used in the testing of the polymer samples.

2.1.1 Calculations

The swell ratio and sol fraction values were calculated in the manner defined by ASTM standard D2765 (Method C). In this method, the sample weight at various points in the procedure and the ratio of the solvent density to polymer density, *K*, are used to calculate the swell ratio. The swell ratio and percentage extracted (sol fraction) were calculated using Equation 1 and Equation 2 shown below.

Equation 1: $Swell\ ratio = \left[\left(W_g - W_d\right)/\left(W_o - W_e\right)\right]K + 1$

Equation 2: $Extract,\% = \left[\left(W_s - W_d\right)/W_o\right]\times 100$

Where:

W_0 = original tube sample weight (the total amount of polymer in the specimen being tested) = fW_s
f = polymer factor (the ratio of the weight of the polymer in the formulation to the total weight of the formulation)
W_s = weight of specimen being tested before sol-gel analysis
W_d = weight of dried gel after procedure - gel fraction
W_e = weight of extract (amount of polymer extracted from the specimen in the test)-sol fraction = $W_s - W_d$
W_g = weight of swollen gel after the immersion period
K = ratio of density of polymer to that of the solvent at the immersion temperature
K = 1.17 for High Density Polyethylene at 110°C and xylene.

Swell ratio has an inversely proportional relationship to crosslink density as presented in Equation 3. As the swell ratio for a sample increases the crosslink density decreases, and vice versa.

Equation 3: (Crosslink Density), $\upsilon_d = -\dfrac{\ln(1-q_s^{-1}) + q_s^{-1} + \chi_1 q_s^{-2}}{\phi_1(q_s^{-1/3} - q_s^{-1}/2)}$

2.2 *ASTM F2214-02 Swell Ratio Testing*

The initial heights of the samples were measured using a digital micrometer with a resolution of 1 µm. The samples were placed on a platform of the SRT-3™ unit, in the orientation for the measured sample height. Swelling measurements were performed using a lightweight ceramic probe.

The test solvent (o-xylene) was injected into the SRT sample chamber and data collection was initiated. The sample height was monitored until steady state conditions were achieved. All testing was performed in compliance with ASTM F2214-02. Three (3) samples were measured.

Instrument:	SRT III (Cambridge Polymer Group)
Software:	Version 4.1s
Solvent:	ortho-xylene with 0.1 wt.% Irganox (anti-oxidant)
Sample rate:	0.1 Hz
Temperature:	130°C

The swell ratio, q_s, is computed from the cubed ratio of the transient sample height H normalized by the initial height H_0.

Equation 4: $q_s = \left(\frac{V_f}{V_o}\right) = \left(\frac{H_f}{H_o}\right)^3$

Where:

V_f = final volume,
V_o = initial volume,
H_f = final height,and
H_o = initial height.

By using Flory's network theory, the crosslink density was calculated using Equation 3.

2.3 ASTM F2381-04 Trans-vinylene Yield

Quantification of the trans-vinylene unsaturations in polyethylene after exposure to radiation can be used as a determinant of the dose level used for sterilizing or crosslinking. The transvinyl index (TVI) was calculated for the provided samples following the procedure outlined in ASTM F2381-04.

2.4 ASTM F2102-01 Oxidation Index

Using a microtome with a pre-cleaned blade, ~200μm thick specimen slices were sectioned, with the orientation of the slice noted. The slices were taken from the clamp region of the tensile samples.

The samples were then placed under the microscope portion of a Bio-Rad Excalibur series FTIR (FTS3000 with a UMA-500 microscope attachment), which had been aligned and calibrated according to CPG Standard Operating Procedures. Each sample was initially placed under the microscope such that the aperture was over the first 200μm from the top surface of the sample. Subsequent scans were taken every 200μm for the first 7mm. After 7mm, readings were taken every 1000μm, to the middle of the sample. The central 500μm of the sample had readings taken at 200μm intervals.

Aperture size: 200μm
scans: 32
step size: 200μm for first 7mm, 1000μm to middle region, 200μm to bulk.
Apodization: Happ-Genzel
Purge: Nitrogen
Calibration: polystyrene

2.5 ASTM D3895-98 Oxidation Induction Time

Standard aluminum pans without lids were used to hold the samples. An indium temperature sweep performed with a standard pan was used as a calibration. Tangent at maximum slope of oxidation curve was used to calculate OIT. Testing was carried out in conformance with ASTM D3895-98: Oxidation Induction of Standard Polyolefins.

3 Results

3.1 ASTM D2765-01 Sol-Gel Content

Analysis of Variance ANOVA showed that at the 95% confidence interval, there was not a statistically significant difference in the swell ratio or % extract for samples 10785-1 through 10785-3 ($p>0.05$, at $\alpha=0.05$). Further observation showed that at the 95% confidence interval there was not a statistically significant difference in the swell ratio or % Extract for samples 10785-4 and 10785-5 ($p>0.05$, at $\alpha=0.05$). Statistical analysis also showed a significant difference in the average swell ratio between samples 10875-1 through 3 and 10785-4 through 10785-5 (p=0.837x10-6, at $\alpha=0.05$).

Table 1: Swell Ratio of tested samples.

Sample	10785-1	10785-2	10785-3	10785-4	10785-5
#1	4.3	4.2	4.1	2.7	2.6
#2	4.9	6.1	4.0	2.8	2.6
#3	4.1	4.5	4.6	2.6	2.3
Average	**4.4**	**4.9**	**4.2**	**2.7**	**2.5**
Std. Dev.	**0.4**	**1.0**	**0.3**	**0.1**	**0.1**

Table 2: %Extract of tested samples.

Sample	10785-1	10785-2	10785-3	10785-4	10785-5
#1	20.7	31.6	26.7	33.4	31.9
#2	30.5	44.9	24.4	33.9	33.2
#3	17.6	30.4	29.9	30.4	30.9
Average	**22.9**	**35.6**	**27.0**	**32.6**	**32.0**
Std. Dev.	**6.7**	**8.1**	**2.8**	**1.9**	**1.2**

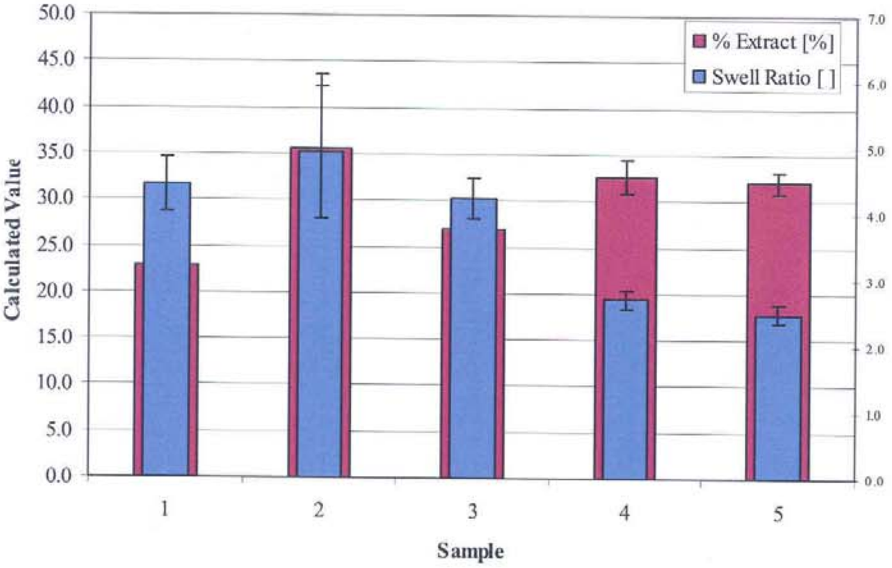


Figure 2: Average swell ratio and %Extract of the tested samples. Error bars are ± 1 standard deviation.

