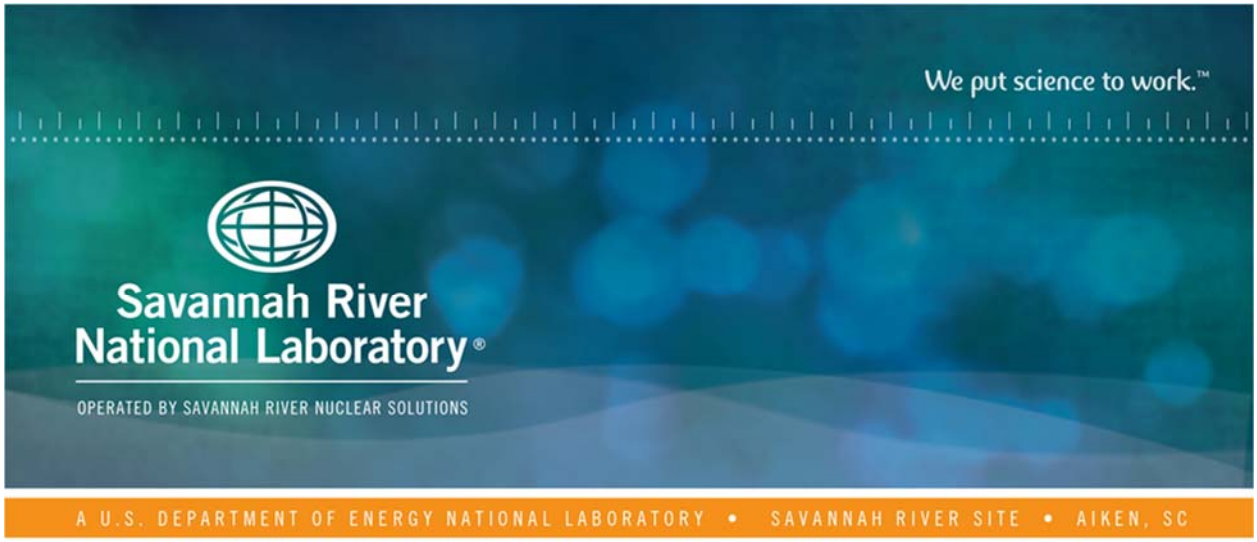
Contract No:

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).

Disclaimer:



SDU7 Interior Liner Testing & Evaluation

T. E. Skidmore

R.C. Hawsey

June 2020

SRNL-STI-2020-00209, Revision 0

DISCLAIMER

Printed in the United States of America

Prepared for
U.S. Department of Energy

SRNL-STI-2020-00209
Revision 0

Keywords: Saltstone, SDU, polymer, liner, containment

Retention: *Permanent*

SDU7 Interior Liner Testing & Evaluation

T. E. Skidmore
R.C. Hawsey

June 2020

Prepared for the U.S. Department of Energy under contract number DE-AC09-08SR22470.

Savannah River National Laboratory®
OPERATED BY SAVANNAH RIVER NUCLEAR SOLUTIONS

REVIEWS AND APPROVALS

AUTHORS:

_____

T. E. Skidmore
Manager, SRNL/Materials Evaluation & NDE

_____

R. C. Hawsey
SRNL/Materials Evaluation & NDE

TECHNICAL REVIEW:

_____

B. J. Wiersma
SRNL/Materials Science & Engineering/Applied Materials Research

APPROVAL:

_____

J. Manna, Manager
SRNL/Materials Science & Engineering

_____

D. T. Wallace
SDU 7-12 Design Authority

ACKNOWLEDGEMENTS

The authors acknowledge the assistance of several individuals for this task. Dr. John Seaman and Dr. Christina Logan of the Savannah River Ecology Laboratory (SREL) coordinated and performed sample immersions and provided extensive photographs of the samples after immersion on a weekly basis. SREL then transferred material to the Savannah River National Laboratory/Materials Science & Engineering organization following immersion. Chandler Hawsey and Patrick Kuzbary (SRNL/Materials Science & Engineering, MS&E) performed lap-shear and tensile testing of all samples, with Chandler Hawsey converting raw data into spreadsheets for data analysis. Lin Thacker and Chandler Hawsey (SRNL/MS&E) assisted with photography of test samples. Fernando Fondeur (SRNL/Separation Sciences & Engineering) performed FTIR spectroscopy on REMA 4CN and BLAIR/Marflex® bromobutyl liner samples for baseline comparison. Joe Galligan (SRNL/Tritium Materials Test Facility) performed initial baseline hardness testing and initiated sample handling and nomenclature.

EXECUTIVE SUMMARY

The Saltstone Disposal Unit 7 (SDU7) project requested the Savannah River National Laboratory (SRNL), Materials Science & Engineering (MS&E) organization to evaluate an alternative bromobutyl liner and adhesives for potential use in SDU7 based on applicable ASTM testing standards. SRNL performed similar testing for the liner system used in SDU6. Bonded and non-bonded samples of the alternative liner (Blair Rubber Marflex™ RCHB60HT) were subjected to specific ASTM tests after immersion in two Saltstone leachate simulants, designated S1 and S2, for 1000 hours at 60 °C. Immersion exposures were performed at the Savannah River Ecology Laboratory (SREL). Post-immersion testing involved mechanical property and hardness testing of base material, lap-shear testing of bonded samples and rubber-to-concrete paver interrogation. The liner exhibited an approximate 40% drop in tensile strength and 25% drop in elongation at failure from baseline values after immersion, though final values are comparable to previous SDU6 liner values and are within liner manufacturer property ranges.

Overall lap-shear strength behavior of the four adhesives showed a similar pattern, with short-term reduction and subsequent increase in peak load values. However, ranking of adhesives varied with the metric used for comparison. Two of the four adhesives tested (Normac 900 and REMA SC 4000) showed overall better behavior, collectively considering immersion performance, lap-shear data and bonded paver interrogation. Lap-shear samples bonded with the REMA adhesive showed the best combination of final retained bond strength, 6-week average bond strength and bond failure mode. Only one paver (REMA SC4000) was noted to have no defects after immersion.

This document details the testing performed and provides conclusions and recommendations. The testing suggests that SDU liner performance is highly dependent upon seam integrity, which collectively depends on a combination of adhesive properties, installation workmanship and inspection/quality control.

TABLE OF CONTENTS

LIST OF ABBREVIATIONS AND ACRONYMS

ASTM	American Society for Testing of Materials
BIIR	Isobutylene-isoprene (butyl) rubber containing reactive bromine
DOE	Department of Energy
DSC	Differential Scanning Calorimetry
EPA	Environmental Protection Agency
EPDM	Ethylene-propylene diene monomer
EPR	Ethylene-propylene copolymer (rubber)
ESCR	Environmental stress-cracking resistance
EVA	Ethylene-vinyl acetate
FML	Flexible membrane liner
FTIR	Fourier Transform Infra-Red
Gray	International Unit of ionizing radiation absorbed, 1 Gy = 100 rad
GRI	Geosynthetic Research Institute
HDPE	High density polyethylene
IIR	isobutylene isoprene rubber
LTLS	Leak-Tight Liner System
MPa	Megapascal (N/mm^2)
MS&E	Materials Science & Engineering
NACE	National Association of Corrosion Engineers
NMR	Nuclear Magnetic Resonance
PSI	Pounds per square inch
Rad	Unit of ionizing radiation energy absorbed (1 rad = 100 erg/g)
SDU	Saltstone Disposal Unit
SEE	Systems Engineering Evaluation
SREL	Savannah River Ecology Laboratory
SRNL	Savannah River National Laboratory
SRR	Savannah River Remediation
SRS	Savannah River Site
SSPC	Society for Protective Coating
TGA	Thermogravimetric Analysis
TTS	Time-Temperature Superposition
XRD	X-Ray Diffraction
XRF	X-Ray Fluorescence

1.0 BACKGROUND

The Saltstone Disposal Unit 7 (SDU7) is a circular concrete tank approximately 375 feet in diameter by 43 feet high, contains 208 roof support columns, with a minimum capacity of 30 million gallons. The columns are 2 feet in diameter. The SDU7 design is similar to SDU6 (Figure 1), which is based on the Syracuse, NY Westcott Reservoir design.

The construction of SDU7 is relying on the lessons learned gained during construction of the Saltstone Disposal Unit 6 (SDU6). SDU6 was required to meet the water leak-tightness criteria of ACI 350.1 as well as having no observation of dye traces at any location exterior to the tank, up to the wetted level of the tank [1-3]. ACI 350.1 criteria were not used for SDU7.

During previous initial SDU6 hydrotesting, external leakage was observed at the wall to floor slab joint. After draining, examination revealed extensive cracking of the floor slab either not identified prior to hydrotesting, or that had been considered only shrinkage cracks. A SEE (Systems Engineering Evaluation) was performed to evaluate options for meeting leaktight requirements [4]. The initial SDU6 design was required to be leaktight without the use of coatings or linings. A coating system (Versiline EC-66 flexible epoxy**,** Blome International) had been specified to protect the interior concrete from chemical attack.

After considering several options, the SEE team concluded that installation of an adhered sheet lining was the most viable option for mitigating the existing cracks and to ensure leaktight containment. The use of spray-applied coatings, including the coating system already specified for concrete protection, with and without fabric or geotextile reinforcement, was also considered. However, due to concern at the time for potential crack propagation and the overall floor condition, the coating manufacturer could not claim leaktightness for their system.

Several polymeric liners were considered possible options for SDU6 based on service conditions and manufacturer recommendations. These included EPDM, EVA, butyl (including halogenated versions), HDPE and other polymers typically used as geomembranes, landfill liners and tank linings. Testing was performed by SREL and SRNL on two liners (REMA Chemoline 4CN bromobutyl elastomer, Marseal M-3500 thermoplastic/Elvaloy® copolymer). Of the two, the REMA Chemoline 4CN system was selected based on superior test performance and material behavior [5-7].

Based on SDU6 experience, the SDU7 project specified the use of a bromobutyl liner to provide a leaktight liner system (LTLS). The REMA 4CN liner used in SDU6 was the preferred liner system for SDU7. Abtrex Industries proposed an alternative bromobutyl liner (Marflex RCHB60HT, Blair Rubber). Abtrex Industries is an approved applicator for Blair Rubber, Polycorp and RubberSource lining materials, but not for the REMA TipTop system previously used in SDU6. Abtrex Industries was awarded the contract contingent upon successful testing of the Marflex RCHB60HT liner system.

The REMA Chemoline 4CN and Marflex RCHB60HT bromobutyl liner materials were initially reviewed based on manufacturer property data and considered comparable, with some variations noted [8]. General properties of REMA Chemoline 4CN and Blair Rubber Marflex RCHB60HT bromobutyl linings are given in Table 1.

The review identified that the Marflex RCHB60HT liner has a higher service temperature (120 °C) than the REMA Chemoline 4CN liner (90 °C) as well as a higher cited tensile strength (1200 vs. 580 PSI). These were considered potential advantages of the Marflex liner or at least not disadvantages. It is noted that liner properties are often published as typical or nominal values. Allowable ranges or minimum/maximum test values are often not reported. The basis for the service temperature ratings for both liners and the range of tensile strength values for the REMA Chemoline 4CN material are unknown.

During SDU6 liner evaluations (2016), the Marflex RCHB60HT pre-cured bromobutyl lining system was not available from Blair Rubber. At that time, Blair Rubber only offered a post-curable bromobutyl lining system, which is not practical for installation within large structures such as the SDUs.

The SDU7 project requested SREL and SRNL to perform testing of the alternative Marflex liner similar to that performed for SDU6. The lining environmental conditions listed below are assumed for the liner in contact with leachate.

- 100% humidity
- pH between 3.7 and 13.7
- Temperature range: -11 °C to 60 °C
- Radiation dose, estimated at 0.82 Mrad over a 25-year period [7]

Figure 1. SDU7 (under construction at right) in Z-Area [9]

Table 1. Typical Properties of REMA Chemoline 4CN and Marflex RCHB60HT Bromobutyl Linings

Product/Manufacturer	Chemoline 4 CN (REMA TipTop)	Marflex RCHB60HT (Blair Rubber)
Material / Thickness	BIIR / 3 mm (120-mil)	BIIR / 1/8 inch (125-mil)
Tensile Strength - ASTM D412	580 psi (range unspecified)	1200 psi (750-2000 psi)
El% at Break - ASTM D412	370% (range unspecified)	350% (200%-600%)
Specific Gravity - ASTM D927	1.25 (EN ISO 1183-1)	1.35 +/- 0.10
Hardness - ASTM D2240 (Shore A)	55 +/- 5	60 +/- 5 (50-65)
Max Operating Temperature	90° C	120° C

2.0 LINING TESTS AND METHODOLOGY

2.1 Test Standards and Basis

Similar to previous SDU6 liner testing, SRR contracted with the Savannah River Ecology Laboratory (SREL) to perform immersion exposures on the Marflex RCHB60HT liner, henceforth described as Marflex. After immersion, samples were transferred to the SRNL/Materials Science & Engineering Section for testing. Post-immersion testing was prescribed in Reference 10. Bonded and non-bonded sheets of Marflex as well as rubber-to-concrete pavers were immersed in Saltstone leachate simulants at a bounding temperature, followed by post-immersion testing for the following attributes:

- 1,000-hour immersion: ASTM D6943-15 [Reference 11]
- Liner mechanical properties: ASTM D412-16 [Reference 12]
- Seam lap-shear strength: ASTM D6392-12/D6214-13 [References 13, 14]
- Hardness testing: ASTM D2240-15 [Reference 15]
- Mechanical point stress test: ASTM D4437-16 [Reference 16]

The 1000-hour immersion period was initially based on the time at peak temperature of 68 °C from a SDU6 one-dimensional thermal model and was used for previous testing of the SDU6 liner [6-7, 17]. The time period exceeds the minimum one-month exposure period in ASTM D6943-15**,** Standard Practice for Immersion Testing of Industrial Protective Coatings and Linings (Method A) [11]. Other documents also address immersion testing of flexible membrane liners, geomembranes and protective linings/coatings [18-22].

For SDU7, an updated two-dimensional thermal model which includes variation in grout fill volume, pouring rates and other operational aspects reduced the peak temperature. Per SDU7 project personnel, the solution temperature for the SDU7 liner testing was reduced to 60 °C.

The simulants used in the current testing are very similar to those used in the SDU6 liner study, modified slightly to account for current or projected grout chemistry modifications. The simulants, designated as S1 (100%) and S2 (50%, diluted from S1), are shown in Table 2. The chemicals used for the simulant make-up include: NaOH, KOH, $Al(NO_3)_3$, $NaNO_2$, Na_2SO_4, NaCl, $NaCO_3$, Na_3PO_4 and ammonium oxalate ($(NH_4)_2C_2O_4$). The S1 simulant solution density is approximately 1.3 g/cc. Simulant make-up is described in References 10, 23 and 24.

Loose liner sheets (with and without bonded seams) and rubber-to-concrete paver samples were immersed in S1 and S2 simulants. An initial 1000-hour immersion test was performed using only one adhesive (NORMAC 900E Ultra Cold Bond Cement + E-Hardener) as recommended by Abtrex and Blair Rubber for typical installation of the Marflex bromobutyl liner. However, due to early observation of edge and seam blistering/debonding and liner mechanical property loss at 1000 hours, the project requested that a second round of 1000-hour immersion testing be performed. At that time, adhesive behavior was attributed to vendor statements that the adhesive had likely not been adequately cured (21 days) prior to immersion. All samples were prepared by Abtrex and submitted to SRR prior to testing.

In the second round of testing, new samples of liner material bonded with four adhesive systems were tested. These were designated as:

- System A (NORMAC 900E Ultra Cold Bond Cement)
- System B (REMA SC4000 and Hardener E-40)
- Systems C1 and C2 (both proprietary Abtrex adhesives).
- C1 samples were designated as P+ and R+ for pavers and sheets
- C2 samples were designated as PE and "RE" for pavers and sheets

Bonded and non-bonded liner samples were removed from immersion every week for 6 weeks to evaluate time-based behavior. Pavers were removed at 500 and 1000-hour intervals for inspection. SREL performed weekly visual examination with all observations recorded in Reference 23. Liner/adhesive system designations are given in Table 3, with SREL/vendor sheet/paver designations given in Table 4.

The second round of System A immersion tests started approximately 3 weeks sooner than Systems B, C1 and C2 due to sample availability from the vendor. Therefore, all samples from all systems were not tested at identical periods. However, an attempt was made to test all samples within ~1 week after immersion bath retrieval to provide approximately the same amount of post-immersion drying time. Upon removal from immersion baths and transfer to SRNL, tensile and lap-shear samples were sectioned from each sheet for testing.

The following sample nomenclature was used:

System (A-D), Tensile (TS) or Lap-Shear (LS), Week (1-6), Simulant 100% (S1) or 50% (S2), followed by individual sample#.

Example: ALSW1-50-1 = System A, Lap-Shear, Week 1, 50% (S2), Sample #1.

