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Determination of the effect of exposure to gasoline components on a high density polyethylene geomembrane using the comprehensive test system

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Abstract

The comprehensive testing system (CTS) for geomembranes was used to test the compatibility of high-density polyethylene (HDPE) geomembrane landfill liner material with chemicals typically found in motor vehicle fuel. The CTS is a testing apparatus specifically designed to test the effects of simultaneously applying mechanical load, fluid head, and chemical exposure on the geomembrane. A combination of these factors is present on the geomembrane material in service, and the CTS provides a laboratory reproduction of actual field conditions. The article provides a description of gasoline based upon the desirable qualities of gasoline and provides background on testing of rubbers used in gasoline-powered engine parts. The test's chemicals were gasoline, motor oil, benzene, ethylbenzene, toluene, xylenes, and iso-octane (2,2,4 trimethyl pentane). This work found that gasoline had an effect on the geomembrane greater than the effect of any of the pure chemicals except ethylbenzene. Benzene, and the other aromatic compounds (ethylbenzene, toluene, and xylenes) are typically the primary regulatory concerns at fuel contaminated sites. The fact that gasoline had a greater effect on the performance of the HDPE geomembrane indicated that chemicals are present in gasoline which can decrease the performance of the containment structures used to hold gasoline, while not having a significant health risk. The clear implication is that risk assessments conducted on facilities must not only include the health risks of chemicals placed in a facility, but must also consider the effect of the chemical on a containment structure. The fact that low-health-risk chemicals may have a great impact on the effectiveness of containment structures leads to a possible synergistic mechanism where the low-health-risk

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chemicals enable a pathway for greater-health-risk chemicals to enter the environment. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Over the past 20 years, geomembranes have found use for the lining of sanitary and hazardous waste treatment, storage, and disposal facilities for preventing ground water contamination. One common source of ground water contamination is motor vehicle fuels. These materials can find their way into waste disposal facilities through a variety of routes, including disposal by homeowners with their municipal solid wastes and disposal of soils resulting from remedial actions at gasoline stations. This paper provides an evaluation of gasoline, and gasoline components on a high-density polyethylene geomembrane using the Comprehensive Testing System (CTS) for geomembranes.

The CTS was developed to better duplicate the conditions that the liner will encounter while in operation in the waste containment facility. Multiple test objectives included the ability to apply compressive load, displacement, and fluid head to the geomembrane, all simultaneously and individually adjustable. Previous geomembrane/chemical compatibility testing using the CTS has focused exclusively on tests of individual chemicals, or complex chemical mixtures, such as landfill leachates, gasoline, and motor oil [1]. These tests showed that the CTS was greatly superior to traditional test methods, such as one-dimensional index tests and multi-axial tests. The results of CTS testing have been correlated to polymer–solvent interaction parameters, such as cohesive energy density differences between the polymer and solvent, and solvent molar volume [2]. This work expands the test database by testing the effects of chemicals typically found in fuel wastes on the geomembrane.

2. Background

Geomembranes are used in solid and hazardous waste landfills, lagoons, building underlayments, and underneath chemical/fuel storage tanks. Geomembranes can be subjected to a wide variety of chemicals when used in a landfill. Of particular interest are petroleum products which readily find their way into a landfill due to their widespread use as lubricants, motor vehicle fuels and solvents. The historical environmental view of these compounds in the environment was to consider simply the health effects of these compounds. This view ignores the possibility that a chemical present having little health risk can have a large effect on containment structures, such as geomembranes used to line landfills and treatment ponds. This section provides a discussion of the properties desirable in gasoline, refining techniques used to produce these products, a discussion of the composition of fuels, and the basis for selecting the mixtures used in this project.

2.1. Gasoline and its key components

While gasoline has been used as a fuel since the late nineteenth century, many factors have forced changes in its composition over the years. Over the past 40 years, in the United States, environmental regulations, primarily driven by air quality concerns, have forced modifications to the composition of gasoline [3]. These regulations are summarized in Table 1. In the USA, gasoline comprises the largest single energy source [4]. Because of the amount of gasoline used, gasoline may enter a variety of situations where it may be disposed in a way where it can be the primary chemical acting on the geomembrane liner.

Gasoline must meet a variety of demanding standards to perform properly in an engine. The octane number of a gasoline is an important measure of its anti-knocking properties. Octane number is determined by testing the gasoline in a test engine. Fuel additives are used to prevent knocking. Historically, tetraethyl lead (CAS number 78-00-2) and other alkyl lead compounds were added to gasoline to reduce knocking. The organo-lead compounds reduced knock by breaking down into lead oxides [5]. The ASTM established two tests for fuel octane numbers, motor octane number (MON) and the research octane number (RON). Both the MON and RON are determined using the cooperative fuels research (CFR) engine. The RON is tested at low engine speeds and simulates light load conditions, while the MON is tested at higher engine speeds and heavier loads, corresponding to heavy load conditions. By definition, the RON and MON of the 2,2,4 trimethyl pentane (iso-octane) is 100 and normal heptane is 0 [5]. Blending octane numbers for various product streams in the refinery are listed in Table 2 [6].

Typically, hydrocarbon constituents of gasoline have 4–12 carbon atoms in their molecular structure [7]. The approximate volume percent composition of unleaded and leaded gasoline is given in Table 3 [8]. Due to the variety of chemical compounds contained in gasoline, combined with the addition of proprietary chemicals to modify the characteristics of the gasoline, each gasoline is chemically different. The USEPA typically considers gasoline to be composed of volatile aromatics, primarily benzene, ethylbenzene, toluene, and xylenes (BTEX). As shown in Table 3, these aromatic hydrocarbons can comprise 20 to 25% of fuels. Mechanisms such as mode of release, and the role volatility and solubility play in mobility, can greatly increase the concentration of BTEX as a fraction of the number of fuel constituents analyzed in ground water. As shown above, gasoline is significantly more complicated.