3.2 ASTM F2214-02 Swell Ratio Testing

The average crosslink density of the various samples varied greatly, with the high value being 1.387 ± 0.370 Mol/dm^3 for sample 10785-5 and the low value being 0.073±0.012 Mol/dm^3 for sample 10785-3. Single factor Analysis of Variance was used to compare the means of the sample groups. It was determined that at the 95% confidence, there was a statistically significant difference in the average crosslink density for the tested samples ($p=9.47\times10^{-7}$, $\alpha=0.05$). The swell ratio testing data is summarized in Table 3, Figure 3 and Figure 4.

Table 3: Average Swell Ratio and Crosslink Density of Tested Samples.

Sample	Swell Ratio	Crosslinked

	[ ]	Density, ν_d [Mol/dm^3]
10785-1	3.965±0.381	0.127±0.021
10785-2	4.721±0.338	0.093±0.012
10785-3	5.470±0.508	0.073±0.012
10785-4	2.106±0.090	0.492±0.063
10785-5	1.555±0.082	1.387±0.370

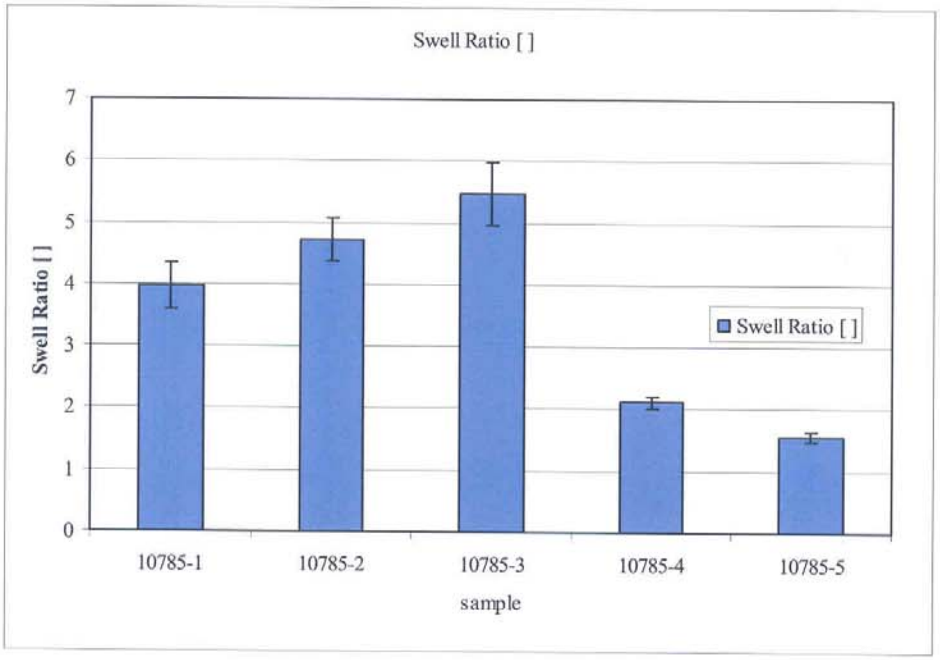


Figure 3: Average Swell Ratio of Tested Samples. Error bars are ±1 standard deviation.

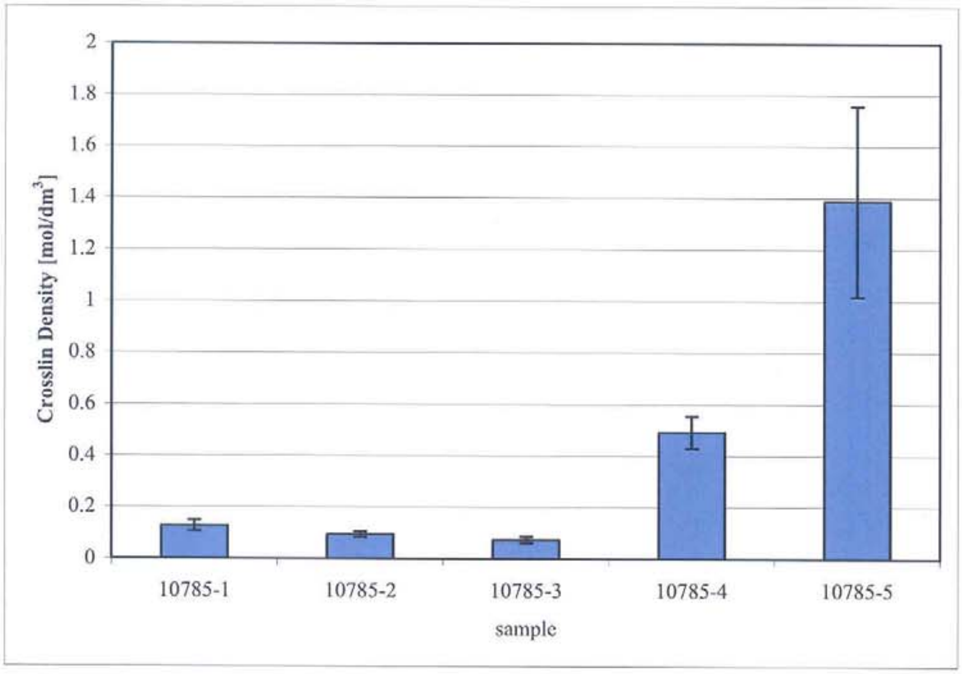


Figure 4: Average Crosslink Density of Tested Samples determined by ASTM F2214. Error bars are ±1 standard deviation.

3.3 *ASTM F2381-04 Trans-vinylene Yield*

The results from the transvinylene yield are shown in Table 4 and in Figure 5. The transvinylene index provides an indication of the uniformity of the received radiation dose through the thickness of the sample, as well as the overall magnitude of radiation dose (a higher TVI usually means a higher radiation dose). The samples tested here show a uniform radiation dose through the thickness of the sample.

Table 4: Average Transvinylene Index of Tested Samples.

