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Effects of Mixed Waste Simulants on Transportation Packaging Plastic Components*

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INTRODUCTION

The purpose of hazardous and radioactive materials packaging is to enable these materials to be transported without posing a threat to the health or property of the general public. To achieve this aim, regulations have been written establishing general design requirements for such packagings. While no regulations have been written specifically for mixed waste packaging, regulations for the constituents of mixed wastes, i.e., hazardous and radioactive substances, have been codified. The design requirements for both hazardous [49 CFR 173.24 (e)(1)][1] and radioactive [49 CFR 173.412 (g)] materials packaging specify packaging compatibility, i.e., that the materials of the packaging and any contents be chemically compatible with each other. Furthermore, Type A [49 CFR 173.412 (g)] and Type B (10 CFR 71.43)[2] packaging design requirements stipulate that there be no significant chemical, galvanic, or other reaction between the materials and contents of the package. Based on these requirements, a Chemical Compatibility Testing Program was developed in the Transportation Systems Department at Sandia National Laboratories (SNL). The program, supported by the U.S. Department of Energy's (DOE) Transportation Management Division, EM-261 provides the means to assure any regulatory body that the issue of packaging material compatibility towards hazardous and radioactive materials has been addressed. This program has been described in considerable detail in an internal SNL document, the Chemical Compatibility Test Plan & Procedure Report (CCTP&PR)[3]

The CCTP&PR presented a comprehensive discussion of chemical compatibility studies on plastic materials which could be used as liners and seals in transportation containers. The report also provided a broad overview of what issues need to be addressed in any program that undertakes chemical compatibility evaluations. It provided general information and proposed a number of tests and procedures for carrying out such a program. Because none of the current mixed waste packaging concepts have received approval, a program was developed to test various properties of a broad range of liner and seal materials. The selected materials were ten plastics having a known chemical resistance to a large number of classes of chemicals. The term plastic, as used in this paper, refers to polymeric materials, which includes both seals and liner materials. The selected plastics were butadiene-acrylonitrile copolymer (Nitrile), cross-linked polyethylene (XLPE), epichlorohydrin (EPI), ethylene-propylene rubber (EPDM), fluorocarbon (VITON™ or Kel-F™), tetrafluoroethylene (TEFLON), high-density polyethylene (HDPE), isobutylene-isoprene copolymer (Butyl rubber), polypropylene (PP), and styrene-butadiene rubber (SBR).

The main threats to seals and liners from anticipated mixed waste compositions are expected to come from strong aqueous base, chlorinated solvents, hydrocarbon solvents, and ketones. Thus, any seal or liner materials used in packaging must be resistant these classes of chemicals and also to radiation. Because few polymers are resistant to all these effects, it is possible that specific polymers must be chosen as container components for different mixed wastes.

In view of the wide variety of waste compositions found throughout the DOE complex, it is not possible to choose one specific simulant mixed waste composition for testing. In addition, since no specific transportation container has been selected or has been specified for certain mixed waste compositions, it is neither possible nor prudent to select a specific waste composition. However, there is information in the open literature and DOE reports that provides adequate guidance on the quantities and characters of the largest waste streams found within the DOE complex. Based on this rationale, four simulant mixed waste compositions were selected. These simulant mixed wastes consist of Hanford Site Tank Waste, chlorinated solvent mixtures, scintillation fluids, and wastes consisting of ketones. Their detailed compositions are described in the Experimental Section.

In this paper, we describe the general elements of the testing program and the experimental results of the screening tests. The implications of the results of this testing are discussed in the general context of packaging development. Additionally, we present the results of the first phase of this experimental program. This phase involved the screening of five candidate liner and six seal materials against four simulant mixed wastes. Since mixed wastes by definition are composed of radioactive and hazardous constituents, the simulant wastes needed to have both of these components present to effectively mimic

real mixed wastes. This objective was accomplished by designing the testing program in such a manner that the candidate materials were first exposed to gamma radiation followed by exposure to the four waste types.

BACKGROUND

The purpose of a Chemical Compatibility Program[4] is to provide a scientifically defensible methodology for measuring the chemical compatibility of potential polymeric liner and seal materials with hazardous wastes. These polymeric materials are those which may be used in current and future container designs for the transportation of hazardous and mixed wastes throughout the DOE complex. The approach for developing such a program was to assess the current state of chemical compatibility testing technology, and to suggest routes that might lead to satisfactory, comprehensive, and reliable chemical compatibility data for use by the U. S. DOE in its Transportation Management Division.

Based on a review of the large body of chemical compatibility information, it is important to be aware of the basic factors that play a role in determining chemical compatibility of polymers (plastics) with various chemical environments. Polymer-environment interactions can be either reversible (absorption leading to plasticization and swelling) or irreversible (oxidation). These may also be referred to as physical (reversible) and chemical (irreversible) interactions, although the physical interactions have a significant chemical aspect in the breaking of secondary interchain bonds. In general, polymers are resistant to weak acids, weak bases, and salt solutions. Strong acids can oxidize polymers leading to embrittlement. Organic solvents cause swelling, softening, and eventually dissolution. Most chemical degradation is system-specific for a particular polymer and fluid or gas. It is unlikely, therefore, that the chemical compatibility information between polymers and any complex waste form being required for regulatory assurance will be found in the literature. For this reason, liner and seal materials selected in the design of transportation packagings will require compatibility testing with simulated wastes to ascertain their chemical resistance to these substances.

The container liner provides a barrier between the waste material(s) and the container structure. The liner itself is not expected to see significant structural loads in service. Emphasis for liner material selection is on their chemical compatibility with any hazardous contents. Liner material properties potentially most affected by chemical exposure are dimensional stability, permeability, and hardness. Stress cracking in the presence of some chemicals may also occur with certain polymers. Seals found in many packages are devices or systems that create a tight union between elements of the container. These devices consist of a polymer that can be or has been modified to a state exhibiting little plastic flow and quick or nearly complete recovery from an extending force. Polymers of this type are referred to as elastomers.

The main threats to seals and liners from the anticipated waste forms are judged to come from strong aqueous base, chlorinated solvents, hydrocarbon solvents, and ketones. Because few polymers are resistant to all these materials, it is possible that different polymers will be chosen as container components for the different waste streams being transported. The candidate liner and seal materials which are known to be chemically resistant to the above described waste forms, are butadiene-acrylonitrile copolymer, cross-linked polyethylene, epichlorohydrin, ethylene-propylene rubber, fluoro-carbon, tetrafluoroethylene, high-density polyethylene, isobutylene-isoprene copolymer, polypropylene, and styrene-butadiene rubber.

Because of the wide variety of waste compositions found throughout the DOE complex, it is not possible to choose one specific simulant waste composition. In addition, since no specific transportation container has been selected or has been specified for certain waste compositions, it is not possible nor prudent to select a very specific waste composition. However, there is sufficient information in the open literature and in DOE reports that provides some guidance on the quantities and character of the larger waste streams found within the DOE complex. Based on this rationale, four simulant mixed waste compositions were selected. To simulate some of the tank wastes at the Hanford Site, a rather simple aqueous solution containing 2 molar sodium nitrate, 0.7 molar sodium nitrite, 2 molar sodium hydroxide, 5.5 molar sodium carbonate, 0.1 molar cesium chloride and 0.1 molar strontium chloride was developed.