ASTM tests of rubbers used within gasoline powered engines (ASTM D-471) utilize five standard reference fuels, listed in Table 4 [9]. These fuels are binary mixtures of 2,2,4 trimethyl pentane (iso-octane) and toluene. These five ASTM reference fuels are widely used to evaluate the effects of gasoline on rubber parts in gasoline-powered engines.

This work sought an evaluation of the effects of gasoline on geomembranes in actual service. EPA currently bases most of its fuel-related risk calculations on BTEX; health considerations comprise knowledge of these compounds as either known or suspected human carcinogens. The surrogate compounds selected to represent gasoline in this work were selected to more accurately duplicate the behavior of gasoline, by adding ASTM

Table 1
Summary of gasoline related air pollution regulations [3]

Year	Agency	Regulation	Purpose
1959	CA	Bromine number, 30 maximum for Southern California	Limit formation of eye irritants, ozone and aerosols
1971	CA	Vapor pressure–9.0 psi maximum	Reduce evaporative hydrocarbon emissions and ozone
1974	US	Unleaded gasoline required in Service Stations	Assure proper fuel exhaust for vehicles equipped with catalytic converters
1976	CA	Sulfur limited to 500 ppm, maximum	Reduce emissions of sulfur oxides
1977	CA	Lead phasedown	Protect public health
1977	US	Manganese banned until a waiver is obtained	Prevent increase in hydrocarbon emissions
1977	CA	Manganese banned	Prevent increase in hydrocarbon emissions
1978	CA	Sulfur limited to 400 ppm, maximum	Reduce emissions of sulfur oxides
1980	US	Lead phasedown	Protect public health
1980	CA	Sulfur limited to 300 ppm, maximum	Reduce emissions of sulfur oxides
1981	US	Substantially similar rule	Control additives and oxygenate use
1989	US	Vapor phase I: 10.5, 9.5, 9.0 psi max summertime	Reduce hydrocarbons emissions and ozone
1992	US	Vapor phase II: 9.0, 7.8 psi max summertime	Reduce hydrocarbons emissions and ozone
1992	US	Oxygen content 2.7% by wt., administered by states	Reduce carbon monoxide in non-attainment areas
1992	CA	Vapor phase I: 7.8 psi max summertime	Reduce hydrocarbons emissions and ozone
1992	CA	Deposit control additive requirement	Reduce emissions due to carburetor and intake valve deposits
1992	CA	Lead banned	Public health
1992	CA	Oxygen content 1.8 to 2.2% wt., wintertime	Reduce carbon monoxide emissions without increasing nitrogen oxide emissions
1994	CA	Required all gasoline to be unleaded	Public health
1995	US	Deposit control additives requirement	Reduce emissions due to carburetor and intake valve deposits
1995	US	Reformulated gasoline simple model	Reduce ozone
		Benzene limited, 1.3% volatile maximum	Reduce toxics
		Oxygen content, 1.5% minimum	Required by Clean Air Act Amendments of 1990
		Vapor pressure, 7.4/8.3 psi maximum	Reduce evaporative hydrocarbons and ozone
		No heavy metals	Protect public health
		Indirect aromatics, ~ 27% maximum	Reduce toxics
		Sulfur, olefins and 90% evaporated < 1990 average levels	Prevent increased emissions by changes in other fuel properties
1996	US	Lead banned for highway fuels	Protect public health
1996	CA	Phase II reformulated gasoline	Achieve maximum cost-effective reductions in criteria and toxic pollutants
		Vapor pressure: 7.0 maximum	Reduce hydrocarbon emissions and ozone
		Sulfur limit: 80 ppm maximum	Reduce sulfur oxides and reduce temporary deactivation of exhaust catalyst thereby reducing hydrocarbon, carbon monoxide and nitrogen oxide emissions
		Benzene limit: 1.2% maximum	Reduce toxics
		Aromatics limit: 30% maximum	Reduce toxics and hydrocarbon emissions

Table 1 (continued)

Year	Agency	Regulation	Purpose
		Olefins limit: 10% maximum	Reduce nitrogen oxide emissions and ozone formation
		90% evaporation point: 330F	Reduce hydrocarbon exhaust emissions
		50% evaporated point	Reduce hydrocarbon and exhaust emissions
		Oxygen content: 0 to 2.7% wt. summertime	Reduce hydrocarbon and carbon monoxide emissions within increasing emissions of nitrogen oxides

test fuels, and selected component interactions, to the traditional BTEX compounds. For these reasons, benzene, ethylbenzene, toluene, xylenes and iso-octane were selected for testing to simulate the behavior of gasoline and motor oil.

2.2. Land disposal of solid wastes

Land disposal in the form of landfills has long been utilized for disposal of waste generated by human activities. Ground water contamination due to land disposal results primarily from the release of leachate generated in the landfill into the underlying ground-water aquifer. Leachate is a liquid generated by the landfill primarily due to percolation of water through the waste materials. Current US EPA guidance for lining solid waste disposal systems suggests a double liner system with a permeability of less than 10^{-9} m/s. The ability of the liner system to provide a barrier to the flow of leachate into the ground-water aquifer is currently an unresolved issue. Liners are slightly permeable to pure water, having a permeability of 1×10^{-9} m/s. However, there is evidence in literature that exposure to other chemicals that may be present in the landfill's leachate may increase the geomembrane's permeability. Furthermore, when low-density non-aqueous phase liquids (LNAPLs) are present in leachate, they form layers of free product on top of the aqueous body. The liner is then exposed to a 'bathtub-ring' of free product, which, itself, may be a mixture of LNAPLs [1].