Sample	TVI
10785-1	0.009±0.004
10785-2	0.017±0.008
10785-3	0.047±0.006
10785-4	0.094±0.008
10785-5	0.110±0.007

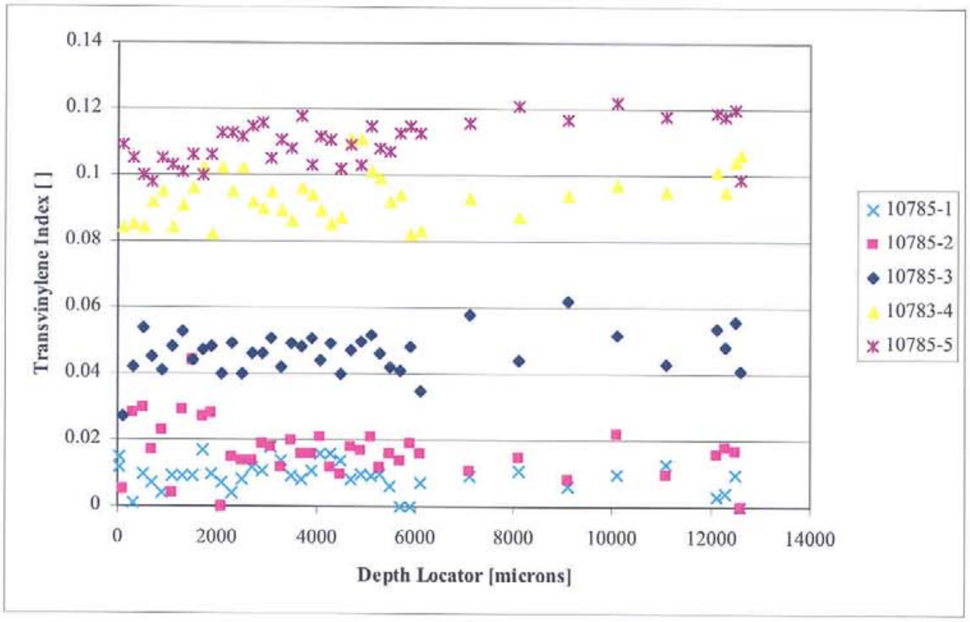


Figure 5: TVI v. sample depth for tested samples.

3.4 ASTM F2102-01 Oxidation

A summary of the Surface and Bulk Oxidation Indices is presented in Table 5 below. Both the bulk and surface oxidation indices for the tested samples were above 3.00 Typically, reduced mechanical properties become present in polyethylene samples at oxidation index values above 1.0.

Table 5: Surface and Bulk Oxidation Indices for Tested Samples.

Sample	SOI	BOI
10785-1	5.20	5.31
10785-2	4.46	4.45
10785-3	4.11	4.09
10785-4	3.51	3.57
10785-5	3.25	3.26

3.5 ASTM D3895-98 Oxidation Induction Time

The average oxidation induction time (OIT) for the tested samples was 0.19 ± 0.01 minutes, as summarized in Table 6. All of the tested samples had very similar oxidation degradation characteristics. Figure 6 shows a plot of the OIT data for sample 10785-1. The oxidation onset was very rapid as seen on the plot. There was also a large exotherm from the sample, indicative of a rapid release in energy from the sample oxidatively degrading.

Table 6: Oxidation Induction Time for the Tested Samples.

CPG Sample #	OIT [minutes]
10785-1	0.18
10785-2	0.20
10785-3	0.20
10785-4	0.19
10785-5	0.18
Average	**0.19**
Standard Deviation	**0.01**

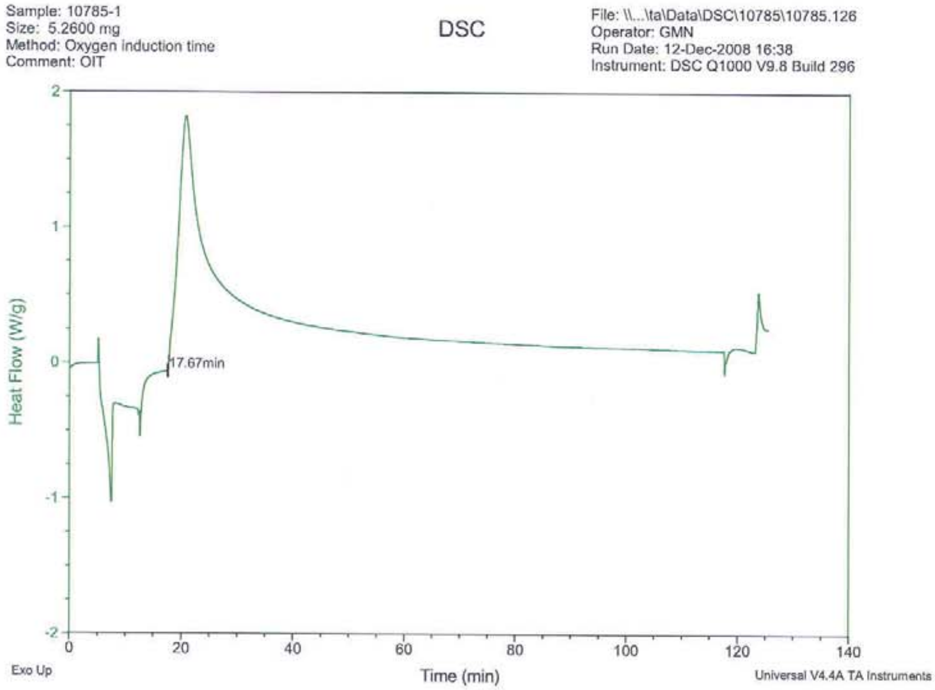
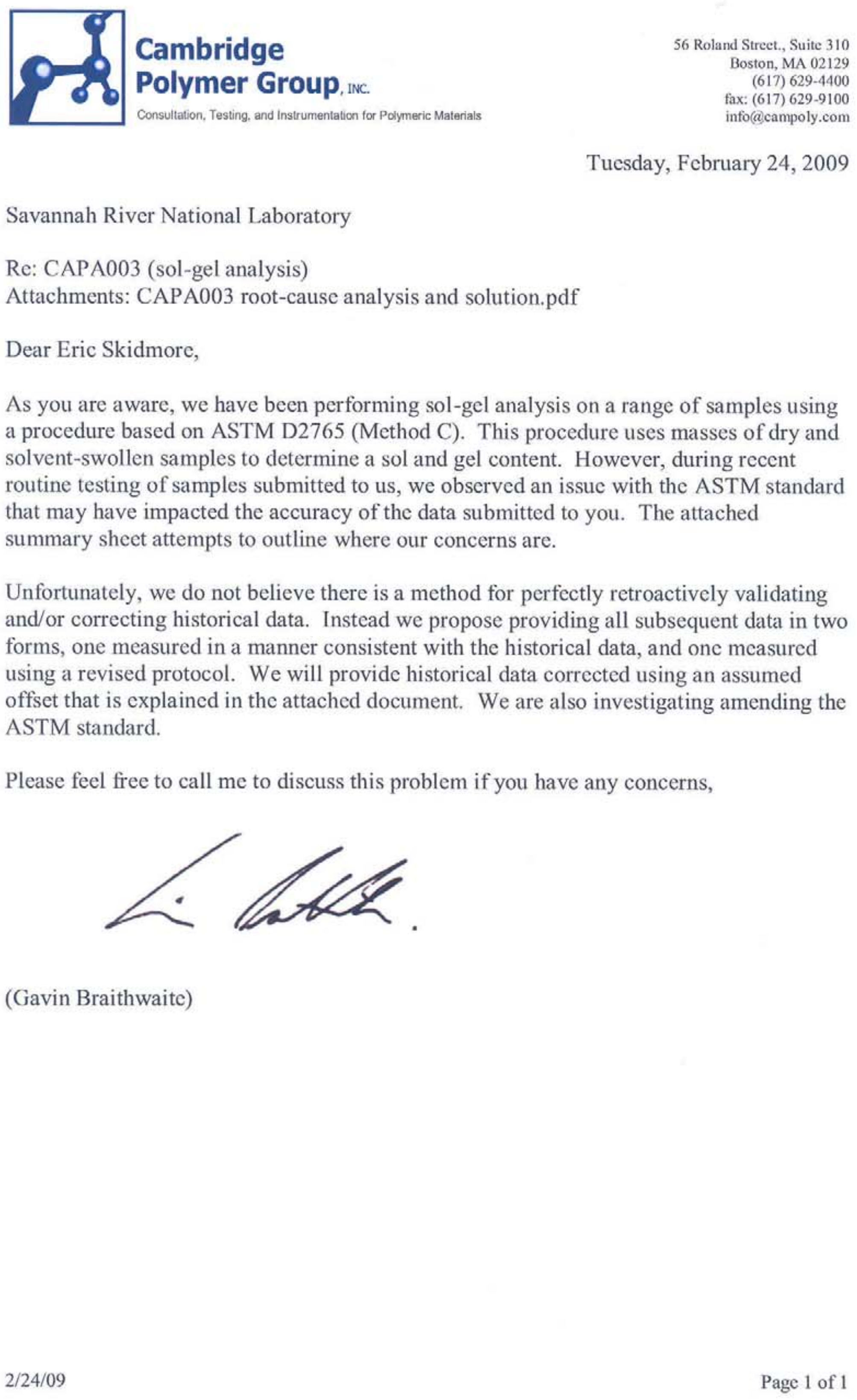


