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TRITIUM LOSS FROM COATED CEMENT PASTE BLOCKS

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The concern with tritium oxide light water exchange arises from the consideration of the disposal of small quantities of lightly tritiated water obtained from the operation of the Los Alamos Meson Physics Facility (LAMPF) and other sources. These wastes could be contained in a casting made from Portland cement and tritiated water. Leaching, evaporation and diffusion of the tritium oxide from the porous castings could result in tritium exchange with environmental hydrogen and subsequent introduction of tritium into the biosphere. Accordingly, the development of an impermeable barrier in the form of a coating for the cement castings is essential to the success of a containment program based on the storage of tritiated cement paste solids.

In work to date, little more has been accomplished than a better definition of the parameters for a thorough study. Emphasis has been placed on use of the most economical coating materials, although no materials were eliminated from consideration on this basis.

Cement Paste Blocks

A strong, dense paste for the cement blocks was desired, hence a mixture with a water/cement (weight) ratio of 0.3 was selected. Variation in this ratio would affect a number of parameters of the movement of water in cement, such as porosity and rate of hydration. All cement pastes contain a certain amount of free water which increases as the water to cement ratio increases and varies with length of time of hydration.

The free, or evaporable, water in a mixture of water to cement of 0.3 (by weight) is about 50 percent of the total water in the paste. This was verified by heating a sample block for 70 hours at 100°C.

The selected mixture (0.3) provides a rather stiff paste. In certain applications, such as one which would require pumping, it is likely that the water to cement (weight) ratio would have to be increased to about 0.5, or additives would have to be introduced to provide a more fluid mix.

A Type I Portland general purpose cement was used for all samples. Retention of tritiated water in blocks prepared from other types of cement may differ somewhat, but this has not been investigated.

Experimental Procedures

Tritiated water which would provide 0.3 to 3 mCi of tritium per block of sample was used to form the paste. Cement and water were thoroughly mixed in a laboratory mixer for ten minutes, then spooned

into glass or polyethylene wide-mouth vessels of 100 to 120 ml capacity. All samples were weighed at the time of forming and again just prior to coating. The weight difference due to moisture loss was noted and the accompanying tritium loss recognized.

The blocks were permitted to cure within their containers for a minimum of two days prior to removal and coating. In several cases, blocks remained within their molds for periods of up to a year before removal for coating application and study. In retrospect all samples should have been cured for the same period of time. However, the results would not be changed significantly.

Coating Materials

The first few groups of samples were coated to convenient and largely uncontrolled thicknesses with materials at hand. It was hoped that this would expedite the determination of which materials might be the most effective barriers to tritium.

Materials used in the preliminary investigation to coat the sample blocks included paving or road asphalt (Federal Specification SS-A-706c, grade AP-1, 120-150 penetration at 77°F); an epoxy-phenolic amine cured formulation, Plasite #1722 (Wisconsin Protective Coating Corp.); a universal quick-drying floor enamel (KOMAC, Denver, CO); a heavy duty resin-base organic solution for penetrating and sealing porous concrete, Peneclear (Penecrete Corp., Denver, CO); saran (vinylidene chloride); hypalon, a chlorosulfonated polyethylene elastomer; teflon "S" (tetrafluoroethylene fluorocarbon resin); heavy duty wheel bearing grease (Quaker State); steep (roofing) asphalt (200° to 215°F temperature range for softening point, minimum ductibility of 2.0 cm at 77°F, penetration between 1.5 and 3.0 mm at 77°F); Silastic 732, a room temperature vulcanizing (RTV) silicone rubber (General Electric); Glyptal, an air-drying or baking gloss enamel (principally rosin modified alkyd resin, aromatic and aliphatic hydrocarbons) designed for electrical resistance properties (General Electric); ceresin, a universal wax derived from purified ozocerite; beeswax; paraffin; and polyethylene.

Asphalt, paraffin and beeswax, applied by dipping, formed coatings much thicker than the less viscous material such as floor enamel, Plasite, hypalon (spray), teflon "S" or Glyptal and were expected to be superior in retaining tritium. However, other of the more viscous materials such as grease or Silastic 732 were noticeably ineffective even at considerable thicknesses.

