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HANFORD PERMANENT ISOLATION BARRIER PROGRAM:  
ASPHALT TECHNOLOGY DEVELOPMENT

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## Hanford Permanent Isolation Barrier Program: Asphalt Technology Development

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### Abstract

An important component of the Hanford Permanent Isolation Barrier is the use of a two-layer composite asphalt system, which provides backup water diversion capabilities if the primary capillary barrier fails to meet infiltration goals. Because of asphalt's potential to perform to specification over the 1000-year design life criterion, a composite asphalt barrier (HMAC/fluid-applied polymer-modified asphalt) is being considered as an alternative to the bentonite clay/high density poly(ethylene) barriers for the low-permeability component of the Hanford Permanent Isolation Barrier. The feasibility of using asphalt as a long-term barrier is currently being studied. Information that must be known is the ability of asphalt to retain desirable physical properties over a period of 1000 years. This paper presents the approach for performing accelerated aging tests and evaluating the performance of samples under accelerated conditions. The results of these tests will be compared with asphalt artifact analogs and the results of modeling the degradation of the selected asphalt composite to make life-cycle predictions.

**Key Words:** asphalt, barriers, long-term stability, accelerated aging, asphalt analogs.

## Introduction

Permanent isolation barriers use engineered layers of natural materials to create an integrated structure with redundant protective features that are designed to divert the movement of infiltrating water from buried radioactive, hazardous, or mixed wastes. A key component of the Hanford Permanent Isolation Barrier (HPIB) is the use of a two-layer composite asphalt system, which provides backup water diversion capabilities if the primary capillary barrier fails to meet infiltration goals. An example of the barrier design is illustrated in Figure 1. The use of the two-layer asphalt system also provides RCRA (Resource Conservation and Recovery Act of 1976) equivalency.

A composite asphalt barrier (HMAC/fluid-applied polymer-modified asphalt) is being considered as an alternative to the RCRA bentonite clay/high density poly(ethylene) (HDPE) barriers for the low-permeability component of the HPIB. It is believed, if not fairly well accepted, that HDPE liners and clay barriers will be incapable of performing over the proposed design life of most surface barriers. Asphalt, on the other hand, appears to be capable of performing to specification over the 1000-year design life criterion. The complex chemistry of asphalt is perhaps its biggest advantage over most other low-permeability construction materials.

Pacific Northwest Laboratory (PNL) is developing asphalt barrier technologies as part of an overall barrier development program that also includes Westinghouse Hanford Company and ICF Kaiser Company. Information being determined includes asphalt longevity, asphalt barrier physical properties, asphalt analogs, RCRA equivalency, and asphalt distortion. Work being carried out includes developing accelerated aging tests

and evaluating the performance of samples under accelerated conditions; comparing the results of the tests with asphalt artifact analogs; and modeling the degradation of the selected asphalt composite to make life-cycle predictions. More details can be found in the PNL Test Plan for Asphalt Technology Development (Freeman and Romine 1994).

### Historical Asphalt Applications

Natural asphalt, or bitumen, has been exploited for a documented 5000 years, and may have been used by prehistoric peoples for a considerably longer period. Available worldwide in surface or readily accessible deposits, asphalt is a transitional phase in the evolution of crude oil, in which lighter, volatile fractions have been removed through evaporation, mechanical processes, thermal alteration, or high pressure (Hellmuth 1989). The state of the material's evolution, differences in the composition of the parent material, and the process(s) to which it has been subjected all account for the extreme variability found in the physical and chemical characteristics of asphalt. Asphalts from a majority of sources share common features, however, which made them attractive to early cultures: a high degree of water repellency, lack of volatility, pronounced adhesiveness, impermeability, and longevity. These same properties have stimulated interest in incorporating asphalt into nuclear waste containment systems.

Wherever natural asphalt outcroppings occur, asphalt artifacts are found in archaeological deposits. The earliest recorded use of asphalt, which dates to 3250 B.C. (~5200 B.P.), comes from the Mesopotamian and Indus civilizations of the Middle East (Forbes 1955). Asphalt was used as mortar, stucco, sealant, waterproofing agent, and

embalming material. It was also an important trade and tribute item throughout the region. Accounts of early asphalt use from this region abound, due primarily to its availability.