Table 2
Laboratory analysis of gasoline refinery cuts [6]

Gasoline cut	Ron	Mon	Hydrocarbon content (vol.%)		
			Olefins	Aromatic	Saturated
Reformate	97.8	87.0	1.4	63.1	35.5
Thermally cracked	70.4	65.1	32.5	9.8	57.7
Catalytically cracked	92.6	80.2	53.3	23.9	22.8
Polymerized	96.8	82.3	100	0	0
Light straight run #1	58.0	58.0	1.3	3.8	94.9
Light straight run #2	61.9	62.0	0.7	2.4	96.9

Table 3
Composition of leaded and unleaded gasoline (vol.%) [8]

Compound	Unleaded	Leaded
Normal/iso-hydrocarbons	55	59
Iso-pentane	9–11	9–11
<i>n</i> -Butane	4–5	4–5
<i>n</i> -Pentane	2.6–2.7	2.6–2.7
Aromatic hydrocarbons	34	26
Xylene	6–7	6–7
Toluene	6–7	6–7
Ethylbenzene	5	5
Benzene	2–5	2–5
Naphthalene	0.2–0.5	0.2–0.5
Benzo[<i>b</i>]fluoranthene	3.9 mg/l	3.9 mg/l
Anthracene	1.8 mg/l	1.8 mg/l
Olefins	5	10
Cyclic hydrocarbons	5	5

2.3. Liner testing

The current method for testing geomembrane liners is the ‘Chemical Compatibility Testing of Wastes and Liner Materials, Method 9090,’ USEPA [10]. This test is conducted by submerging the liner material in the chemical of interest for specified periods of time, after which, a battery of standardized index tests is performed on the material. Concerns have been raised regarding the ability of these tests to simulate the actual conditions the geomembrane liners are exposed to in a landfill.

A wide range of other tests exists, many now codified as American Society of Testing and Materials (ASTM) tests. These may be broken into index and performance tests: index tests isolate individual sample properties, such as the use of a dumbbell-shaped sample to obtain standard materials-strength data (see the tests listed in Table 5); performance tests attempt to develop strength or integrity data in a manner representative of field application. A discussion of these categories, with comparative data indicating the need for a new test method, is available in Stessel and Goldsmith [11].

Table 4
Composition of ASTM D-471 reference fuels

Fuel type	Composition (% by vol.)	
	2,2,4 Trimethyl pentane (iso-octane)	Toluene
Reference fuel A	100	0
Reference fuel B	70	30
Reference fuel C	50	50
Reference fuel D	40	60
Reference fuel E	0	100

Table 5
Minimum properties for smooth geomembranes [15]

Property	Test method	Minimum property
Minimum thickness (mil)	ASTM D751, D1593 or D5199	54
Average thickness (mil)		60
Density (g/cc)	ASTM D792(b) or D1505	0.940
Carbon black content (%)	ASTM D1603	2.0 to 3.0
Carbon black dispersion	ASTM D3015	A1, A2, B1
Tensile properties (each direction)	ASTM D638 Type IV, 5 cm per min NSF 54, Modified	
Tensile strength at yield (ppm)		130
Tensile strength at break (ppm)		243
Elongation at yield (%)	1.3 in. gauge length	13
Elongation at break (%)	2.5 in. gauge length	560
Tear resistance (lb)	ASTM D1004	45
Puncture resistance (lb)	FTMS 101, Method 2065	80
ESC (h)	ASTM S1693, B	1500
Dimensional stability (% change)	ASTM D1024 (1 h at 100C)	±2

Further discussion of performance testing systems is available in Stessel and Gopal [12]. The comprehensive test system for geomembranes (CTS) attempts to duplicate the structure of the landfill surrounding the geomembrane, the effects of wastes, through applied loads, and the effect of waste placement through the application of cyclic displacement. The mechanical simulation of landfill conditions is combined with introduction of fluids that may be present in landfill leachate resulting in the ability to test the effects of chemical exposure with simultaneous loads. CTS testing has provided a means to evaluate the interactions between polymer and solvent. Further, CTS test data have been correlated to the polymer solvent interaction parameter and differences in the cohesive energy density (CED) between polymer and solvent [13]. These differences are related to the solubility of the chemical in the polymer [1].

3. Experimental method, materials, and techniques of analysis

The following sections describe the test apparatus, its use in this testing program, and data analysis techniques utilized.

3.1. Comprehensive Testing System

The Comprehensive Testing System (CTS) was developed at the University of South Florida for testing simultaneous application of mechanical loads, chemical exposures and other environmental factors, such as elevated temperature on geomembranes. The CTS was developed in response to deficiencies discussed above. Its key attributes are:

(1) apply compression to simulate the weight of the landfill; (2) apply controlled displacements for stress/strain, cyclic, and relaxation testing; (3) apply fixed forces to conduct creep tests; (4) read and store forces and displacements; (5) allow independent application of fluid head; and (6) read and store pressure in the bottom chamber so as to detect membrane integrity by detecting fluid passage through the membrane.

A simplified drawing of the configuration of the CTS test unit is shown in Fig. 1. The CTS consisted of a test cell filled with granular media designed to apply loads to the geomembrane through pistons mounted on a compression tester capable of applying cyclic loads. The CTS was originally constructed in 1987, and had undergone a series of modifications to attain its current configuration. Details of its design, configuration and operation are available in Stessel [14]. Its use in this work is discussed below.