The combination of nitrate and nitrite anions represent the oxidizing chemical species while the hydroxide and carbonate anions simulated the corrosive nature of the tank wastes. The last two constituents, cesium and strontium, simulated the radioactive component in this large volume waste stream. To simulate the sizable inventories of chlorinated hydrocarbons mixed wastes, a solution of 50% by volume of trichloroethylene, 25 % chlorobenzene, 24% carbon tetrachloride and 1% cerium (III) 2-ethyl hexanoate was selected. This mixture of chemicals was believed to qualitatively represent the chlorinated solvent waste streams at the DOE sites. The cerium salt simulated uranium and other actinide elements because of similarities in ionic radii and redox properties. Similarly, to simulate liquid scintillation fluids and/or fuel hydrocarbons, a solution of 33% toluene, 33% xylene, 32% dioxane with 1% water was used. The water component was meant to simulate tritiated water found in some mixed wastes. Finally, to simulate ketones, a solution of 60% MEK and 39% MIK containing 1% cerium (III) acetyl acetonate hydrate was used. It should be mentioned that ketones were solvents frequently used in the nuclear fuel reprocessing cycle.

The variables in chemical compatibility testing represent those factors that are meant to simulate the conditions under which the material will be used under normal and, in some cases, abnormal conditions. Specifically, the more important of these variables include exposure temperature, exposure time, radiation dose, and waste liquid concentration.

Some standard testing methods specify exposure temperatures of 23°C and 50°C. Since the purpose of this program is to evaluate the effects of hazardous materials on transportation container components, it is worthwhile to mention that the Department of Transportation (DOT) regulations in 49 CFR 173.24 (e)(3)(ii) require chemical compatibility testing at temperatures of 18, 50, and 60°C. Since this program's goal is to support the development packaging used in transport of mixed waste, we have chosen the set of temperatures whose basis is in DOT requirements, i.e., 18, 50, and 60°C.

As with exposure temperatures, in standardized testing methods, the duration of exposure varies with each test protocol. However, regardless of the actual test duration, most groups involved in chemical compatibility testing agree that what is required is a three-level approach involving short-duration, intermediate, and long-duration exposure. The short duration tests are considered a good way to screen materials for further testing. Intermediate duration are considered to be 4 months in length. Long duration tests are considered by some to be more than 4 months in length. DOT specifies such a testing duration scheme for its plastic packaging used for liquid hazardous materials. Accordingly, we have selected exposure times of 7, 14, 28, and 180 days to include short and long duration times.

With regard to radiation dose, some international standards recommend that materials be exposed to absorbed doses ranging from 10^5 to 10^{10} rad. While the doses recommended by these standard span a range where no effects in material properties are expected, to where plastic materials are expected to be severely damaged, the transportation containers for mixed wastes are not expected to receive doses above 10^4 rad. We have selected γ-radiation doses of 143,000, 286,000, 571,000, and 3,672,000 rad from a ^{60}Co source. These radiation values were calculated based on γ-ray dose rate data available to us for the projected components of a pump submerged in a specific storage tank at Westinghouse Hanford Co. These data indicate a maximum γ-ray dose rate in the range of 750 to 850 R/hr. The maximum dose rate of 850 rad/hr was used in calculating the dose that container materials will receive from a ^{60}Co source at SNL. Using this dose rate, the four doses described above were calculated for 7, 14, 28, 180 day exposures, respectively.

A final variable for chemical compatibility testing is waste concentration. Practitioners of chemical compatibility evaluations generally believe that liner and seal materials should be tested with the actual concentration of waste. However, exposure to pure chemicals is generally rejected since it does not simulate actual conditions where concentrations are usually lower. This is especially true where complex mixtures of many chemicals are concerned. A generally accepted concentration is exposure to 10 times the expected actual concentration. This value is considered a good way to simulate a worst-case situation. For transportation containers, such a worst-case scenario could involve the evaporation of the contained waste, i.e., leakage of the more volatile components from a container. For this reason we selected a mixture of pure chemicals at their full strength as a worst-case condition.

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A variety of properties have been proposed and used for evaluating liner and seal materials. Of primary interest to most organizations is resistance to chemicals in wastes. For organizations concerned with mixed waste forms, the materials' resistance to both chemicals and radiation are of interest. Where low-levels of radiation are expected, resistance to chemicals may be of greater interest. Chemical compatibility is usually based on static physical test data gathered after exposure of the material to a chemical (leachate, surrogate, or simulant). By far the simplest of such testing involves changes in mass and dimensions. Since specific gravity measurements combine these two units in one method, this method is particularly attractive for screening tests. Physical test data may also include tensile properties such as tensile strength, yield strength, elongation at break, elongation at yield, and some others. These one-dimensional, short-term, simple tests are easily accomplished in the laboratory. Additional physical tests may include tear and puncture resistance of the plastics. However, since liners and seals in packaging applications are not expected to be exposed to such failure modes, the latter tests will be omitted.

Traditionally in plastics and rubber testing, the static physical tests led by hardness and tensile stress/strain measurements are used to indicate changes and degradation. The stress/strain properties are related to the molecular makeup of the polymer, so that any attack or alteration in the polymer structure is manifested by stress/strain changes. Most of these specified polymer physical tests, whether in tension, compression, shear, or bending (a combination of all three modes), have been adapted from traditional methods for metals. In polymer technology, it is assumed that a simple, single test of short-term mechanical nature at an arbitrary combination of time, temperature and one physical state is useful for evaluating the general performance of plastic materials. A special consideration is the fact that in physical testing the value and meaning of observed changes are not always clear. Is no change in values necessary to ensure compatibility, or is a change of 5%, 10%, etc. acceptable?

The proposed testing strategy shown in Figure 1 uses a screening technique to limit the number of materials being subjected to more comprehensive testing. In this strategy, screening criteria values of 10% for specific gravity and 0.9 g/m²/h for VTR were selected. These values were chosen because they have been cited in the literature[4] as qualitative criteria in determining the chemical resistance of materials used in liner applications. As shown in Figure 1, those materials which exhibit lower values are determined to pass the screening test while those with higher values fail the tests. These latter materials are then eliminated from further testing. All testing data is compiled in a material database which is available to packaging designers or additional parties within and external to the DOE. The selection of specific gravity and VTR as screening tools is based on the availability of national standards, i.e., ASTM D792[5] and ASTM D814[6], that describe the use of these properties to test plastics. These tests can be easily performed with inexpensive laboratory equipment, and these tests provide data on materials consistent with their intended application. For example, where a material exhibits changes in specific gravity, i.e., changes its density, the materials may be losing some of the specific desirable properties for which they were selected. Such properties might be flexibility, radiation resistance, and chemical resistance. The use of permeability in evaluating materials for sealing applications is certainly obvious. What may not be as obvious is the 0.9 g/m²/hr pass/fail criteria value for permeability rates. While this value may be valid for flexible liners used in hazardous waste landfill applications[4], its application to packaging components may be tenuous. However, since permeability rates are used in packaging regulations, i.e., by the DOT in Appendix B of 49 CFR 173, there seems to be some validation for its use.

