



Project Summary

Liner Materials Exposed to Hazardous and Toxic Wastes

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A research project was undertaken to assess the relative effectiveness and durability of a wide variety of liner materials when exposed to hazardous wastes under conditions simulating various aspects of service in waste storage and disposal facilities. The materials studied included compacted soil, admixes, sprayed-on asphalt, and 32 polymeric membranes. Four partially crystalline polymeric sheetings were not compounded for use as liners but were included in the study because of their known chemical resistance and their use in applications requiring good chemical and aging resistance.

The lining materials were exposed in test cells to 10 hazardous wastes (two acidic, two alkaline, three oil, a blend of lead, a pesticide, and an industrial waste) and three media of known composition—deionized water, 5% aqueous solution of salt, and a saturated solution of low-concentration (0.1%) organic tributyl phosphate. The polymeric materials were also exposed to wastes or environmental conditions under a variety of procedures that included primary one-sided exposure, immersion testing, two types of outdoor exposure, and a pouch test. Some of the exposures were as long as 2700 days. New methods for testing polymeric materials are presented.

This Project Summary was developed by EPA's Hazardous Waste Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Land disposal studies in the early 1970's clearly indicated the need for positive control measures to prevent contamination of the surface water and groundwater that might result from storage and disposal of hazardous wastes on the land. The use of man-made liner materials of low permeability appeared to be a feasible means of preventing the pollutants in hazardous wastes from entering the groundwater. Some lining materials have been in use for 20 years or more to impound water. Liners have also been used to impound brines and some wastes. A wide range of materials differing in permeability, composition, construction, and cost have been used or are potentially useful for confining possible pollutants. Nevertheless, available data on the relative performance and service lives of specific materials exposed to certain wastes are meager. To guide and perhaps eventually regulate the use of liners in these applications, the U.S. Environmental Protection Agency (EPA) needed considerably more information.

This project was undertaken in 1975 with the following board objectives:

1. To determine how a selected group of lining materials is affected by exposure to a range of typical hazardous wastes over a relatively extended period (2 years).
2. To determine the durability and cost effectiveness of polymeric membranes, sprayed-on membranes, admixed materials, and natural soils as liners for hazard-

ous waste storage and disposal facilities.

3. To estimate the effective lives of 12 liner materials exposed to six types of nonradioactive hazardous waste streams under conditions that simulate those encountered in waste impoundment and disposal facilities.
4. To develop information needed for selecting specific lining materials to confine hazardous wastes in specific installations.
5. To develop methods for assessing the relative merits of the various lining materials for specific applications and for determining their service lives.
6. To develop indicator tests that could be used to select lining materials for given applications.
7. To help EPA develop effective controls for the proper disposal and management of hazardous wastes.

Results of this project have been reported over the past several years in various preliminary documents. The final report, summarized here, presents the results of the complete project and includes information on the exposure of lining materials for periods of up to 2700 days (most of the exposure data are for periods of up to 1350 days, however).

Materials and Methods

Types of Liners Used

This research program determined the effects of exposing a broad range of selected liner materials to a range of wastes, sludges, and test media under a variety of test conditions for periods of up to 2700 days. The four types of liner materials included in the program were:

- One compacted soil of low permeability
- Three admixes (asphalt concrete, polymer-treated bentonite and sand mixtures, and a hydraulic cement)
- One sprayed-on membrane of an emulsified asphalt on a nonwoven fabric
- Thirty-two different commercial polymeric sheetings based on the following polymer types:
 - Butyl rubber
 - Chlorinated polyethylene
 - Chlorosulfonated polyethylene
 - Elasticized polyolefin
 - Neoprene

Polybutylene
Polyester elastomer
Polyethylene (low- and high-density)
Polypropylene
Polyvinyl chloride

The polymeric materials covered a range of thicknesses, manufacturers, and crosslinked and thermoplastic variations of the same polymers, and some were fabric-reinforced sheetings.

Single samples of sheeting of polybutylene, low- and high-density polyethylene, and polypropylene were included in the study because of their promising characteristics and use in pipes and containers for handling corrosive chemicals. None of the sheetings contained carbon black, and none were designed specifically for use as linings for waste disposal facilities.