3.2. Geomembrane test samples

The geomembrane liner samples tested were 1.5 mm (60 mil) thick HDPE obtained from GSE Lining Technology, of Houston, TX. Manufacturer's specifications for this material are presented in Table 5, GSE Lining Technology [15]. To reduce variation, test samples were obtained from the same roll of HDPE. For CTS testing, samples 40 cm by 40 cm (16 in. x 16 in.) were cut from this roll and drilled for the passage of the NC threaded rods and bolts used for clamping the grips and the top and bottom clamping

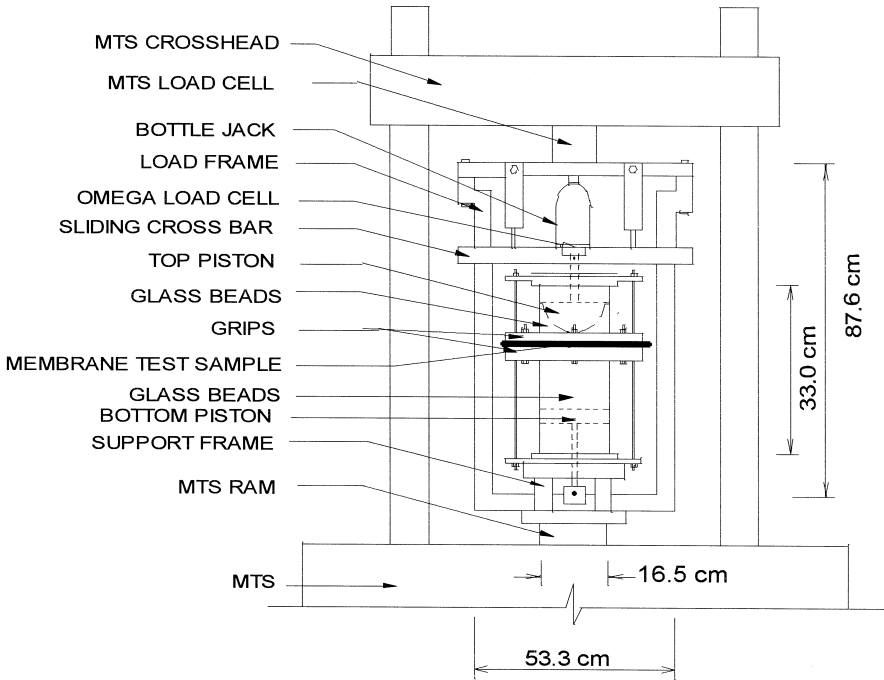


Fig. 1. Comprehensive Testing System.

plates. Samples were inspected for surface imperfections that might lead to undesired modes of failure during testing. Samples exhibiting imperfections such as scratches or grooves were rejected due to possible stress concentration at these defects.

3.3. Test chemicals

The chemicals used to evaluate the geomembranes in this project were obtained from Fischer Scientific, and met American Chemical Society certification. Gasoline and motor oil were obtained from local retail outlets. The chemicals used in this project, their Chemical Abstract Services (CAS) number, synonyms, and hazardous waste number (if applicable) are listed in Table 6.

Solubility of the test chemicals in polyethylene can be determined from the differences in cohesive energy density of the polymer and solvent. The cohesive energy density consists of three parts, dispersive forces, hydrogen bonding forces, and polar interactions. The solubility is calculated from the squares of the differences between each component of the cohesive energy density [1].

3.4. CTS testing

The CTS used an MTS Systems (MTS) load frame and hydraulic ram. The displacement of the ram was measured by a linear voltage displacement transducer (LVDT) located in the ram. The cyclic displacement of the ram was controlled by the MTS's function generator which produced a sinusoidal function with a frequency of 0.012/s and an amplitude of 2.5 cm (1 in.) cyclic displacement. This resulted in an average displacement rate of 3.9 cm/min (1.5 in./min). The total displacement was obtained by manually increasing the displacement during the return stroke of the first five cycles as shown on Fig. 2. The total manual displacement was 3.81 cm (1.50 in.) and the cyclic displacement was 2.54 cm (1 in.), resulting in a maximum total displacement of 6.35 cm (2.5 in.). Tests ran for 4000 s, or approximately 1 h; the sample was thus exposed to 48 cycles, or 43 cycles after the completion of ramping. Fig. 3 shows the rationale for that test duration: by that time, the stress difference between the maximum and minimum displacement had reached an approximate steady-state, indicating that the energy being added to the membrane was approximately constant. Analysis focused on the nearly steady-state segment of the data.

Table 6

List of chemicals used, CAS numbers, synonyms, and waste characteristics (40 CFR 302)

Hazardous substance	CAS number	Synonym	Source	EPA waste number
Benzene	71432		Fischer Scientific	U109, D018
Ethylbenzene	100414		Fischer Scientific	
Gasoline, 93 octane			Shell Oil Company	
2,2,4 Trimethyl pentane	540841	Iso-octane	Fischer Scientific	
Toluene	108883	Methylbenzene	Fischer Scientific	U220
Xylenes, mixed isomers	1330207	Dimethylbenzene	Fischer Scientific	U239

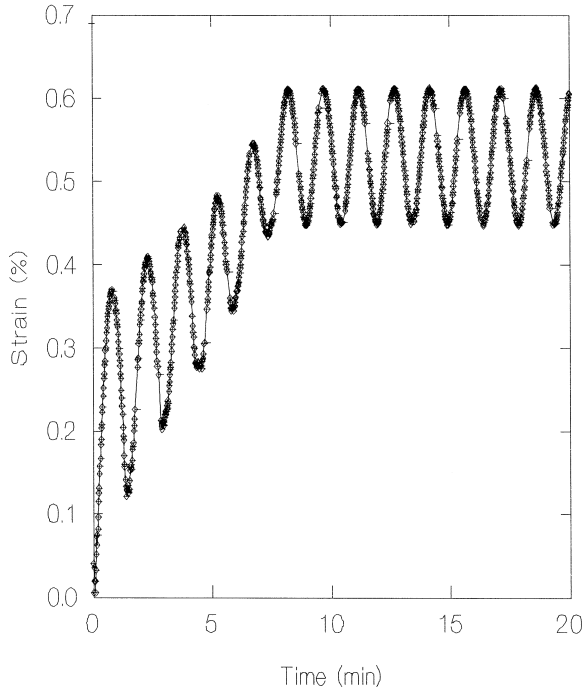


Fig. 2. Plot of strain during displacement showing manual increases during cyclic loading.