Figure 6: Plot of DSC oxidation induction time run for sample 10785-1.



Cambridge
Polymer Group, INC.
Consultation, Testing, and Instrumentation for Polymeric Materials

56 Roland Street., Suite 310
Boston, MA 02129
(617) 629-4400
fax: (617) 629-9100
info@campoly.com

Tuesday, February 24, 2009

Savannah River National Laboratory

Re: CAPA003 (sol-gel analysis)
Attachments: CAPA003 root-cause analysis and solution.pdf

Dear Eric Skidmore,

As you are aware, we have been performing sol-gel analysis on a range of samples using a procedure based on ASTM D2765 (Method C). This procedure uses masses of dry and solvent-swollen samples to determine a sol and gel content. However, during recent routine testing of samples submitted to us, we observed an issue with the ASTM standard that may have impacted the accuracy of the data submitted to you. The attached summary sheet attempts to outline where our concerns are.

Unfortunately, we do not believe there is a method for perfectly retroactively validating and/or correcting historical data. Instead we propose providing all subsequent data in two forms, one measured in a manner consistent with the historical data, and one measured using a revised protocol. We will provide historical data corrected using an assumed offset that is explained in the attached document. We are also investigating amending the ASTM standard.

Please feel free to call me to discuss this problem if you have any concerns,

(Gavin Braithwaite)

Cambridge Polymer Group, INC.
Consultation, Testing, and Instrumentation for Polymeric Materials

MEMO

56 Roland Street
Boston, MA 02129
(617) 629-4400
fax: (617) 629-9100
info@campoly.com

2/10/2009
Re: anomalous mass readings during gravimetric analysis of swollen polymer films
Re: CPGCAPA003

Executive summary

The standard procedure for determining the swell ratio of a crosslinked polymer film is based on ASTM standard D2765. This standard calls for the weighing of a polymer film before and after swelling in a suitable solvent. The standard is ambiguous on the exact method to be used for weighing the samples. CPG has identified an issue arising from this ambiguity that potentially causes erroneous results. Outlined in this document are two possible sources of error for this method that may result in the perceived mass of the sample being measured as less than anticipated. Also provided is a solution to this problem. We believe that historical data generated by CPG using D2765 has been impacted by these erroneous results. We propose correcting historical data where possible, and providing both a corrected and uncorrected version of the data (for historical cross-reference) going forward. The correction allows the historical data and correct data to be mapped to within 6% of each other. We are also seeking to amend D2765 to correct this ambiguity. An example of the deviations in the data, and the correction applied is shown in Figure 1. The data is corrected by the subtraction of 28 mg from the apparent sample mass using the original calculation.

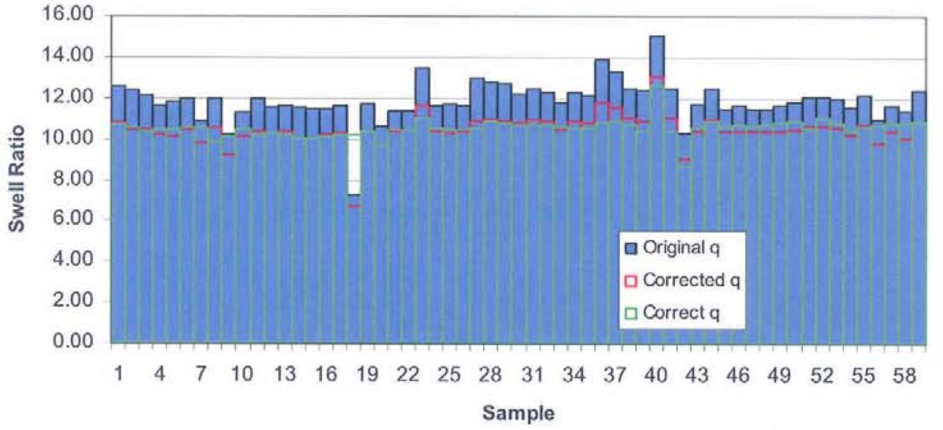


Figure 1: Example of original, correct and corrected data. Original data is that calculated using the original procedures. Correct data is data calculated using the revised procedure. Corrected data is the swell ratio corrected by assuming a fixed offset to the mass measured, as outlined below.

The impact of this weight error on the reported swell ratio for a specific sample set depends primarily on the size of the sample, and the true final swell ratio. Corrected data will be provided in amended reports. However, the final dry sample mass analyzed is normally of the order of 0.1-0.3 g. Therefore a discrepancy of 28 mg results in a maximum error in the dry sample mass of 15%. For a true swell ratio of 10 the error in the incorrect swell ratio is approximately 15%.

Outline of issue

The samples are routinely vacuum dried in their measurement vessels at an elevated temperature to drive off solvent. They are then sealed using the provided lid and allowed to cool in a desiccator for 24 hours. This procedure was intended to ensure that solvent was fully evaporated and that no moisture could be reabsorbed from the atmosphere. However, it was observed that the mass of the jar/sample/lid combination did not appear to be consistent with the mass of the sample/jar and lid taken separately. Two possible sources of error have been determined. Experimentally, this issue can be seen by examining actual observed data in a recent experiment. If the inferred lid mass error is calculated as:

inferred lid mass error = mass(inferred lid) – mass(actual lid)
= mass(lid/sample/jar) – mass(sample/jar) – mass(actual lid)

Then this can be plotted as shown in Figure 2.