EXPERIMENTAL

Material properties that should be evaluated to assess the suitability of potential seal and liner materials in mixed waste packaging designs are mass and density changes, Vapor Transmission Rates (VTR), hardness, modulus of elasticity, tensile strength, elongation, compression set, and stress cracking. In this section, we describe the experimental aspects of a chemical compatibility testing program. However, before discussing the testing program itself, a description of the four simulant mixed waste forms and the selected plastics is given.

The four simulant mixed waste forms selected above consist of an aqueous alkaline simulant tank waste, a chlorinated hydrocarbon mixture, a simulant scintillation fluid, and a ketone mixture. The aqueous

simulant contains of 179 g sodium nitrate, 50 g sodium nitrite, 82 g sodium hydroxide, 32 g sodium carbonate, 17 g cesium chloride, and 16 g strontium chloride dissolved in 1 L of deionized water. The chlorinated hydrocarbon simulant consists of a mixture of 500 mL trichloroethylene, 250 mL chlorobenzene, 240 mL carbon tetrachloride, and 30 g cerium(III) 2-ethyl hexanoate. The simulant scintillation fluid is a mixture of 333 mL toluene, 333 mL xylene, 323 mL dioxane, and 1 mL water. The ketone simulant is a mixture of 600 mL methyl ethyl ketone (MEK), 390 mL methyl isobutyl ketone, and 30 g cerium acetyl acetonate hydrate.

Screening Studies

Since the measurement of all the above mentioned material properties were expected to be costly and time-consuming, screening tests were implemented which used relatively severe exposure conditions such as high temperatures and high radiation levels to quickly reduce the number of possible materials for full evaluation. The evaluation parameters used in the screening study consisted of specific gravity changes in liners and changes in permeability rates [Vapor Transport Rates (VTR)] in seals. These parameters were evaluated using standardized test methods such as those developed by the American Society for Testing and Materials (ASTM). For specific gravity changes, ASTM D792 was used. In evaluating permeability rate changes, ASTM D814 was used. A reduction in the number of materials requiring more complete evaluation was dependent on some of the materials not passing certain acceptance criteria. These criteria and the rational for their selection are described in detail in the Discussion Section of this report.

Sample Preparation. Standardized test methods were used to cut, condition, and test the materials. The geometry of the material samples was that specifies by the test method. The samples were cut using an expulsion press and dies (Part # 22-16-00) manufactured by Testing Machines Inc., Amityville, NY. For example, the rectangular (1" x 2" x 0.125") samples required for specific gravity measurements were cut in the expulsion press fitted with an Expulsion Straight Edge Die (Part #23-10-06). Similarly, the circular samples (2.69" diameter x 0.125" thick) required for VTR measurements were cut in the expulsion press fitted with an Expulsion Die specifically designed for ASTM D814 testing (Part # 23-00-00). The press and dies permitted the cutting of multiple samples of uniform dimensions. The individual samples were visually checked to assure that none had nicks or other imperfections prior to their use. As recommended by ASTM D618[7], the plastics were conditioned at a standard temperature of 23°C (73.4°F) and a relative humidity of 50% for at least 24 hours prior to the testing process. This was done by storing the cut samples in a desiccator (Fisher Scientific, Part # 08-615) filled with magnesium nitrate hexahydrate (Fisher Scientific, Part # M46-500, 500 g) and saturated with water. Procedures for generating this constant relative humidity environment are describe in ASTM E104[8]. During conditioning, the samples were stacked atop each other and separated from each other using a metal spiral (Slinky Jr., James Industries, Inc., Part # 126).

Sample Irradiation. The pre-cut liner and conditioned seal samples were first exposed to gamma radiation from an underwater ^{60}Co source at SNL[9] using a water-tight stainless steel canister (volume ~ 4 Liters). All the samples (of one candidate material) required for compatability testing in each of the four simulant waste streams were placed in one canister. This involved 12 samples for VTR measurements or 20 samples for specific gravity measurements. The samples were loaded into a metal basket in the same configuration as was used to condition the samples, i.e., the samples were stacked atop each other and separated a metal spiral. The basket was inserted into the canister and the canister was sealed. The loaded canister was lowered into the pool to a depth of 6 feet, purged with slow steady flow (~ 30 mL/min) of dry air, and allowed to come to thermal equilibrium at 60°C. Once thermal equilibrium was obtained, the canister was lowered into its irradiation location in the pool and the exposure timing started to obtain the desired radiation dosage. The highest dose rate currently available at the Low Intensity Cobalt Array (LICA) Facility is ~ 210 krad/hr. Thus for a screening study where a gamma dose of 286,000± 5% rad was required, the samples were exposed for approximately 1.5 hours. After the samples received the calculated radiation dosage, the canister was removed from the pool and the samples were replaced in the conditioning chamber. The samples were then surveyed by SNL Health Physics personnel and subsequently returned to us for the remainder of the testing. No more than 24 hours elapsed between the time the samples had been exposed to radiation and when the samples were exposed to the simulant wastes.

Sample Exposure to Chemicals. The general exposure protocol for specific gravity involved placing four specimens of each plastic material into a container (cell), and exposing them to each of the wastes for 14 days at 60°C. The four specimens were bundled together using nylon cable ties. Within each bundle, the specimens were separated through the use of ~1/16" (~ 2 mm) metal pins as spacers. This allowed for the ready access of the waste simulant to all surfaces of each specimen. A tapered pint glass canning jar (Kerr Group, Inc., Los Angeles, CA, Part # 70610-00518) was loaded with the five bundled test specimens and then filled with 300 mL of the test solution. Care was taken to ensure that sufficient waste was present to expose the entire surface area of all the samples. For relatively insoluble materials, ASTM D543[10] recommends about 10 mL/in^2 (~1.6 mL/cm^2). After filling with liquid waste, the metal lid and band were attached to the jar and tightened. This cell was immersed in a water bath maintained at 70°C. After approximately one minute of immersion or after the rate of bubble evolution from the canning jar subsided, the jar was removed from the water bath, the metal band was tightened, and the jar was placed in secondary container which was then placed in an oven (Blue M, Model OV-490A-2) maintained at 60°C. The container was kept in this oven for 14 days.

VTR measurements were performed according to the procedures describes in ASTM D814. Here is a general description of the methodology. For specific experimental details, the standard test method should be consulted. The VTR cells consisted of 1/2 pint glass Mason jars (Kerr Group, Inc., Los Angeles, CA, Part # 70610-00105B). Each of the three jars was filled with approximately 200 mL of the test solution. For elastomeric materials, ASTM D543 recommends about 40 mL/in^2 (~6.2 mL/cm^2). The seal specimen and metal band were loosely attached. The three jars were placed in an upright configuration (seal and metal band facing up) into the oven thermostated at 60°C. These jars were held at this temperature for one hour. They were then removed from the oven, sealed tightly, and then weighed on an analytical balance (Mettler-Toledo Inc., Hightstown, NJ, Model AT200 or PM2000). The respective weight of each jar was recorded and the jars were returned to the oven. At this time however, the jars were placed in the oven in an inverted position, i.e., with the seal and metal band facing down. The jars were again removed from the oven and reweighed after 24 hrs. They were then returned to the oven and kept in the oven for the remainder of the 14 days. After this time period, the jars were removed from the oven and reweighed. It should be noted that where flammable and toxic organic materials were used, e.g., the simulant scintillation fluids, the ketone simulants, and the simulant chlorinated hydrocarbon mixture, the jars were placed in a metal paint can (Wellborn Paint Manufacturing Company, unlined paint can, gallon capacity, Part # 3239001) and the can was tightly sealed. These precautions were required because the oven was not rated to handle flammable liquids. Thus a means to minimize the evolution of flammable vapors had to be developed. This was accomplished by confining any potentially generated vapors in a sealed secondary containment vessel (the paint can).