Several series of blocks were coated with varying thicknesses of asphalt, wax and paraffin. The technique for forming the thicker coatings consisted of dipping the block into the hot material for a few seconds, removing it and permitting it to set, then repeating this cycle until the desired thickness was achieved.

Certain coatings were used which were not applied by dipping because of the high temperature of the material in the liquid state. In the case of saran and polyethylene, the blocks were wrapped and sealed in thin films of the material. In another instance, a cement-paste-filled polyethylene container was sealed and the container itself was considered as a coating.

The quantity of coating applied is easily determined by weighing the sample before and after coating. Determination of thickness, however, is much more difficult and, in these tests, it frequently was not uniform. Suggested methods for thickness measurement included direct measurement using micrometer calipers, the eddy current method,

the beta probe and radiography. The eddy current equipment requires that the specimen be conductive; the beta probe uses a special contacting device which is not particularly suited to the shape of the sample. Radiography, however, was successful in graphically illustrating coating thickness on X-ray photographic plates. With certain coatings such as Plasite, thicknesses less than about 0.127 to 0.178 mm were not detectable although a 0.20 mm coating was measured along the bottom of the sample. The first steep asphalt coated specimen showed a coating thickness of 2.41 mm on the lower half of a side on which the coating was typically 0.89 to 1.14 mm. The measurements confirmed the nonuniform coating conditions and served to support revised coating procedures in the latest tests.

Examination of Exchange Phenomena

The purpose of leach, or in this case "exchange," testing of radioactive solids is to determine the rate of loss of the isotope to its environment. Where encapsulated or "fixed" wastes are buried, the most serious consequences of this loss are related to contamination of ground water. The testing is conducted, therefore, in a water environment. In these experiments, the cement paste blocks were placed in 500 ml of demineralized water in a 0.95-liter polyethylene freezer container. The blocks with thick asphalt coatings were immersed in 1.5 liters of water in a four-liter polyethylene container.

The water, in all cases, was changed and samples were collected at weekly intervals for a short period and thereafter at regular four week intervals. The tritium content of the collected samples was determined through use of an organic-liquid scintillator using 0.5 ml of sample in a 12 ml cocktail. The cocktail, Aqua-sol, uses a xylene solvent with naphthalene for removal of quenching, a solute and two wavelength shifter phosphors. Normally the samples were counted for 100 minutes and the efficiency was about 30 percent.

One uncoated block was allowed to dry in an open hood to determine the rate of loss of tritiated water to an air environment. Twice each week the sample was placed in a sealed vessel for periods of one-half to six hours, the atmosphere of the vessel was transferred to an evacuated ionization chamber and tritium activity was determined. The data, which indicate a rather high initial rate of loss, are provided in Table 1.

The mechanism by which tritium is released from a material is complex, and in many cases may be a combination of several processes [1]. Movement through a coating may occur by diffusion through microscopic openings, or by tritium exchange of the tritiated water with hydrogen of the free and combined water in the cement paste or of the coating itself. Diffusion plays a major role with porosity affecting its rate to a high degree.

Methods of preventing escape of tritium to the environment would include fixing it into a compound which will not permit exchange or diffusion of hydrogen or water, or coating a tritiated cement paste with such a compound. The first may be possible but the method has not been investigated in this study. For the second suggestion, it is likely that in certain of the plastics, hydrogen is tightly bound and will not exchange and the materials are impervious to moisture. The study of plastics is being expanded.

Other substances, such as beeswax, contain tightly bound hydrogen

Table 1

Tritium Release from an Uncoated Block in Air

Total activity in block - 2.05 mCi

Days after Removal from Container	Tritium Release Rate %/sec	Calculated Cumulative Percent Release of Tritium
1	3.27×10^{-5}	1.4
5	5.02×10^{-6}	4.7
8	2.68×10^{-6}	5.4
12	1.61×10^{-6}	5.8
15	8.49×10^{-7}	6.4
19	1.54×10^{-6}	6.6
22	5.95×10^{-7}	6.8
26	9.32×10^{-7}	6.9
28	4.10×10^{-7}	7.0

and are very effective barriers. It is possible that materials which contain no hydrogen may prove superior. None of these hydrogen-free materials have been tested as yet.