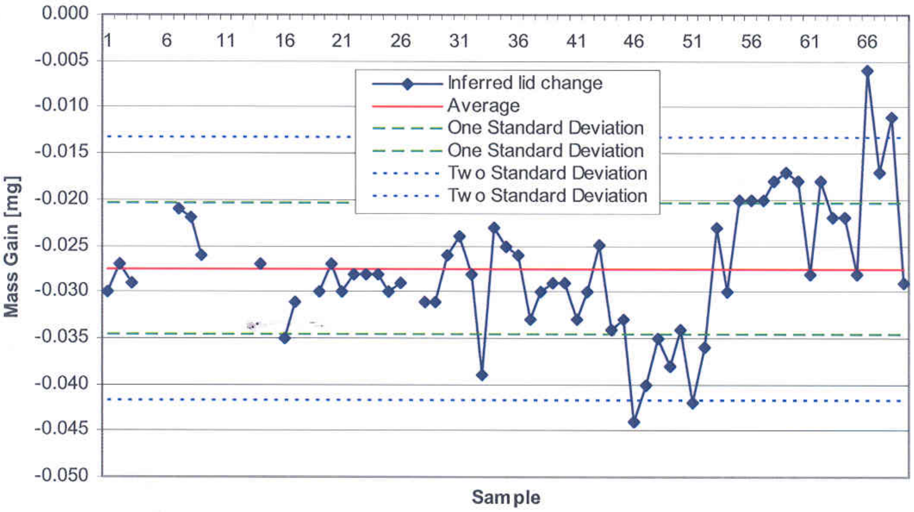


Figure 2: Inferred mass change of lid (gain is positive) for actual experimental set, (69 samples). Note that these data are <u>not</u> from the same sample type.

Lid mass change

During root-cause-analysis, it became apparent that the lids may change mass during this baking procedure. From weighing the lid before and after the vacuum oven step, lids do appear to change mass, although not consistently. This phenomenon (presumably either dehydration and rehydration, degradation, or absorption of solvent into the lid liner) should be consistent across all samples, but the data does not support this hypothesis (see).

Density change in measured material

The standard procedure seals the jar with the lid when hot and then allows the entire assembly to cool. It has been observed that the lid is often hard to remove because of a vacuum effect, implying a lower internal pressure. One can estimate the mass change due to the change in air density as the jar is heated.

Using the ideal gas equation:

$$PV = nRT \tag{1.1}$$

Where:

P = *pressure (Pa)*
V = *volume* (m^3)
R = *ideal gas constant* = 8.314472 $J \cdot mol^{-1} \cdot K^{-1}$ = 8.314472 $m^3 \cdot Pa \cdot K^{-1} \cdot mol^{-1}$
T = *temperature (K)*
n = *number of moles of gas*= m/M
M = *the molar mass*

the combined gas law says that:

$$\frac{PV}{Tm} = \frac{R}{M} = c \tag{1.2}$$

where c is constant.

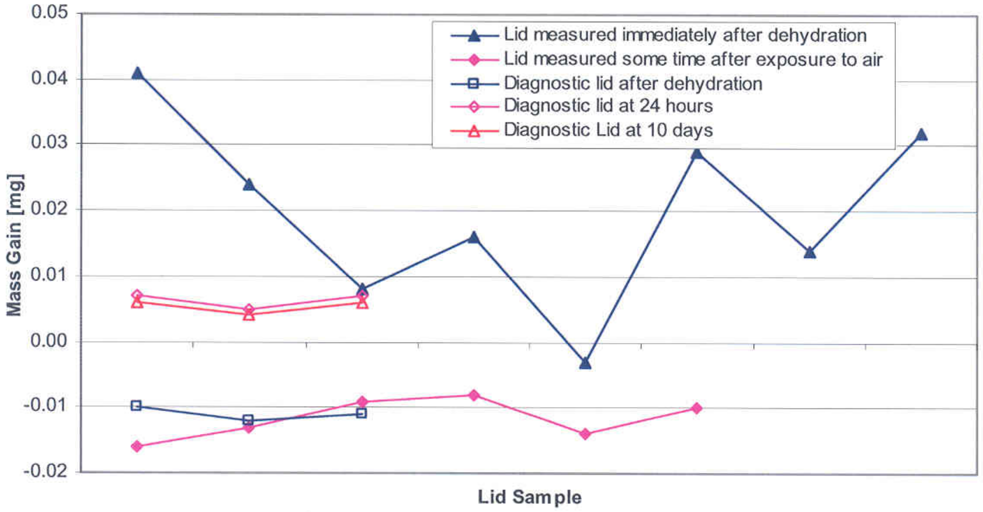


Figure 3: Mass change relative to initial "out of box" mass immediately after dehydration (blue), at approximately 24 hours (pink) and at over one week (red) for two different sets of samples (solid symbols experimental values, open symbols diagnostic test samples), with 6-8 replicates in each set.

If a jar is heated up the air expands, therefore once it is sealed, the mass of gas inside the jar is different from that at room temperature. In this case, the volume is constant and the change in mass is:

$$\Delta m = m_2 - m_1 = \frac{M}{R}\left(\frac{P_2V_2}{T_2} - \frac{P_1V_1}{T_1}\right) = \frac{MV}{R}\left(\frac{P_2}{T_2} - \frac{P_1}{T_1}\right) \tag{1.3}$$

If we assume that air is composed purely of nitrogen and that a 2 oz jar is used then:

M = 14.01 g/mol for nitrogen 75% composition and 16 g/mol oxygen 25% composition = 14.41 g/mol
V = 2 oz jar contains 71 g of water (measured) = 0.000071 m^3
R = 8.314 J·mol^{-1}·K^{-1}

Comparing a <u>heated</u> jar against a control jar at room temperature, the pressures are constant (1 atm or 10^5 Pa), therefore there is a difference in mass between the jars:

$$\begin{aligned}\Delta m &= \frac{MVP}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ &= 12.31\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\end{aligned} \tag{1.4}$$

Note that the mass on cooling does not change since the "hot" jar is a closed system and is being compared to the "cold" jar directly.

T_1 = room temperature = 20 C = 295 K
T_2 = 100 C = 373 K

Therefore:

$$\Delta m = 12.31\left(\frac{1}{373} - \frac{1}{293}\right) = -9.0mg \tag{1.5}$$

Although this value is low compared to what we measure, it supports the idea of a mass <u>loss</u> due to a systematic measurement error resulting from a poorly defined protocol.

Solution

The solution to this issue is to ensure that all readings, where possible, are taken without the presence of the lid, under ambient conditions. This is not possible for one measurement, of the wet sample where safety concerns require a sealed vessel. However, this measurement can be taken immediately after weighing the cap directly, and before any heating steps. We therefore do not feel this measurement is likely to be impacted. Going forward, results will be reported in two manners:

1. The results will be reported with all mass readings determined to remove the impact of heating on the jar/lid combination. These readings will be termed the "correct" readings
2. The results will be provided calculated using the old method. These results will be termed "historical" and will be provided to allow cross-referencing with previous reports.

Correction

Clearly the calculated deviation assuming gas density changes does not fully explain the deviations from the data. Therefore there is no quantitative method for correcting these data if the measurements included lid masses explicitly. For data that cannot be corrected directly, an alternative method will be required. Figure 2 clearly demonstrates that if enough samples are measured, there is an implicit mass change in the lid that could be used to correct all measurements where the lid/sample/jar was measured in combination. For the data in Figure 2, this error is a loss of 28 mg with a standard deviation of 7 mg. Therefore by adding this value to the correct measurements, an estimate for the historical data can be obtained. This process is demonstrated in Figure 4. It can be seen that the correction method proposed here, brings the uncorrected data to within 6% of the true value in all cases.