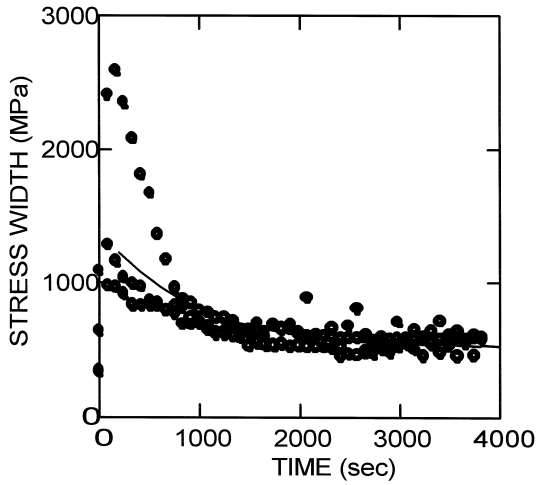


Fig. 3. Difference between maximum and minimum stress for benzene.

The CTS test cell was constructed from a 15-cm (6 in.) nominal diameter, schedule 40 stainless steel pipe machined to an inside diameter of 15.24 cm (6.000 in.). The cell top and bottom were originally from a 6-in. diameter Soil Test permeameter modified to permit the passage of piston shafts and fittings for permeant introduction and pressure measurement. Additional sealing against gas permeation was provided by a viton o-ring.

Permeant was delivered to the test cell under 170 kPa (25 psi) of air pressure. Test fluid was placed in a pressure vessel that was connected to the test cell by Teflon[®] tubing using Swagelok[®] fittings. Upon entering the test cell, the test chemical passed around the edges of the piston, which did not seal against the cylinder walls, through the granular media, through the various layers of glass cloth and filters, finally to encounter the GM sample. A polycarbonate shield, vacuum blower system, and personal protective equipment provided worker safety.

The MTS control panel provided outputs from the MTS's load cell and linear displacement transducer, which indicated the displacement and load on the GM. The MTS was calibrated: its load cell was within 1% full range, and the LVDT within 1% of the reading for the range utilized. An Omega load cell, having an accuracy of 0.25% of full scale, and Brainard–Kilman linear displacement transducer, having an accuracy of 0.10% of full scale, were mounted to the inner load frame allowing determination of differences between the actual loads and displacement of the GM and the values recorded by the MTS's instrumentation. An Omega pressure transducer/indicator was attached to the lower cell to determine pressure in the cell, which would indicate a breach of the GM.

The outputs of these instruments were fed into a computerized data acquisition system consisting of a micro-computer equipped with an analog-to-digital (A/D) convertor card. A spreadsheet macro enabled data to be acquired directly from the A/D card into Microsoft Excel. The spreadsheet was programmed to perform calculations of stress, strain, slack, and delta modulus. The results of the calculations were displayed on a near-real-time basis in graphical form on the screen during testing, greatly aiding the evaluation of test progress. All the data were stored on a diskette in Microsoft Excel format for further analysis.

3.5. Data analysis techniques

Stress was defined as the ratio of the load applied to the area perpendicular to the application of load. The cross-sectional area of the membrane was calculated as the product of thickness and circumference of the sample held within the grooved area of the grips. Stress could be mathematically represented as

$$\sigma = \frac{L}{2\pi rS} \quad (1)$$

where σ = stress (N/cm²), L = applied load (N), r = radius of the test sample held within the grooved area of the grips (cm) and S = thickness of the sample (cm).

Due to the multi-axial deformation of the sample, the strain (ϵ) was computed as the square root of the change in area divided by the original area of the test sample before

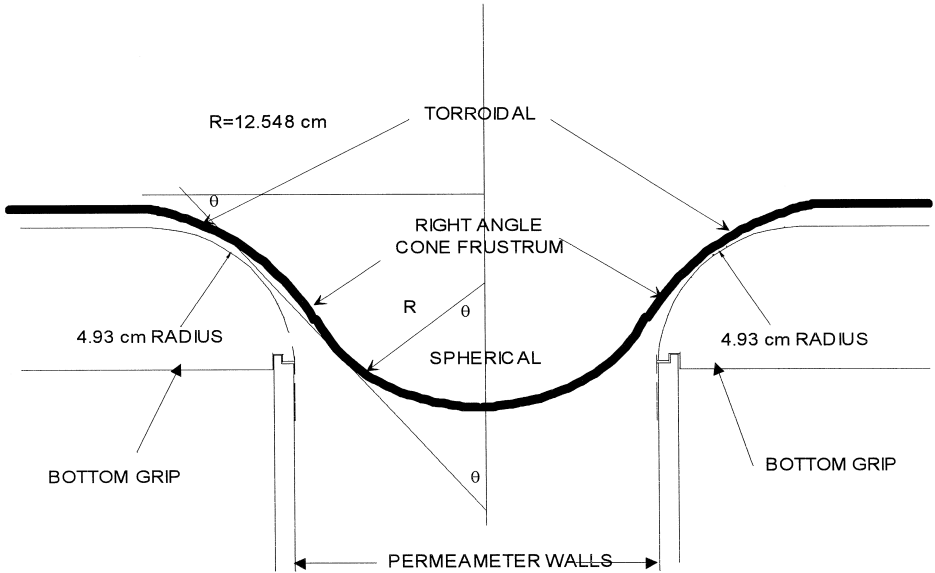


Fig. 4. Geometry of CTS test.