Table 2: Saltstone Bleedwater Simulant Salt Solution (S1) and Rationale [23, 24]

Species	Conc. (M)	Rationale
Na^+	6.73	Maximum [Na^+] per SWPF WAC is 7.0 M; however, total cation/anion inventory had to be reduced to avoid precipitates
Al^{3+}	0.22	Approximates historically measured [Al^{3+}] in Tank 50
K^+	0.06	Maximum [K^+] per SWPF WAC
OH^-	2.30	Maximum [OH^-] per SWPF WAC
NO_3^-	2.35	Approximates historically measured [NO^{3-}] (average) in Tank 50; meets corrosion inhibitor requirements
NO_2^-	0.90	Nitrite is added at approximately double the upper concentration recorded in Tank 50 since Ref. 41 indicates higher nitrite concentrations in future salt batches from the Tank Farm
CO_3^{2-}	0.20	Approximates historically measured [CO_3^{2-}] in Tank 50
SO_4^{2-}	0.18	Maximum [SO_4^{2-}] per TF WAC
Cl^-	0.11	Maximum [Cl^-] per TF WAC
PO_4^{3-}	0.05	[PO_4^{2-}] is limited by solubility (refer to latter text on preparing simulants); concentration higher than maximum measured in Tank 50
$C_2O_4^{2-}$	0.01	Approximates historically measured [$C_2O_4^{2-}$] in Tank 50

Table 3. List of SREL Liner/Adhesive System Designations

Adhesive System	Description
System A	BLAIR Marflex liner + Normac adhesive
System B	BLAIR Marflex liner + REMA adhesive
System C1	BLAIR Marflex liner + C1 adhesive (Abtrex/proprietary)
System C2	BLAIR Marflex liner + C2 adhesive (Abtrex/proprietary)

Table 4. Liner Sample/Paver Designations (Vendor/SREL)

System	Sheet/Paver	Marking/Label	Simulant (S1 or S2)	Removal Time
A	Paver	A01	S1	500 hrs
A	Paver	A02	S1	1000 hrs
A	Paver	A15	S2	500 hrs
A	Paver	A16	S2	1000 hrs
A	Sheet (no seam)	A03	S1	Week 1
A	Sheet (no seam)	A04	S1	Week 2
A	Sheet (no seam)	A05	S1	Week 3
A	Sheet (no seam)	A06	S1	Week 4
A	Sheet (no seam)	A07	S1	Week 5
A	Sheet (no seam)	A08	S1	Week 6
A	Sheet (lap seam)	A09	S1	Week 1
A	Sheet (lap seam)	A10	S1	Week 2
A	Sheet (lap seam)	A11	S1	Week 3
A	Sheet (lap seam)	A12	S1	Week 4
A	Sheet (lap seam)	A13	S1	Week 5
A	Sheet (lap seam)	A14	S1	Week 6
A	Sheet (no seam)	A17	S2	Week 1
A	Sheet (no seam)	A18	S2	Week 2
A	Sheet (no seam)	A19	S2	Week 3
A	Sheet (no seam)	A20	S2	Week 4
A	Sheet (no seam)	A21	S2	Week 5
A	Sheet (no seam)	A22	S2	Week 6
A	Sheet (lap seam)	A23	S2	Week 1
A	Sheet (lap seam)	A24	S2	Week 2
A	Sheet (lap seam)	A25	S2	Week 3
A	Sheet (lap seam)	A26	S2	Week 4
A	Sheet (lap seam)	A27	S2	Week 5
A	Sheet (lap seam)	A28	S2	Week 6
B	Paver	PR-01	S1	500 hours
B	Paver	PR-02	S1	1000 hours
B	Paver	PR-03	S2	500 hours
B	Paver	PR-04	S2	1000 hours
B	Sheet (lap seam)	RR-01-S1	S1	Week 1
B	Sheet (lap seam)	RR-02-S1	S1	Week 2
B	Sheet (lap seam)	RR-03-S1	S1	Week 3
B	Sheet (lap seam)	RR-04-S1	S1	Week 4
B	Sheet (lap seam)	RR-05-S1	S1	Week 5
B	Sheet (lap seam)	RR-06-S1	S1	Week 6
B	Sheet (lap seam)	RR-01-S2	S2	Week 1
B	Sheet (lap seam)	RR-02-S2	S2	Week 2
B	Sheet (lap seam)	RR-03-S2	S2	Week 3
B	Sheet (lap seam)	RR-04-S2	S2	Week 4
B	Sheet (lap seam)	RR-05-S2	S2	Week 5
B	Sheet (lap seam)	RR-06-S2	S2	Week 6
C1	Paver	P+01	S1	1000 hours
C2	Paver	PE-01	S1	1000 hours
C1	Paver	P+02	S2	1000 hours
C2	Paver	PE-02	S2	1000 hours

Table 4. Liner Sample/Paver Designations (Vendor/SREL) - continued

System	Sheet/Paver	Marking/Label	Simulant (S1 or S2)	Removal Time
C1	Sheet (lap seam)	R+01-S1	S1	Week 1
C1	Sheet (lap seam)	R+02-S1	S1	Week 2
C1	Sheet (lap seam)	R+03-S1	S1	Week 3
C1	Sheet (lap seam)	R+04-S1	S1	Week 4
C1	Sheet (lap seam)	R+05-S1	S1	Week 5
C1	Sheet (lap seam)	R+06-S1	S1	Week 6
C2	Sheet (lap seam)	RE-01-S1	S1	Week 1
C2	Sheet (lap seam)	RE-02-S1	S1	Week 2
C2	Sheet (lap seam)	RE-03-S1	S1	Week 3
C2	Sheet (lap seam)	RE-04-S1	S1	Week 4
C2	Sheet (lap seam)	RE-05-S1	S1	Week 5
C2	Sheet (lap seam)	RE-06-S1	S1	Week 6
C1	Sheet (lap seam)	R+01-S2	S2	Week 1
C1	Sheet (lap seam)	R+02-S2	S2	Week 2
C1	Sheet (lap seam)	R+03-S2	S2	Week 3
C1	Sheet (lap seam)	R+04-S2	S2	Week 4
C1	Sheet (lap seam)	R+05-S2	S2	Week 5
C1	Sheet (lap seam)	R+06-S2	S2	Week 6
C2	Sheet (lap seam)	RE-01-S2	S2	Week 1
C2	Sheet (lap seam)	RE-02-S2	S2	Week 2
C2	Sheet (lap seam)	RE-03-S2	S2	Week 3
C2	Sheet (lap seam)	RE-04-S2	S2	Week 4
C2	Sheet (lap seam)	RE-05-S2	S2	Week 5
C2	Sheet (lap seam)	RE-06-S2	S2	Week 6

2.2 Test Methods

Details for each of the test methods performed by SRNL/MS&E as identified in Reference 10 are provided.

2.2.1 Tensile Testing – ASTM D412-16 [12]

Samples of non-bonded liner material were tested per ASTM D412-16, Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers [12]. Samples were die-cut using a brand-new die meeting Die C dimensions (Figure 2). Samples were tested using a 1000 N load cell at a crosshead/displacement rate of 20 inches/minute per ASTM D412, which allows other displacement rates if specified. Tensile and lap-shear tests were both performed on an MTS tensile machine (Model C43-504), located at the SRNL Hydrogen Technology Research Laboratory (HRTL), Figure 3. A minimum of 5 tensile samples were tested from each sheet of the base liner material for replication. Approximately 65 tensile samples from non-bonded liner sheets were tested (5 baseline + 5 samples per panel per week for 2 simulants).

Figure 2. ASTM D412-15 Die C with tensile sample of Marflex RCHB60HT

Figure 3. MTS tensile machine (Model C43-504), SRNL Hydrogen Technology Research Laboratory

2.2.2 Lap-Shear Testing – ASTM D6392/D6214

Several methods to evaluate the integrity of geomembrane seams are discussed in ASTM D7700 [25]. Two of these standards were used to evaluate the lap-shear strength of the alternative bromobutyl liner seams. These standards are essentially similar in approach but are applicable to different types of liners. This approach was used for testing the REMA Chemoline 4CN material for the SDU6 liner in 2016. These are:

- ASTM D6392-12, Standard Test Method for Determining the Integrity of Non-reinforced Geomembrane Seams Produced using Thermo-Fusion Methods [13].
- ASTM D6214-13, Standard Test Method for Determining the Integrity of Non-reinforced Geomembrane Seams Produced using Chemical Fusion Methods [14].

Technically, the SDU liner may not be considered a geomembrane and the MARFLEX liner (as was the SDU6 liner REMA 4CN) is bonded via use of adhesives, rather than by thermal fusion methods that might be used to join HDPE liners or solvent methods as might be used for joining PVC-based materials though the adhesives used do contain a fair amount of solvent. A similar standard for testing solvent-welded seams in non-reinforced PVC geomembranes is ASTM 8172-18 [26]. Product data sheets and SDS information on the Normac and REMA adhesives are given in References 27-31.

Both standards include lap-shear and T-peel tests. Only the lap-shear configuration was tested since it best represents actual installation and testing both configurations would increase the total number of samples. Only lap-shear tests were performed for the SDU6 liner. The authors of Reference 22 note that peel adhesion tests may be more sensitive to chemical/aqueous degradation than lap-shear tests. ASTM D4896 provides a good discussion on the interpretation and use of lap-shear data, though it is mostly applicable to rigid adherends [32].

Both ASTM D6392 and D6214 test methods specify lap-shear tests to be performed on 1” wide samples at a crosshead speed of 20 inches/minute unless otherwise specified. Lap-shear samples were cut across the 2” lap joint, approximately 6” in length, with 2” of material past each end of the joint.

It is noted that the joint configurations for the REMA and MARFLEX bromobutyl liner test samples are significantly different. The REMA 4CN materials tested in 2016 were bonded as a skived butt-splice joint (approximately ¾” bond length) whereas the MARFLEX liner samples in the current testing were joined as a lap-seam with skived edges. There are pros and cons to each joint configuration, but fundamentally both are acceptable if adequate bond strength and leak integrity is attained.

The splice joint has a reduced bond surface area but provides a smooth flat profile. Splice joints may be left uncovered or covered with a cap strip depending on design requirements. The lap-seam joint with skived edges provides a larger bond area but has a stepped profile. The current MARFLEX RCHB60HT lap-shear samples are essentially similar to the MARSEAL M-3500 lap-shear samples tested in 2016, but with the skived edge. Both joint configurations are shown in Figures 4 and 5.

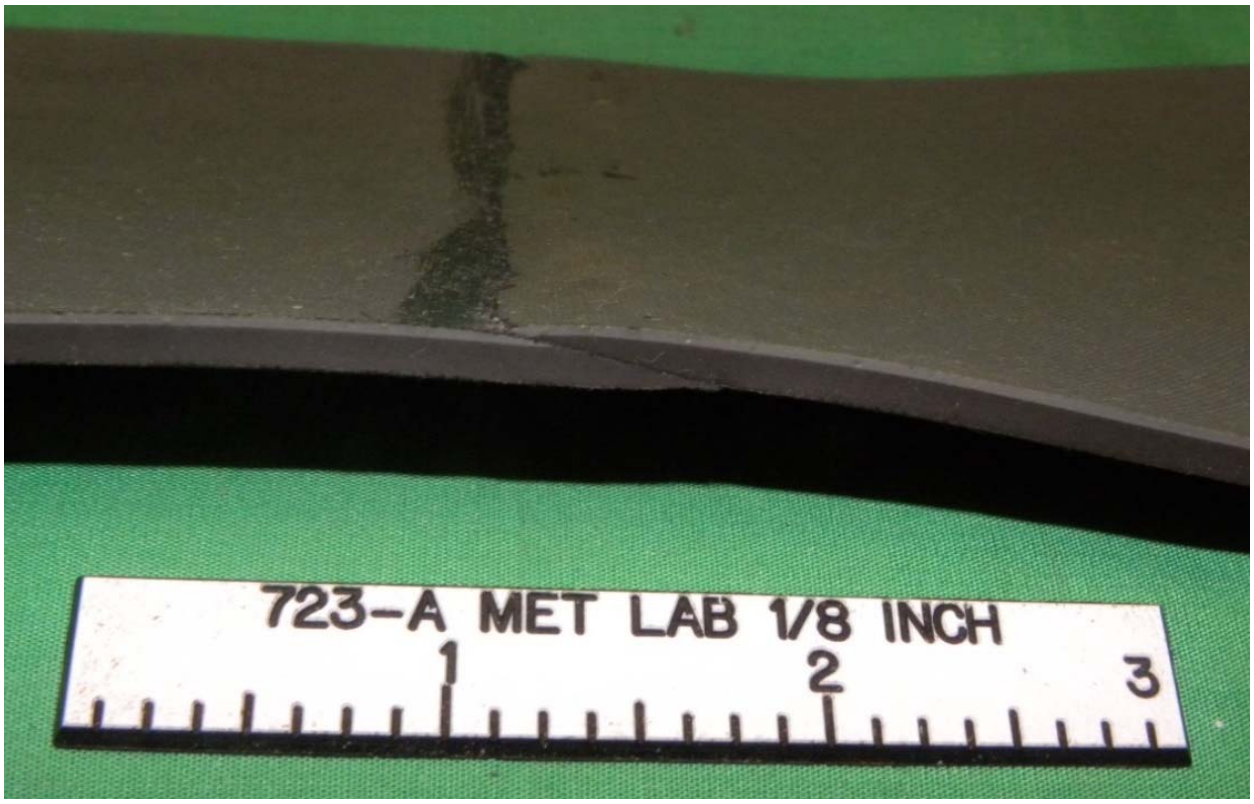


Figure 4. Splice joint configuration for REMA 4CN (installed in SDU6), ~ ¾" joint width)

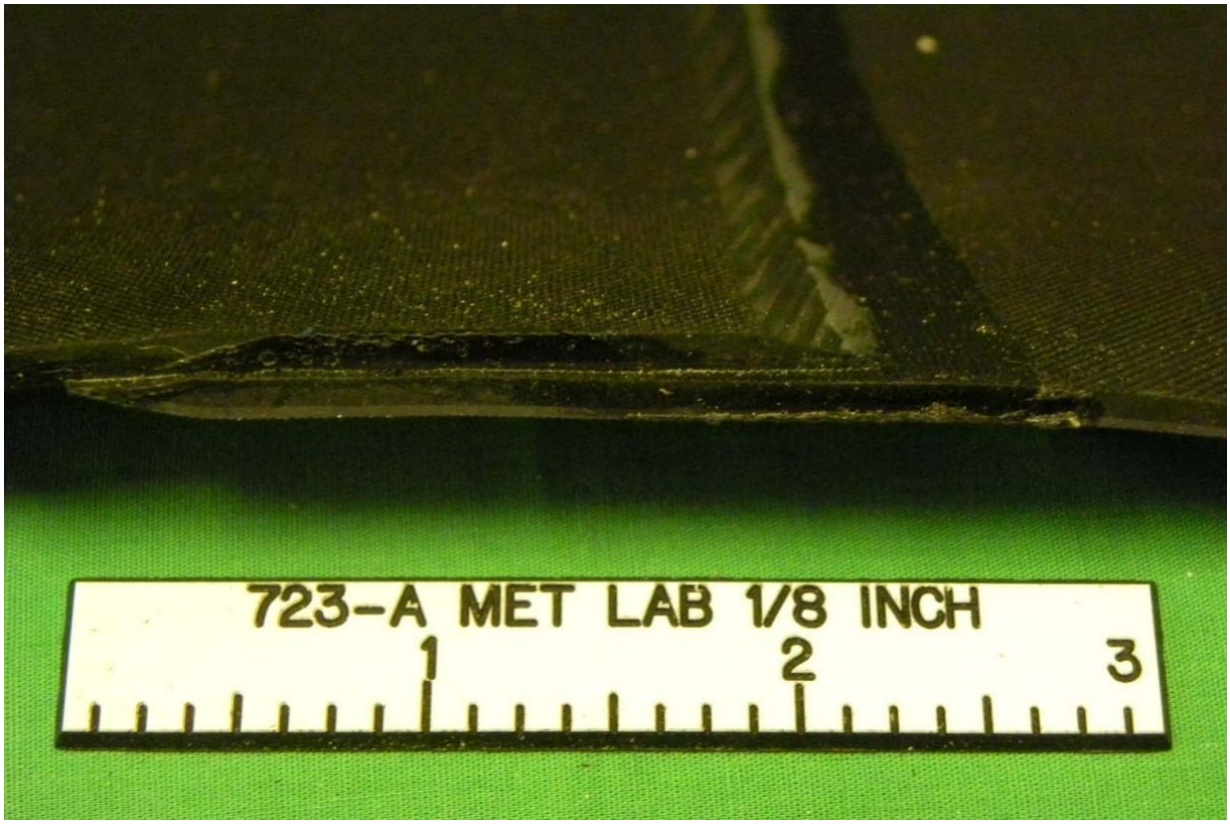


Figure 5. Lap-joint configuration for MARFLEX RCHB60HT samples, ~ 2" bond width

Approximately 226 lap-shear samples, including baseline (non-immersed) samples were tested for weekly intervals and both S1 and S2 simulants.

For System A, only three 1" wide samples could be cut from each post-immersion sheet due to the sample orientation provided by the vendor. Thinner samples could possibly have been tested, with peak loads normalized to a 1" width, but it was judged best to test all samples in the same manner for direct comparison. Cutting thinner samples with consistent width also proved to be more difficult.

For Systems B, C1 and C2, a minimum of 4 samples were tested for all systems, with 5-6 samples tested in some cases, depending on exact dimensions of the original pieces provided from the vendor. The outer edges were not included due to the taper from the skived joint. Skived edges on the sheets reduced the effective width for sample sectioning.

2.2.3 Liner Bonded to Concrete Paver Interrogation

ASTM D4437, Standard Practice for Non-destructive Testing (NDT) for Determining the Integrity of Seams used in Joining Flexible Polymeric Sheet Geomembranes, was used to evaluate the integrity of the liner bonded to concrete pavers [16]. It is acknowledged that ASTM D6392, D6214 and D4437 standards are explicitly written for geomembrane materials, not specifically for rubber tank linings, but the methods were considered relevant for SDU liner comparison purposes.

Prior to rubber adhesion, the concrete pavers were coated by Abtrex personnel with a surfacer (Versiline CP-83 MP) and a conductive primer (Conductive Primer #75) as will be installed in the SDU. The surfacer smooths out the surface, while the conductive primer allows for spark/holiday testing of the liner seams.

ASTM D4437 covers many different tests for determining the integrity of geomembrane/landfill liner seams. As in SDU6 liner testing, only the point contact method was performed in the current testing, using a blunt flathead screwdriver (approximately ¼" width) with rounded edges to interrogate the perimeter edges and seams of the bonded sheets to check for bond integrity.

This is recognized to be a subjective method, as the force and angle imposed during the interrogation is not controlled or measured. However, an attempt was made to keep the probing method consistent for all samples. The main goal was to find suspect or clearly debonded areas, not to forcibly make reasonably well-bonded areas fail. The edges of the screwdriver were rounded to avoid sharp corners. The screwdriver was lightly pushed against the seam or edge joint to find areas with little to no resistance. Examples of liner edge to concrete bond and seam interrogation are shown in Figures 6 and 7.