Wastes Tested

The wastes studied represented several general types, including two acidic wastes (one with a pH < 1.0), two alkaline wastes (one with a pH of > 12.5), one industrial waste (with high concentrations of trace metals and organics), one lead waste, three oil wastes, and one pesticide waste. In addition, three test fluids of known composition were included as reference points: Deionized water, 5% solution of salt and water, and saturated solution of tributyl phosphate (0.10%). The first two fluids could be used as standard references, as many of the wastes that are encountered contain water and salt. The saturated solution of tributyl phosphate was included to assess the effect that occurs when polymeric membranes absorb an organic chemical in an aqueous solution of known low concentration.

Test Methods

Four major types of exposure tests were conducted on the lining materials:

1. *One-sided exposure to the wastes.* In this primary test of the project, liner specimens about 0.092 m² (1 ft²) were mounted in cells (Figure 1), and a 0.030-m (1-ft) head of waste was placed on them. This test was designed to simulate a liner at the bottom of a pond. The permeability of the material could be assessed by collecting seepage below the liner specimen. Durability was measured in terms of property retention after two exposure periods. All four

types of lining materials were included in this exposure test.

2. *Two-sided exposure to the wastes by immersion.* Samples of 16 polymeric membrane liners were suspended in the tanks of the above cells containing 13 waste liquids and test media. In most cases, two specimens of a membrane were placed in the liquid, withdrawn at two different times, and subjected to a series of tests, including measurement of dimensions, weight increase, volatiles content, extractables content, and such physical tests as tensile, tear, and puncture resistance.
3. *Outdoor exposure.* Two types of outdoor exposure were conducted. The first exposed polymeric membrane samples to weathering, and the second exposed samples intermittently to both weathering and a waste. In the first exposure, three specimens for each of the polymeric membranes were placed on a roof rack in Oakland, California (Figure 2). One specimen was removed after each of three time periods. The specimens were measured for dimensional changes and then tested in a manner similar to those in the immersion test. In the second type of outdoor exposure, polymeric membrane liner specimens were used to line small tubs that contained wastes (Figure 3). This test allowed assessment of weather and waste exposure on the liner below, above, and at the interface of the waste and air, and it tested the effect of directional orientation. The liner specimens in the tubs contained a field seam so that the effects of waste on seam strength could also be assessed.
4. *Pouch test.* Pouches fabricated from polymeric membranes were filled with wastes and sealed (Figure 4). The sealed pouches were immersed in deionized water and exposed for extended periods. The permeability of the membranes could be assessed by measuring at various time intervals the weight change of the pouch and the conductivity and pH changes of the deionized water in which the