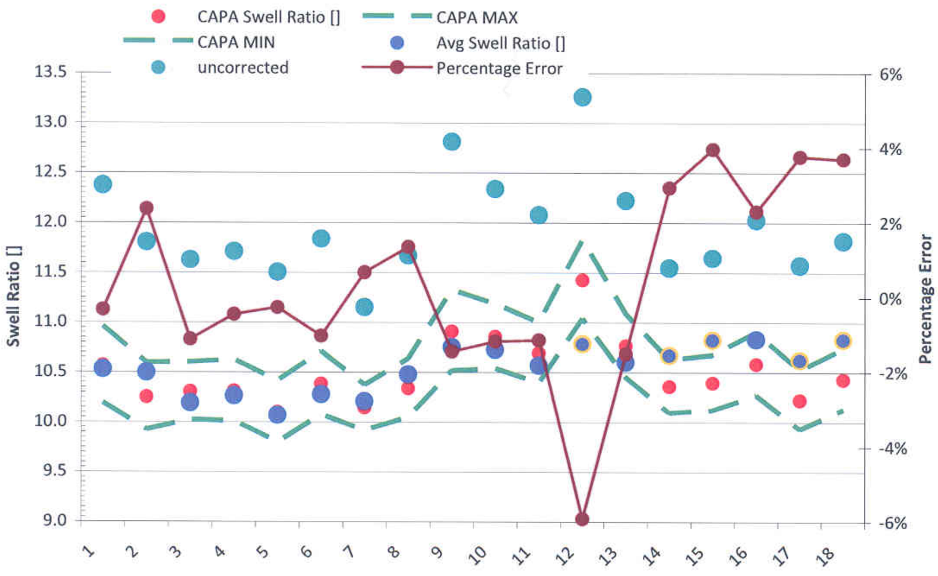


Figure 4: Example of corrected data for swell ratio. Light blue dots represent the swell ratio as calculated using the lid/sample/jar measurement. Red dots represent the swell ratio calculated using the jar/sample measurement without the lid. Green dotted lines represent the corrected value with plus/minus one standard deviation included in the calculation. Blue/grey dots are the corrected values. Brown line is the percentage error between the correct value (red dots) and the corrected value (blue/grey dots).

Background

Thus the historically reported swell ratio, gel content, crosslink density (if applicable) and molecular weight between crosslinks (if applicable) can be corrected as shown below. The results of this correction for one particular set of data are shown in Figure 1. The fundamental equations utilized in this analysis are outlined below, per ASTM D2765:

$$\text{Swell Ratio, } q_s = \frac{W_s - W_d}{W_o - W_e}K + 1 = \frac{W_s - W_d}{W_d}K + 1 \qquad (1.6)$$

$$\text{Sol-fraction (\%), } S = \frac{W_s - W_d}{W_o} \times 100 = \frac{W_s - W_d}{W_s} \times 100 \qquad (1.7)$$

$$\text{Gel-fraction (\%), } G = 100 - \frac{W_s - W_d}{W_o} \times 100 = 100 - \frac{W_s - W_d}{W_s} \times 100 \qquad (1.8)$$

Where:

W_0 = original tube sample weight (the total amount of polymer in the specimen being tested) $= fW_s$

f = polymer factor (the ratio of the weight of the polymer in the formulation to the total weight of the for

W_s = weight of specimen being tested before sol-gel analysis

W_d = weight of dried gel after procedure - gel fraction

W_e = weight of extract (amount of polymer extracted from the specimen in the test)-sol fraction $= W_s -$

W_g = weight of swollen gel after the immersion period

K = ratio of density of polymer to that of the solvent at the immersion temperature

This ratio is approximately 1.07 for low-density polyethylene at 80 °C and 1.17 for high density polyethylene at 130 °C. It is 0.643 for Ethyl Vinyl Acetate[1] at 110 °C[2]

With the swell ratio known, the crosslink density (1.9) and molecular weight between crosslinks (1.10) can also be calculated for the tested samples. Note that these parameters are not reported for any materials other than Xylene/UHMWPE combinations.

$$\text{Cross-link density, } \upsilon_d = -\frac{\ln(1 - q_s^{-1}) + q_s^{-1} + \chi_1 q_s^{-2}}{\phi_1(q_s^{-1/3} - q_s^{-1}/2)} \qquad (1.9)$$

$$\text{Molecular weight between crosslinks, } M_c = (\bar{\upsilon}\upsilon_d)^{-1} \qquad (1.10)$$

Where:

q_s = swell ratio

χ_1 = heat of mixing (Flory interaction parameter) $= 0.33 + 0.55/q_s$

ϕ_1 = molar volume of solvent $= 136\ cm^3 mol^{-1}$ for xylene

$\bar{\upsilon}$ = specific volume of the polymer $= 920\ gcm^{-3}$

All chemical parameters were obtained from ASTM standard F2214-02 and ASTM standard D2765.

---

[1] Calculated from density of trichlorobenzene given in MSDS and average of EVA grades from matweb.com.

[2] This data is specific to EVA in TCB at 110 °C. However, a fourth specimen was run for sample 10794-4.

Correction

The equations outlined above can be used to correct the invalid sample parameters relatively easily. However, this correction assumes that the average mass deviation recorded in the data presented in Figure 2 is consistent across all experiments. If the subscript "c" is used to represent the "correct" values of *q*, W_d and *G*, and $W_{dc}=W_d-e$, where *e* is the correction applied to the mass, then the following relationships can be determined:

$$\begin{aligned} q_s &= \frac{W_s - W_d}{W_o - W_e}K + 1; q_{sc} = \frac{W_s - W_{dc}}{W_o - W_e}K + 1 \\ q_{sc} &= \frac{q_s W_d + e(K-1)}{W_d - e} \end{aligned} \qquad (1.11)$$

$$\begin{aligned} G &= 100 - \frac{W_s - W_d}{W_s} \times 100; G_c = 100 - \frac{W_s - W_{dc}}{W_s} \times 100 \\ G_c &= G\left(\frac{W_d - e}{W_d}\right) \end{aligned} \qquad (1.12)$$

These formulae can then be used to correct the crosslink density and molecular weight between crosslinks, if required. Example corrected data for swell ratio are shown in Figure 1 and the equivalent gel-fraction data is shown in Figure 5. In two separate experiments on similar materials, the apparent mass loss in the lid was 23 mg ± 2 mg (12 samples) and 28 mg ± 7 mg (59 samples), where the uncertainty represents one standard deviation. According to the Student t-Test these values are statistically indistinguishable. We have chosen to use 28 mg as the correction, *e* as representing the largest number of samples.

