Contract No. and Disclaimer:

Investigation of Radiation and Chemical Resistance of Flexible HLW Transfer Hose - 10393

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ABSTRACT

A chemical transfer hose constructed of an EPDM (ethylene-propylene diene monomer) outer covering with a modified cross-linked polyethylene (XLPE) lining was evaluated for use in high level radioactive waste transfer applications. Laboratory analysis involved characterization of the hose liner after irradiation to doses of 50 to 300 Mrad and subsequent exposure to 25% NaOH solution at 93 °C for 30 days, simulating 6 months intermittent service. The XLPE liner mechanical and structural properties were characterized at varying dose levels. Burst testing of irradiated hose assemblies was also performed. Literature review and test results suggest that radiation effects below doses of 100 kGy are minimal, with acceptable property changes to 500 kGy. Higher doses may be feasible. At a bounding dose of 2.5 MGy, the burst pressure is reduced to the working pressure (1.38 MPa) at room temperature. Radiation exposure slightly reduces liner tensile strength, with more significant decrease in liner elongation. Subsequent exposure to caustic solutions at elevated temperature slightly increases elongation, suggesting an immersion/hydrolytic effect or possible thermal annealing of radiation damage. This paper summarizes the laboratory results and recommendations for field deployment.

INTRODUCTION

The Savannah River Site (SRS) has stored high-level radioactive waste in carbon steel underground waste tanks for many years. A major effort is underway to expedite tank closure and reduce environmental impact. During tank closure operations, the ability to make emergency or short-term transfers is needed. Transfer piping and jumper assemblies are normally made of Type 304L stainless steel that is corrosion-evaluated per ASTM A262. However, the time and cost for fabrication and installation of corrosion-evaluated stainless steel piping can be prohibitive, particularly for a short-term transfer or unusual configurations. The use of robust chemical transfer hose for such tasks was proposed and a candidate product was identified. Such transfers would only occur within underground diversion boxes for secondary containment. However, process compatibility and materials performance issues needed to be addressed.

MATERIALS AND SERVICE CONDITIONS

The candidate hose is constructed of a modified crosslinked polyethylene (XLPE) liner, reinforced with a spiral-plied synthetic fabric with double wire helix, and an abrasion-resistant cover made of ethylene-propylene diene monomer (EPDM). The same hose has been successfully used as the core hose in a low-level, aboveground radioactive waste hose-in-hose transfer system in the same facility. The hose is rated from -40 °C to 121 °C at a working pressure of 1.38 MPa and can be cleaned using open-end steam up to 0.35 MPa or in a bath containing 10% NaOH solution up to 100 °C. Operating temperature limits vary with the specific chemical media. The specific hose formulation is proprietary. A sample of the hose liner material was analyzed by Fourier Transform Infrared (FT-IR) spectroscopy. The liner was confirmed to primarily consist of low-density polyethylene (LDPE), with possible blending of ethylene-propylene diene monomer (EPDM). The outer covering was confirmed to be EPDM. Aluminum silicate, polypropylene and iron were also detected by X-ray diffraction. The use of precipitated silica or aluminosilicates as a filler in polyethylene and other plastics is common [1].

Service Conditions

The chemistry of high-level radioactive waste solutions is very complex, with nearly all known elements present in some amount. The chemistry is generally dominated by sodium hydroxide, sodium nitrate and sodium aluminate with a pH of 13 or greater. A bounding free hydroxide concentration was estimated at 25% for test purposes. High pH from sodium hydroxide was expected to dominate the chemical resistance of the hose, in absence of significant organics. The waste solution exhibits a viscosity of approximately 10 centipoise (cP) and a specific gravity of ~1.3. The maximum operating pressure anticipated is 1.04 MPa and the maximum operating temperature is 93 °C. Lower temperatures are likely in service. For safety reasons and inability to inspect the hose after installation, the operating life of the hose was limited to six months. A bounding continuous dose rate of ~580 Gy/hr corresponds to a cumulative dose of ~2.5 MGy.