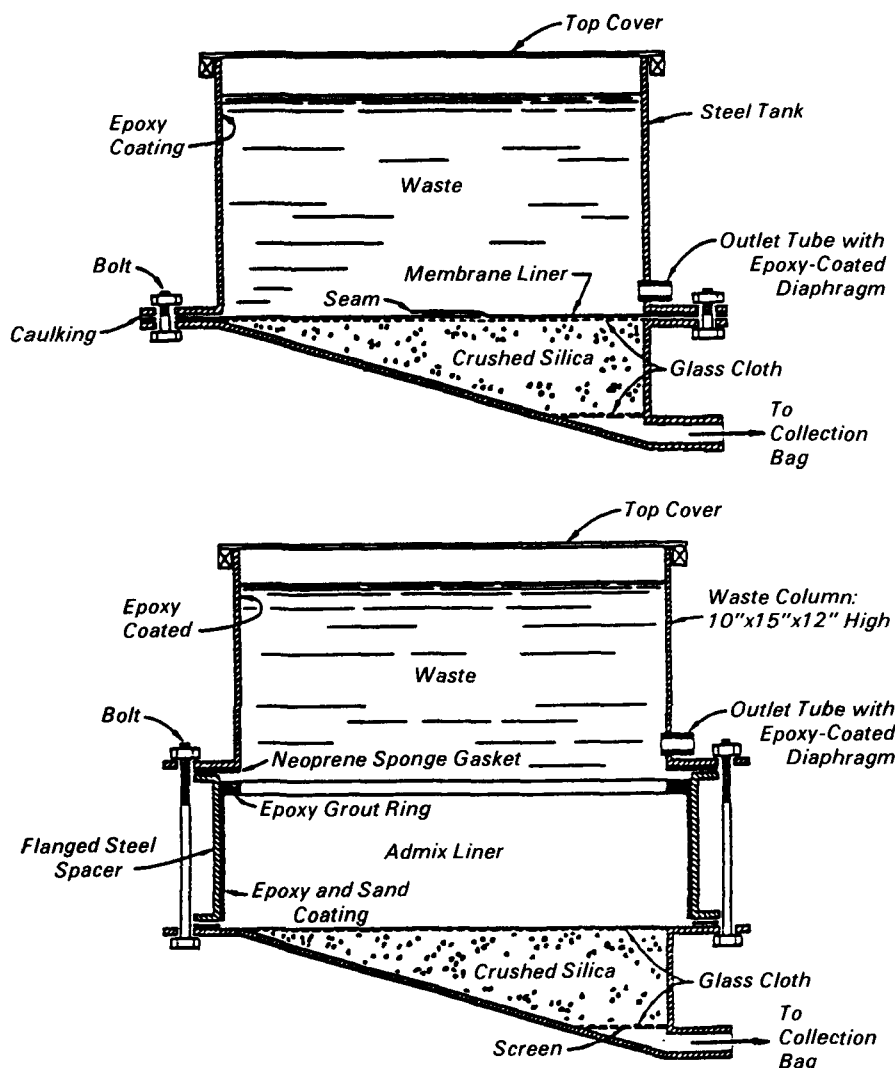


Figure 1. Design of cells for long-term exposure of membrane liners (top) and soil and admix liners (bottom) to various hazardous wastes.

pouches were placed. When the pouches were eventually dismantled, dissected, and tested, they also yielded information on one-sided exposure to waste.

The duration of these tests ranged up to 2700 days for the primary tests, 1456 days for the immersion test, 1231 days for the roof rack test, and more than 2500 days for some of the tubs. Some of the pouch tests ran as long as 2000 days.

In addition to the exposure studies, a variety of special tests were developed for the polymeric membranes. These included analyses for ash, volatiles, and extractables and a pyrolysis test to measure general composition.

Results and Conclusions

The project was concerned principally with the chemical compatibility of materials as measured by the liner's absorption of the waste solution, changes in mechanical properties, and (in some cases) changes in permeability. Results indicated that some of the liner materials performed satisfactorily in contact with certain wastes. But because waste combinations can be highly specific, compatibility testing is needed to select a liner for a given waste.

Lining Materials

Soil Liner

Specimens of the native soil liner performed quite satisfactorily during the

6.5 years of exposure to each of the six waste liquids—low-alkalinity waste (spent caustic), lead waste, oily wastes (slurry oil and Oil Pond 104), and pesticide waste. Combinations of the soil liner with the acidic wastes were eliminated in the screening tests because of apparent incompatibility.

With all wastes, the 1-ft-thick soil liners showed low permeability ($2.0 - 3.1 \times 10^{-8} \text{ cm s}^{-1}$), which they maintained throughout the exposures. The apparent insensitivity of the native soil to various chemicals is probably related to its high ratio of nonclay to clay minerals in the fraction smaller than $2 \mu\text{m}$. Another feature of this soil that may contribute to its insensitivity is the high salt content (it had been dredged from the channels in the Carquinez Straits in California and had dried on land). Except for the possible migration of copper, the other five metals tested (cadmium, chromium, lead, mercury, and nickel) did not appear to migrate more than 2 cm (0.8 in.) into the liner during 958 days of exposure to Oil Pond 104, which contained these trace metals.

Asphalt Cement

Combinations of the asphalt concrete and the oily wastes were eliminated in the screening tests. But in spite of the low permeability and good mechanical properties for the 6.4-cm- (2.5-in.-)thick asphalt concrete, the liner was deficient in several other exposures. Both specimens leaked when in contact with the strong acid ($\text{HNO}_3\text{-HF-HOAc}$). Some of the aggregate at the surface was dissolved, and the asphalt itself hardened severely during exposures that were relatively short (40 and 199 days). Leaks also developed in the specimens below the spent caustic and lead wastes. The lead waste contained sufficient oily constituents to cause the asphalt concrete to become almost a slush. Some seepage also occurred through the specimens below the water. We conclude that this type of lining material should not be used with wastes that contain oily compounds and that thorough testing of the aggregates is necessary. Also, a thickness of 6.4 cm (2.5 in.) may be insufficient even for water and compatible dilute wastes.