Comprehensive Evaluations

Those materials passing the screening tests will be evaluated using four different radiation doses, three temperatures, and four exposure times for each of the four waste forms described above. The radiation levels chosen are 143,000, 286,000, 571,000, and 3,672,000 rads of γ-radiation from a ^{60}Co source. The exposure temperatures selected were 18, 50, 60°C. Exposure times of 7, 14, 28, and 180 days will be used. In addition to the specific gravity and permeability testing, the response of these materials will be further evaluated based on their dimensional changes (ASTM D471), hardness changes (ASTM D2240), tensile property changes (ASTM D412, D638, and D945), stress cracking (ASTM D1693), and compression set changes (ASTM D395).

RESULTS

VTR Measurements

VTR testing provides a measurement of the rate of vapor transmission of a volatile liquid through a seal material. This type of testing provides a steady-state measure of the rate of vapor and liquid transmission through relatively thin plastics. While the calculated values of VTR can not be directly converted to traditional permeability values, the VTR values can be used to give a figure of merit for permeability. For

the purposes of these screening tests, these values of VTR were used as a criteria for determining whether the material passed or failed the exposure protocol.

Figure 2 shows the results of the screening of six seal materials, in triplicate, in the aqueous simulant mixed waste for 14 days at 60°C. As can be seen from the data, all materials exhibited VTR values below 1 g/hr/m^2, i.e., all seal materials passed this screening test. In addition, the data presented in this figure shows that both EPDM and SBR exhibited the lowest VTR. These results suggest that either materials could be used in the construction of packagings transporting aqueous, caustic waste containing large concentrations of sodium nitrate and sodium nitrite. This suggests that seals from these materials might be suitable in packagings intended to transport Hanford Tank waste. Depending on other factors such as cost of the seal materials, a further down-selection of seal materials is possible.

Figure 3 shows the results of similar screening in chlorinated hydrocarbon simulant mixed waste. As can be seen in the figure, all materials, with the exception of VITON, had VTR values greater than 1 g/hr/m^2. Since the pass/fail criteria was 0.9 or ~ 1 g/hr/m^2, only the VITON passed the screening test with an average VTR of 0.25 g/hr/m^2.

Figure 4 presents the results for the simulant scintillation fluid mixed waste. All materials failed the screening tests. A close inspection of the data in the figure reveals that Butyl and VITON had two samples with relatively low values (< 10 g/hr/m^2) of VTR and one sample with high Vapor Transmission Rates (VTRs). Since the average value from the three samples was used to establish whether the material passed or failed the screening tests, these materials while not passing still had the lowest VTR values. Specifically, VITON exhibited the lowest VTR value of 14.2 g/hr/m^2.

Figure 5 shows the results of VTRs for the ketone mixture simulant waste through seal materials at 60°C. While none of these materials passed these screening tests, Butyl rubber came closest to passing the tests. This material had a VTR of 1.5 g/hr/m^2. The data shows that EPDM also had relatively low VTR values.

To summarize the results of the screening tests, while all seal material passed exposure to radiation and the aqueous simulant mixed waste, the EPDM rubber exhibited the lowest VTR of 0.05 g/hr/m^2. When exposed to radiation and chlorinated hydrocarbon simulant mixed wastes, only VITON passed these screening tests with a value of 0.25 g/hr/m^2. None of the seal materials tested passed the screening tests in either the simulant scintillation fluid mixed waste or the ketone mixture simulant waste. However, VITON and EPDM had the lowest VTR values, respectively, in these wastes. These results are consistent with chemical compatibility data reported in the literature. However, since these screening tests combined radiation and chemical effects, it can be concluded that radiation effects, i.e., γ-radiation at a dose of 286,000 rads, plays little, if any role in affecting the resistance of these materials to these chemical effects at 60°C. It should, however, be mentioned that a different conclusion might be reached on the effects of a combination of radiation and chemical exposure if some other evaluation criteria is used. For example, if tensile property changes had been selected instead of VTR values, different conclusions might be reached. The resolution of determining which effect, radiation or chemical, predominates will be accomplished in the next phase of this testing program.

Specific Gravity Measurements

Specific gravity testing provides a direct measurement of the density of the materials. Since density values reflect possible physical changes in materials, these measurement can give some indication of whether the material has changed in mass and/or in volume. These changes in turn might indicate whether the chemicals to which the material has been exposed has affected the material's composition. For example, some of the components of the material such as plasticizers or other constituents of the plastic might be leached out of them.

A change in the density of the material might also indicate swelling. Swelling can be important when selecting appropriate liner materials for packagings because liners can be structural components of the package. If liners swell, the change could have undesirable effects on the performance of the package.

The specific gravity data for liner materials is presented in Figures 6 - 9. The data shows that all liner materials with the exception of polypropylene passed the screening tests in the four simulant waste types.

Figure 6 shows the specific gravity changes of the liner materials when exposed to radiation and the aqueous simulant mixed waste at 60°C. Several features in the data should be noted. In spite of the fact that most materials exhibited a positive change in the specific gravity, three samples (HDPE, Kel-F, and TEFLON) for each of the different materials were found to have negative changes in specific gravity. The samples which exhibited this behavior can be recognized in the graph by a completely blackened area. While this observation was also found in the three other waste types, we will only provide a discussion of this phenomenon here. Since the determination of specific gravity by ASTM D792 involves only the measurement of sample mass, a negative value for specific gravity would suggest that the effected samples had a mass loss. However, a close examination of the data for the affected samples revealed that these actually had an increase in mass. Without performing additional measurements on these materials, the origin of the negative specific gravity change can only be speculated upon. One such speculation is that the observed mass gain is due to adsorption effect. In such a process, the sorbed species causes a greater increase in the volume of the sample. If the volume component of the sample increases to a greater extent than does the mass, a net decrease in the specific gravity would be observed. Since the test method did not involve dimensional measurements, it was not possible to confirm this hypothesis. Another explanation of this effect is that during the exposure to the wastes, a component of the material was leached from the sample. This preferential leaching of material components could be masked by the simultaneous uptake of chemical species. It is not unreasonable that a desorbed species would have a greater specific gravity than an adsorbed species. To confirm either of these speculations, additional testing would be required. What is certain in the data shown in Fig. 6 is that Kel-F exhibited the lowest value of percent change, i.e., -0.08%.

In Figure 7, the specific gravity change of liner materials when exposed to radiation and chlorinated hydrocarbon simulant mixed waste at 60°C are shown. As was previously mentioned, polypropylene failed to pass the 10% criterion. This material exhibited a specific gravity change of 10.9%. The material with the greatest resistance to radiation and chemicals, as indicated by the smallest change in specific gravity, was HDPE. This material had a percentage change value of 4.12%. Interestingly, the fluorocarbon material was the only material in this waste to exhibit negative specific gravity changes of 6.43%.