Tritium Release Rates from Coated or Uncoated Blocks

In this paper, release or loss rate refers to the percentage of the total quantity of tritium initially included in the sample block which is found in its water environment after a certain period.

Three series of cement paste samples were mixed with the following tritium contents:

Series "T" - About 0.32 mCi per block

Series "H" - About 3.0 mCi per block

Series "W" - About 2.3 mCi per block

Figures 1 and 2 illustrate the increase in percentage released over a period of time. The uncoated control samples, of course, release or lose tritium most readily. The first control sample of the "T" series has lost about 60 percent of its tritium content in 72 weeks, with half of this amount being lost in the first six weeks.

Figure 1

Comparative Release of Tritium from Coated and Uncoated Tritiated Cement Paste Blocks Immersed in Water

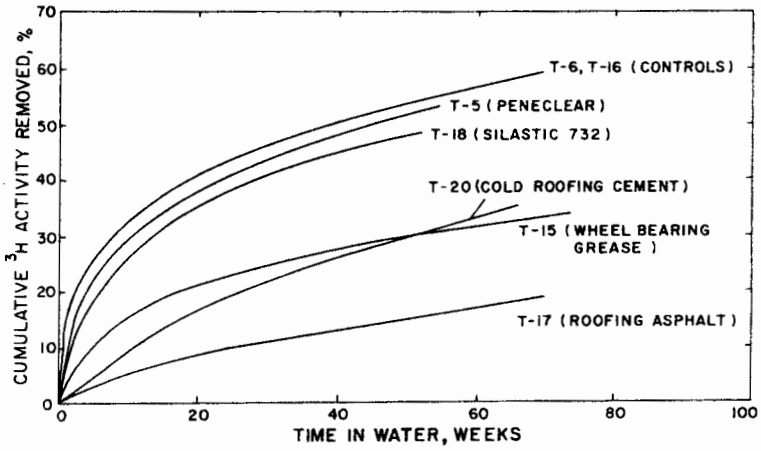
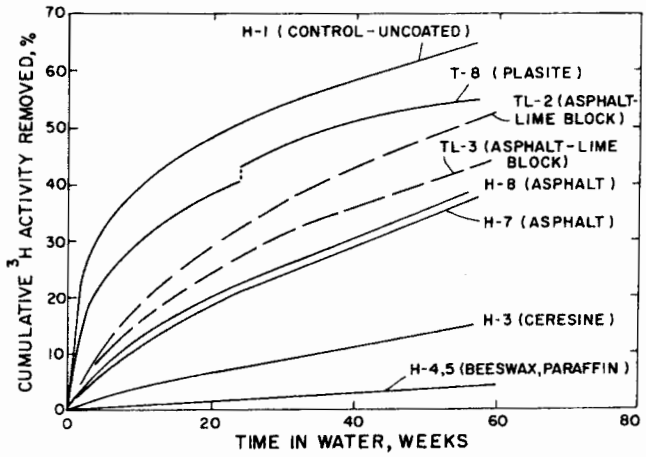


Figure 2

Comparative Release of Tritium from Coated and Uncoated Tritiated Cement Paste Blocks Immersed in Water Including Data for Two Asphalt-tritiated Lime Blocks



Many of the curves indicate this rapid initial loss. With the more effective barriers such as asphalt, the cumulative release curve is nearly linear, indicating a rather uniform release rate throughout the test.

The beeswax and paraffin curves indicate that these materials provide the most effective barriers. It must be pointed out, however, that for the samples indicated in Figures 1 and 2, samples H-4 and H-5 are among those with the thickest coatings. The asphalt coatings, other than H-7 and H-8 which were immersed in hot asphalt for extended periods, are relatively effective barriers and the use of asphalt is being studied in some detail.