Bentonite and Sand Mixtures

Polymer-treated bentonite and sand mixtures were tested in cells containing the lead, pesticide, slurry oil, and Oil Pond 104 wastes. These liners had been

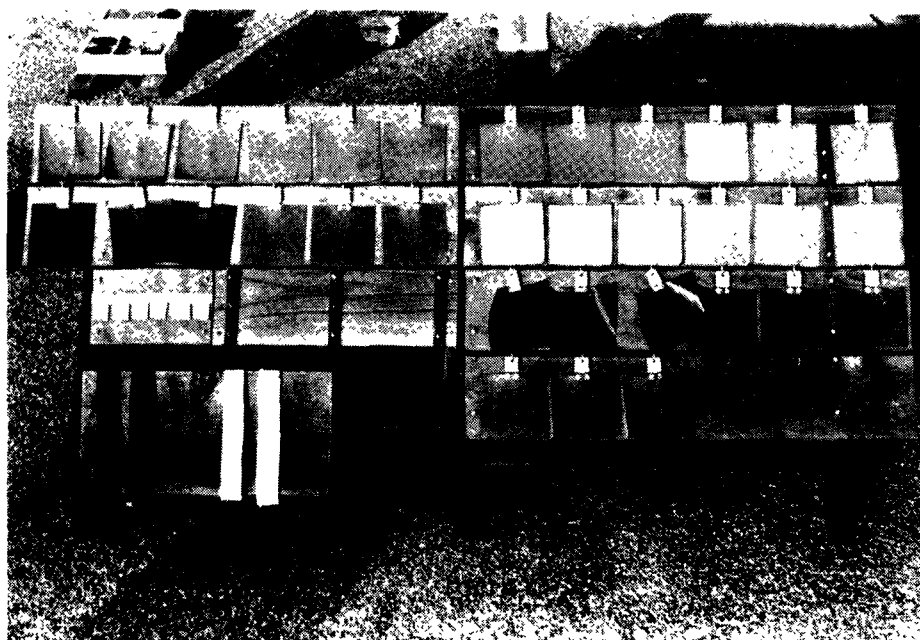


Figure 2. Exposure rack loaded with polymeric membrane specimens. The rack is exposed at a 45° angle to the south.