deformation. Since the vertical displacement was the control parameter for the test, surface area had to be computed from this displacement value. The geometry of the deformation was assumed to consist of three portions, (1) the top portion of a torroidal area at the cell wall defined by the bottom grip, (2) a spherical area in the center of the GM, and (3) a right angle cone frustum joining the other two portions, as shown on Fig. 4. The total displacement (h) was considered to be the sum of the displacements resulting from each of these three portions of the curve. The surface area could be determined from these heights using the appropriate equations. As data reduction was performed in a spreadsheet, repetitive solving of simultaneous equations was not possible. The clear third order geometry allowed curve-fitting of a polynomial with $r^2 = 1.00$. The resulting equation is:

$$SA = 494.469 + 24.23(x) + 1.590(x^2) - 0.062(x^3) \tag{2}$$

where x is the vertical displacement of the test sample in centimeters, and SA is the resultant membrane surface area in cm^2 . The curve fit had an error of less than 0.025% for a displacement of 3.75 cm (1.5 in.) [16].

Strain in the GM as a function of applied stress is shown in Fig. 5. After a few cycles, the system reached steady state, where the loads (stresses) resulting from the displacement(strains) were relatively constant. The delta modulus, ΔE , was defined to describe the mechanical response of the system:

$$\Delta E = \frac{(\overline{\sigma_{\max}} - \overline{\sigma_{\min}})}{(\overline{\epsilon_{\max}} - \overline{\epsilon_{\min}})} \tag{3}$$

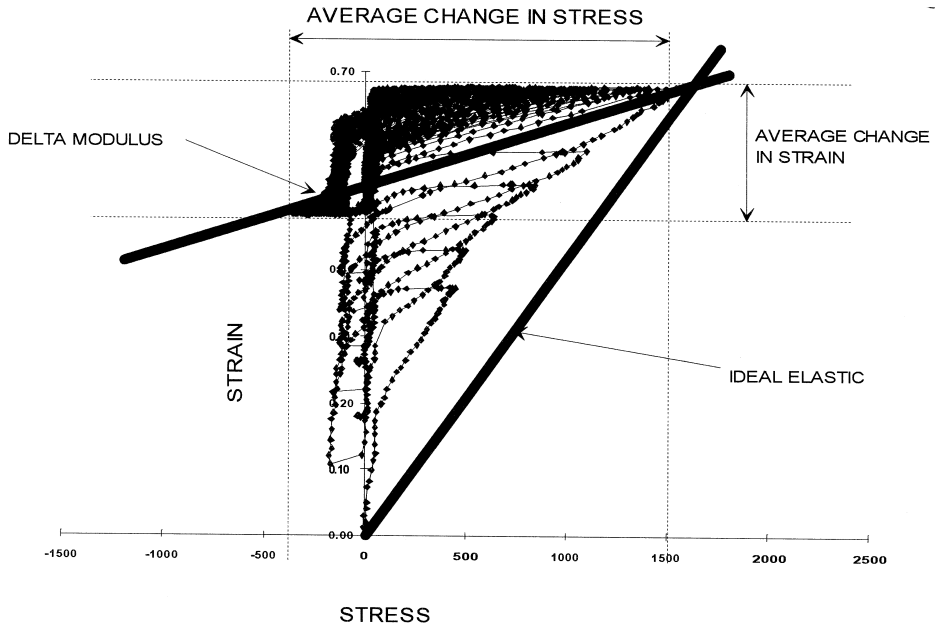


Fig. 5. Stress–strain plot for geomembrane subjected to cyclic loading by the CTS.

where σ and ϵ are the stress and strain [1]. The delta modulus provides a single-parameter measure of the material's elasticity/plasticity and strength as revealed under cyclic loading.

The strain energy is the amount of mechanical energy dissipated in a hysteresis loop. Strain energy was measured by determining the area of the hysteresis loops. A typical hysteresis loop is shown on Fig. 6. The formula for strain energy is:

$$W = \sum_{i=1}^n \bar{\sigma}_i (\epsilon_i - \epsilon_{i-1}) \quad (4)$$

where n is the number of measurements made in the individual cycle, $\bar{\sigma}_i$ is the average stress in the i th time step during a cycle and ϵ_i is the i th strain measurement. The greater the strain energy during a given cycle, the more energy required to deform the geomembrane. Greater mechanical strength also indicates that less damage has been accumulated in the geomembrane.

3.6. Statistical analyses

The CTS testing data reduction produced the delta modulus and strain energy. Once the values of these parameters were obtained, the data were statistically evaluated using Systat for Windows, Version 7.0. Box plots were prepared to identify trends in the data. Box plots can be ordered by median or other value and adjacent box plots provide the easiest comparison of data [17]. Analysis of variance (ANOVA) of the delta modulus

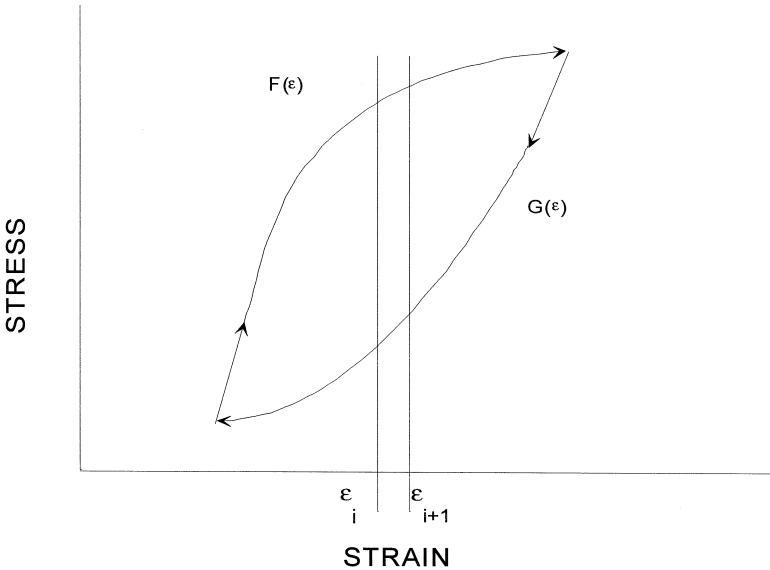


Fig. 6. Calculation of strain energy.

data was conducted to determine if statistically significant differences in geomembrane performance were present. These differences would be the result of the chemical exposure. The data were sorted by chemical and post-hoc tests were conducted using the Tukey wholly-significant-differences (WSD) method, a single analysis sufficient to determine whether statistically significant differences between treatments existed for a balanced data set [18].