EXPERIMENTAL

Compatibility testing consisted of two parts: 1) chemical/thermal/radiation effects on the hose liner and 2) burst testing of irradiated hoses. Baseline mechanical tests were performed on full-size 3” ID hose but are not reported here. The wire/fiber reinforcement dictates mechanical robustness and bend radius. Test samples of the modified XLPE liner were obtained from the hose manufacturer. The samples were cured on the same mandrel used to cure actual hoses, but with a thin Teflon sheet behind the liner for mold release. The as-cured liner tube was then die-cut into tensile specimens per ASTM D638 [2]. The samples were irradiated to doses of 0.5, 1.0, 2.5 and 3.0 MGy at a dose rate of ~4 kGy/hr.

A few samples were also irradiated at a slightly lower rate (1.7 kGy/hr) to evaluate the potential for dose rate effects. Dose rate effects are well-known to occur in polymers and can be significant, though such effects are of less concern for short operating periods. Some samples were irradiated only, with others subsequently immersed in 25% NaOH solution at 93 °C for 30 days. Short sections of 25.4 mm nominal ID chemical transfer hose were also irradiated to doses of 1.0, 2.5 and 3.0 MGy for burst testing, respectively.

RESULTS

Mechanical Testing

Tensile tests of the liner material were performed per ASTM D638 for sample type IV, using a crosshead speed of 50 +/- 10% mm/min. The values for tensile strength and elongation at failure are given in Table 1 and represent the average of three samples for each condition. The variation within each sample condition was minimal.

Table 1. Tensile properties for the modified XLPE liner at various conditions.

Sample Description	Irradiation	Ultimate Tensile Strength (MPa)	Elongation at Failure (%)
Irradiated In Air @Room Temperature	0 MGy	14.5	190
	0.5 MGy	11.8	100
	1.0 MGy	11.3	76
	2.5 MGy	7.7	20
	3.0 MGy	6.9	14
Irradiated In Air @Room Temperature + 30day immersion in NaOH @ 93 °C	0.5 MGy + NaOH	12.4	251
	1.0 MGy + NaOH	8.6	90
	2.5 MGy + NaOH	7.0	32
	3.0 MGy + NaOH	6.1	33

At 0.5 MGy, the tensile strength is reduced by approximately 18%, with elongation reduced by 47%. This is comparable to a 50% elongation reduction criterion often imposed on nuclear cable insulations, or alternatively, a reduction to 50% absolute elongation. At 1.0 MGy, tensile strength is reduced by 22% and elongation is reduced by 60%, with 76% absolute retained elongation. At 1.0 MGy, the hose liner would still pass the 50% absolute elongation criterion.

However, at 2.5 MGy, the absolute elongation is reduced to 20%, well below the 50% arbitrary criterion. A dose of 2.5 MGy is higher than the dose typically used for qualification of nuclear cables and motors [3, 4]. For samples exposed to radiation and then immersed in 25% NaOH at 93 °C for 30 days, the chemical/thermal exposure slightly reduced tensile strength and increased elongation, with the exception of 0.5 MGy. The cause of higher elongation at 0.50 MGy is unknown. A possible cause is that different degradation mechanisms (crosslinking vs. chain scission) could be competing at this dose range. Chain scission of crosslinks already present from the curing process could occur at some threshold dose, with increased crosslinking at higher doses. The elongation values for samples at 2.5 and 3.0 MGy plus chemical/thermal exposure are notably similar, but higher than for samples exposed to radiation only.

These results indicate that NaOH exposure is not significantly detrimental and 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. This is a possible artifact of exposing the material sequentially rather than synergistically, which is the ideal case.

X-Ray Diffraction

X-ray diffraction (XRD) analysis was performed on the liner samples after irradiation to evaluate effects on polymer crystallinity. XRD spectra for the XLPE liner samples are shown in Figure 1. As expected, the crystallinity of the polymer liner increases with dose, though the relative increase is minor. The estimated % crystallinity values are 27% (0 Mrad), 29% (0.5 MGy), 31% (1.0 MGy), 32% (2.50 MGy) and 33% (3.0 MGy), respectively.