Figure 8 shows the specific gravity changes of liner materials when exposed to simulant scintillation fluid mixed waste at 60°C. In this waste, the cross-linked polyethylene (XLPE) exhibited the greatest resistance to radiation and chemicals. This material exhibited a percentage change of only -0.02%. While not as good as XLPE, HDPE also had a rather low percentage change in specific gravity of -0.60%.

Finally, Figure 9 gives the specific gravity change of liner materials when exposed to a ketone mixture simulant mixed waste at 60°C. For this waste type, the HDPE material appeared to have the greatest resistance to radiation and chemicals. This material exhibited a percentage change of only -0.6% in specific gravity.

To summarize the specific gravity testing data, while all materials with the exception of polypropylene (in chlorinated hydrocarbons) passed the screening criteria of 10% specific gravity change, Kel-F, HDPE, and XLPE were found to offer the greatest resistance to the combination of radiation and chemicals. However, since the meaning of negative specific gravity changes are not understood at this time, the selection of these materials are somewhat tenuous.

As was established by the VTR measurements, the results of the specific gravity measurements are consistent with what has been generally reported in the literature about the chemical resistance of materials used in liner applications. However, this work has demonstrated that the candidate materials are resistant not only to chemicals alone but also to a combination of radiation and chemicals. Since such data is not available in the literature, this work provides valuable data to suppliment the chemical compatibility literature.

CONCLUSIONS

We have developed a chemical compatibility program for the evaluation of transportation packaging components which may be used in transporting mixed waste forms. Consistent with the methodology outlined above, we have performed the first phase of this experimental program to determine the effects of simulant mixed wastes on packaging materials. This effort involved the screening of 10 plastic materials in 4 liquid mixed waste simulants. These plastics were butadiene-acrylonitrile copolymer rubber, cross-linked polyethylene (XLPE), epichlorohydrin rubber, ethylene-propylene rubber (EPDM), fluorocarbon, tetrafluoroethylene (VITON and Kel-F), high-density polyethylene (HDPE), isobutylene-isoprene copolymer rubber, polypropylene, and styrene-butadiene rubber. The selected simulant mixed wastes were (1) an aqueous alkaline mixture of sodium nitrate and sodium nitrite; (2) a chlorinated hydrocarbon mixture; (3) a simulant liquid scintillation fluid; and (4) a mixture of ketones. The testing protocol involved exposing the respective materials to 286,000 rad of gamma radiation followed by 14 day exposures to the waste simulants at 60°C. The seal materials or rubbers were tested using Vapor Transport Rate (VTR) measurements while the liner materials were tested using specific gravity as a metric. For these tests, a screening criteria of 0.9 g/hr/m^2 for VTR and a specific gravity change of 10% was used. Those materials which failed to meet these criteria were judged to have failed the screening tests and will be excluded in the next phase of this experimental program. Based on this work, it was concluded that while all seal materials passed exposure to the aqueous simulant mixed waste, EPDM and SBR had the lowest VTRs. In the chlorinated hydrocarbon simulant mixed waste, only VITON passed the screening tests. In both the simulant scintillation fluid mixed waste and the ketone mixture simulant mixed waste, none of the seal materials met the screening criteria. For specific gravity testing of liner materials the data showed that while all materials with the exception of polypropylene passed the screening criteria, Kel-F, HDPE, and XLPE were found to offer the greatest resistance to the combination of radiation and chemicals.

ACKNOWLEDGMENTS

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5. Standard Test Method D792, "Density and Specific Gravity (Relative Density) of Plastics by Displacement," ASTM, Philadelphia, PA, 1991.
6. Standard Test Method D814, "Rubber Property - Vapor Transmission of Volatile Liquids," Volume 9.01, ASTM, Philadelphia, PA, 1993.
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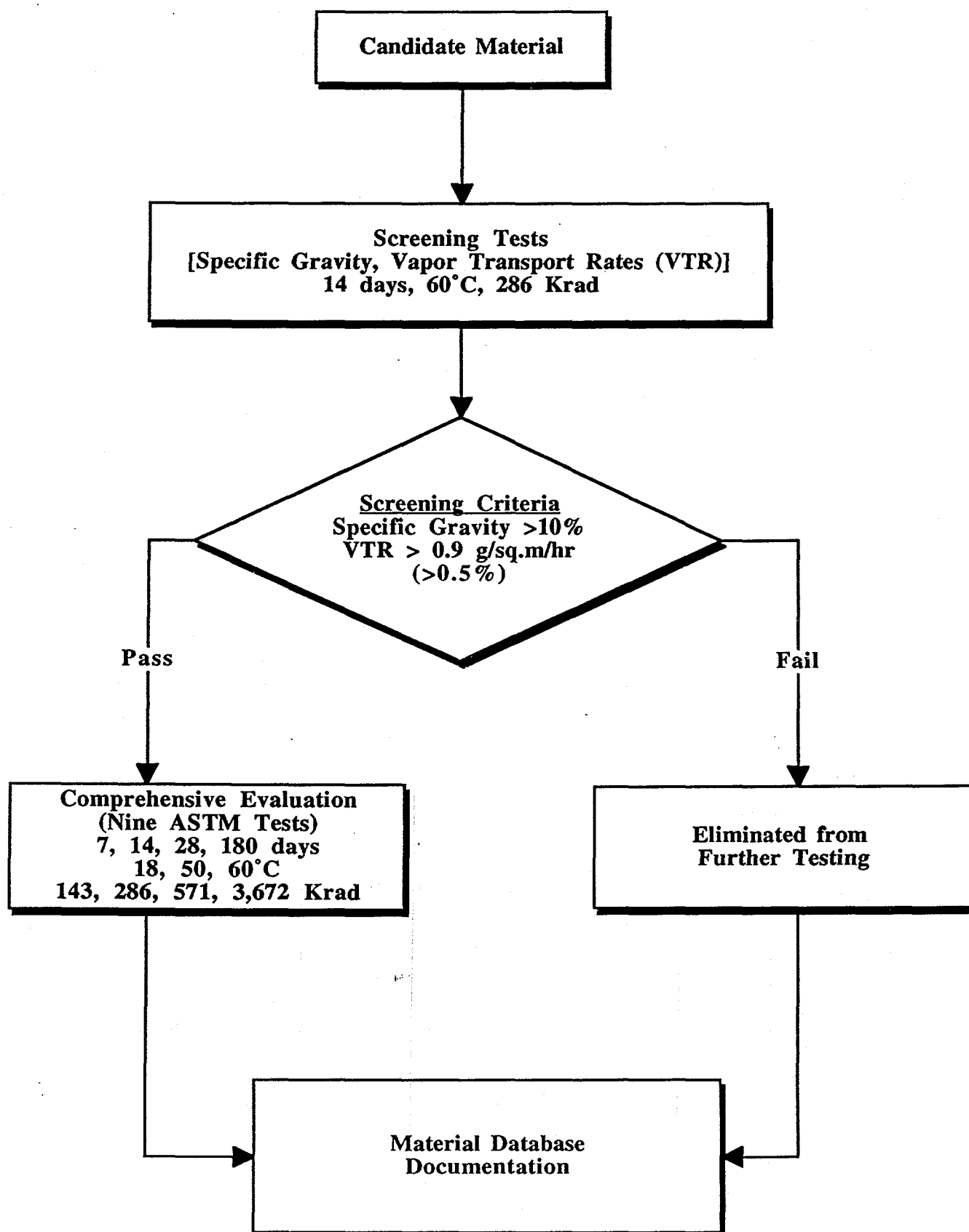10. Standard Test Method D543, "Resistance of Plastics to Chemical Reagents," Volume 8.01, ASTM, Phila., PA, 1993.