Figure 6. Seam interrogation on System C1 Paver, S2 Simulant, 1000-hour immersion
(black markings denote easily debonded regions)

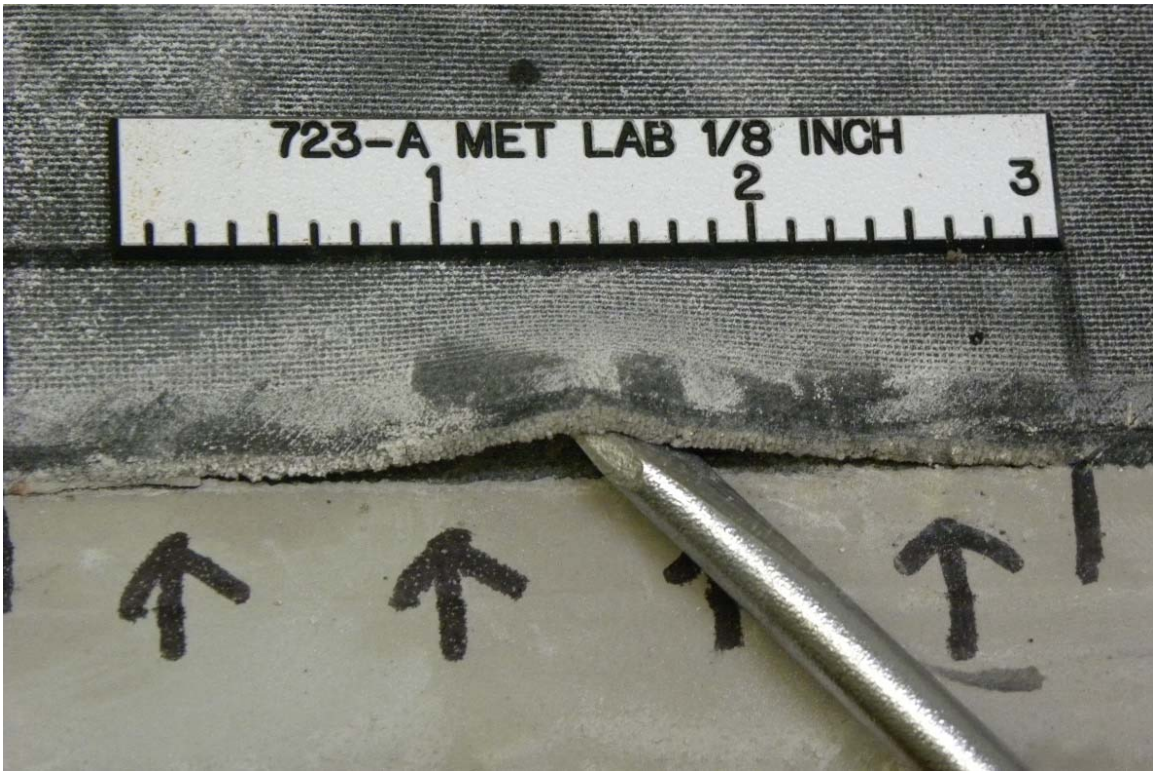


Figure 7. Rubber/concrete edge interrogation, System C1 Paver, S2 Simulant, 1000-hour immersion
(several regions of the liner edge were visually observed to be debonded prior to physical interrogation)

3.0 TEST RESULTS

A summary of test results was provided to SRR for project schedule and liner procurement decisions, as documented in G-ESR-Z-00032, Rev.1 [33]. The results are further discussed in this document.

3.1 Mechanical Property Data

3.1.1 Tensile Strength

Mechanical property data for the base liner material are graphically shown in Figures 8-13. The data shown in Figures 8 and 9 represent the average of the data set for the particular simulant (S1-100% or S2-50%) and weekly interval over 6 weeks. Tensile strength is the load at failure divided by the initial cross-sectional area of the tensile sample in the gage length. Strength values were measured in MPa (N/mm^2) and converted to PSI. The elongation at failure is based on the crosshead displacement at failure minus the original gage length divided by the original gage length (2 inches). These data represent approximately 65 tensile samples.

In Figure 8, the average baseline tensile strength (~825 PSI) is significantly less than the nominal 1200 PSI value quoted by the liner manufacturer, but it is on the lower end of the vendor's observed range (750-2000 PSI). The average tensile strength more sharply dropped during the first week of immersion, but subsequent values appear to level off toward a value of approximately 500 psi for both S1 and S2 simulants. The trendline of the average weekly values for the S1 simulant is relatively smoother than for the S2 simulant. The data suggest no significant effect of simulant variation on tensile strength reduction.

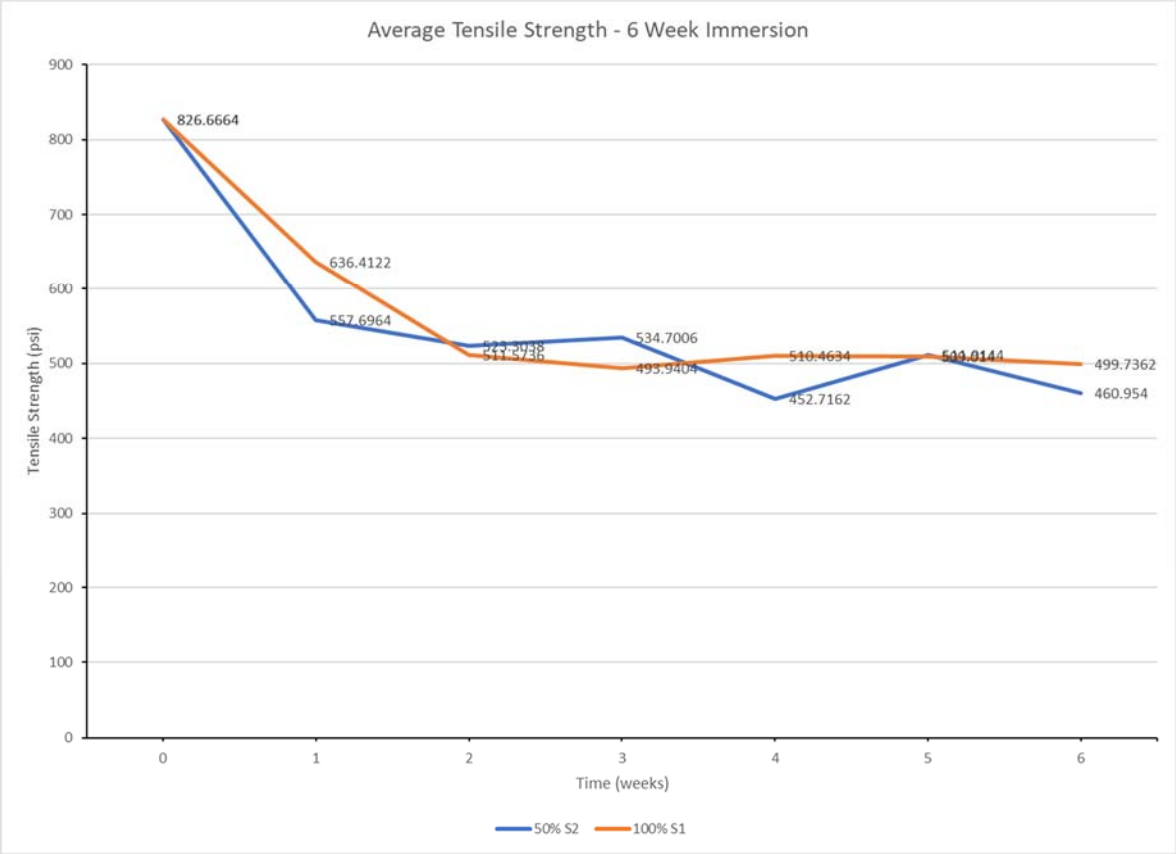


Figure 8. Average liner (non-bonded) tensile strength vs. immersion time

The average final tensile strength (~500 PSI) is approximately 60% of the baseline average value (825 PSI), a 40% reduction. The 500 PSI value is also approximately 67% of 750 PSI (37% reduction), the lowest end of the range cited by Blair Rubber for tensile strength of the MARFLEX liner.

The specific reason for this much change in baseline values or from minimum manufacturer values is unknown. The Saltstone leachate simulants are not particularly aggressive toward bromobutyl and most elastomers and polymers compared to other fluids such as hydrofluoric, sulfuric and hydrochloric acids and other industry chemicals for which bromobutyl liners have been successfully used [34]. Some of the effect may be attributed to the limited number of samples, though test values were relatively consistent. Some of the effect may be due to hydrolysis or fluid absorption rather than actual chemical degradation, which may explain the asymptotic behavior. True chemical degradation would likely be more severe and progressive.

The tensile strength reduction observed (~40 %) is significantly greater than the <20% reduction criterion established in the test plan. The 20% acceptance criterion is comparable to that used in the Compass Chemical Resistance Guides for Elastomers and similar references for ranking performance [35, 36]. In Reference 34-35, materials exhibiting a <15% loss in tensile strength (or swelling change) over 30 days to 1 year are given an "A" rating, indicating excellent resistance, with little to no swelling, softening or surface deterioration. References 35-36 give B, C and NR (Not Recommended) ratings for <30%, <60% and >60% losses in tensile strength, respectively.

While the tensile strength reduction of the MARFLEX bromobutyl liner exceeds the 20% loss criterion, the absolute value (500 PSI) is only ~12% less than the average final tensile strength of the REMA 4CN bromobutyl liner tested for and installed in SDU6. No loss criterion was established in SDU6 liner testing.

Tensile strength is certainly important and an easy property to measure, but the relative significance of tensile strength for a liner that is bonded to concrete compared to a loose geomembrane is not well-defined. The mechanical integrity of the liner is likely more important for areas subject to movement or under constant strain such as at the wall to floor joint in the SDU, either during hydrostatic testing or grout pouring.

3.1.2 Elongation Data

Figure 9 shows elongation at break values, with a reduction over time in both simulants. The average retained elongation at break values at week 6 are approximately 380-420% (average 400%). Ignoring the trend lines for interval time periods, these values represent an average reduction of elongation at break of approximately 25% from baseline.

Both the initial baseline average elongation (~540%) and the final values at 6 weeks (380-420%) are all within the range of values cited by the liner manufacturer (Blair Rubber, 200-600%, nominal 350%). The final values are also comparable to the nominal elongation at failure value cited for the REMA Chemoline 4CN liner used in SDU6 (380%).

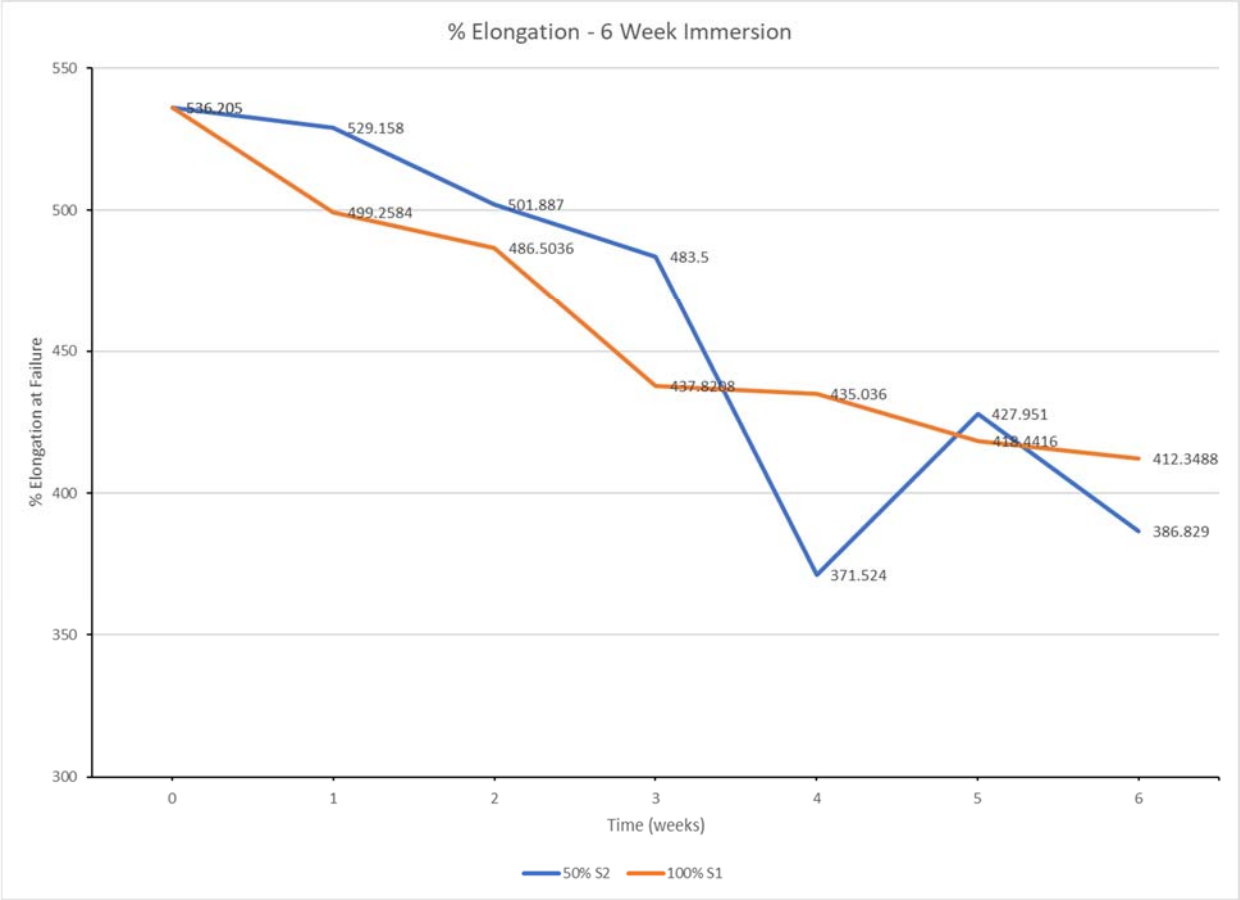


Figure 9. Average elongation to failure vs. immersion time

The 25% reduction in elongation is slightly over the 20% loss criterion in the test plan, but it is far less than the near-40% reduction observed in tensile strength. The absolute retained values are also within the range cited for the base material by the manufacturer and are very close to the nominal value cited (350%). These values also well exceed the values determined by the project as necessary to accommodate movement at the wall/floor joint (80%).

The reasons for reduced elongation at failure and the variation in % reduction in tensile strength vs. elongation are unknown. The drop in % elongation was less sharp at the first week interval compared to the tensile strength reduction.

The average elongation at break curves appear less asymptotic than the tensile strength data, though the S1 (100%) simulant data appear to be slightly leveling near 400%. Individual sample data for tensile samples are shown graphically in Figures 10-13. The reason for the sharper drop at Week 4 for simulant S2 is unknown, but two of the samples for Week 4 in Figure 12 had noticeably lower elongation values than the other 3 samples. Longer exposures would possibly be needed to verify long-term behavior and equilibrium elongation values.

As with tensile strength, the significance of reduced elongation at break values for a bonded liner has not been established. The property is likely more critical for areas where maximum displacement is expected.

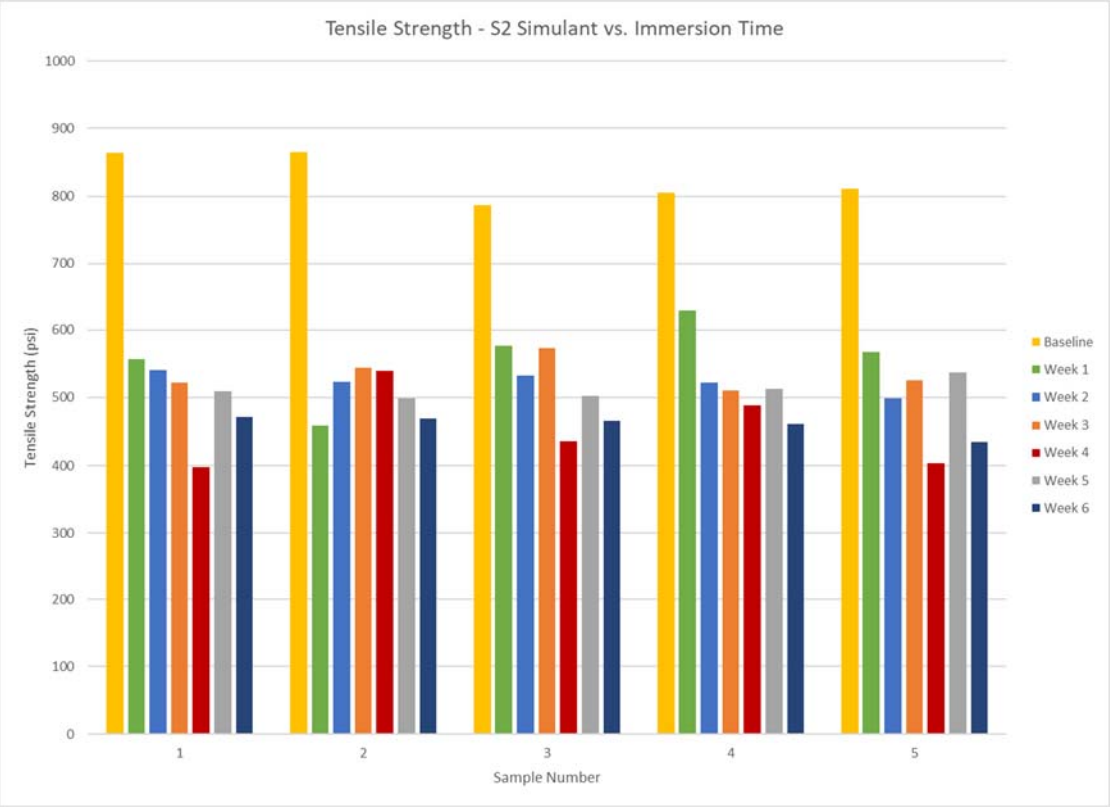


Figure 10. Tensile strength data for liner samples (S2 – 50% simulant)

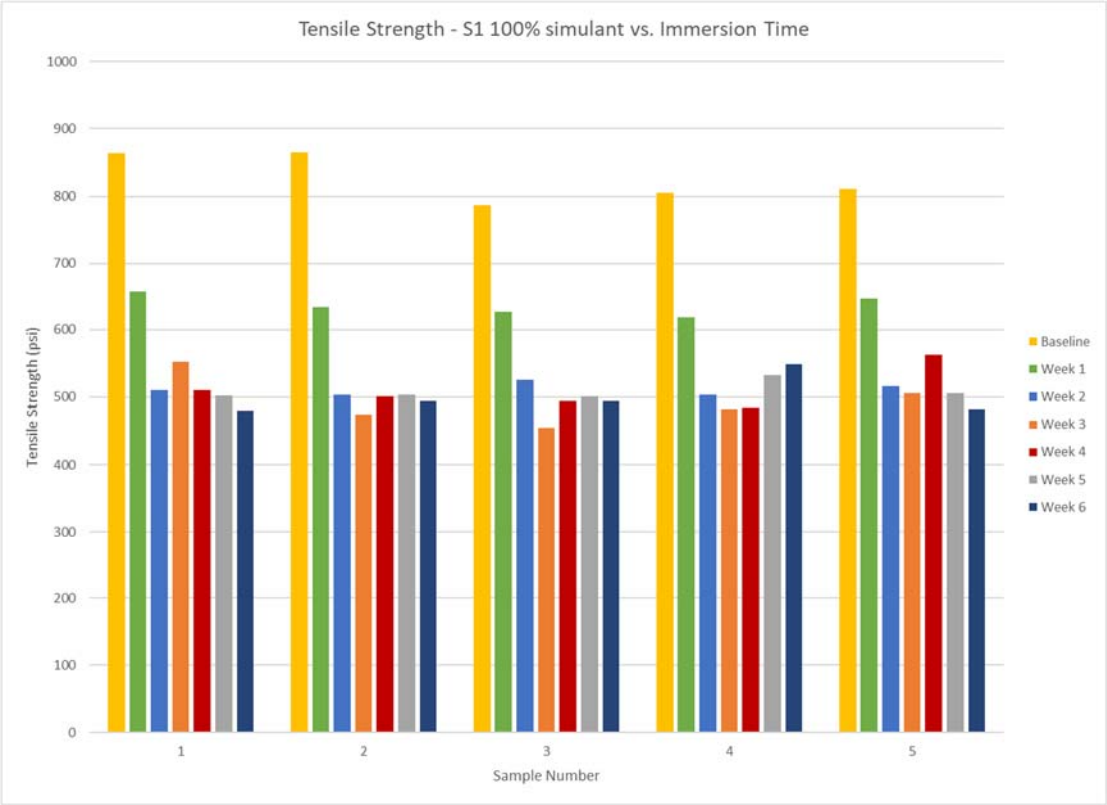


Figure 11. Tensile strength data for liner samples (S1 – 100% simulant)