Asphalt from Val de Travers in Switzerland was used by prehistoric lake dwellers as a preservative for underwater building supports (Nellensteyn 1938). There are numerous accounts of prehistoric asphalt use in North America, ranging from the famous "Seneca Oil" of the Seneca Indians of the northeastern United States (Giddens 1974) to Florida and Texas (Dedera 1976), into the Mexican Gulf states of Tamaulipas and Vera Cruz, where asphalt was used as flooring in temple mounds 3000 years old (Muir 1926), and west into Utah and Wyoming (Dedera 1976).

Some of the best documented accounts of asphalt use in North America come from the Santa Barbara Channel region of California, where its use was reported by early Spanish explorers (Fages 1875). Asphalt artifacts dating to 5000 years B.P. have been recovered from archaeological sites throughout the region (Rogers 1929; Heizer 1943; Gutman 1979, 1983; Moratto 1984). Many reported artifacts from the Santa Barbara Channel were found in graves, which makes them most suitable as analogs of a buried moisture barrier (the composite asphalt barrier).

#### Role of Asphalt in Permanent Isolation Barrier

The composite asphalt layer provides a redundant, but important, backup to the overlying earthen layers. It must be able to reduce infiltration to less than  $1.6 \times 10^{-9}$  cm/s, which exceeds the RCRA requirements by almost 2 orders of magnitude. A

composite asphalt barrier was selected for use in the HPIB for several reasons. Low air void, high-asphalt-content hot-mix asphalt concretes (HMAC) are noted for low permeability and have mechanical properties needed to withstand subsidence events. Furthermore, HMAC covers have been shown to be effective in preventing root and animal penetration. Studies with vegetation growing above an asphalt layer show that roots are unable to penetrate an 8-cm-thick asphalt/aggregate layer. Similarly, animals (ground squirrels and prairie dogs) confined to digging in shallow soil immediately above an asphalt layer were unable to penetrate the 8-cm-thick layer (Cline et al. 1982). Finally, HMAC is a widely used construction material with well-documented engineering properties and construction techniques. The construction technology is already deployed and readily available for large-scale testing and demonstration for utilization in the HPIB.

Although there is a great deal known about HMAC properties, the effects of aging in a buried environment for long times is unknown. Measuring or estimating physical degradation rates of the asphalt components of the HPIB is required to evaluate long-term barrier performance. Changes in properties of the asphalt binder, such as storage and loss moduli, and permeability need to be known as a function of age.

A number of examples and references can be used to infer the long-term behavior of asphalt. As noted above, asphalt has been used for several thousand years as a barrier to water infiltration because of its impermeable nature (Forbes 1955). However, most of the data available on the performance properties of asphalt barriers are from freshly manufactured materials. A large portion of this information is available in

literature associated with the use of asphalt as a matrix for solidification of low-level radioactive wastes (Fitzgerald et al. 1970; MRM Partnership 1988; Fuhrmann et al. 1989). Some of the data associated with solidification of low-level radioactive wastes will be useful, but generally those data do not address the specific needs of subsurface barriers. The work discussed in this paper is designed to fill some of the technology gaps as needed for the HPIB.

### **Asphalt Technology Development**

Several activities are being conducted or are planned to provide data to support the life-cycle predictions for the composite asphalt component of the HPIB.

1. Develop a defensible accelerated aging test procedure to allow measurements of asphalt barrier properties as a function of age for a minimum of 1000 years.
2. Age potential asphalt materials over a range of conditions expected in the subsurface environment, including temperature, oxygen content, moisture, and the presence of gases or ions produced by the underlying soil and waste forms.
3. Measure the changes in fundamental asphalt barrier properties using standard and modified testing procedures to provide the database of information required to assess the long-term performance of the asphalt barrier system.

4. Supplement and validate the laboratory aging data by comparing with several-hundred to several-thousand-year-old asphalt artifacts from Santa Barbara, California, and other archaeological sites.
5. Estimate the response of aged asphalt materials to a range of disruptive stresses such as a subsurface subsidence and/or seismic events through computer simulations and limited laboratory and field tests.