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                    ┌─────────────────────────┐
                    │   Candidate Material    │
                    └─────────────────────────┘
                                 │
                                 ▼
        ┌──────────────────────────────────────────────────┐
        │                 Screening  Tests                 │
        │ [Specific Gravity, Vapor Transport Rates (VTR)]  │
        │          14 days, 60°C, 286 Krad                 │
        └──────────────────────────────────────────────────┘
                                 │
                                 ▼
                          Screening Criteria
                        Specific Gravity >10%
                          VTR > 0.9 g/sq.m/hr
                              (>0.5%)
              Pass                              Fail
```

Figure 1   Chemical Compatibility Testing Strategy

Comprehensive Evaluation
(Nine ASTM Tests)
7, 14, 28, 180 days
18, 50, 60°C
143, 286, 571, 3,672 Krad

Eliminated from
Further Testing

Material Database
Documentation
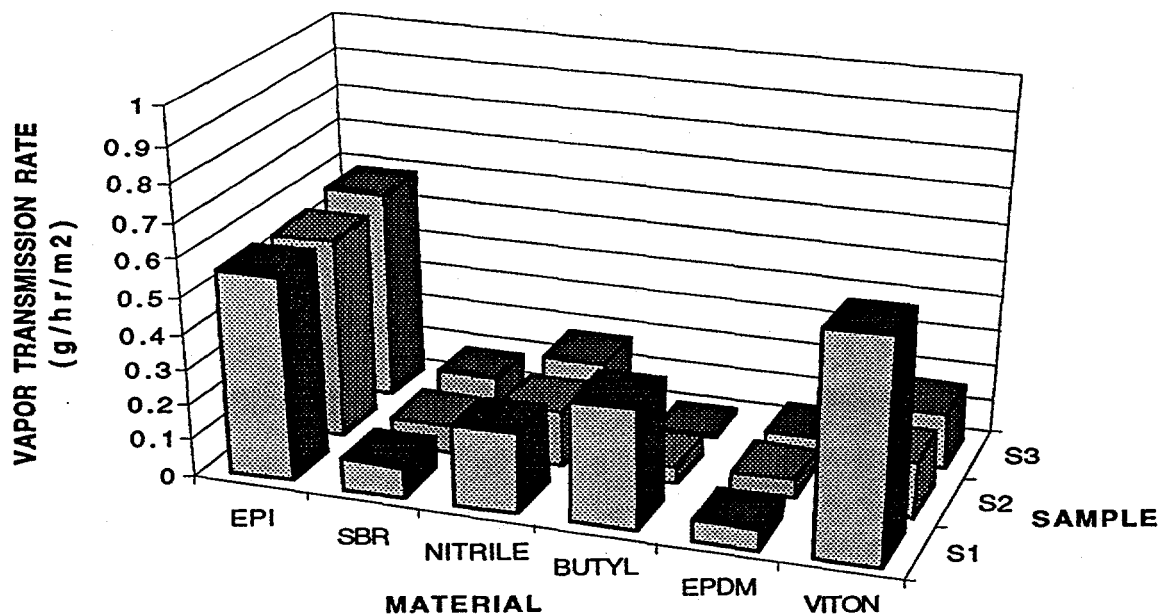
Figure 2   VTR of aqueous simulant mixed waste through seal materials at 60°C.
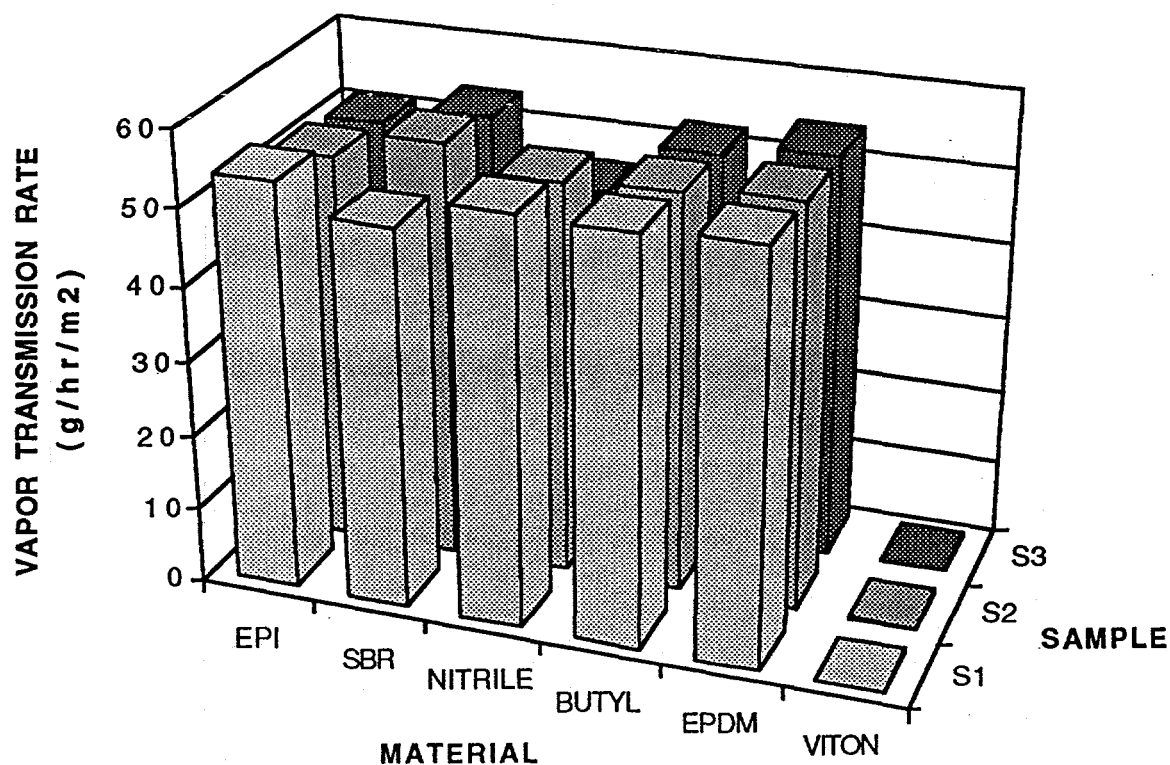

Figure 3   VTR of chlorinated hydrocarbon simulant mixed waste through seal materials at 60°C. (Note scale change from previous figure)
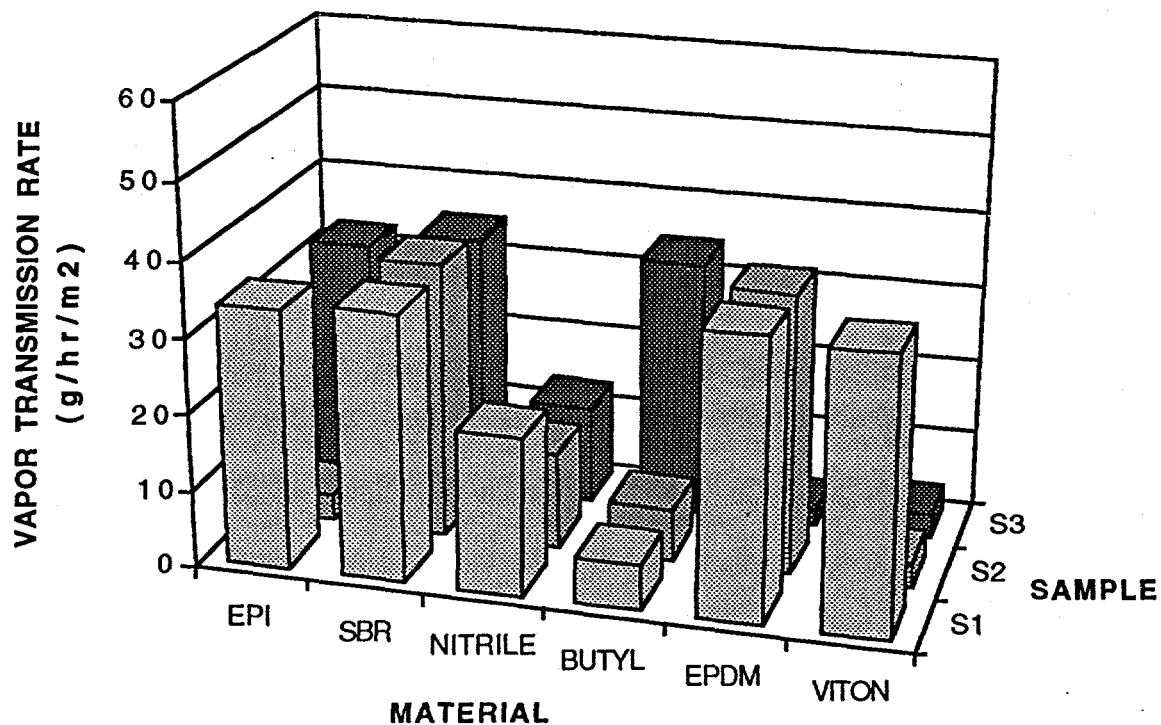
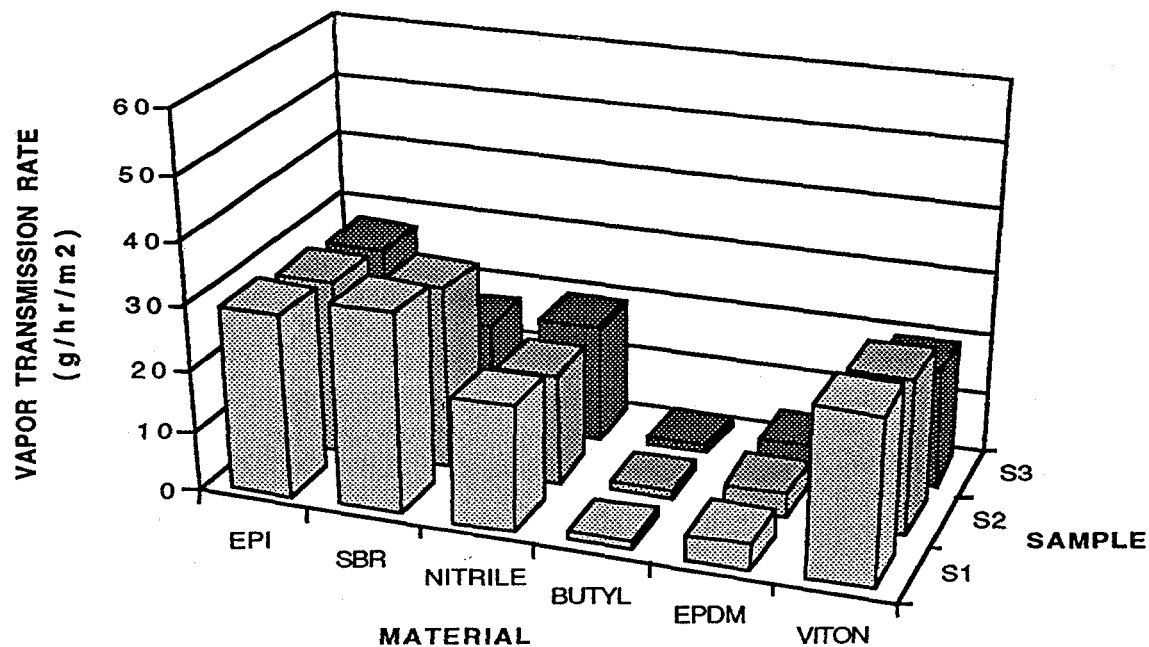Figure 4   VTR of simulant scintillation fluid mixed waste through seal materials at 60°C.