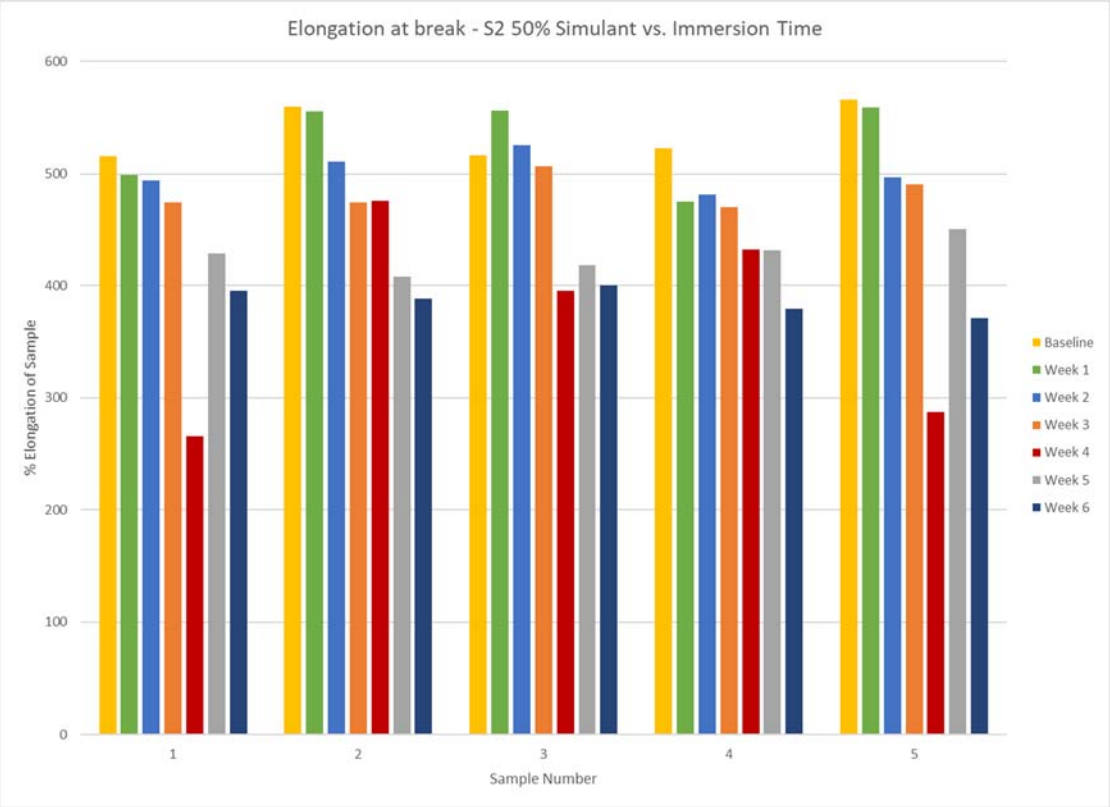


Figure 12. Elongation at break data - S2-50% simulant vs. Immersion Time

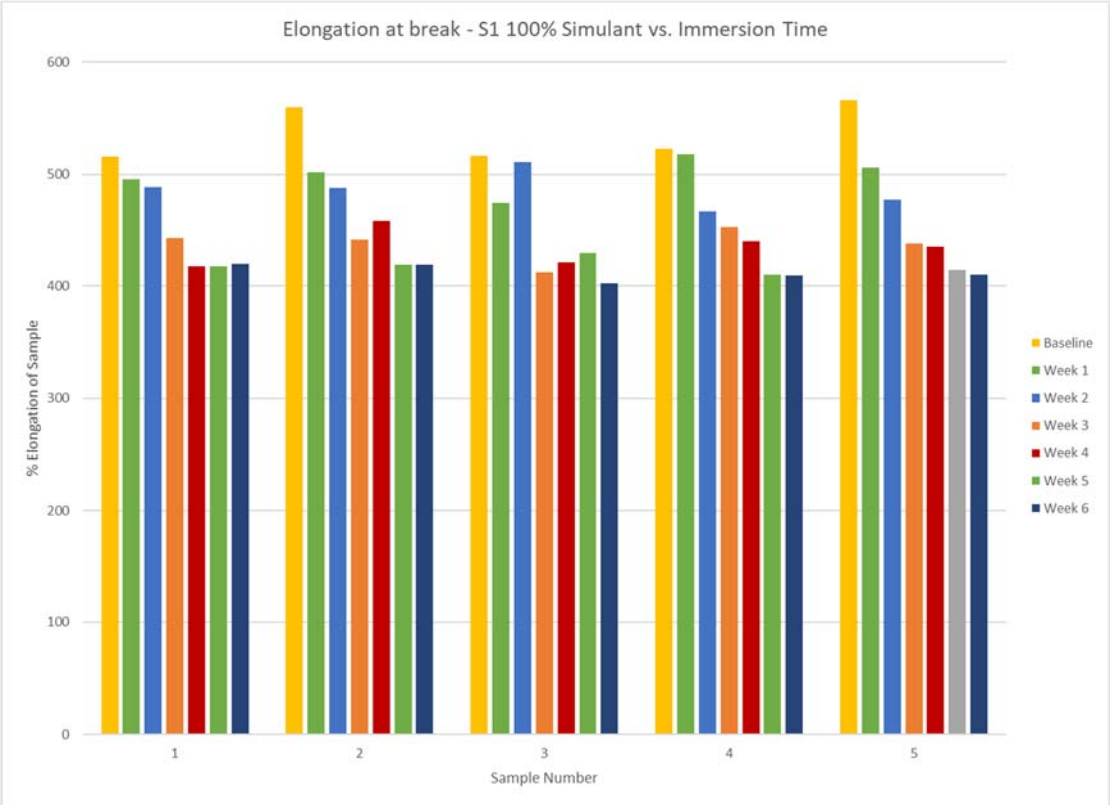


Figure 13. Elongation at break data - S1 100% simulant vs. Immersion Time

3.2 Lap-Shear Data

Lap-shear data for all samples and adhesive systems are shown in a master graph in Figure 14. Lap-shear strength is usually reported in load/bond width (typically lb-force/inch or N/mm). Bond stress can also be reported as load/bond area. Approximately 226 lap-shear samples were tested, including baseline (non-immersed) samples. These data represent the average of the data set for the particular simulant (S1 or S2) and weekly interval.

In some cases, the peak load values were reached with samples cleanly debonding or peeling apart soon thereafter. However, in other cases, peak loads were reached with samples still remaining intact until the mechanical extension limit of the Instron machine was reached. Therefore, peak load values do not necessarily completely represent sample behavior.

Elongation data were derived for the lap-shear samples. Elongation at failure data are not normally reported for lap-shear samples as the values are not the same as elongation for base material. This is because lap-shear samples have no reduced gage length as compared to true tensile samples. The elongation of the lap-shear samples is a combination of extension of the tab sections outside the bond area and extension of the bonded joint, as the samples do not stretch uniformly throughout the entire length of the sample. The majority of extension occurs in the loose non-bonded regions.

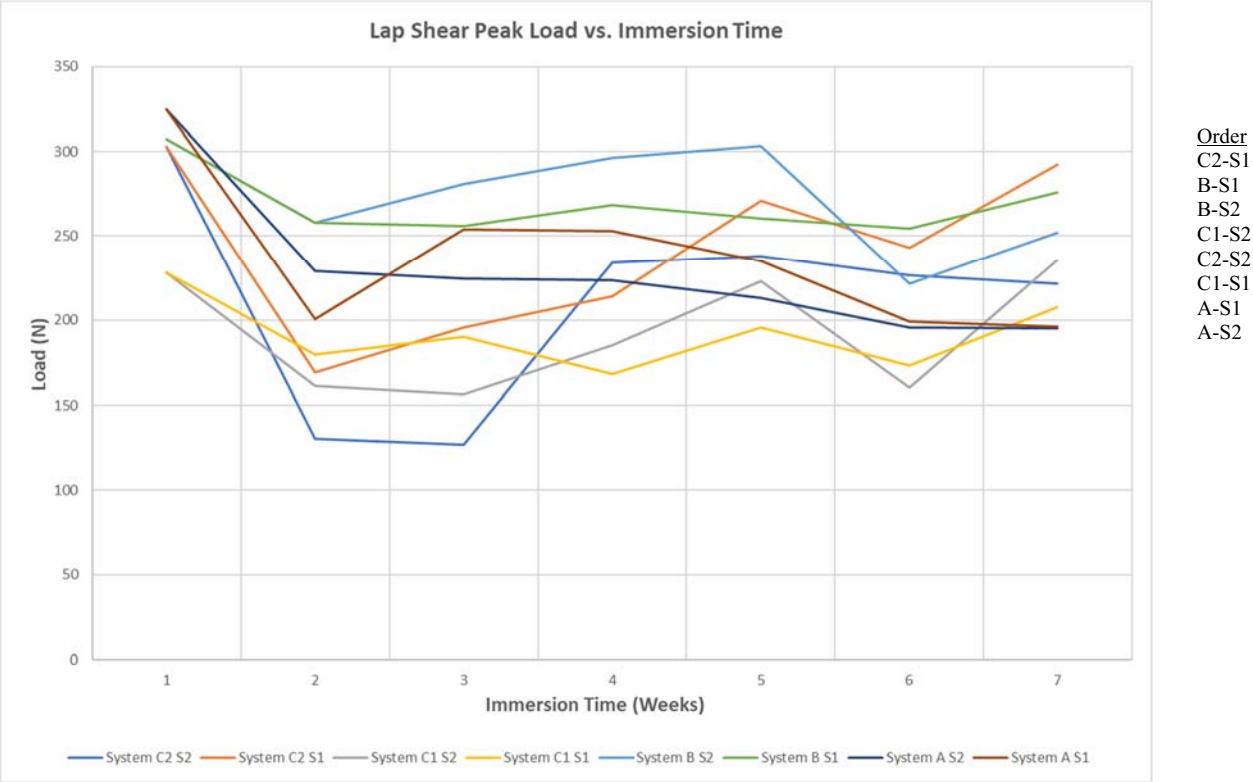


Figure 14. Master graph of lap-shear data (trendlines of average values at each test interval)

In the test plan (Reference 10), project personnel requested data on the tensile stress values (for unbonded samples) and lap-shear stress values (for bonded samples) at an elongation value of 80%, the maximum elongation estimated by the project to accommodate radial growth of the SDU structure, based on a radial deflection of 1.28 inches at the base of the wall [37].

As previously stated, the elongation at failure values for non-bonded tensile samples of the liner after 1000 hour immersion are approximately 400%. This value is far greater than the 80% elongation value required for radial growth of the SDU structure. The stress state for liner sheets bonded to the walls and floors and for seams in regions not bonded to the wall/floor joint to allow movement may vary from the stress state in dumbbell tensile samples. However, the margin for elongation to failure for the liner itself appears significant.

The tensile stress vs. elongation values for liner tensile samples (Week 6) are shown in Figures 15-16. Elongation values were based on an initial gage length of 33.274 mm (1.31 inches). Elongation values were initially only calculated at failure, but were later derived from crosshead displacement data for each sample. Figure 15 shows at approximately 80% elongation, the tensile stress for Week 6-S2 samples is estimated at 130-140 PSI. The curve for sample #5 in Figure 15 is atypical with cause unknown. Figure 16 shows slightly higher stress values (140-160 PSI) for Week 6-S1 samples. The shape of all curves in Figure 16 is similar, though the tensile stress for sample# 4 is relatively higher. The average tensile stress at approximately 80% elongation for all S1 and S2 samples is estimated at 150 PSI, or approximately 30% of the tensile stress at failure (~500 PSI).

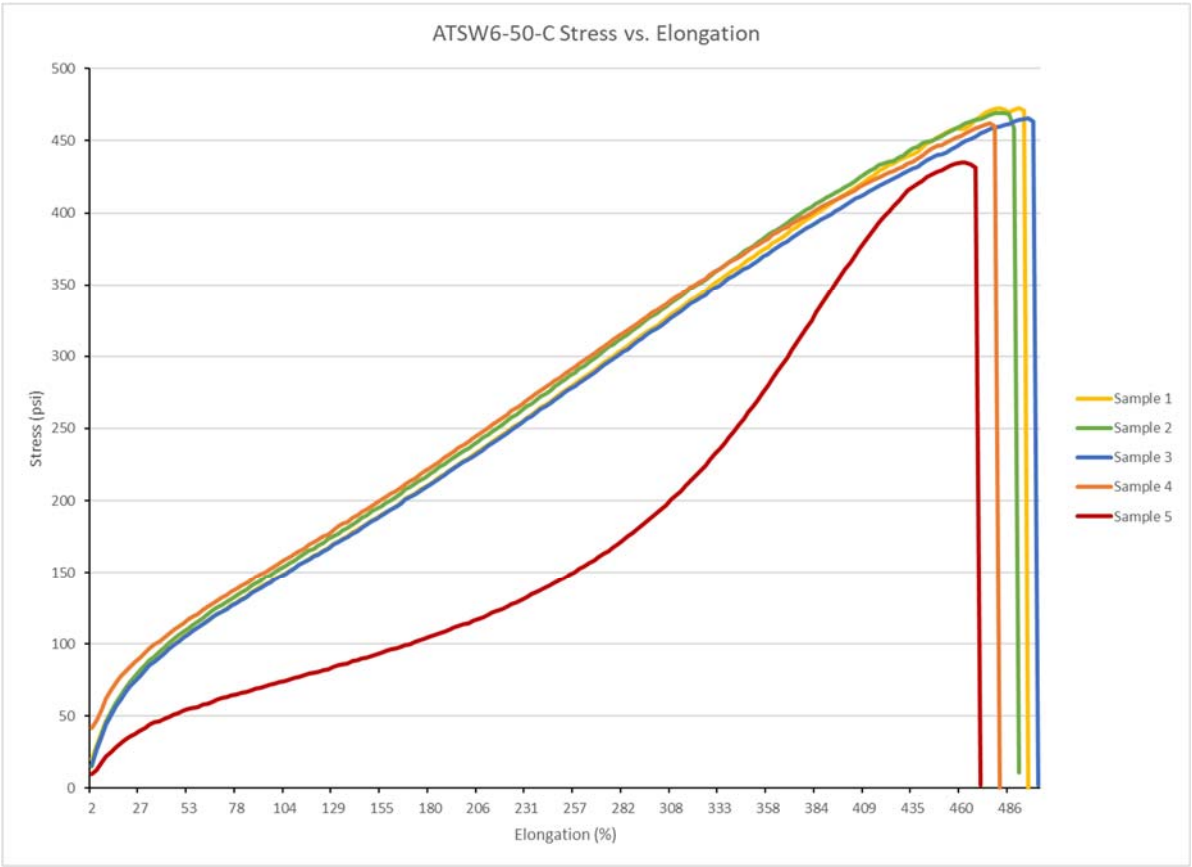


Figure 15. Tensile Stress vs. Elongation (Week 6, 50% - S2)

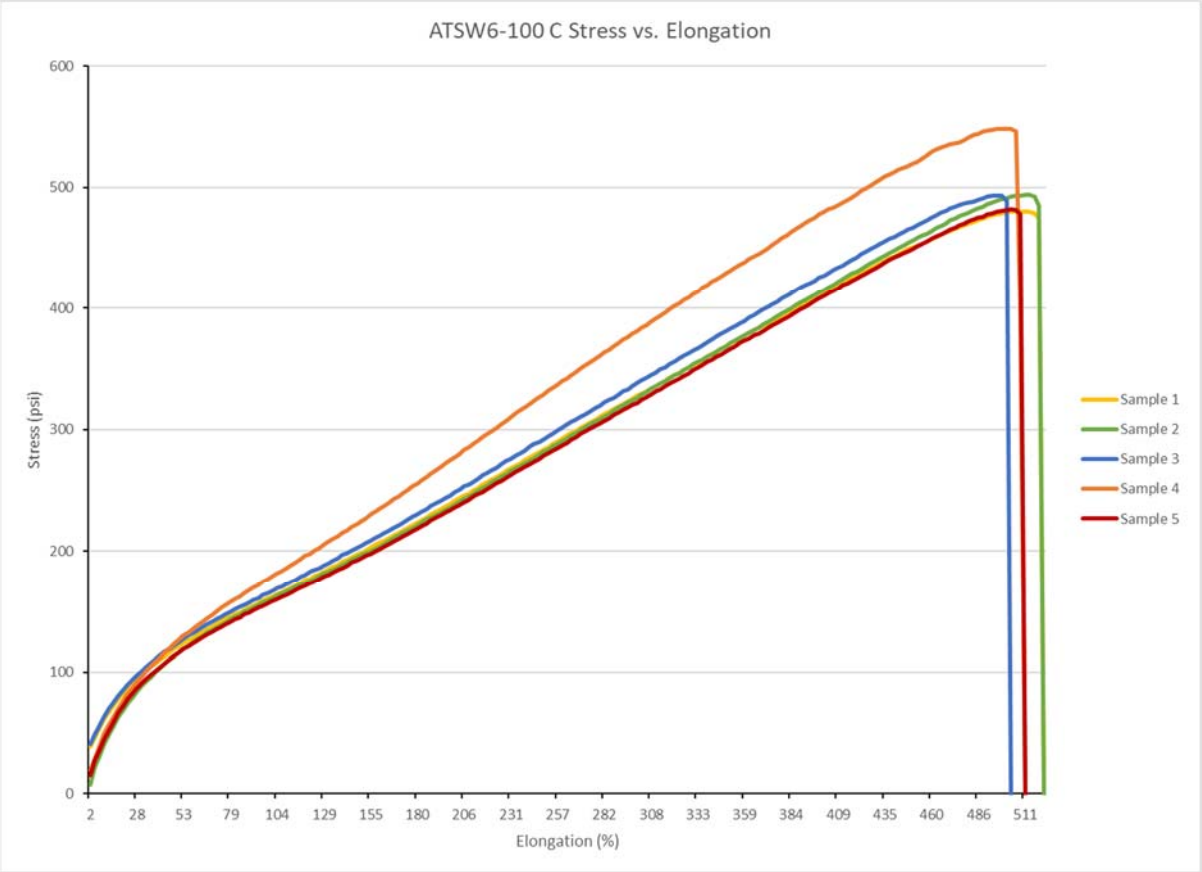


Figure 16. Tensile Stress vs. Elongation (Week 6, 100% - S1)

Determining the lap-shear stress at a specific elongation value for lap-shear samples is more complex. The elongation of lap-shear samples is often not reported, as the primary parameter of interest is the bond strength at failure. The entire length of the bonded sample does not elongate uniformly during testing, in contrast to the gage length of a tensile sample. The elongation value can vary with the basis original length. Assuming samples were approximately gripped just outside the bond edge, the length in between the grips that can stretch is approximately 2 inches (50.8 mm). The base liner in the grips stretches much more easily than the bonded region. The bond area is approximately 1" x 2" or 2 in^2. The cross-sectional area of a single layer of the lap-shear samples is approximately 1" x 0.125" = 0.125 in^2. The elongation solely in the bonded region cannot be determined from existing data.