4. Results

Box plots of delta modulus and strain energy by chemical are presented in Figs. 7 and 8, respectively. The highest delta modulus observed was for Reference Fuel A (iso-octane) (52.76 MPa, 7641 psi), followed by xylenes (47.65 MPa, 6901 psi). Gasoline and the aromatic compounds had delta moduli that varied from a low of 21.95 MPa (3179 psi) for ethylbenzene to 47.65 MPa (6901 psi) for xylenes. Water, which was the control, had a delta modulus that was in the middle of the range of values observed (34.23 MPa). This indicated that some of the chemicals increased the mechanical strength measured by delta modulus of the geomembrane relative to the control, a substance that should have minimal effect on HDPE. The differences were not statistically significant for strain energy, but were quite significant for delta modulus. That distinction suggests that water has a greater interaction with the particles in the granular media possibly due to its polarity and ability to form hydrogen bonds. These hydrogen bonds may have wetted the granular media to a greater extent than the organic chemical, and reduced the friction between the granular media particles. The delta modulus of mixtures of iso-octane with toluene and iso-octane with xylenes were between the delta

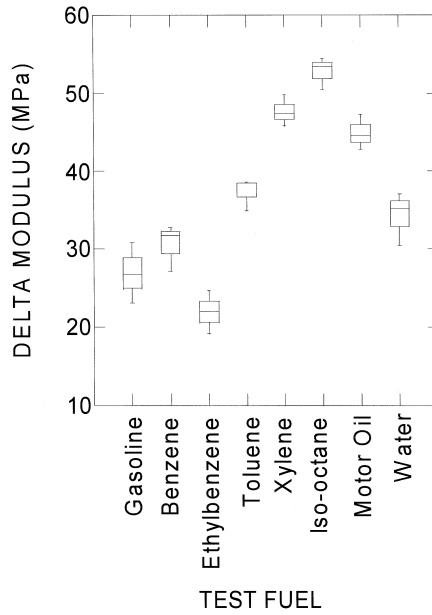


Fig. 7. Box plot of delta modulus by test fuel.

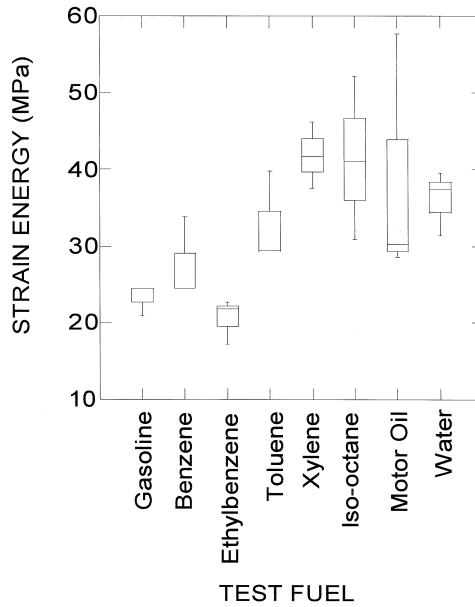


Fig. 8. Box plot of strain energy by test fuel.

moduli of the pure components. This indicated that a relationship between the concentration of a chemical in the mixture and delta modulus was present.

ANOVA of the delta modulus data showed statistically significant differences in delta modulus for 14 of the 28 possible pairs of different chemicals at a confidence level of 95%. The results of the ANOVA comparing the individual chemicals with gasoline and motor oil are listed in Table 7. Statistically significant differences in the delta modulus was based solely on the chemical to which the geomembrane sample was exposed and the delta modulus increased with the differences in solubility between the chemical and HDPE based on cohesive energy density differences for all chemicals except water. No statistically significant differences in strain energy, as a function of chemical of exposure, were found using the multiple comparison technique. The box plot of the strain energy (Fig. 8) shows a trend between the strain energy and the chemical of exposure.

The lack of significance differences in the strain energy values while delta modulae (cyclic stress differences) were statistically significant indicated that the effects of chemical attack were most apparent at the extremes of the loading curves, the minimum and maximum strain. Strain energy involves the force required to displace the geomembrane the desired distances dynamically. On the other hand, delta modulus is measured at the minimum and maximum displacement, where the rate of strain is zero. Strain energy measures the forces required to move the geomembrane, both the stress accumulated in the geomembrane and the shear forces required to move granular media. If variations in the shear forces are sufficiently large, they can mask the variations in stresses accumulated in the geomembrane, resulting in strain energy measurements that could not be correlated to material properties. A general trend between strain energy and delta modulus can be seen, as expected. However, this trend showed substantial variability, which indicated that the variation in the shear forces generated within the granular media may have been large enough to distort the actual relationship present between the strain energy and material properties.