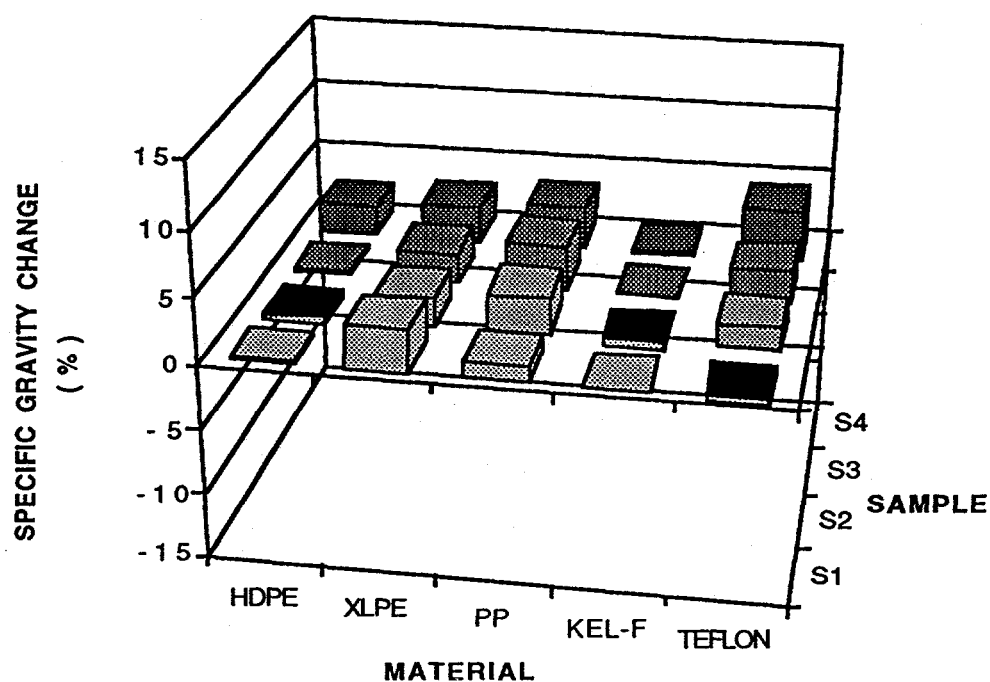Figure 5   VTR of ketone mixture simulant mixed waste through seal materials at 60°C.

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Figure 6   Specific gravity changes in aqueous simulant mixed waste by liner materials at 60°C (Note that bars with dark areas on top represent negative values)
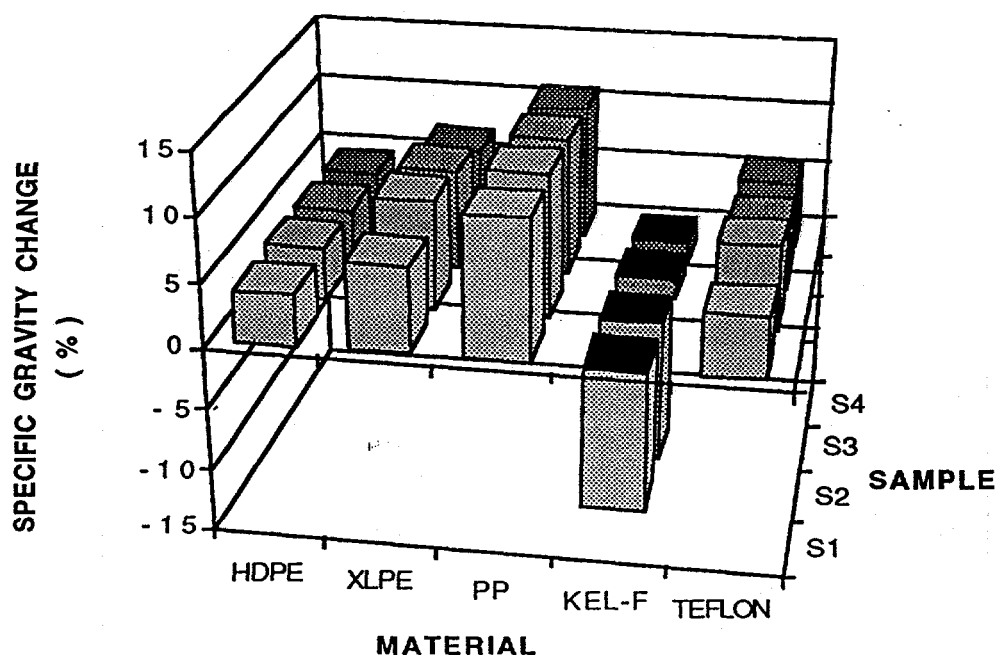

Figure 7   Specific gravity changes in chlorinated hydrocarbon simulant waste by liner materials at 60°C
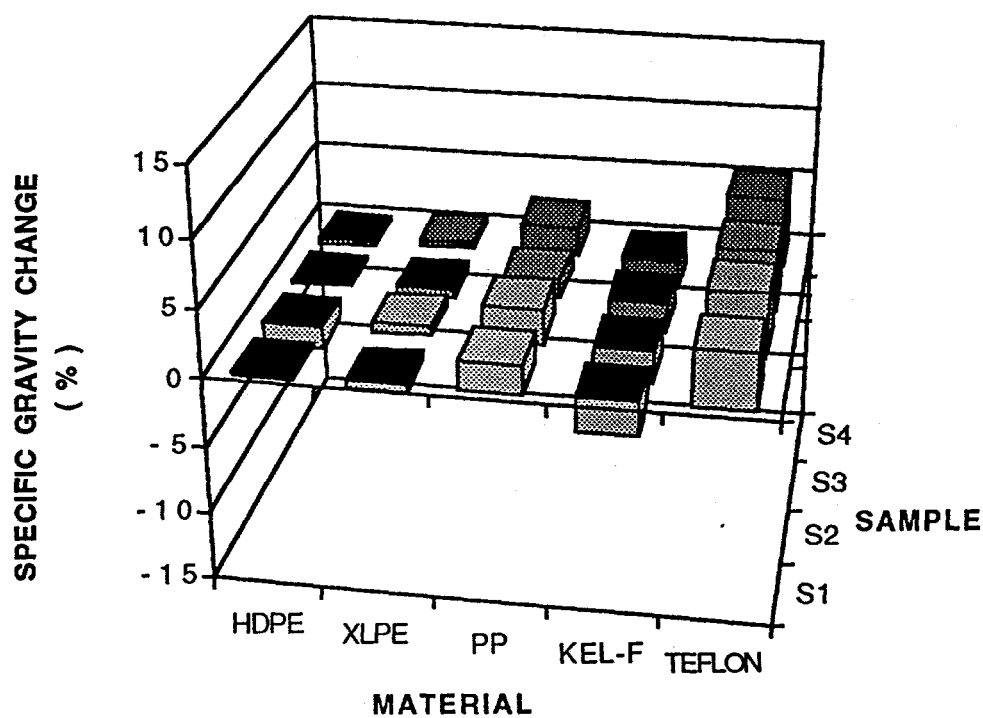
Figure 8   Specific gravity changes in simulant scintillation fluid mixed waste by liner materials at 60°C
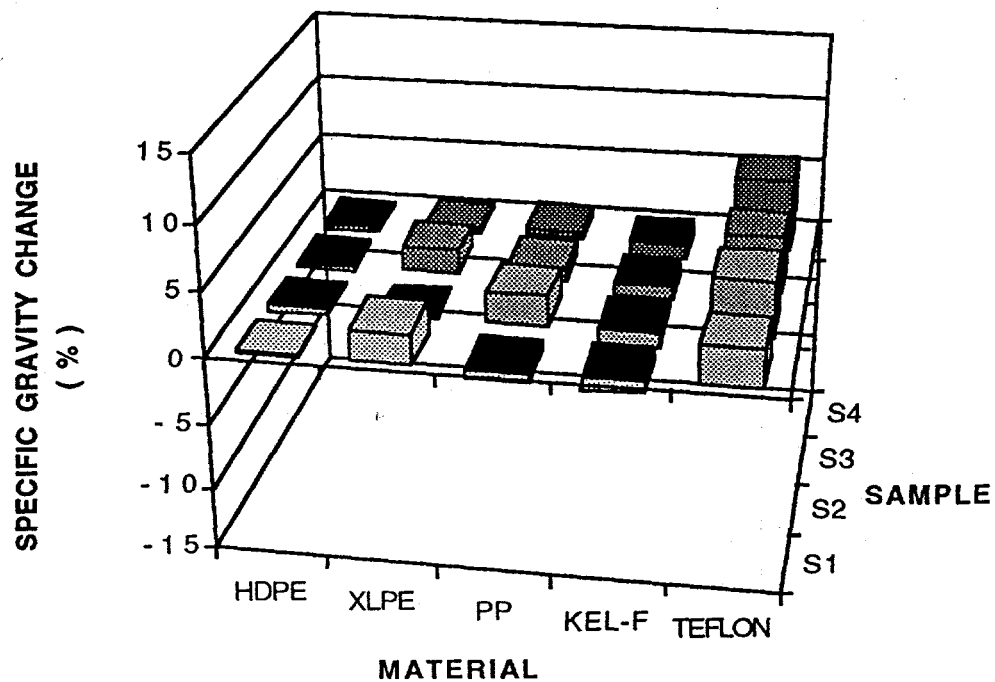

Figure 9   Specific gravity changes in ketone mixture simulant mixed waste by liner materials at 60°C