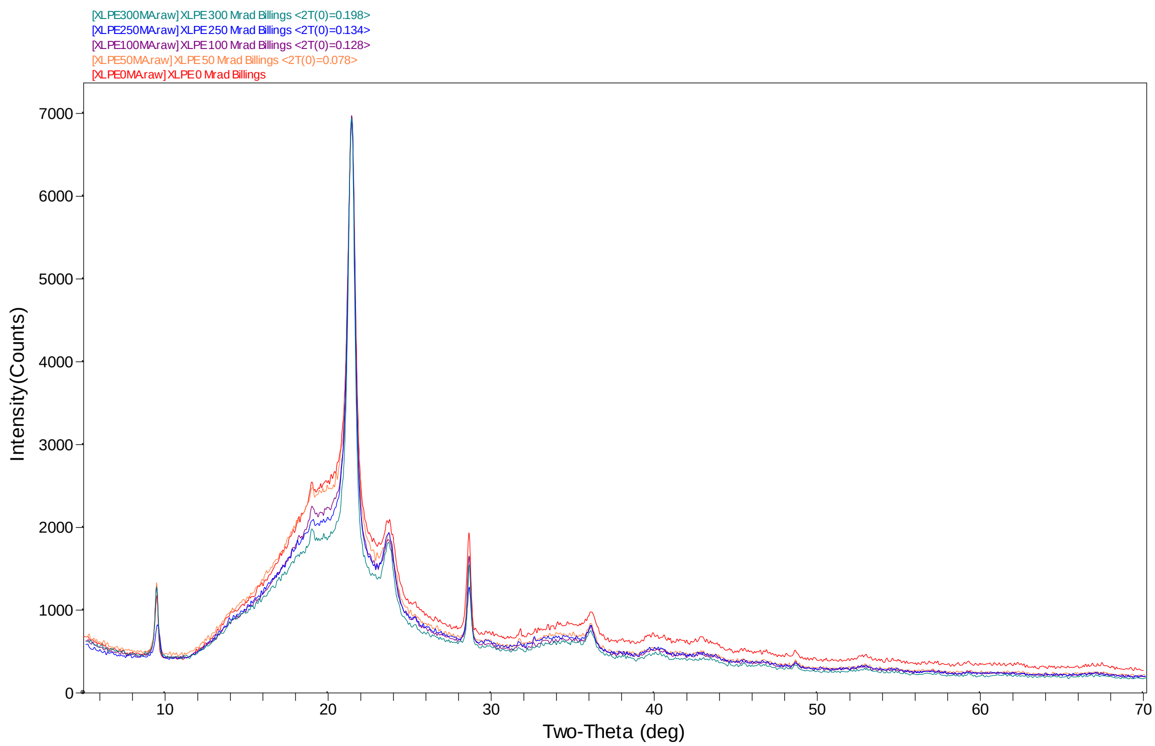

Figure 1. XRD spectra for baseline and irradiated modified XLPE hose liner.

FT-IR Spectroscopy

The liner samples were analyzed by Fourier Transform Infrared (FT-IR) spectroscopy to determine radiation effects on the polymer backbone (Figure 2). 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. 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.