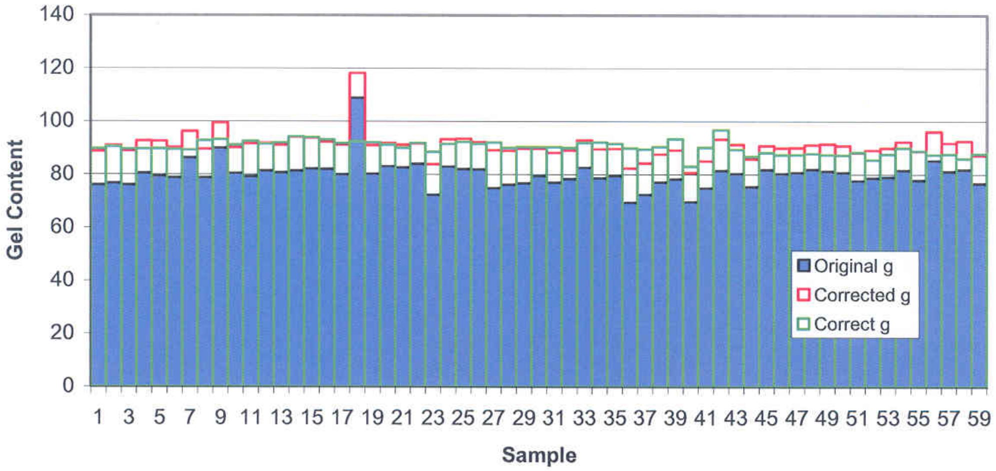


Figure 5: Example of original, correct and corrected data. "Original g" is that calculated using the original procedures. "Correct g" is data calculated using the revised procedure. "Corrected g" is the old gel-content corrected by assuming a fixed offset to the mass measured, as outlined above.

Cambridge Polymer Group, INC.
Consultation, Testing, and Instrumentation for Polymeric Materials

MEMO
56 Roland Street
Boston, MA 02129
(617) 629-4400
fax: (617) 629-9100
info@campoly.com

2/10/2009
Re: correction of gravimetric data
Re: CPGCAPA003
Project: 10785

See attached documents "CAPA003 cover letter.pdf" and "CAPA003 root-cause analysis and solution.pdf" for explanation.

Provided here are the corrected data for project number 10785. If specific analysis is required please contact us and we will be happy to analyze the data in manner that you require. Figure 1 presents the swell ratio data before and after correction. Figure 2 presents the gel-content data before and after correction. Figure 3 presents the percent extract data before and after correction. Table 1 presents all of the corrected values. In the following graphs "Original" refers to the previously reported data, "corrected" refers to the revised data corrected using the procedures outlined elsewhere and "correct" is data calculated avoiding the issues outlined in the accompanying document. Not all data has the "correct" value available.