The stress difference (delta modulus) and strain energy tended to be similar by chemical, that is, chemicals with high strain energies also had high stress differences. A

Table 7
ANOVA results and solubility in HDPE sorted by average delta modulus

Chemical	Average delta modulus (MPa)	ANOVA results probability the same as:		Solubility in HDPE (MPa)
		Gasoline	Motor oil	
Ethylbenzene	21.96	0.403	0.000	2.50
Gasoline	26.90	1.000	0.000	
Benzene	30.52	0.740	0.000	6.60
Water	34.23	0.074	0.005	1239.00
Toluene	37.33	0.005	0.063	6.60
Motor oil	44.85	0.000	1.000	
Xylenes	47.65	0.000	0.366	10.77
Iso-octane	52.76	0.000	0.046	43.56

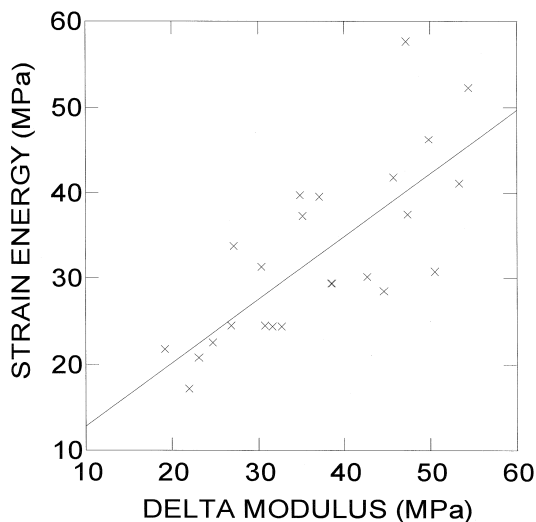


Fig. 9. Strain energy as a function of delta modulus.

plot of strain energy as a function of the delta modulus for the chemical is shown on Fig. 9. Theoretically, one would expect that when the geomembrane is exposed to a chemical having a greater change on the mechanical properties of HDPE, both the stress extremes and the amount of energy required to deform the geomembrane would decrease. This decrease was the general effect observed in this study. Further, the delta modulus result and strain energy could be correlated to show statistically that the materials having a higher delta modulus also had higher strain energy.

5. Discussion

The chemicals tested were components of gasoline, gasoline itself, and motor oil. The effect of each of the pure chemicals, as measured by delta modulus, can be related to the solubility of the chemical in HDPE. This indicated that the mechanism of the change in material properties of HDPE is related to the interaction between the polymer and solvent. The most striking result was the fact that gasoline had one of the lowest delta modulae, lower than all chemicals tested except ethylbenzene.

Four of the pure chemicals tested—benzene, toluene, ethylbenzene, and xylenes—have long been regarded as the primary contaminants of concern at gasoline contaminated facilities due to composition and health risk assessments. Early CTS work focused on these chemicals for this same reason. The results of this investigation raises concerns regarding the suitability of selecting chemicals for testing containment structures based on the health effects of the chemical: Gasoline had a larger effect on the high-density polyethylene geomembrane than any of the major chemicals of concern which gasoline contains. ANOVA showed that no group of constituent chemicals clearly explained the mechanical effects of oil and gasoline (see Table 7). A strong argument exists for further

study of the examination of synergistic effects of chemicals on barrier–material resistance. With the possibility for concentrated exposure of liner materials to layers of LNAPLs and DNAPLs (dense NAPLs), such interactions may well occur.

These results suggest that chemicals should be selected for evaluation that represent the waste that will be disposed in the facility. In a complex mixture of chemicals, it is likely that there will be chemicals present which have a greater effect on the geomembrane than the primary chemicals from a health risk viewpoint. This complicates risk assessments of facilities in that all chemicals must be considered when evaluating the life of the containment structure. The presence of chemicals at a facility which may have large impacts on the containment structures, but little health concern provides a possible additional synergistic effect where a low-health-risk chemical may facilitate the release of greater risk chemicals.

6. Conclusions and recommendations

Differences were observed in the results of testing the effects of chemical exposure on geomembranes using the CTS. The differences showed a direct relationship to the solubility of high-impact chemicals in HDPE. The CTS has shown that the performance of a geomembrane when exposed to a chemical can be evaluated and the effect of an individual chemical can be determined in a statistically meaningful manner.

Gasoline is a complicated mixture of hydrocarbons and additives, some of which are proprietary. Health risk from fuels is principally assessed using the major aromatic constituents of gasoline, which were those tested: benzene, toluene, ethylbenzene and xylenes (BTEX). The other chemical tested, iso-octane, is used to assess possible damage to fuel-system plastic and rubber components. Gasoline a greater effect on the mechanical performance of the geomembrane than any individual BTEX component; iso-octane had very little effect.

Thus, the key conclusion is that the gasoline tested had a greater effect on the geomembrane barrier material than any of the individual components deemed significant in environmental impact assessment. The implication is that the risk associated with gasoline disposal must consider two separate conditions: (i) the effect of gasoline on the containment, or how the gasoline will effect barrier materials so as to cause its release into the environment; and (ii) the health risks of the compounds comprising gasoline.

One might then generalize the conclusion: leachate components that may cause a breach of a containment system may not be the same constituents that pose the greatest threat to public health, once released.

The work remaining in this arena further illustrates the issue. Leachates may be viewed as having three components, which stratify on the liner: dense non-aqueous-phase liquids, water with dissolved materials, and less-dense non-aqueous-phase liquids. This work primarily dealt with the latter; it therefore has applicability to situations where free product exists, such as underlayment for storage tanks overlain by a low-permeability roof or pavement. In landfills, where materials from a multitude of sources might have been placed, the possible chemical-risk interactions include all leachate constituents that may work to penetrate the liner, which would then liberate a leachate containing a

separate, possibly-overlapping, list of materials that pose a significant health risk. Thus, facility breaching might be an issue for investigation entirely separate from health, suggesting further study in that arena alone. Such materials might include chemical with higher water-solubility than previously investigated, such as organic acids from microbial degradation. For example, if MTBE survives allegations in the popular press concerning alleged health effects to motorists, it would be well to test it, or other oxygenates.

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