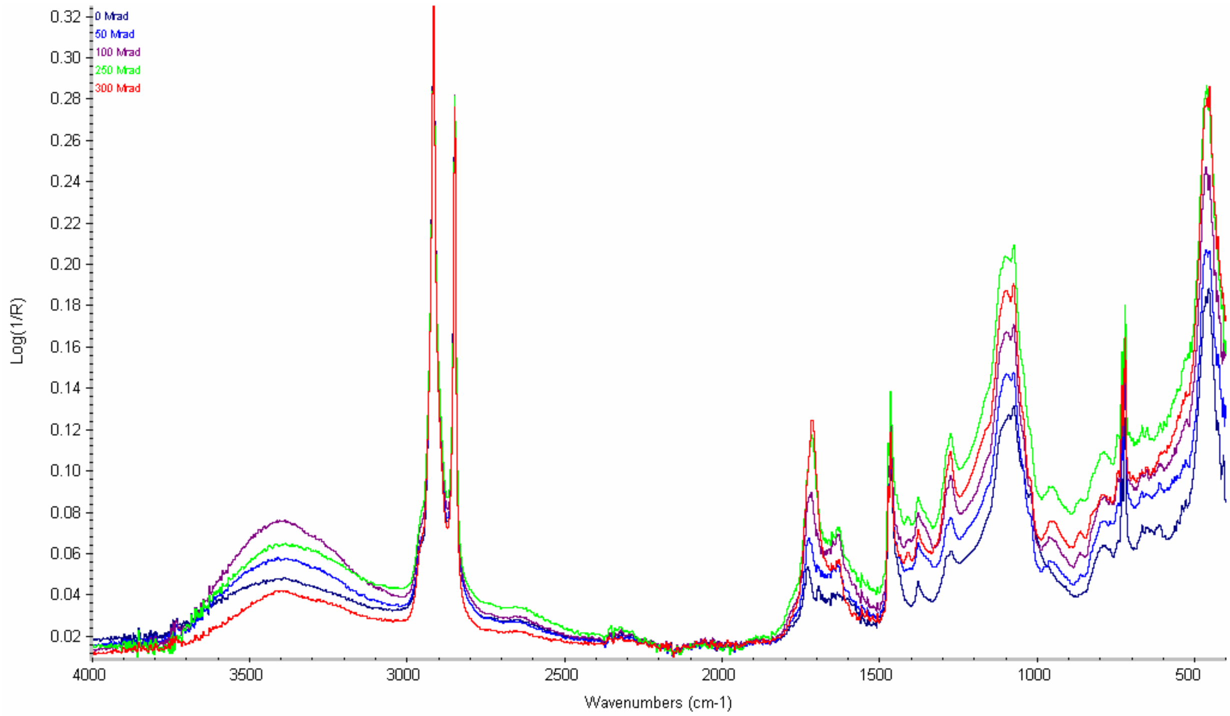

Figure 2. FT-IR spectra for baseline and irradiated XLPE liner.

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. C-Cl peaks are possibly indicated at ~700 cm^{-1}, which may be indicative of chlorinated polyethylene (CPE). This is not conclusive, as the modified proprietary XLPE liner may or may not be blended with CPE.

Raman Spectroscopy

Raman spectroscopy is often used to complement FT-IR spectroscopy for polymer/organic analysis. 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. Raman spectra of XLPE after irradiation and exposure to 25% NaOH solution are in Figure 3. The spectra are very similar, with the top curve representing baseline material and lower curves at progressively higher doses. However, the ratio of carbon-carbon stretch to hydrogenated carbon shows a minimum with applied radiation.