In Table 5, the average 6-week values of shear stress (load/bond area) and tensile stress in the liner at the lap-shear joint (load/single layer cross-sectional area) at 80% elongation are estimated for S1 and S2 simulants. These values were derived from crosshead displacement and load data for each lap-shear sample for each adhesive system. Bond stress values are relatively low due to the large bond area.

Table 5. 6-Week Lap-Shear Stress and Tensile Stress (single layer) at 80% Elongation

System	6-Week Lap-Shear Bond Stress (psi)	6-Week Tensile Stress (psi)
A	11.5 (S1), 8.9 (S2), 10.2 (avg)	183.7 (S1), 141.4 (S2), 162.6 (avg)
B	12.0 (S1), 10.0 (S2), 11.0 (avg)	191.8 (S1), 160.3 (S2), 176.1 (avg)
C1	11.7 (S1), 11.0 (S2), 11.4 (avg)	186.1 (S1),175.5 (S2), 180.8 (avg)
C2	12.8 (S1), 11.04 (S2), 11.9 (avg)	204.9 (S1), 176.7 (S2), 190.8 (avg)

3.3 Durometer Hardness

Durometer hardness testing was performed per ASTM D2240 using an A-scale instrument. For the liner, the hardness was tested on the black/thicker side, as this side will be exposed to fluid in service. The underlying thinner gray side may influence overall "composite" hardness value but probably not significantly due to the total thickness of the material. It is noted that in ASTM D2240, the sample thickness should be 0.24" or greater. Thinner material can be plied to meet the minimum requirement. Since the primary goal of hardness testing in this case was to evaluate changes due to immersion rather than for quality control, the reduced liner thickness is not considered relevant.

A few Durometer measurements were taken on the gray side for comparison, with the hardness values reading similar to the black side for the baseline sample. For the immersed samples, the gray neoprene bonding layer exhibited slight softening (~45-50A). This is not considered significant as the gray layer will be applied on the adhesive/concrete side and will not be exposed directly to the chemistry.

The hardness of the MARFLEX liner material is specified as 50-65A. A typical Durometer hardness range for elastomers is +/-5A. Multiple Durometer hardness measurements were taken per sheet and reported as an average. Measurements were taken away from edges to minimize edge effects. No significant trend in hardness data could be determined for either simulant over the immersion period, but all measured values were within the 50-65A range.

3.4 Paver Interrogation

Concrete pavers with bonded liner sheets with seams are shown in Figures 17-28. Pavers were marked and designated as listed in Table 4. Pavers marked with Axx numbers were bonded with System A (Normac) adhesive. Pavers marked as PR-xx were bonded with the REMA adhesive (System B). Pavers marked as P+xx and PExx were bonded with Abtrex C1 and C2 adhesives respectively. The perimeter and seam edges were interrogated using a blunt screwdriver (corners slightly rounded, no sharp point loads), approximately ¼" width tip.

This is a subjective method, but a best effort was made to interrogate all locations using the same manual pressure at the same angle for fair comparison. Forces and angles were not measured or controlled. Areas that were easily debonded or where fluid (simulant or adhesive) was observed to squeeze out under applied pressure were marked with arrows and lines as shown in the photographs.

Pavers bonded with each adhesive system are discussed below. A summary of paver observations is given in Table 6.

System A pavers (Figures 17-20) showed many small localized areas, some pavers more than others, that all seemed to be related to the tie gum or the very thin skived layer at the edge. These appear to be either due to trapped air pockets or blisters at the edge. None were noted to expel fluid when pressed. All of these areas were relatively shallow, only extending approximately 1/16"-1/8" into the skived edge and did not extend under the bulk thickness of the bonded sheet, at least not without significant effort.

System B paver PR-03 (Figure 23) was considered the only paver to be defect-free. No areas of delamination or debondment were found on that particular paver with reasonable interrogation effort. Paver PR-04 (Figure 22) showed one area with about 1" length of debonding, found by lightly tapping the screwdriver along the edge, which finds a weak spot relatively well. Areas tend to be either well-bonded or relatively easily debonded.

In comparison, System C1 and C2 pavers showed relatively more extensive debonding or expelling of fluid upon pressing. For example, paver P+01 (S1-1000 hrs) exhibited an area approximately 2" long that was not well-bonded and could be worked loose with minimal effort. Several areas of weeping fluid were observed, with some being observed prior to or just after transfer from SREL without pressure or interrogation and some being noted during interrogation. Paver P+02 (S2-1000 hrs) was found essentially loose along the majority of the entire length of the seam (Figure 26). Upon interrogation, the bond was found to be relatively weak and could be propagated with negligible effort. Another debonded area, approximately 3-4" length around perimeter, was observed on the same paver.

Similar observations were made for System C2 pavers (PE-01 and PE-02) though with perhaps less overall length of perimeter or seam being affected. Paver PE-02 (S2-1000 hrs) in Figure 28 shows debonding at one corner, approximately 1" along the perimeter on one side and approximately 2" along the perimeter on the other side.

Paver seam/sheet bonding behavior is complicated by the fact that adhesive behavior is a combination of workmanship (edge skiving, pressure applied, amount of adhesive/coverage, cure time, air entrapment and other factors), inherent adhesive properties and possible exposure effects. Distinguishing between the effects of these factors is difficult. It is assumed that all paver and sheet samples were bonded and cured in accordance with adhesive manufacturer instructions and by personnel experienced with each adhesive system.

In summary, System A pavers exhibited many small unbonded regions along the edges of seams and skived edges. The cause is unknown, but may be attributed to air entrapment, solvent evaporation or workmanship issues. None of the areas were observed to extend much beyond the outermost skived edge of either the seam or sheet perimeter. These regions did not seem to get progressively worse from examination at 500 and 1000 hrs in either simulant. These observations are consistent with those made by SREL personnel [23].

These regions were not observed on other adhesive systems and samples. The cause of the edge blistering/delamination is unknown and may be related to workmanship, application method, cure times or other factors. The impact of such regions on leaktightness is also unknown. These regions did not seem to get progress from 500 to 1000 hrs in immersion, but the regions were also not subject to any significant hydrostatic pressure.

Only one paver (System B, REMA, PR-03) showed essentially defect-free behavior, with no significant blistering, debonding or fluid seepage observed. This observation indicates that if this adhesive is properly applied and cured, defect-free seams can be made. Other System B pavers showed minor debonded regions and/or expelled fluid. The cause of variation in paver performance with a given adhesive system is unknown.

In comparison, System C1 and C2 pavers showed more extensive delamination or debonding, regions of leaking fluid and/or easily loosened material. Based on these observations, System C1 and C2 pavers are considered unsatisfactory. It is unknown whether the observed behavior of System C1/C2-bonded sheets and pavers is due to workmanship, inadequate sample preparation/curing or inherently inferior adhesive properties, at least under the conditions tested. The C1/C2 adhesives may simply not be compatible with or well-suited for bromobutyl liners.

Table 6. Summary of Paver Interrogation/Observations

System	Marking	Simulant	Immersion Time	Observations
A	A01	S1	500 hrs	Many small disbonded regions, 1/8” deep, edges and along seam
A	A02	S1	1000 hrs	Many small disbonded regions, 1/8” deep, edges and along seam
A	A15	S2	500 hrs	Fewer small disbonded regions 1/8” deep, along seam
A	A16	S2	1000 hrs	Fewer small disbanded regions, 1/8” along edge and seam
B	PR-01	S1	500 hours	Few disbanded regions, along edge, ¼” deep, slight fluid
B	PR-02	S1	1000 hours	Few disbanded regions, along edge, ¼” deep, slight fluid
B	PR-03	S2	500 hours	No disbanded or delaminated areas noted
B	PR-04	S2	1000 hours	Few disbonded regions noted, one region (~1” long”) in seam
C1	P+01	S1	1000 hours	Many disbonded regions, majority of seam, expelled fluid
C2	PE-01	S1	1000 hours	Several disbonded regions, ½” deep, expelled fluid
C1	P+02	S2	1000 hours	Many disbonded regions, majority of seam, expelled fluid
C2	PE-02	S2	1000 hours	Several disbonded regions, ½” deep, expelled fluid