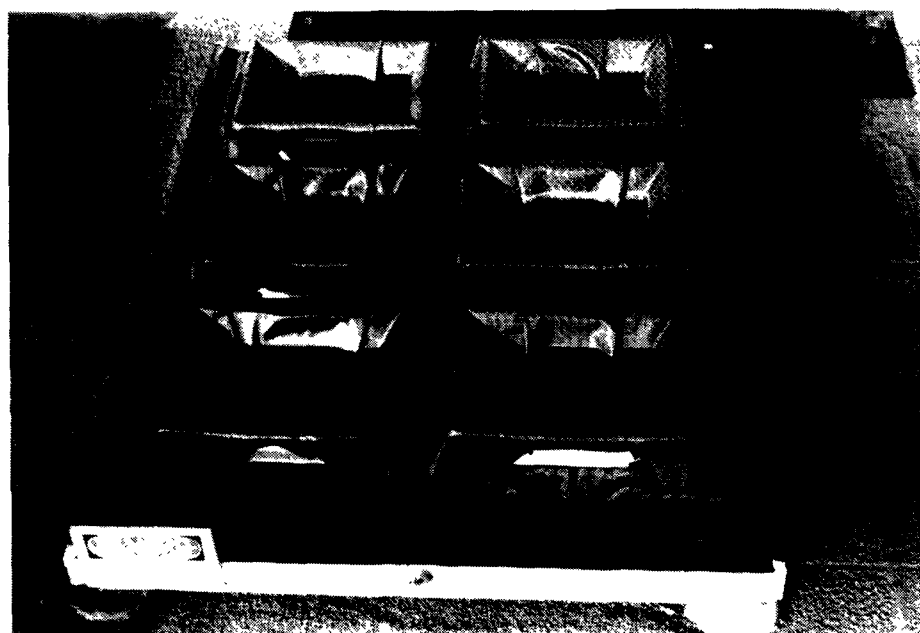


Figure 3. Open exposure tubs lined with polymeric membranes and partially filled with hazardous wastes. The tubs were covered with chicken wire and placed in a shallow basin lined with an elasticized polyolefin membrane. During rainy weather, these cells were protected by a corrugated plastic cover.

eliminated from exposure with the acid and strong alkaline wastes in the screening test. The 13-cm-(5-in.-)thick specimens exhibited low permeability ($<10^{-8}$ cm s $^{-1}$), though the bentonite

A specimens showed significantly lower permeability than the bentonite B specimens. This type of lining material is probably not satisfactory for oily wastes, since considerable fingering of

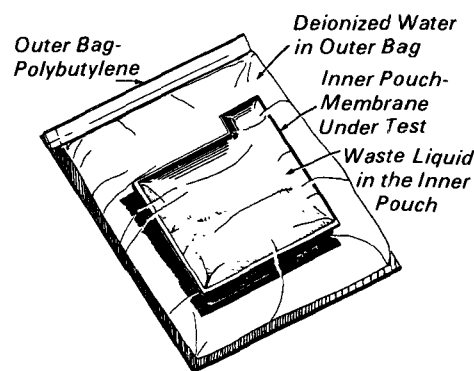


Figure 4. Schematic of a pouch assembly showing inner pouch made of membrane material under test. The pouch is filled with waste liquid and sealed at the neck. The outer polybutylene bag, which can be easily opened, is filled with deionized water.

the waste into the liner mass took place during the 980 days of exposure. None of the oil broke through the liner to be collected in the base, however. Even though some flow through the liner occurred, the distribution of the metals at the various depths was uniform. The use of a soil cover on the liner to produce an overburden could probably reduce the fingering effect and reduce the flow.

Soil Cement

The 10-cm- (4-in.-) thick soil cement specimens showed resistance to spent caustic, the lead waste, the two oily wastes, and the pesticide waste. Soil cement had been eliminated from exposure to the strong acid waste (HNO $_3$ -HF-HOAc) in the screening test. No seepage occurred in and of the specimens. In the five that were recovered and tested, actual increases occurred in compressive strength. Metal concentrations were uniform through the depth of the liner.

Sprayed-On Asphalt

When exposed to spent caustic, pesticide waste, and water, the sprayed-on asphalt showed good performance. A leak developed in one of the specimens in a cell containing brine. The sprayed-on asphalt had been eliminated from exposure to the oily and the highly acidic wastes during screening. In contact with the lead waste, it has softened considerably. In all cases, it absorbed water. Compatibility tests would thus be appropriate when considering

sprayed-on asphalt for any impoundment linings, and all oily or highly acidic wastes should be avoided.

Polymeric Membranes

Among the polymeric materials, those that were partially crystalline showed the least absorption of wastes and largely retained their physical properties best. These materials included sheetings of elasticized polyolefin, polyester elastomer, high- and low-density polyethylene, polybutylene, and polypropylene. The last four of these were not compounded for use as specific liner membranes but were tested because of their potential use in liner materials. Some of these materials showed considerable swell in oily wastes. Also, important properties were lost when elasticized polyolefin was exposed to the highly alkaline waste (slop-water) and when polyester elastomer was exposed to the highly acidic waste (HNO_3 -HF-HOAc).

Polyvinyl chloride (PVC) membranes varied considerably from sample to sample and were highly variable in the wastes. The need for compatibility testing was quite apparent. Test results for the specific materials tested varied from major weight losses to significant increases, and from near embrittlement to severe softening. This variation indicated the effects of compound differences (e.g., plasticizers).