#### Accelerated Aging Procedure Development

The protocol must identify conditions that can accelerate the asphalt aging mechanisms sufficiently that a 1000-year exposure to a subsurface environment similar to that expected for the HPIB can be simulated in a manageable time (weeks or months). Ideally, the accelerated aging test conditions would simply accelerate the normal aging mechanisms (e.g., chemical reactions) without causing entirely different reactions to occur. The accelerated aging test procedure will be developed based on procedures developed by the Strategic Highway Research Program (SHRP). These procedures will be modified to better reflect the subsurface environment and loading experienced by the asphalt barrier. Results of the accelerated aging tests will be compared with asphalt analogs (ancient asphalt artifacts) to try to associate an aging time to the accelerated exposures.

## Aging Mechanisms

Much research has been performed on understanding the mechanisms of asphalt aging (Mill 1990; Petersen 1990; Quddus and Khan 1990). The majority of the work has been associated with the asphalt pavement industry, where the time frame of consideration is about 15 to 30 years (the design life of a typical modern pavement). In that research, scientists have employed accelerated aging tests using elevated temperature levels, increased O<sub>2</sub> concentrations, and time to simulate aging over the life cycle of pavement (Bell 1990; Petersen 1990). Development of accelerated tests and interpretation of experimental results have been based on the analysis of a large number of samples which were aged in the field (Bell 1990; Petersen 1990; Quddus and Khan 1990). These field-aged samples were exposed to moisture, actinic light, temperature extremes, and dynamic and static loads from traffic. Recent results have established a good correlation between laboratory accelerated aging procedures for asphalt binders (pure asphalt) and naturally aged asphalt binders in the field (SHRP 1992). Another potential aging mechanism is biological decomposition. However, rates of biodegradation are estimated to be very low, in the range of a few centimeters in 1000 years (Luey and Li 1992).

The environment for subsurface barriers is much different from those for asphalt pavements. The asphalt layers will not be subjected to temperature extremes (pavement temperatures up to 60°C are not uncommon), ultraviolet (UV) radiation, or heavy traffic. The temperature of the installed barrier should remain below ~20°C once covered by ~ 4.5 m of soil layers. The soil layers also preclude any exposure of the

asphalt to UV radiation, which is a major initiator of oxidation reaction with organic materials. Some oxidation of the asphalt is still expected, but rates of oxidation should be substantially lower than those for surface-exposed asphalt pavements.

### Material Composition

The susceptibility of asphalt/aggregate mixtures to various degradation mechanisms also depends on the chemical composition of the asphalt and aggregate (Petersen et al. 1974; Halstead 1985; Tuffour and Ishai 1988; Petersen 1990). The chemical composition of asphalt varies greatly, depending on the source of the crude stock and on the refining techniques employed in the manufacturing. The following variations are typical:

- type and concentration of heteroatom species
- ratio of aromatic to aliphatic carbon
- ratio of aromatic to aliphatic hydrogen
- molecular size distribution
- type and content of polar and neutral species.

These variations have a significant impact on the physical properties of an asphalt. The chemical composition will affect the way an asphalt or asphalt mixture responds to aging (accelerated or natural). As asphalts age they stiffen and become more susceptible to cracking. The PNL work is specifically addressing the following aging mechanisms:

- intramolecular oxidation
- uptake of molecular oxygen

- loss of volatiles
- molecular self-assembly
- poly-condensation reactions.

The HMAC to be used for the HPIB is composed of approximately 92.5 wt% aggregate. The chemical composition of aggregates also varies substantially and may influence asphalt aging, physical properties of the mixture, and susceptibility to stripping of the asphalt from the aggregate (Petersen et al. 1974). Aggregates also vary in physical properties such as porosity, gradation, and surface texture. These physical properties have a major influence on the asphalt/aggregate bonding and, hence, to mechanical stability of the mixture. For these reasons, it will be important to include aggregate in designing aging experiments because the effect of aggregate on test samples must be characterized.

#### Test Conditions

During the development of the accelerated aging procedure, only the asphalt binder and polymer-modified asphalt will be exposed to accelerated aging conditions and analyzed chemically and physically. The feasibility of accelerated aging HMAC samples will be evaluated at a later date. The results of these experiments will be compared against the results from control experiments and unaged and asphalt artifact analog experiments. This analysis is expected to tie the results of the accelerated aging experiments to a time line defined by unaged and asphalt artifact experiments. This will

provide the support required to establish the longevity of the materials used for the composite asphalt barrier.