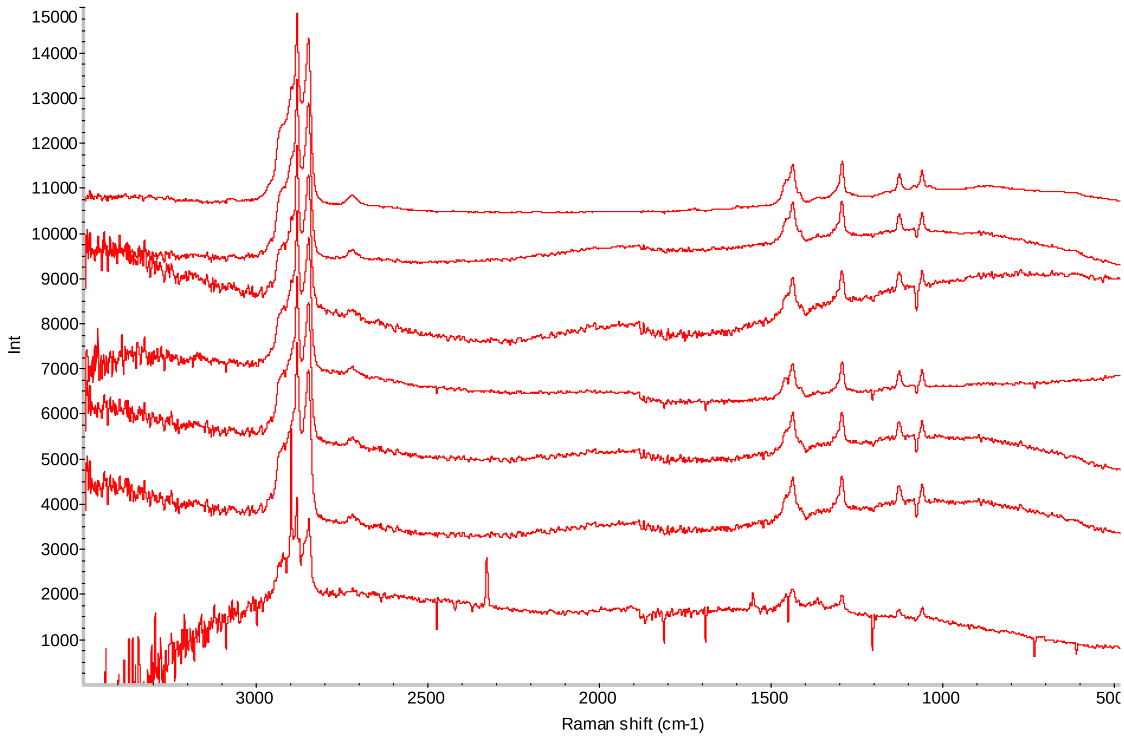

Figure 3. XLPE Raman spectra after radiation and chemical exposures.

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 to 3.0 MGy. 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 4 shows the increase in aromatic content vs. dose.

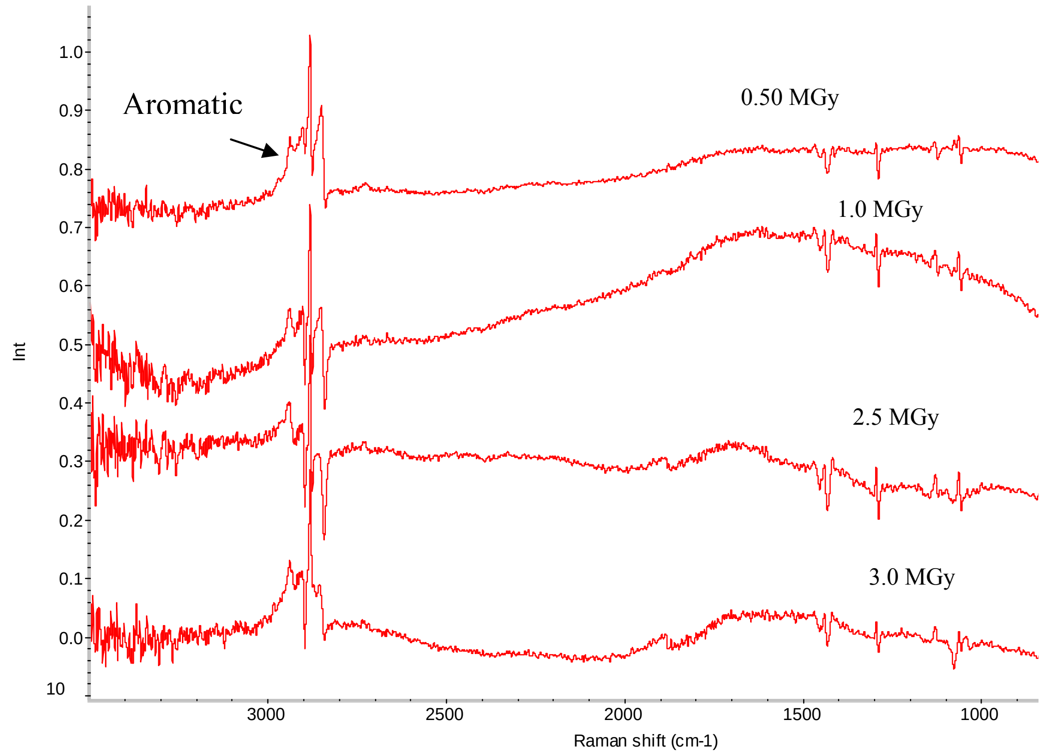

Figure 4. Increase in the polymer aromatic (carbonaceous) content vs. radiation.

Burst/Leak Testing

Per ASTM D380, a minimum length of 18 inches (45.7 cm) for burst tests [5, 6]. However, such lengths could not be irradiated to a uniform dose in the irradiation chamber. Therefore, shorter samples (23 cm) were only irradiated to doses of 1.0, 2.5 and 3.0 MGy, respectively. The 25.4 mm diameter hose has the same working pressure rating (1.38 MPa) as the actual 76.1 mm diameter hose to be used. The hose sections were burst tested using stainless steel stems (Dixon stem #RMS-11) and #156 Boss clamps (plated iron). Swaged-on fittings are typically preferred for the wire-reinforced hose. However, these are only rated to 6.9 MPa and do not allow for a complete burst.