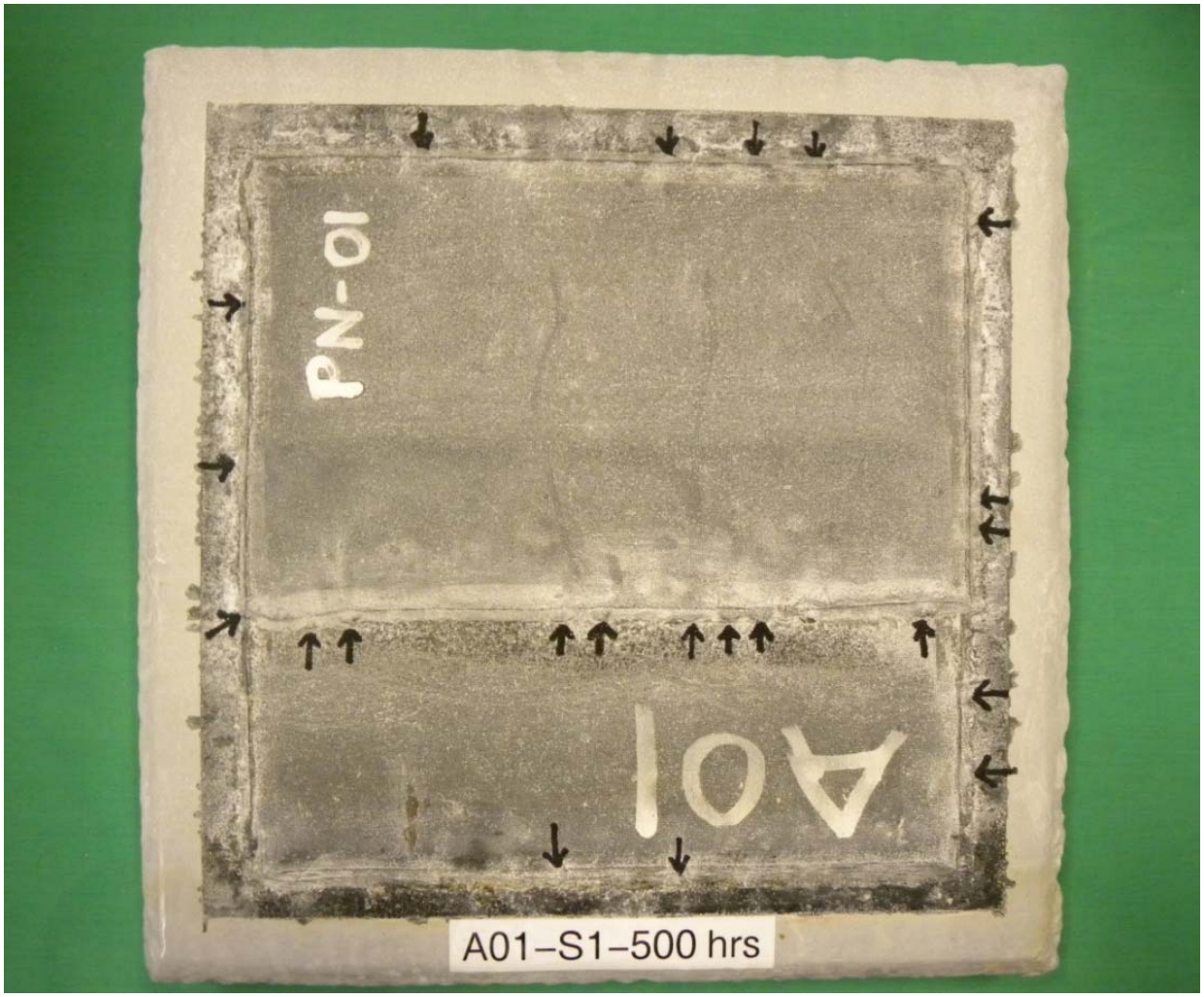


Figure 17. System A Paver, S1 simulant, 500-hour immersion

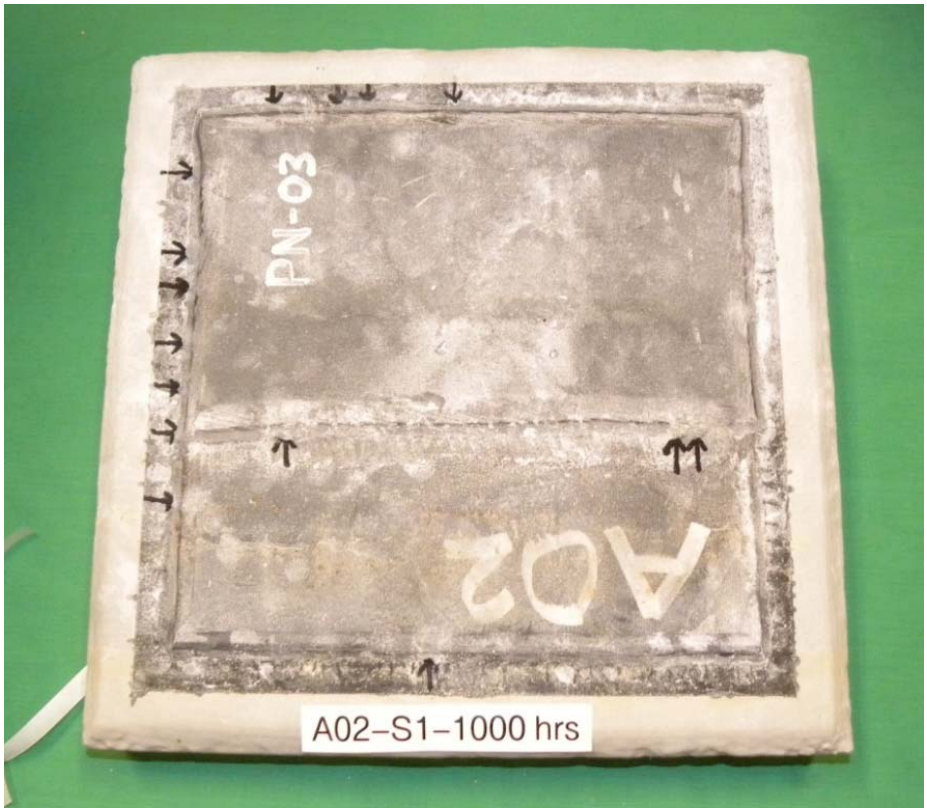


Figure 18. System A Paver, S1 Simulant, 1000-hour immersion

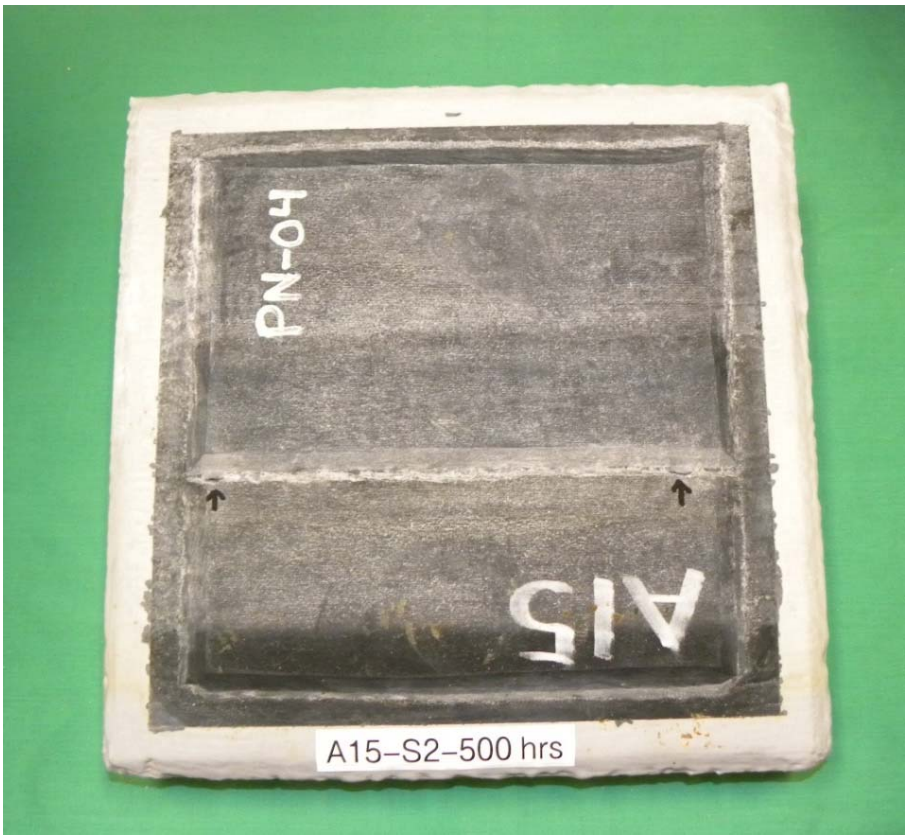


Figure 19. System A15 Paver, S2 simulant, 500-hour immersion

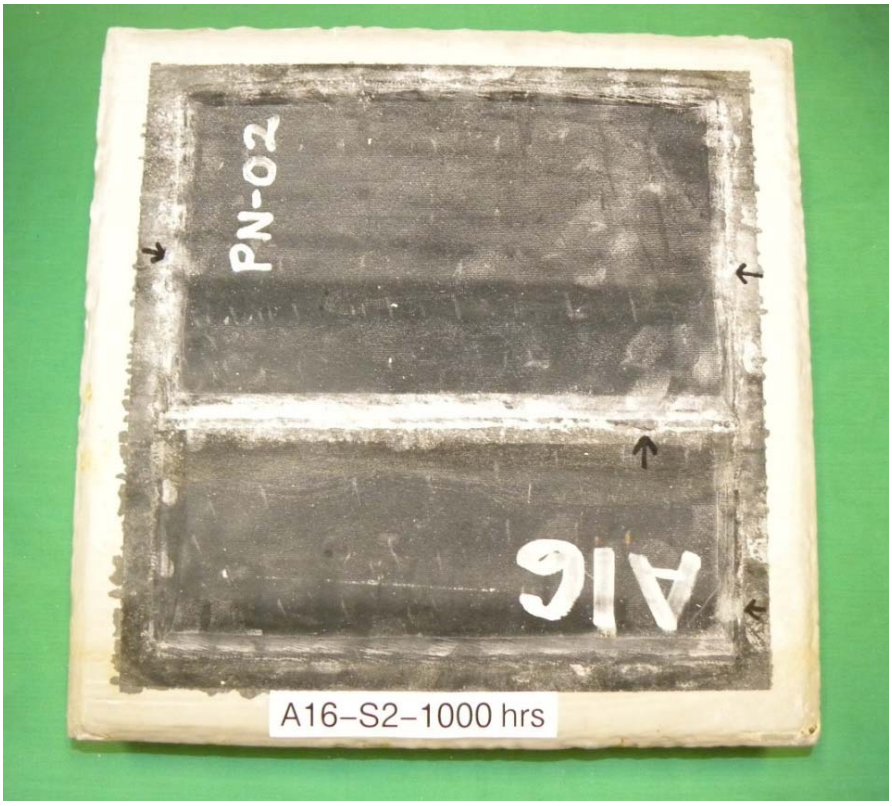


Figure 20. System A Paver, S2 Simulant, 1000-hour immersion

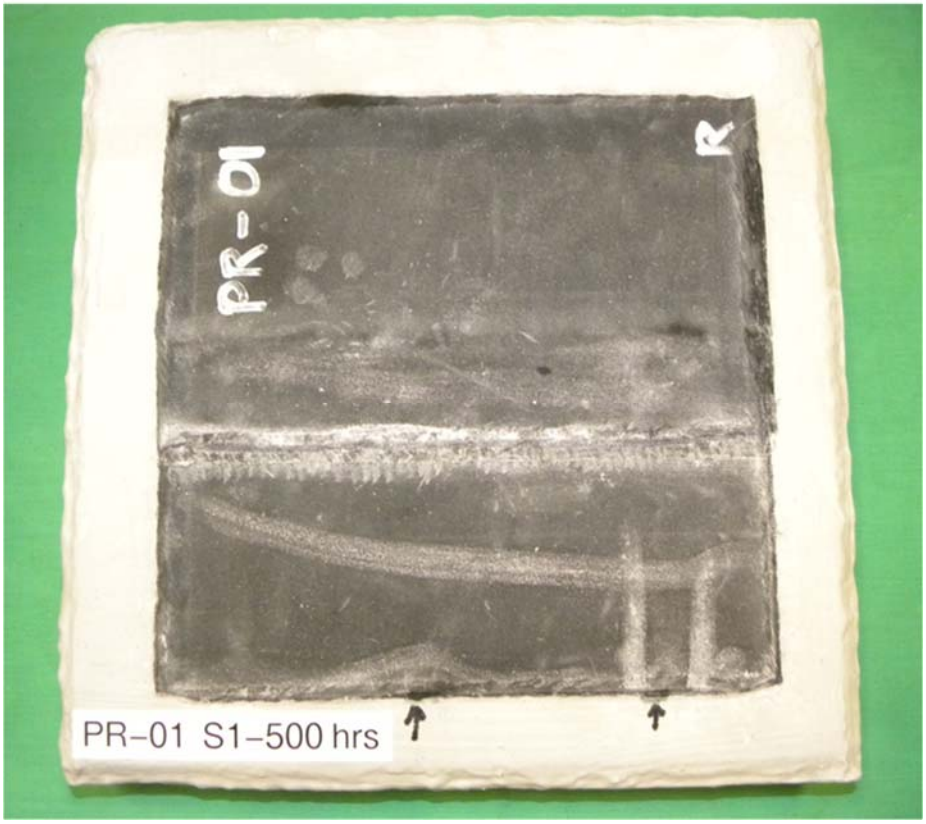


Figure 21. System B (REMA) Paver, S1 Simulant, 500-hour immersion

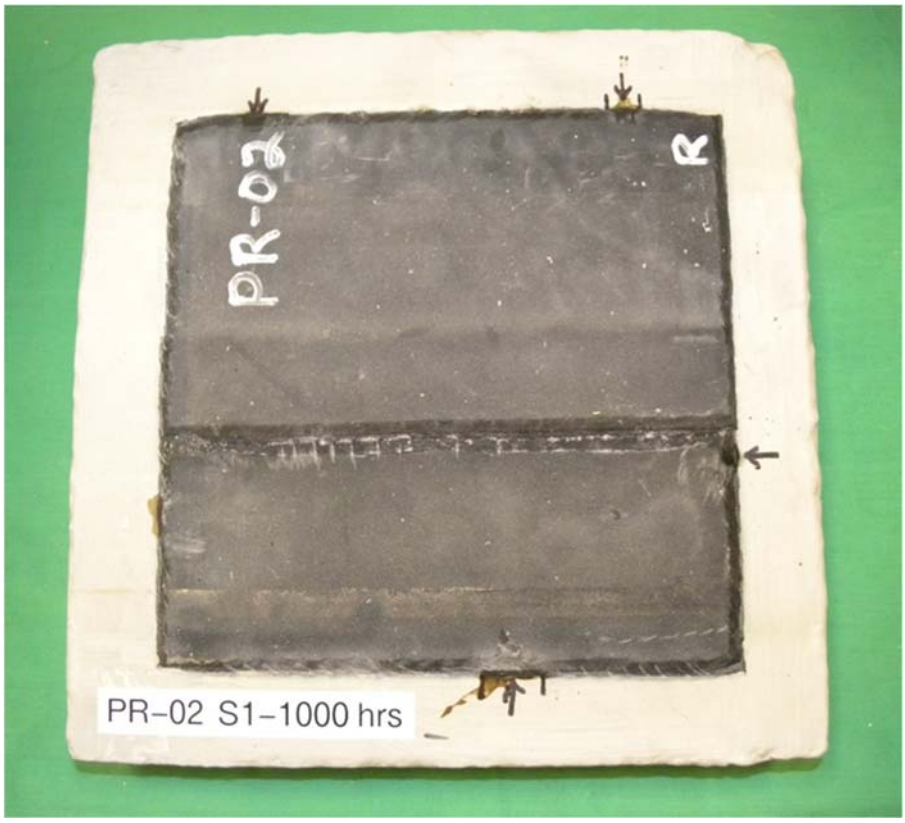


Figure 22. System B Paver, S1 Simulant, 1000-hour immersion

Figure 23. System B Paver, S2 simulant, 500-hour immersion (no defects or debonded areas)

Figure 24. System B Paver, S2 Simulant, 1000-hour immersion

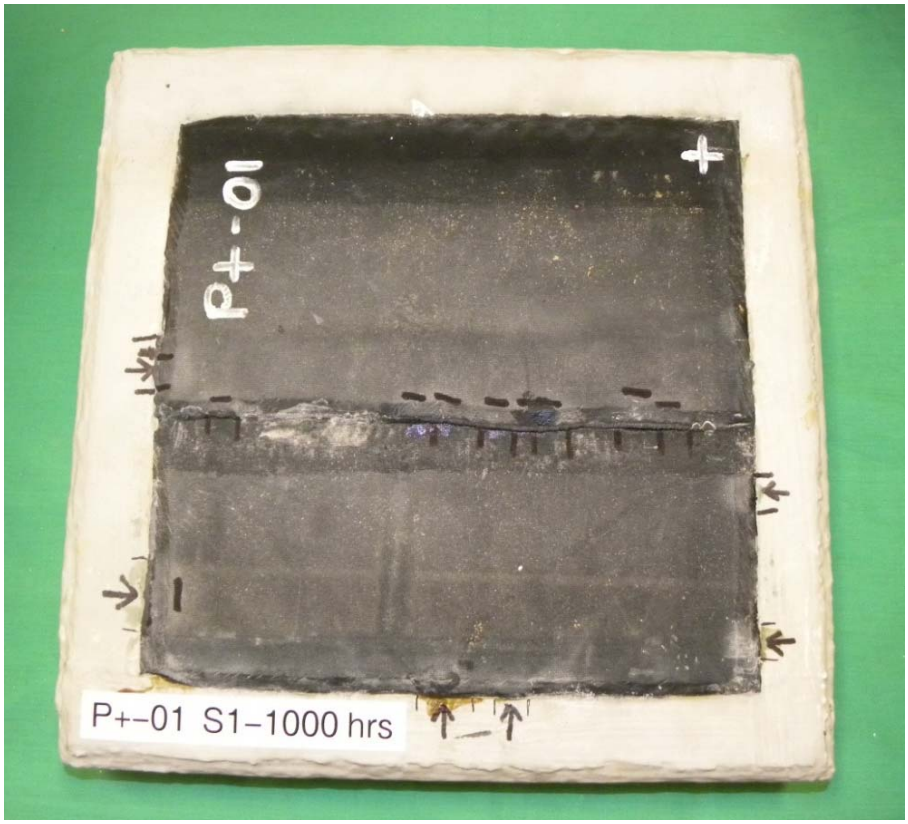


Figure 25. System C1 Paver, S1 Simulant, 1000-hour immersion

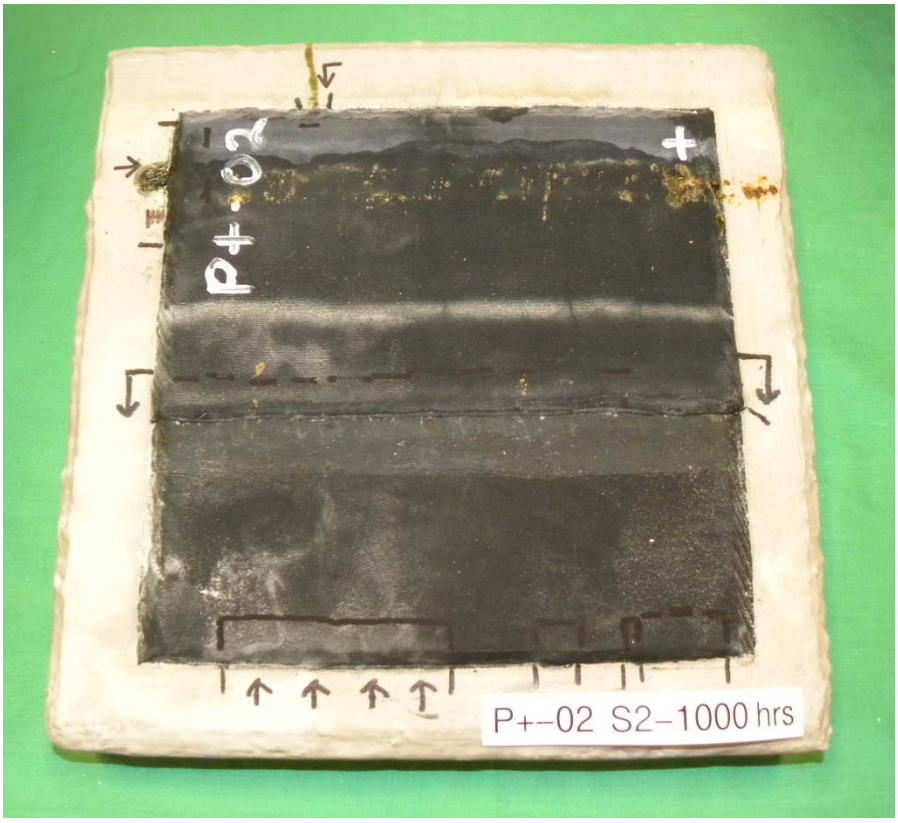


Figure 26. System C1 Paver, S2 Simulant, 1000-hour immersion

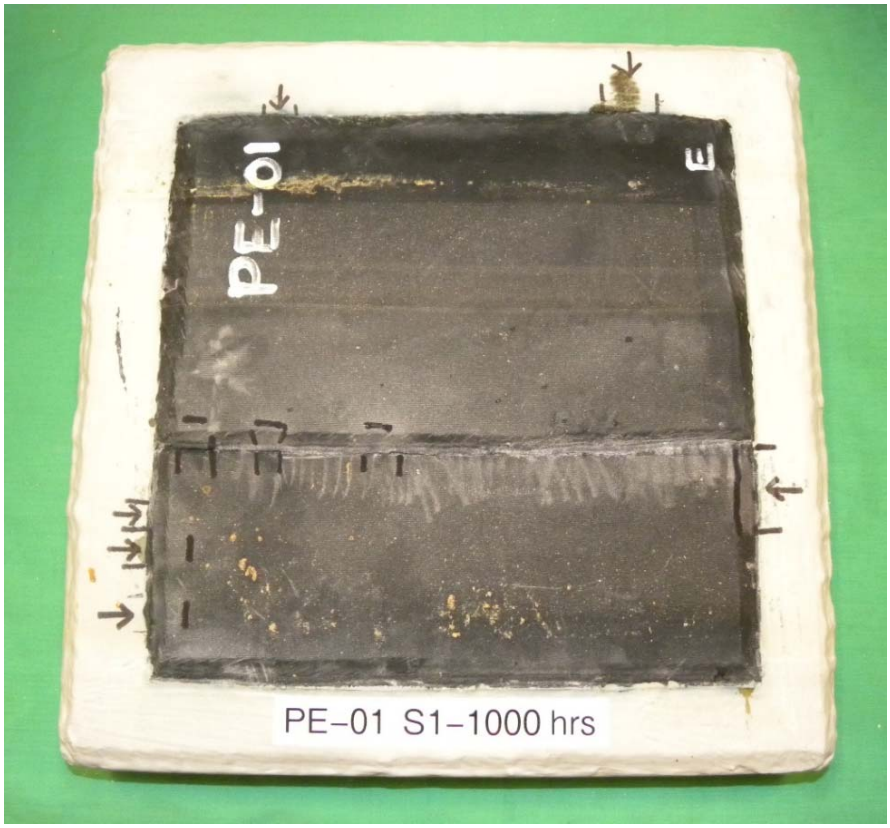


Figure 27. System C2 Paver, S1 Simulant, 1000-hour immersion

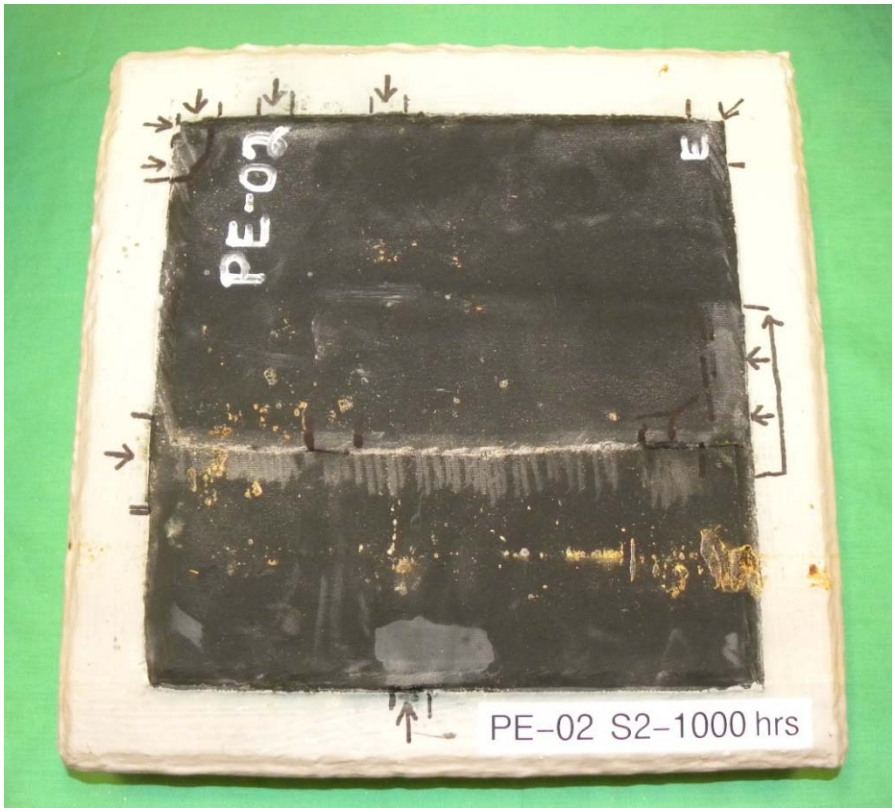


Figure 28. System C2 Paver, S2 Simulant, 1000-hour immersion

4.0 DISCUSSION & OBSERVATIONS

4.1 Base Liner Mechanical Properties

The average tensile strength (~825 PSI) of the MARFLEX liner was reduced by approximately 40% during the 1000-hour immersion test to a relatively asymptotic value of 500 PSI for both S1 and S2 simulants. The trendline of the average tensile strength values for the S1 simulant is relatively smoother than for the S2 simulant, cause unknown. The data suggest no significant effect of simulant composition on tensile strength reduction. The absolute value (500 PSI) is only ~12% less than the average final tensile strength of the REMA 4CN bromobutyl liner tested for and installed in SDU6.

The average elongation at break (540%) of the MARFLEX liner was reduced by approximately 25% to around 400%. The elongation data showed some leveling off, but less asymptotic behavior than the tensile strength data. All values were within the range cited by the liner manufacturer (Blair Rubber, 200-600%, nominal 350%). The final values are also comparable to the nominal elongation at failure value cited for the REMA Chemoline 4CN liner used in SDU6 (380%).

The apparent reductions in tensile strength (~40 %) and elongation at failure (~25%) both exceed the 20% property loss threshold for acceptance in the test plan. The criterion is consistent with chemical compatibility rating references and was included in the test plan to provide an objective comparison point. It is noted that no such property loss criterion was established in SDU6 liner testing.

If the 20% property loss threshold were an absolute criterion, the MARFLEX liner would not be acceptable for the intended service. Ideally, the mechanical properties of the liner should not significantly change with exposure, indicating excellent compatibility. However, the property changes observed should be viewed with perspective. The post-immersion properties are not significantly different from those of the REMA liner installed in SDU6, though the % reduction in properties of the REMA liner was less. The post-immersion properties of the MARFLEX liner also well exceed the minimal requirements determined by the project for movement at the wall/floor joint.

4.2 Lap-Shear Data/Behavior

The overall lap-shear behavior of all samples and adhesives showed similarity, with early reduction in peak load values in the first 1-2 weeks, followed by subsequent increase in later weeks. Some observations from the lap-shear data show a spike in lap-shear strength between weeks 3 and 4 in systems B, C1, C2, but not system A. This may be attributed to slippage in the grips, likely caused by the rubber samples thinning too quickly before the self-tightening grips could not tighten sufficiently to hold the samples. Salt precipitation on the surfaces also made the samples slippery. This was corrected by making a shim out of untested smooth rubber and sandpaper to grip the sample.

Observations for each adhesive system are described below. Metrics used for adhesive system comparison are given in Table 7. System A had the lowest values in all but one category (baseline bond strength, the highest). System B had the highest values in the most categories listed in Table 7 (3 total), and had the second-highest values listed in the most categories (4 total).