Five asphalts will be used to develop the accelerated aging procedure: U.S. Oil and Refining AR-4000 asphalt, the asphalt specified for use in the prototype HPIB; and four different asphalts from the Strategic Highway Research Program - Materials Reference Library (SHRP-MRL). The MRL asphalts will be chosen to represent a range of different types of asphalts available around the world. Asphalts from Venezuela, California, and Texas will be used to evaluate differences in aging among asphalts of varying chemistry.

Asphalt binders will be exposed in vessels pressurized with air up to 300 psi and temperatures up to 100°C. The residues from these exposures will be analyzed chemically and rheologically to relate chemical changes to changes in physical properties. The following chemical and physical procedures will be used to characterize the asphalt binders before and after accelerated aging:

- quantitative infrared spectroscopy (IR)
- high pressure liquid chromatography-size exclusion chromatography (HPLC-SEC)
- Rheological Properties (storage modulus, loss modulus, creep compliance, viscosity vs. temperature).

Tests being conducted in FY 1994 are primarily being directed at developing a defensible accelerated aging test and obtaining baseline data on performance of the barrier components. This work will provide data on chemical and physical properties

for the components of the HPIB as a function of oxygen (air) concentration, temperature, and time of conditioning. It is expected that the chemical and physical properties of the aged materials will be substantially different from those of newly produced materials. Data obtained in these tests will provide the basis for determining the best accelerated aging conditions for simulating extremely long-term exposure conditions. Data from the long-term exposures will be used to estimate barrier properties after extremely long periods.

### Analytical Techniques

It is critical that the data generated in this study have a firm connection to past data, which will be ensured by reproducing data reported in the SHRP-MRL. This will provide a validation of our procedures and techniques while also providing a baseline of properties for unaged materials.

Infrared (IR) spectroscopy will be used to monitor changes in chemical functional groups present in asphalt barrier components as a result of accelerated aging conditioning (Petersen 1986). Quantitative functional group analysis will be performed to specifically characterize the following products of oxidative aging: phenolic, pyrolic, sulfoxide, carbonyl, ketone, carboxylic acid, and anhydride functionalities. Samples for analysis by IR and HPLC will be recovered from the asphalt mixtures and neat asphalt coupons by dissolving a portion of the sample in spectral-grade tetrahydrofuran (THF). HPLC-SEC will be used to measure changes in the molecular size distribution caused by condensation reactions and loss of volatiles. In this technique, samples are dissolved in a

suitable solvent and passed through a column of macroreticular styrene-divinylbenzene beads. These beads have very small openings (5 Å and greater). The smaller molecules in the samples will be retained in the openings (retention time is a function of molecular size), while larger molecules will be carried along in the eluent. Through this mechanism a separation based on molecular size is achieved. HPLC-SEC data will be used to monitor the increase in the molecular size distribution as the result of oxidative aging (Jennings 1985). HPLC-SEC will also be used to evaluate self-assemblage in the asphalt (Brule et al. 1986; Glover et al. 1987). HPLC-SEC data, with weight change data, will be used to determine the loss of volatiles.

Changes in elastic and viscous properties of the aged asphalt binder will be determined by rheological techniques. Both oscillatory and rotation techniques will be used to monitor changes in storage, loss, and relaxation moduli and storage, loss, and creep compliance. These data describe how the asphalt binder ( and ultimately the HMAC) will respond to forces imposed by the barrier if subsidence beneath the asphalt layer occurs. Procedures will be similar to those outlined by SHRP for Dynamic Shear Rheometry, but will be expanded to obtain the full "Master Curve" that describes the rheology of the asphalt binder. These properties can be used to estimate the properties of the HMAC layer without the need to age the entire HMAC matrix by using time/temperature superposition to obtain certain physical properties of HMAC samples, such as indirect tensile strength. If the changes in rheological properties is known as a function of age, the expected increase in stiffness of the asphalt can be simulated by reducing the temperature of the HMAC when determining mechanical properties. This

would eliminate problems associated with exposing compacted HMAC specimens to high pressures, which can result in microfracturing and other physical damage if the pressure is released too rapidly.