Room temperature burst pressure values for baseline and irradiated hoses are in Figure 5. Baseline values ranged from 5.9-9.7 MPa, with an average of 8.4 MPa. The hose manufacturer quotes a theoretical burst pressure of 7.45 MPa, providing a ~5X safety factor over the working pressure rating (1.4 MPa). The theoretical calculation is based on fabric strength and number of plies, not an average test value. However, vendor burst test results from 187 samples of similar hose give an average of 9 MPa with a standard deviation of 0.63 MPa. Using a 3σ rule, the lowest acceptable burst pressure is 7.14 MPa. Burst tests performed on 76.1 mm diameter hose failed at 7.6 MPa, similar to the 7.45 MPa theoretical value.

The average burst pressure of five 1” ID baseline samples (8.38 MPa) is only slightly less than one standard deviation below the 9 MPa average value quoted above, or 8.4 MPa. The cause for the single burst value of 5.9 MPa is unknown. If this value is anomolous, the average burst pressure is increased to ~9 MPa. Additional tests are needed to establish a better statistical basis.

According to the hose manufacturer, there can be a lot of variation in burst tests on shorter samples due to coupling/hose interaction. This is likely less of an issue for the robust composite 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.

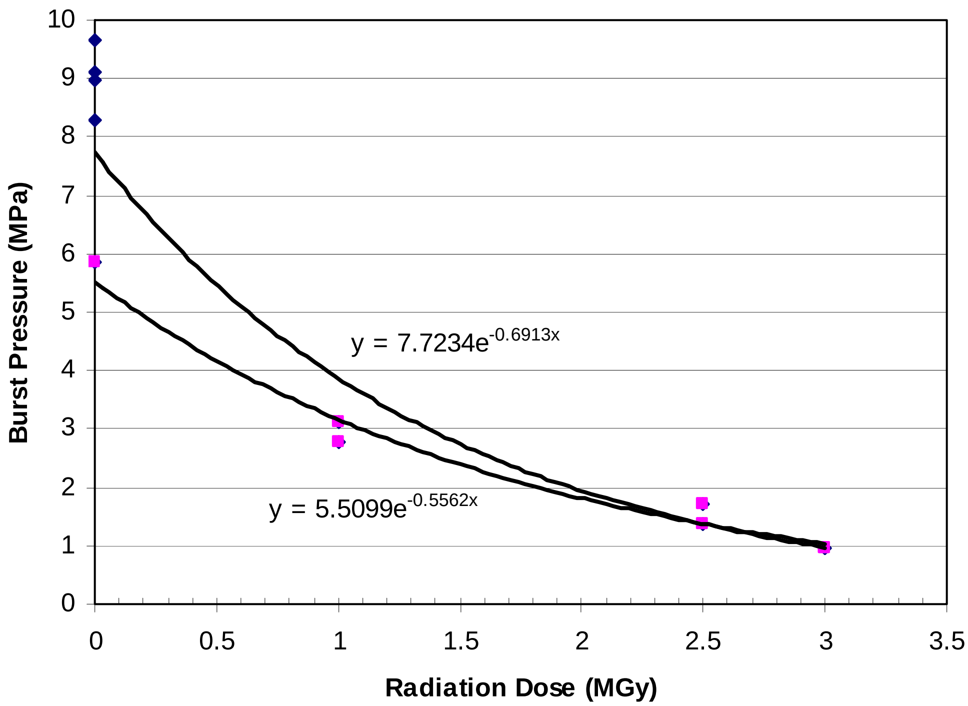

Figure 5. Burst Pressure (MPa) vs. Radiation Dose (MGy).

Burst pressures at doses less than 1.0 MGy were not determined. The estimated burst pressure in Figure 5 at 0.5 MGy is approximately 4-5.5 MPa. The higher curve in Figure 5 represents an exponential fit including all data but the lower 5.9 MPa value. 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 (1.04 MPa). Actual values may be higher if there is a threshold dose below which radiation has no measureable effect on burst pressure.