System A

System A samples experienced a steady decline in bond strength retention as testing progressed. System A did have the highest average baseline bond strength. However, the “final” System A peak load values were the lowest of all systems, though interval values for System C1 were lower (Week 5). System A also had the lowest average % retention in both S1 and S2 simulants and 100% samples at 52.8% and 55%, respectively. The only noticeable trend in the retention is between the first two weeks of testing the retention increased, which could have been caused by the samples becoming more saturated. Another factor to note for System A samples is that shims were not used. Deterioration at the seam was also noted in later System A samples prior to testing.

System B

System B showed overall more retention of lap-shear strength over time than other samples, though the 6-week final strength of the System C2 samples (S1 only) was higher than the final values for System B. Notable for System B samples is that the majority failed outside the bond in the base material, which is desirable. System B had the second highest average % retention of lap-shear strength in both sample groups, at 75.6% (S1) and 80.9% (S2), respectively. In addition, System B samples showed the highest 6-week overall average bond strength. There was also less deterioration of the bond at the edges noted prior to testing as compared to System A samples.

System C1

System C1 samples seemed to follow the same trend as System B, also requiring the use of shims to minimize slipping from the grips before failure. System C1 had the highest % lap-shear strength retention in both simulants, at 81.9% and 81.5% for the S1 and S2 simulants, respectively. System C1 experienced less slippage than System B. However, baseline System C1 bond strength values were lower than all other systems and were only marginally higher than the final values for System A, which were the lowest final values for all adhesives.

System C2

System C2 samples followed the same trends as Systems B and C1, with shims required to avoid slippage. Another difference noted in System C2 was the difference in the weld geometry, as there was more noticeable deterioration at the edges of the weld in C2 prior to testing compared to B and C1. This may have been a factor in the difference in results between C2 and the other three systems. System C2 had the second lowest average % retention of the four systems, at 63.7% and 65.9% for the S2 and S1 simulants respectively. System C2 experienced less slippage during the testing, which may be attributed to the shims, or possibly the deterioration at the weld being more noticeable than the other systems, allowing failure to occur before slippage became an issue. C2 also showed the most variation in final 6-week values for S1 and S2 simulants (65.7 and 49.8 lb/inch, respectively).

Table 7. Comparison Metrics for Adhesive Systems (values are averages per condition)

System	Baseline Bond Strength (lb/inch)	Final Bond Strength - S1 (lb/inch)	Final Bond Strength - S2 (lb/inch)	% Bond Strength Retained S1	% Bond Strength Retained S2	6-week Avg S1 (lb/inch)	6-week Avg S2 (lb/inch)
A	72.9	44.1	43.9	52.8	54.9	50.1	47.9
B	69.1	62.0	56.6	75.9	80.9	58.9	60.4
C1	51.3	46.7	52.9	81.5	81.9	51.9	50.9
C2	68.1	65.7	49.8	65.9	63.7	44.1	51.9

Note: Highest values per category in green, 2ND-highest values in blue, lowest values in red

4.3 Liner Bonded to Concrete Paver Behavior

Strict interpretation of acceptance criteria outlined in the test plan (no delamination) would mean that none of the adhesives tested are acceptable. This is true for bonded sheet panels as well as pavers. Delamination was not specifically defined, but the intent was to note areas that may be suspect for either leakage or reduced bond integrity.

All pavers, with one exception, showed at least some degree of disbondment or delamination. Only System B (REMA) showed one paver that is considered defect-free, though this was not observed for all System B pavers. This suggests that System B can be very effective if properly applied and cured.

System A pavers showed many minor regions of blistering and/or debonding along the bonded seams and around the liner perimeter, though these regions appeared to be limited to the skived edge and did not progress farther into the bonded joint. It is unknown whether this behavior would progress over time in immersion after installation. The behavior was observed fairly early during SREL immersions and did not progress significantly from 500 to 1000-hour intervals. The cause of the edge blistering or debonded areas is unknown, but was not observed in other System pavers.

In comparison, the C1 and C2 Abtrex adhesives exhibited more extensive delamination, both in terms of the affected bond length and depth of penetration, also the relative ease of debondment. Edges could be lifted and debonded with relatively little effort. This behavior is consistent with the delamination observed in bonded sheets during immersion by SREL. It is assumed that these adhesives were applied and cured per product requirements.

The pre-immersed sheets and pavers are assumed to have been prepared as they would be during actual installation prior to service. It is noted that none of these samples were subjected to head pressure during immersion, so joint integrity at bounding hydrotest conditions cannot be determined from this evaluation.

Collectively, these observations indicate that liner seam performance is significantly dependent on the quality of the application, as well as the inherent properties of the adhesive. The best adhesive can fail if not properly applied and cured. This aspect is likely the most important of any seamed liner system.

4.4 REMA 4CN vs. MARFLEX Comparison

A brief comparison of test results for the MARFLEX and REMA 4CN liners is provided in Table 8. It is recognized that while both liners were tested in essentially the same manner, some variations exist. The main variations are: 1) interval data were not obtained for REMA 4CN material, 2) variation in the lap-shear joint configuration, 3) only one adhesive tested for the REMA 4CN material and 4) use of Die C vs. Die D for tensile samples. Values in Table 8 are overall averages unless otherwise specified.

Table 8. Comparison of REMA 4CN (SDU6, 2016) and MARFLEX RCHB60HT (current)

Property/Metric	REMA 4CN	MARFLEX
Baseline Tensile Strength (psi)	584.7	825
Final Tensile Strength (psi)	556 (S1), 579.8 (S2)	500 (S1), 460 (S2)
% Retained Tensile Strength	95.1 (S1), 99 (S2)	60.6 (S1), 55.8 (S2)
% Tensile Strength (Baseline/Nominal)	80.7	68.8
Lap-Shear Strength (lb/inch)	61.5 (baseline), (56.4, 61.8)	A (44.1, 43.9), B (62.0, 56.6) C1 (46.7, 52.9), C2 (65.7,49.8)
% Retained Lap-Shear Strength	101 (S1), 91.7 (S2)	A (52.8, 54.9), B (75.9, 80.9) C1 (81.5, 81.9), C2 (65.9, 63.7)

Note: Data for lap-shear are given for both S1 and S2 simulants as (S1 value, S2 value).

Overall, the MARFLEX liner showed a greater reduction in liner mechanical properties and lap-shear strength than the REMA 4CN liner installed in SDU6. The REMA 4CN liner showed only a ~5% reduction in average tensile strength and ~8% reduction in average lap-shear/bond strength after 6-week immersion S1 and S2 simulants in previous testing. The degree of curing for the REMA 4CN material prior to immersion is unknown. In comparison, the MARFLEX liner showed a near-40% reduction in average tensile strength, 25% reduction in elongation at break and lap-shear reduction in current testing.

However, the final average tensile strength of the MARFLEX liner was only ~12% less than the final average tensile strength of the REMA 4CN liner. Final average lap-shear bond strength values of MARFLEX in current testing ranged from ~180-280N (41-63 lb-force), with the higher end of the range comparable to the 250-275N (56-62 lb-force) range observed for REMA 4CN lap-shear samples in previous testing.

Direct comparison of SDU6 and SDU7 liner test data is difficult due to variation in simulant compositions, immersion bath temperatures and lap-shear sample configurations. The limited number of samples in both test rounds may be a factor, but results in most cases were relatively consistent. Side-by-side testing of both liners under the exact same conditions and joint configurations would ideally be required to evaluate the effect of such variations.

4.5 FTIR Spectroscopic Analysis

Analysis of the REMA 4CN and MARFLEX bromobutyl liners was performed via FTIR (Fourier Transform InfraRed) spectroscopy by SRNL (F. Fondeur/Separation Sciences & Engineering). FTIR spectroscopy is commonly used to analyze and identify polymeric and organic materials. Testing was performed for generic comparison only. Other methods such as Raman spectroscopy and NMR (nuclear magnetic resonance) spectroscopy are used to analyze polymeric materials and molecular structures. Methods such as XRF (X-ray fluorescence) and XRD (X-ray diffraction) can be used to identify elements and crystalline compounds that may be present as fillers, stabilizers and other additives. Thermal methods including TGA (Thermogravimetric Analysis) and DSC (Differential Scanning Calorimetry) can be used to differentiate materials based on their thermal properties. A good discussion of bromobutyl compounding and formulation ingredients is given in References 34, 38-42.

The analysis performed was not intended to identify all aspects of the liner formulation, as several tests would likely be required to obtain such information. Specific formulations of both bromobutyl liners may be obtained with non-disclosure agreements (NDAs) if lining manufacturers are willing to provide.

Butyl (IIR) rubber is essentially a copolymer of isobutylene and about 2 mol% isoprene, with structure below [Figure 29, Reference 38]. Bromobutyl is made by blending elemental bromine in a hexane solution of butyl rubber at 50 °C. Final bromobutyl grades typically have about 2 wt% bromine. Butyl rubber is typically sulfur-cured, whereas halogenated versions can be cured either by sulfur or peroxides for crosslinking, depending on saturation levels. Zinc oxide (ZnO) is commonly used as a curing agent with stearic acid and other accelerators [34, 38-42].

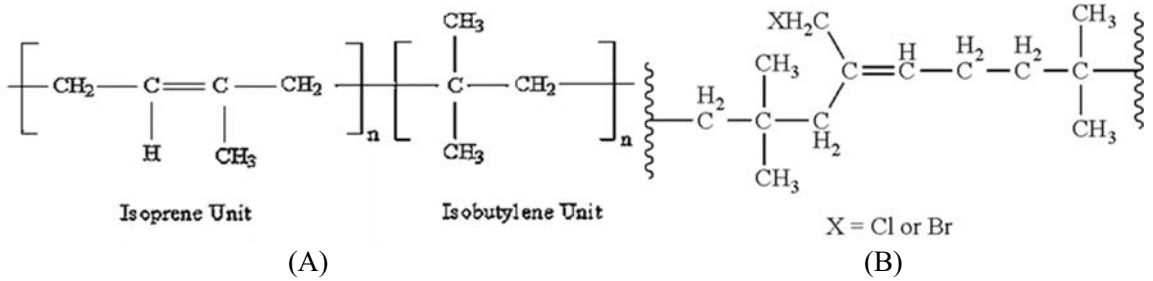


Figure 29. General structure of butyl (IIR) rubber (A) and halobutyl structure (B) [38]

The FTIR spectra for bromobutyl and neoprene bonding layers for both REMA 4CN and MARFLEX liners are given in Figures 30-33. Neoprene (polychloroprene) is distinguished by peaks at wavenumbers of 1743, 1650 and 1530 cm^{-1} (see red spectrum in Fig. 30) while the FTIR spectrum of bromobutyl rubber is distinguished by the doublet at 1381 and 1368 cm^{-1} due to the tert-butyl group (-C-$(CH_3)_3$). C–Cl stretches appear from 850–550 cm^{-1}, while C–Br stretches appear at slightly lower wavenumbers from 690-515 cm^{-1}. In terminal alkyl halides, the C–H wag of the –CH_2X group is seen from 1300-1150 cm^{-1} [41].

The FTIR spectrum for bromobutyl in Figure 30 is similar to the reference FTIR spectra for bromobutyl shown in Figure 31 (Reference 41). Only minor variations are observed. Figure 30 also shows the FTIR spectra of the Rema 4CN material for different positions across the cross-section of the two bonded layers. The spectra at the interface (spectrum colored red) showed a relatively higher concentration of neoprene (as if the neoprene penetrated into the bromobutyl layer) but also a relatively high concentration of CH_2 groups, polar and unsaturated groups (C=O and C=C) possibly indicating a third substance, possibly natural rubber. The spectra in Figure 30 suggests the neoprene layer contains a silicate filler (including quartz) while bromobutyl liners appear to contain a carbon filler.

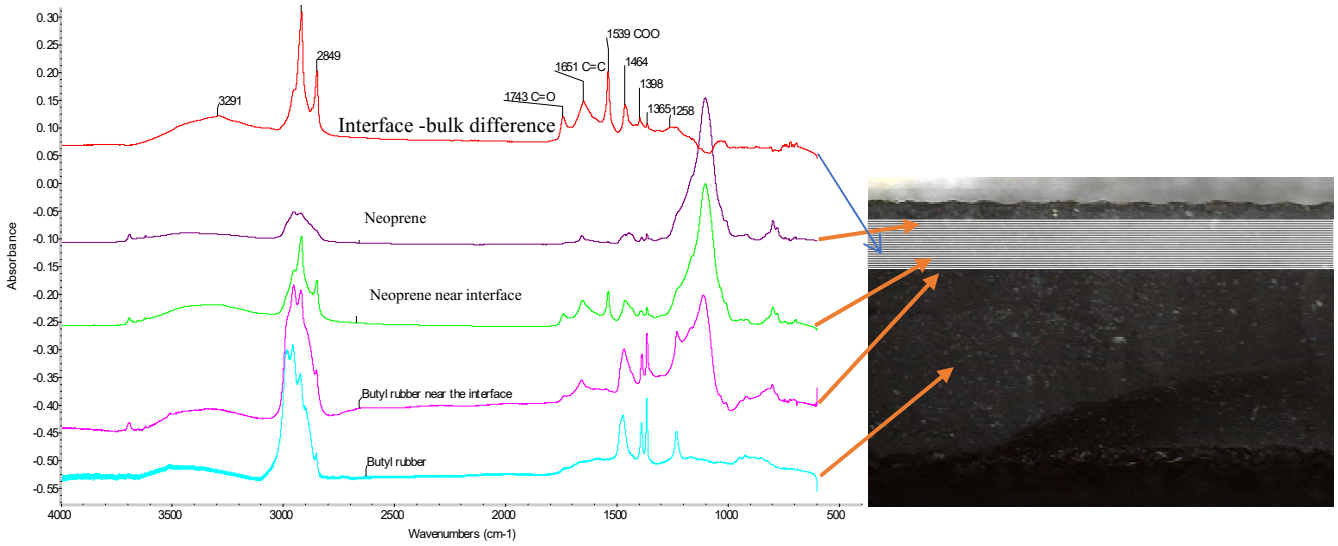


Figure 30. FTIR Spectra for REMA 4CN (bromobutyl base layer, neoprene bonding layer)

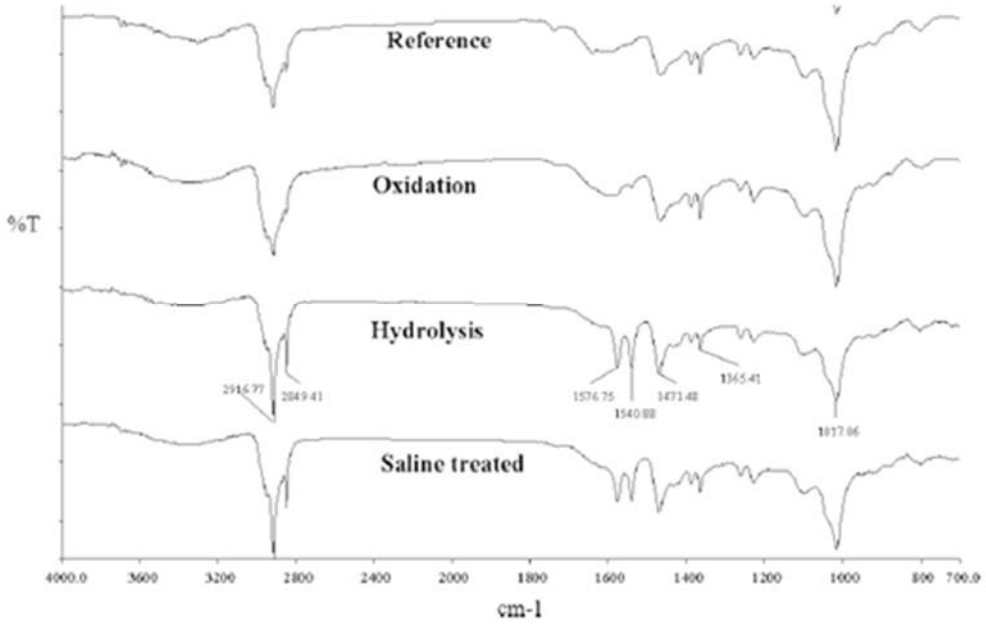


Figure 31. Reference FTIR spectra for bromobutyl elastomer [41]

In the case of the Marflex double-layer material, the FTIR analysis indicate a clean interface between the neoprene and bromobutyl layer. The interfacial spectrum (top spectrum in Figure 32) obtained by subtracting both the bromobutyl and the neoprene layers indicate an enrichment of unsaturated groups (C=C), polar groups (C=O) and possibly OH (or NH) groups.

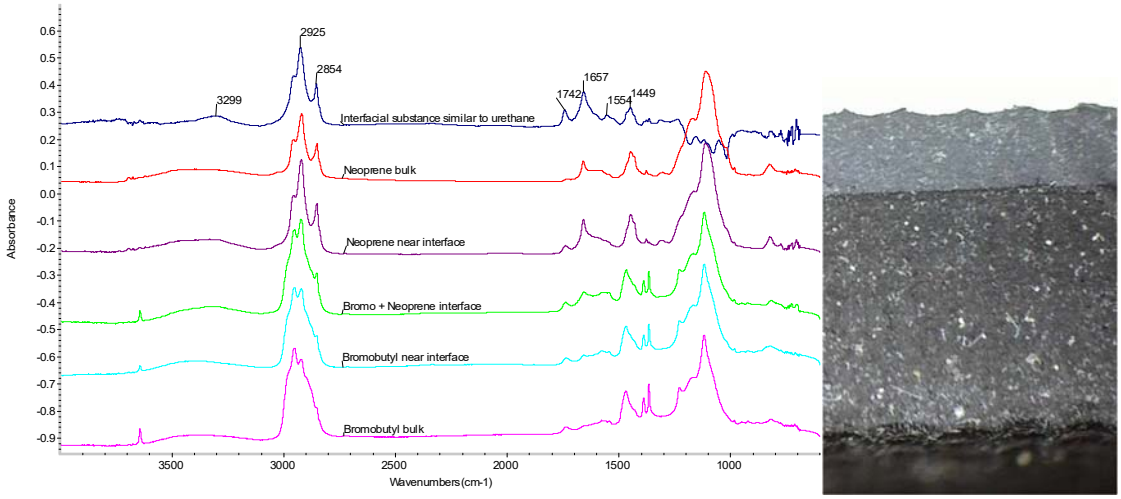


Figure 32. FTIR Spectra for MARFLEX Bromobutyl Liner

To determine differences between the two bromobutyl layers, the FTIR spectra of the REMA 4CN and MARFLEX bromobutyl layers are shown in Figure 33. The primary difference appears to be the presence of a large peak at ~1118 cm^{-1} in the MARFLEX bromobutyl layer, which is absent in the REMA 4CN bromobutyl layer. This peak is most likely attributed to a silicate filler, which has a strong IR peak around 1100 cm^{-1}. Variations in peak positions and the number of peaks is seen with different forms of silica from amorphous silica to quartz. Amorphous clay, for example, has a very intense, broad peak centered at 1095 cm^{-1}, while quartz exhibits an intense broad band around 1100 cm^{-1} combined with sharper bands at 795, 775 and 690 cm^{-1} [43]. Overall, with exception of the silicate/quartz filler in the MARFLEX, both materials appear to be very similar in composition.