### Accelerated Permeability Analysis

One of the primary properties that will be used to determine asphalt barrier performance is hydraulic conductivity. The two-layer asphalt system must be able to meet overall barrier infiltration requirements, i.e., equivalent to  $1.6 \times 10^{-9}$  cm/s. Measuring a hydraulic conductivity this low requires modification of standard permeability testing protocols. Also, because the permeability is much different for asphalt aggregate mixtures, the permeability of the HMAC must be measured directly and cannot be extrapolated from measurements on the asphalt binder alone.

A procedure to measure the hydraulic conductivity of the HMAC component of the HPIB is being developed in FY 1994. The test vessel is similar to those used in determining the hydraulic conductivity of compacted soils (ASTM D-2434 1993). Permeability measurements are performed on standard Marshall compacted HMAC samples. The permeameter is made with a 4.5-in.-i.d. Plexiglas tube with Plexiglas end caps. The bottom one-half inch of the annulus is filled with cured Silicone-RTV. The remainder of the annulus is filled with asphalt cement. The cell is gasketed, capped, and pressurized with a 2.5-m tall falling head water column. The conductivity is determined by monitoring the inflow of water into the sample with a pipette mounted at the top of the water column.

### Asphalt Analogs

Archaeological asphalts are expected to provide valuable data on asphalt aging, not available from any other source, linking accelerated aging results to a time line for buried asphalt. This information can then be used to evaluate the performance of the asphalt components of the HPIB. The analysis of the seep materials and the asphalt artifacts provides a unique opportunity to study the aging response of an asphaltic material in a depositional environment analogous to that of the Hanford barriers. The range in the ages of the artifacts corresponds to the anticipated design life of the Hanford barriers.

### Artifact Sources

Archaeological samples were selected from the Santa Barbara region based on the availability of artifacts for testing and the large base of information on the source and use of asphalt in the region. The source of the asphalt used in the artifacts was determined using nickel/vanadium (Ni/V) ratios (Gutman 1979; Gutman 1983). There are also very detailed ethnographic accounts on asphalt processing methods (Hudson et al. 1978). Artifacts used in this study will be limited to those recovered from buried sites to best simulate the environment of the asphalt layer in the HPIB. A second set of asphalt artifacts is currently being identified to provide corroborating data on how asphalt ages in a buried environment.

## Age Determinations

Radioactive carbon dating will be used to determine the age of the artifact.

Wherever possible, specimens of shell, bone, or wood charcoal reported to have been found in the same graves as the selected artifacts will be obtained from the museums and radiocarbon dated. Ideally, materials to which asphalt is found adhering will be selected. It will be assumed that the radiocarbon age of the sample is representative of the length of time that the artifact have been buried in the grave sites. If objects from the same grave cannot be obtained, specimens found nearby in the same geological layer will be used. When asphalt is found adhering to an object to be dated, it will be mechanically removed, if possible, or removed by solvents. The asphalt will be recovered from the solvent under vacuum conditions for later chemical analysis.

## Chemical Analysis

Asphalt artifacts and samples obtained from the asphalt seeps will be analyzed to provide data for estimating the rate and degree of chemical changes in the asphalt artifacts. Neat asphalt from the seeps and neat asphalt mixed with pitch, following the proportions described in the anthropological literature, will be analyzed as controls. Deviation of chemical properties in the artifacts from these controls will be interpreted as change attributable to long-term internment. Analyses will include HPLC-SEC and IR as described previously.

## **Aging Control Asphalt**

The ability of the accelerated aging procedure to reproduce chemical changes found in artifacts will be determined by exposing asphalt recovered from seeps near the artifacts to accelerated aging conditions described previously. Both neat asphalt and asphalt/pitch mixtures will be exposed to evaluate the influence of pitch on asphalt aging characteristics. Exposures will occur over a range of air pressures and temperatures determined by the results of the accelerated aging procedure development task.

## **Conclusions**

Asphalt has many desirable characteristics for an excellent long-term moisture barrier as part of the HPIB. However, the required data on changes in properties over hundreds to thousands of years are not available. These data will be obtained through the use of accelerated aging tests coupled to analysis of several-thousand-year-old asphalt artifacts.

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**Figure Caption:**

**Cross Sectional View of the Hanford Permanent Isolation Barrier Showing Position of Asphalt in Barrier Profile**