These results do not account for pressure at temperature. NAHAD guidelines recommend that hose working pressure be reduced by 30% if operating between 66 °C and 107 °C. Hose manufacturer representatives confirm this applies to the candidate hose. This reduces the true working pressure from 1.38 to 0.97 MPa, which is slightly less than the anticipated service pressure (1.04 MPa). Alternatively, a 30% reduction of normal burst pressure (6.9 MPa) gives a burst pressure of 4.83 MPa. This is similar to the room temperature burst pressure estimated at 0.5 MGy and burst values obtained for full-size hose performed at 93 °C, with no radiation exposure.

Gas Generation

During radiolysis, polymers absorb a portion of the energy which produces changes in the polymer structure. This can result in gas generation. The specific amount and type(s) of gas liberated depends on the polymer type and other factors. Some gases liberated may be toxic or corrosive such as HCl, or flammable such as hydrogen.

Gas generation rates are often expressed in terms of G-values, which represent the number of molecules of gas liberated per 100 electron volts (eV) of energy absorbed. 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. Gas generation of EPDM elastomers are expected to be bounded by that of polyethylene.

Based on weight of the hose per length without the wire helix, a composite polymer density was estimated at 1.18 g/cc. At a 0.50 MGy dose with a hose thickness of 0.76 cm and a G(flammable) value of 4.1, the gas generation rate at room temperature was estimated at 4.67 cm^3 per cm^2 of hose. This value assumes atmospheric pressure, a uniform dose through thickness and no attenuation of gamma radiation. For a 20 foot (609 cm) length of 76.1 mm ID hose, the surface area of the exposed liner is estimated at 14, 586 cm^2.

Multiplying the surface area by the gas generation rate per area gives ~ 68 L flammable gas evolved per 609 cm length of 76.1 mm ID hose at 0.50 MGy. This translates to a gas generation rate of about 1.36L of flammable gas per 0.01 MGy for a 609 cm length of hose, or 0.22L per 0.01 MGy per cm length.

As the hose can be changed out between transfers, the time duration of concern is a single transfer. Assuming a bounding dose rate of 0.58 kGy/hr and transfer duration of 20 hours, the dose per transfer is estimated at 0.012 MGy. This results in approximately 1.63L of flammable gas generated per transfer for a 609 cm length of 76.1 mm ID hose at room temperature. Correcting for the effect of elevated temperature gives:

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

Assuming an activation energy of 2.51 kJ/g-mole for H_2 formation, the gas constant as 8.314 J/K-mole and a maximum service temperature of 93 °C , the ratio of the G (flammable gas) value at 93 °C (366.15K) to the G (flammable) value at room temperature (298K) is calculated as 1.22 or a ~ 22% increase in the room temperature G value (4.1) to 4.96 at 93 °C, thus increasing the flammable gas generation rate to 5.7 cm^3 per cm^2 of exposed hose or about 1.97L per 20-hour transfer.

CONCLUSIONS AND RECOMMENDATIONS

The test results suggest a maximum “safe” dose limit of 0.5 MGy for the candidate hose, given anticipated operating conditions. Higher doses may be tolerated depending on the required safety factor, service conditions expected and increased operating history. Burst values at 0.50 MGy are estimated at ~4.1-5.5 psi, providing a 3-4X safety factor over the working pressure (1.38 MPa) and a 4-5X safety factor over the operating pressure (1.04 MPa), at room temperature. At elevated temperature, the margins are reduced.

At a bounding continuous dose rate of 0.6 kGy/hr, the 0.5 MGy limit will be reached in ~ 1.2 months or about 11.6 kGy per 20 hour transfer. Therefore, approximately 40 transfers may be performed before the 0.50 MGy dose is reached. The bounding dose rate is likely conservative for most transfers, so refined dose rate calculations may possibly extend service life. Exposure to 25% NaOH at 93 °C for 30 days did not subsequently embrittle the irradiated hose liner, representing six months of planned service. Additional testing is recommended to better understand the degradation mechanisms, particularly at the lower, more realistic doses anticipated. A graded approach involving post-service examination after a limited number of transfers is recommended to validate laboratory test results.

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