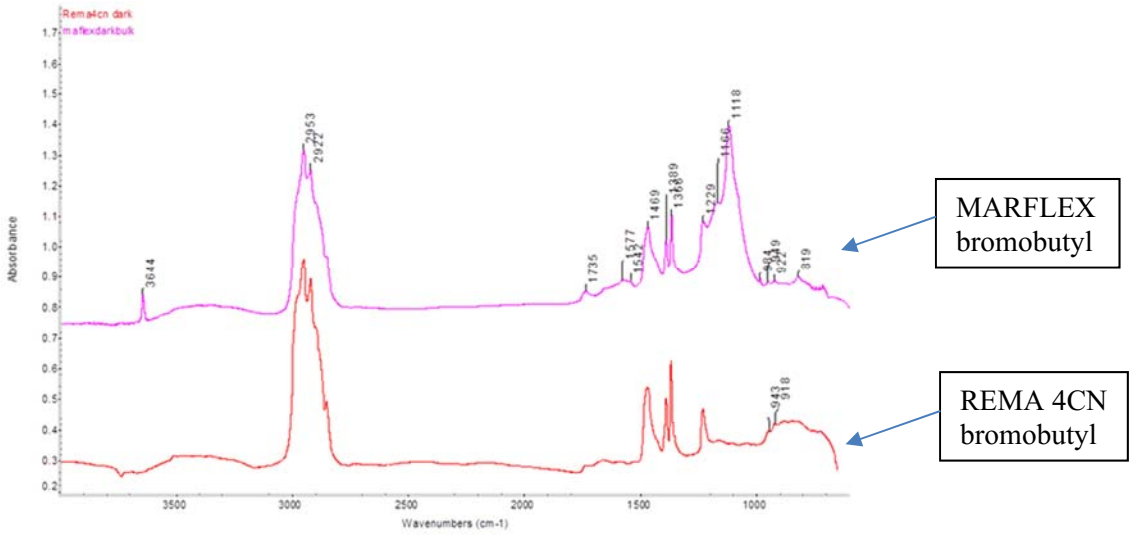


Figure 33. FTIR Spectra overlay of REMA 4CN and MARFLEX dark (bromobutyl) layers (Note absence of a silicate filler peak in the 1100-1000 cm^{-1} region in the REMA4 CN spectrum)

Similarly, close FTIR examination of the neoprene layer in the MARFLEX and REMA 4CN liners showed minor variations in the neoprene material used in both materials (see Figure 34). The neoprene rubber used in the REMA 4CN material showed a higher concentration of C=C groups (1539 cm^{-1}) and quartz (filler or impurity) while the MARFLEX material has a higher concentration of the -CH-C(CH_3)=CH_2. The specific effects and implications of these variations on liner bonding and performance are not known.

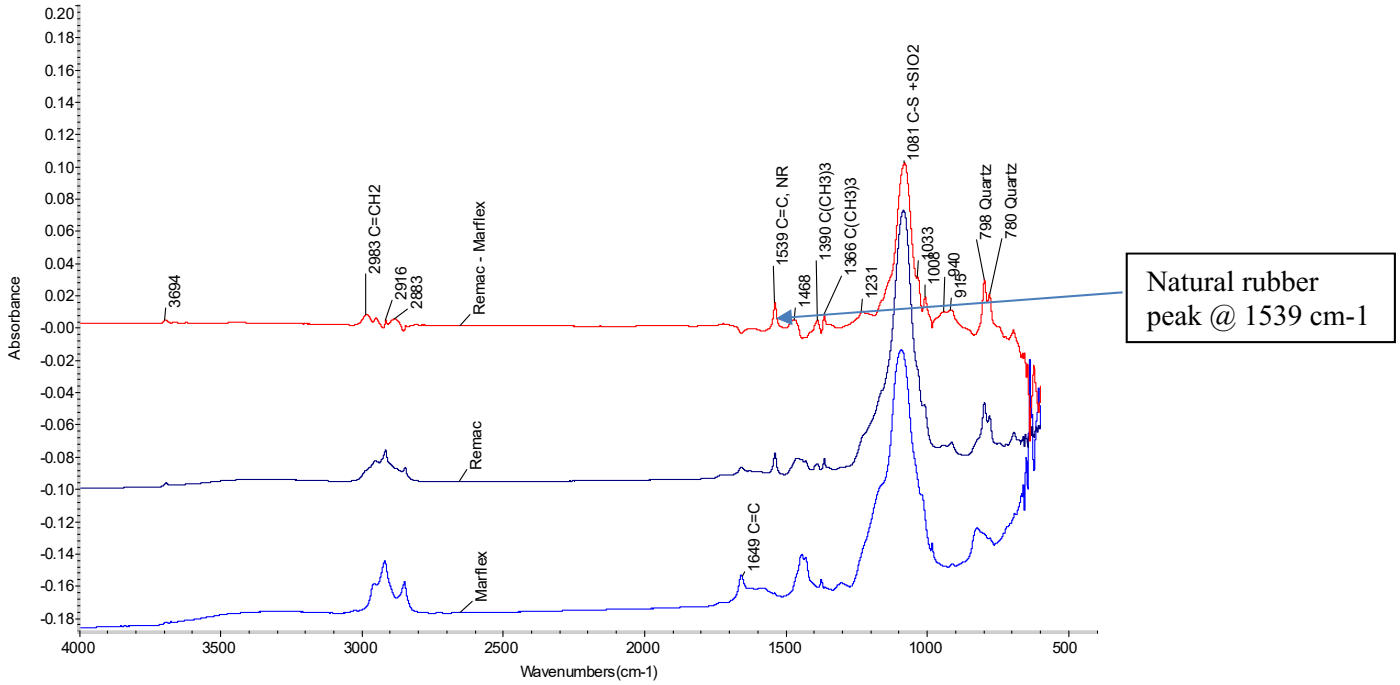


Figure 34. FTIR spectra overlay of REMA 4CN and MARFLEX grey (neoprene) bonding layers (note features associated with natural rubber (1539 cm^{-1}) and isobutylene (1390 and 1366 cm^{-1}) in the REMA 4CN layer relative to the MARFLEX layer

4.6 Considerations for Enhanced Testing

Based on experience from previous and current SDU liner testing, as well as knowledge and input from other test standards, references and polymer degradation studies, SRNL provides a few recommendations for consideration to improve the understanding of liner performance in the SDU environment or similar applications. These are not intended to reflect inadequacies of current or previous test results.

- T-peel or peel strength tests may not reflect stresses imposed during SDU liner installation or in service, though some references suggest that peel strength tests may be more sensitive to immersion/chemical effects than lap-shear tests.
- Short-term mechanical tests (lap-shear or peel) provide information on effects of chemical/immersion and temperature on seam integrity but do not evaluate the effect of chronic stress (creep or stress-relaxation), such as may be imposed in areas of radial growth during hydrostatic testing or service.
- Test panels or sheets ideally should be immersed in the flat or non-stressed condition, unless the effect of stress is of interest and the degree of stress imposed is well-controlled. Testing panels in both stressed and non-stressed states may be worth performing, particularly for seamed samples.
- The potential for leakage at seams due to hydrostatic pressure and the relationship between lap-shear or peel strength and leak performance has not been established. Stronger bonds are generally preferred, but lower strength bonds may provide satisfactory leak performance.
- Current and previous tests are reasonable screening tests based on applicable ASTM standards for SDU liner compatibility. It is recognized that a 1000-hour exposure is limited compared to the cumulative SDU liner service life and that the length of immersion time varies with different standards.

  For liner service life prediction, a broader testing approach could be performed as done for long-life polymeric components such as nuclear reactor electrical cable insulations, HDPE geomembranes/piping, radioactive waste containment packaging and elastomeric O-rings in critical applications [44-48].

  The general approach in such studies is to expose samples of interest at multiple accelerated temperatures (and/or radiation dose rates), with critical properties aged to failure or target degradation points. The time to failure data are then collectively used to develop aging models using time-temperature-superposition (TTS) principles.

  A primary degradation mechanism for polymers in oxygen-bearing environments is thermo-oxidation. Butyl rubber is known to have excellent resistance to thermo-oxidation, but a literature review on the aging behavior of butyl rubber compounds may also be worth performing.

  SRNL can provide a detailed test plan and cost/schedule estimate for such efforts upon request.

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Following 1000-hour immersion, the average tensile strength and elongation at failure values for the MARFLEX RCHB60HT bromobutyl liner were reduced approximately 40% and 25% from baseline values, respectively. Tensile strength data showed relatively sharper initial drop and subsequent asymptotic behavior than the elongation data.

5.2 Liner mechanical property reductions exceeded the 20% loss criterion established in the test plan. However, the final average tensile strength (500 PSI) of the MARFLEX liner is only ~12% less than that of the REMA 4CN liner previously tested and installed in SDU6. The final average elongation of the MARFLEX liner (~400%) is within the baseline range reported by the liner manufacturer and slightly higher than the 350% nominal reported value.

5.3 Lap-shear data showed similar behavior for all adhesives, with an early drop in peak load values and recovery in later weeks. This may be attributed to thermal (post-cure) effects during immersion or other mechanisms. Similar behavior may have occurred in previous REMA 4CN testing, but interval data were not obtained. It is acknowledged that the data sets per condition are limited, increasing the impact of individual values on the average, though sample data sets were relatively consistent. Statistical analysis of the data was not performed.

5.4 Lap-shear adhesive performance varied with the comparison metric. System A (NORMAC) showed good overall bonding, but several localized regions of blistering or delamination were observed at the skived edge. System A showed the most loss in lap-shear strength from baseline (~45%). Systems B (REMA) and C1 (Abtrex) retained the most of their initial bond strength, with System B having the highest 6-week average strength value for both simulants. Most System B samples failed in base material rather than layers peeling apart. Retained bond strength values for Systems A and C2 were ~20% lower than those for System B or C1. System C1 showed the lowest baseline lap-shear strength. System B showed the most consistent metrics of all adhesives tested.

5.5 Bonded paver behavior was mixed. System A pavers showed overall good bonding, but exhibited many small regions of delamination/blistering at the skived edge around the perimeter and along the seam. It is unknown whether these areas would eventually cause leakage. They did not seem to progress from 500 to 1000-hour inspections. Only one paver (System B, REMA, PR-03, 50% simulant, 500 hrs) was considered defect-free, though other System B pavers showed minor localized debonding. System C1 and C2 pavers showed more extensive delamination in terms of affected bond length, depth and ease of debonding. Paver/seam performance strongly depends on a balance of inherent adhesive properties and application workmanship.

5.6 The correlation between absolute values of lap-shear strength or rubber-to-concrete bond strength and resistance to leakage has not been established. Ideally, changes in bond strength should be minimal, indicating chemical/thermal stability. Stronger bonds are generally preferred, but lower strength bonds may provide satisfactory leak performance. The success of any lining system is highly dependent upon the quality of lining installation.

6.0 REFERENCES

[1] SDU 6 Procurement Specification, C-SPP-Z-00008, Revision 4

[2] Savannah River Remediation M-TC-Z-00008, Task Requirements and Criteria, Revision 6

[3] ACI 350.1-10, Reported by ACI Committee 350, Specification for Tightness Testing of Environmental Engineering Concrete Containment Structures (ACI 350.1-10) and Commentary

[4] Y-AES-Z-00002, Revision 0, Saltstone Disposal Unit (SDU) 6, Floor and Roof Repair Study

[5] SRR-LWP-2009-00001, Liquid Waste System Plan, Revision 20, March 2016

[6] SREL R-16-002 SDU Liner Performance Testing, J. C. Seaman, J. Cochran and E. Dorward

[7] SRNL-STI-2016-00568, Revision 0, SDU6 Interior Liner Testing & Evaluation, T.E. Skidmore, September 2016

[8] G-ESR-Z-00031, Revision 0, Mega-SDU Leak Tight Liner System

[9] https://www.energy.gov/em/articles/srs-reaches-milestone-construction-large-scale-disposal-unit

[10] G-ESR-Z-00030, Revision 1, SDU 7 Plan for Testing Liner Samples

[11] ASTM D6943-15, Standard Practice for Immersion Testing of Industrial Protective Coatings and Linings

[12] ASTM D412-16, Standard Test Methods for Vulcanized Rubber and Thermoplastic Elastomers-Tension

[13] ASTM D6392-12, Standard Test Method for Determining the Integrity of Nonreinforced Geomembrane Seams Produced Using Thermo-Fusion Methods

[14] ASTM D6214-13, Standard Test Method for Determining the Integrity of Field Seams Used in Joining Geomembranes by Chemical Fusion Methods

[15] ASTM D2240-15, Standard Test Method for Rubber Property-Durometer Hardness

[16] ASTM D4437-08 (R2013), Standard Practice for Non-destructive Testing (NDT) for Determining the Integrity of Seams Used in Joining Flexible Polymeric Sheet Geomembranes

[17] M-CLC-A-00241, Rev. 0, M.A. Shadday Jr., “Saltstone Pouring in Vault#2”, August 17, 2005.

[18] NACE Standard TM0174-2002, Item No. 21206, Standard Test Method, Laboratory Methods for the Evaluation of Protective Coatings and Lining Materials on Metallic Substrates in Immersion Service.

[19] ASTM D3912-10, Standard Test Method for Chemical Resistance of Coatings and Linings for Use in Nuclear Power Plants

[20] NACE SP0892-2007, Item No. 21060, Standard Practice, Coatings and Linings over Concrete for Chemical Immersion and Containment Service

[21] SW-846 Test Method 9090A: Compatibility Test for Wastes and Membrane Liners

[22] EPA/600/2-88/052, Lining of Waste Containment and Other Impoundment Facilities, Matrecon, Inc. for Risk Reduction Engineering laboratory, Office of Research and Development, U.S. EPA, September 1988.

[23] M. Shapiro, J. Lott, C. Logan, and J.C. Seaman, 2020, SDU 7 Liner Performance Testing: Data Report. SREL Doc. No. R-20-0003.

[24] G-ESR-Z-00018, Rev.1, Proposed Simulant Salt Solution For Evaluating the Resistance of the SDU LTLS to Chemical Attack, August 2019

[25] ASTM D7700-12, Standard Guide for Selecting Test Methods for Geomembrane Seams

[26] ASTM D8172-18, Standard Test Method for Shear and Peel Strength of Solvent-Welded Seams with Nonreinforced Geomembranes

[27] Normac® 900E-Ultra Cold Bond Cement, Section 5: Endurabond™ Cement Specification, www.blairrubber.com

[28] Safety Data Sheet, 900E-Ultra Rev.4, Normac Adhesive Products, Inc., https://www.normacadhesives.com/products

[29] Safety Data Sheet, E-Hardener, Rev. 2, Normac Adhesive Products, Inc., https://www.normacadhesives.com/products

[30] Safety Data Sheet# RTT-IND-004, Rev.6, SC-4000 Cement, REMA Tip Top, http://www.rematiptop.com/safety-data-sheets-ind.html

[31] Safety Data Sheet# RTT-IND-013, Rev.6, E-40 Hardener, REMA Tip Top, http://www.rematiptop.com/safety-data-sheets-ind.html

[32] ASTM D4896 − 01 (R2016), Standard Guide for Use of Adhesive-Bonded Single Lap-Joint Specimen Test Results

[33] G-ESR-Z-00032, Rev.1, SDU7 Liner Testing Results

[34] Anticorrosive Rubber Lining: A Practical Guide for Plastics Engineers, Plastics Design Library, C. Chandrasekaran, Ed., 2017

[35] Chemical Resistance Guide for Elastomers III, A Guide to Chemical Resistance of Rubber and Elastomeric Compounds, Compass Publications, 2005

[36] Chemical Resistance Guide for Elastomers II, A Guide to Chemical Resistance of Rubber and Elastomeric Compounds, Compass Publications, 1995

[37] C-CLC-Z-00115, Rev.0, SDU7 Tank Calculation

[38] Exxon Bromobutyl Rubber Compounding and Applications Manual, https://www.exxonmobilchemical.com/en/library/library-detail/2252/bromobutyl_rubber_compounding_and_applications_manual_en

[39] "The Cure Chemistry of Brominated Butyl Rubber: A Mode1 Compound Approach", DaiTen James Thom, Master of Science (Engineering), Queen's University, Kingston, Ontario, Canada December, 1999

[40] Essential Rubber Formulary, Plastics Design Library (PDL) Series, Chellappa Chandrasekaran, Editor, 2007.

[41] J. Charles, S. Muthusamy, "Comparative study of butyl rubber (IIR) and bromobutyl rubber (BIIR) based on FTIR, dielectric and thermal studies", Proceedings on International Conference on Recent Advances in Applied Sciences (ICRAAS 2016), Volume II.

[42] Rubber Technology Handbook, Ed. W. Hofmann, Hanser Publications, 1989.

[43] http://www.irdg.org/the-infrared-and-raman-discussion-group/ijvs/ijvs-volume-2-edition-3/a-guide-to-identifying-common-inorganic-fillers-and-activators-using-vibrational-spectroscopy/

[44] NUREG/CR-6384-Vol.1, BNL-NUREG-52480-Vol.1, "Literature Review of Environmental Qualification of Safety-Related Electric Cables: Summary of Past Work", M. Subudhi, 1996

[45] "Long Term Behaviour of Low and Intermediate Level Waste Packages Under Repository Conditions", T. RAMSØY, G.C. CHRISTENSEN, P. VARSKOG , Institute for Energy Technology, Kjeller, Norway in IAEA-TECDOC-1397, Long term behaviour of low and intermediate level waste packages under repository conditions, Results of a co-ordinated research project 1997–2002, June 2004

[46] "Oxidative Resistance of High-Density Polyethylene Geomembranes", Mueller, W. and Jakob, I., Polymer Degradation and Stability, Elsevier Science Ltd. Vol. 79 (2003) pp. 161-172.

[47] SAND98-1942, "New Methods for Predicting Lifetimes in Weapons, Part 1- Ultrasensitive Oxygen Consumption Measurements to Predict the Lifetime of EPDM O-Rings", K. T. Gillen, M. Celina, R.L. Clough, G.M. Malone, 1998.

[48] SRNL-STI-2015-00683, Revision 0, CSR Behavior and Aging Model for the Viton® Fluorelastomer O-Rings in the 9975 Shipping Package, A.J. McWilliams, W.L. Daugherty, T.E. Skidmore, December 2015