Crosslinking normally causes a polymer to swell less and be more resistant to change in liquids. This quality was observed in the chlorinated polyethylene (CPE) lining materials, which in all but one case experienced less swelling and fewer property changes with the crosslinked materials. In contrast, a thermoplastic ethylene propylene rubber (EPDM) sheeting had significantly lower swelling in the wastes than a crosslinked EPDM, which is the usual type of EPDM sheeting used for liners. Recognize, however, that considerable differences do exist in the EPDM rubbers, some of which can be crystalline and would reduce swelling.

Two membrane liners showed distinct incompatibility with specific wastes, though the time to failure was about 1 year. The polyester elastomer in the strong acid (HNO_3 -HF-HOAc) failed completely and cracked. The elasticized polyolefin absorbed considerable amounts of the alkaline slopwater waste and showed a major increase in permeability after about 1 year in the pouch test.

Wastes

In order of their overall detrimental effects on the lining materials, the 13 wastes and test media used in the project can be grouped as follows:

- Acidic wastes
- Alkaline wastes
- Brine and industrial wastes
- Lead waste
- Oily wastes
- Trace organic test liquid
- Deionized water and pesticide waste

The more acidic and the more alkaline wastes of the various groups were the more aggressive to the lining materials.

Among the wastes included in the program, those with oily constituents generally caused the greatest swelling and loss in properties. In the case of the PVC membrane, however, two nonoily wastes caused significant loss of plasticizer and thus stiffening of the PVC specimens.

A trace (<0.1%) of an organic species such as tributyl phosphate in an aqueous solution can cause severe swelling and loss of physical properties of some membrane liners after long exposure. Considerably varied reactions occurred among the 16 membranes immersed in the tributyl phosphate solution. Partially crystalline materials showed the fewest effects of the trace organics in the wastes.

Nonhomogeneity of the wastes and the sampling can pose major problems in the compatibility testing and selection of lining materials for a given facility. More laboratory data are needed to develop background correlations with field exposure and actual service. Some of the wastes stratified so that the waste at the bottom of a cell or tank had a considerably different composition from that at the top. Thus the specimens exposed horizontally at the bottom of a cell were not exposed to the same waste that suspended specimens were exposed to at the top. Such could also be the case with a pond liner when exposure at the bottom is compared with exposure near the top. Thus the possibility exists that a test specimen in a compatibility test may not be exposed to a representative waste from the impoundment or to a waste from a critical area in the pond. Two of the wastes were saturated with salts that crystallized out of the waste onto the liner, thus exposing the liners to wastes different from those in the waste solution. Constant agitation of a nonhomogeneous waste during a compatibility test

may be a solution, but it may not result in the worst exposure condition. A procedure using agitation should be studied.

Test Methods

The various test methods used revealed significant differences among the liners for each type of waste. Generally, a correlation appears to exist among the results of the different methods used.

Test duration should be as long as possible. The 12- and 24-month exposures originally set in the contract are far too short for estimating service lives unless the latter are relatively short. Also, the number of exposure periods was inadequate for projecting some of the physical properties because of inherent sources of error arising from the nature of these tests. The primary and immersion tests performed in this project were inadequate because they generally included only two exposure periods.

Immersion Test

An immersion test can be adapted for use as a compatibility test of a lining material with a given waste if at least four time exposures are used with at least 1 month between exposures. But additional investigation of the immersion test should be run to develop correlation with actual experience.

Tub Test

The tub test demonstrates that different locations within an impoundment can have significantly different effects on the retention of properties by a liner. This test also shows the greater severity of effects on liners at the interface between the waste and the weather.

Pouch Test

The pouch test used in this project with only thermoplastic and crystalline membranes shows considerable promise for assessing the effects of a waste liquid in contact with a polymeric membrane liner. Efforts should be undertaken to increase the applicability of this type of test to crosslinked sheeting and to stiff, thick sheetings. The test was run primarily with thinner sheetings that could be heat-sealed or solvent-seamed. The pouch tests, however, may have to be run for extended periods of time to observe long-term effects, and they may require interpretation until they have been used extensively.

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Robert Landreth is the EPA Project Officer (see below).

The complete report, entitled "Liner Materials Exposed to Hazardous and Toxic Wastes," (Order No. PB 85-121 333; Cost: \$23.50, subject to change) will be available only from:

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