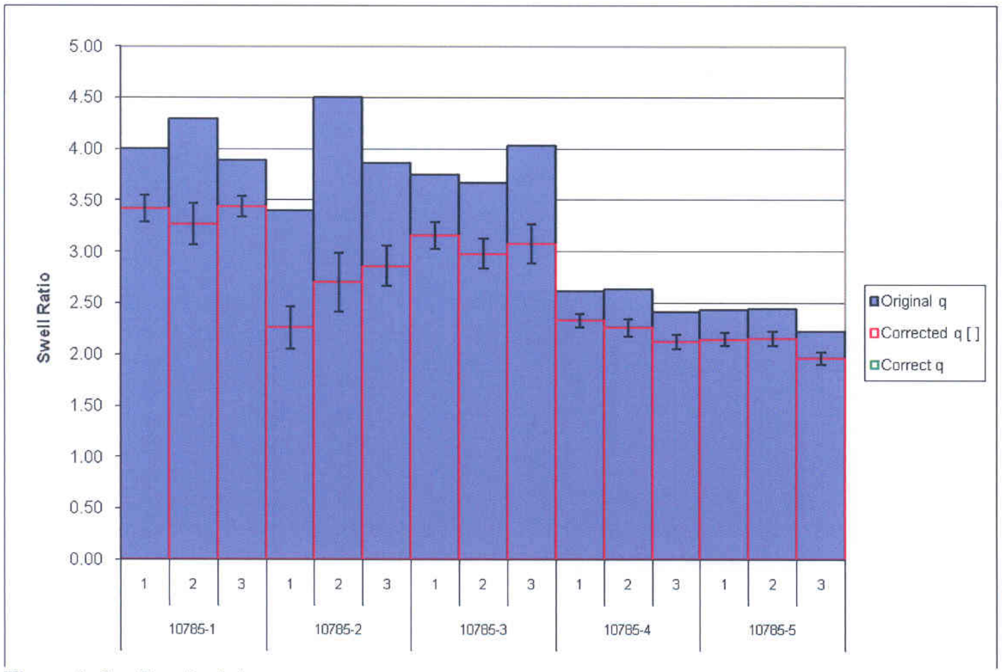


Figure 1: Swell ratio data

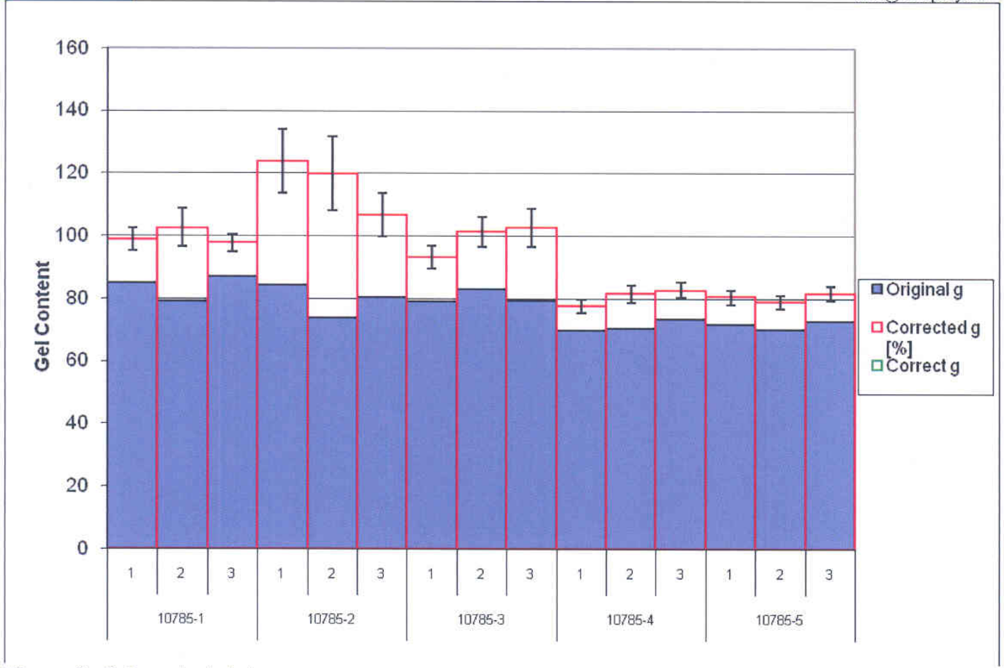


Figure 2: Gel content data

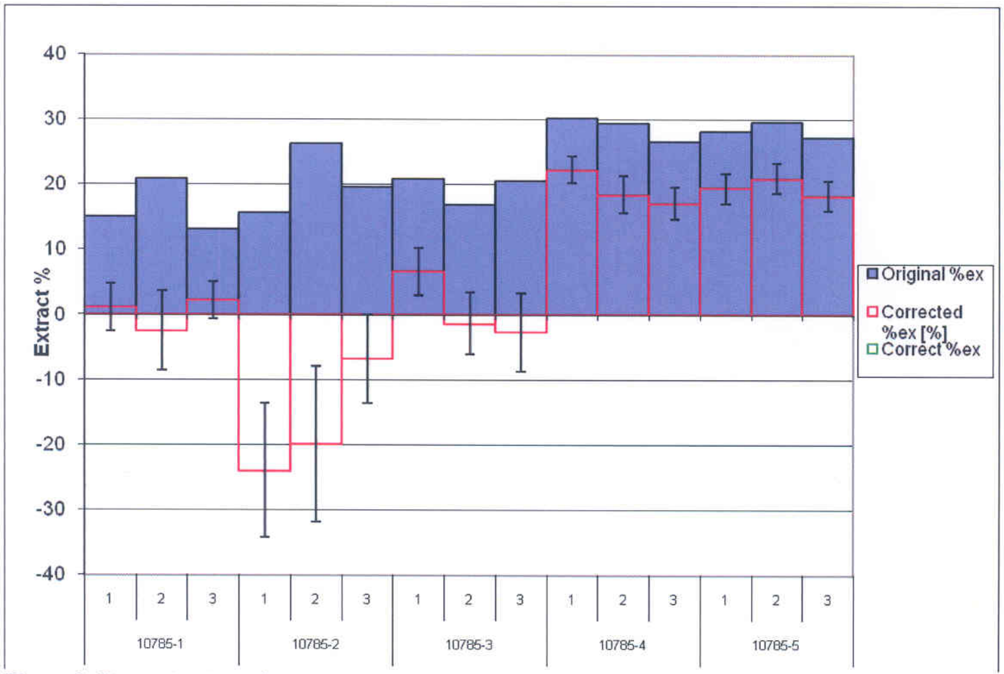
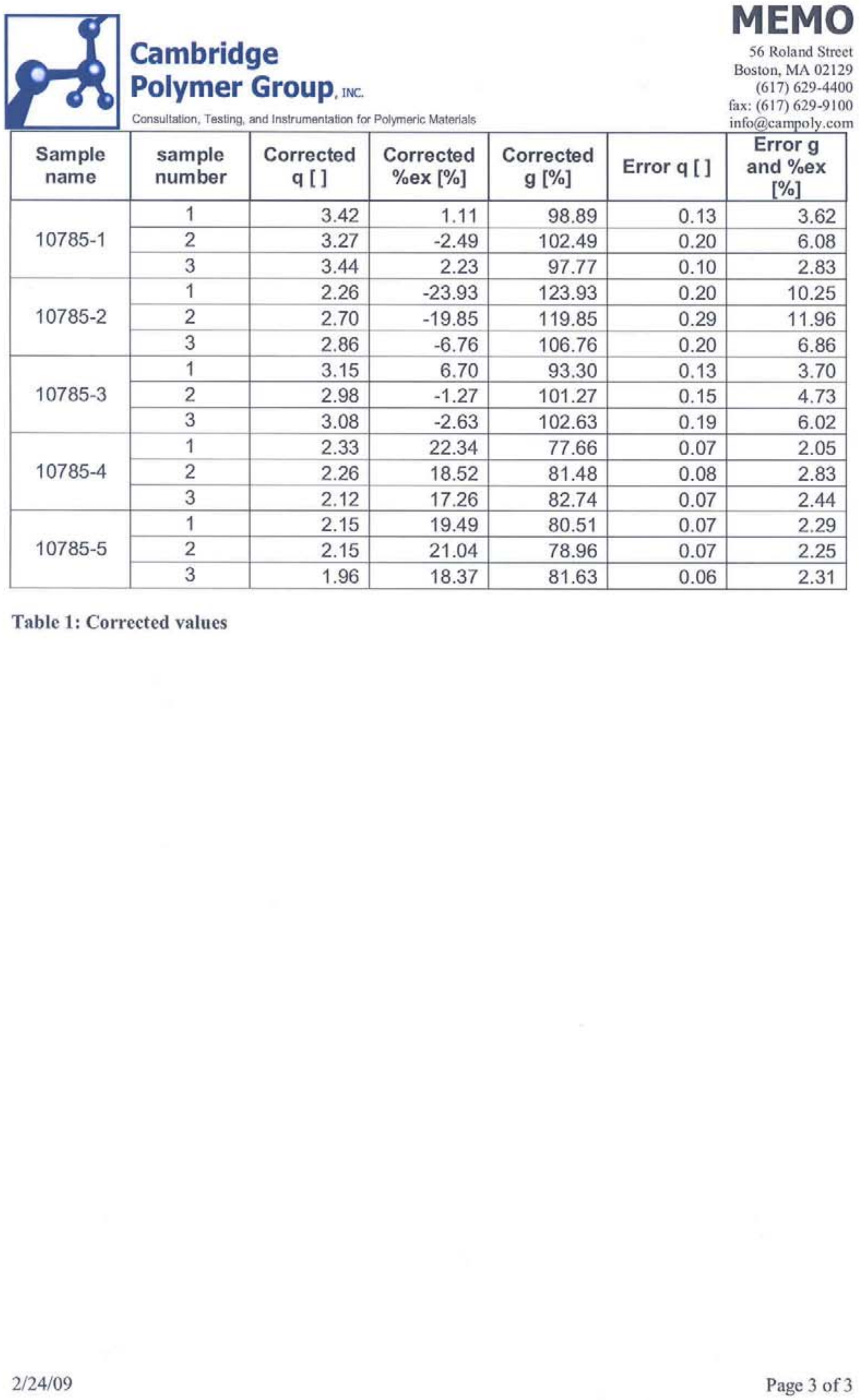


Figure 3: Percent extract data



Cambridge
Polymer Group, INC.
Consultation, Testing, and Instrumentation for Polymeric Materials

MEMO
56 Roland Street
Boston, MA 02129
(617) 629-4400
fax: (617) 629-9100
info@campoly.com

Sample name	sample number	Corrected q [ ]	Corrected %ex [%]	Corrected g [%]	Error q [ ]	Error g and %ex [%]
10785-1	1	3.42	1.11	98.89	0.13	3.62
	2	3.27	-2.49	102.49	0.20	6.08
	3	3.44	2.23	97.77	0.10	2.83
10785-2	1	2.26	-23.93	123.93	0.20	10.25
	2	2.70	-19.85	119.85	0.29	11.96
	3	2.86	-6.76	106.76	0.20	6.86
10785-3	1	3.15	6.70	93.30	0.13	3.70
	2	2.98	-1.27	101.27	0.15	4.73
	3	3.08	-2.63	102.63	0.19	6.02
10785-4	1	2.33	22.34	77.66	0.07	2.05
	2	2.26	18.52	81.48	0.08	2.83
	3	2.12	17.26	82.74	0.07	2.44
10785-5	1	2.15	19.49	80.51	0.07	2.29
	2	2.15	21.04	78.96	0.07	2.25
	3	1.96	18.37	81.63	0.06	2.31

Table 1: Corrected values

Distribution:

N.C. Iyer, 773-41A
R.L. Bickford, 730-A
G.T. Chandler, 773-A
K.E. Ziegler, 773-41A
W.L. Daugherty, 730-A
B.J. Wiersma, 773-A
W.L. Isom, 704-26F
M. Hubbard, 241-162H
A.S. Liutkus, 241-162H
D.J. Clark, 241-162H
A.J. Tisler, 704-26F
E.J. Freed, 704-56H
D.C. Bumgardner, 704-56H
A.W. Wiggins, 704-26H
T.E. Britt, 704-60H
S.T. French, 730-1B
Document Control, 703-43A