Figure 3 shows the fractional release per week of residual tritium as a function of immersion time. The figure indicates that the exchange or release mechanism is complex and cannot be clearly defined at this time.

Figure 3

Fractional Release per Week of Residual Tritium as a Function of Immersion Time

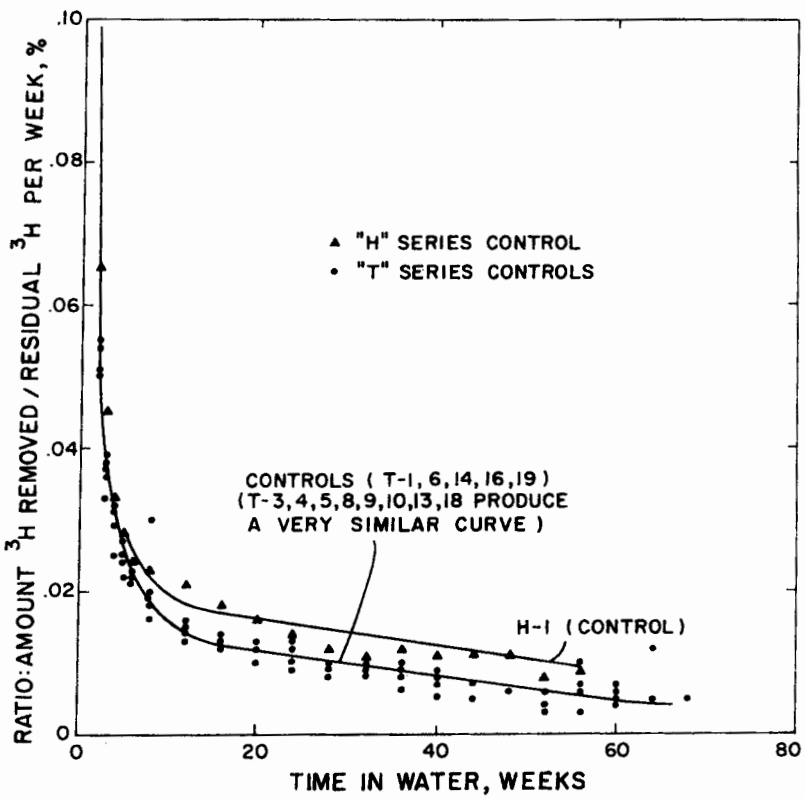
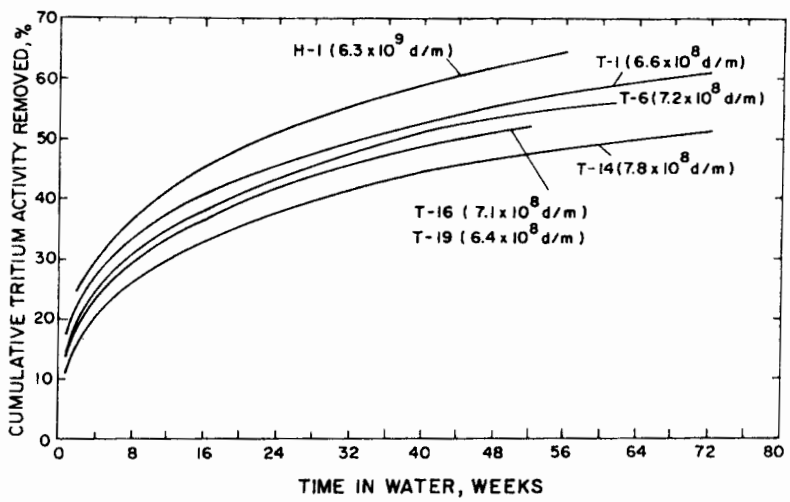


Figure 4 provides cumulative removal curves for a number of control samples. The curves are very similar, indicating a high initial loss of tritium which decreases rather uniformly. Samples T-1, T-6, T-14 and T-19 are all from the same cement-tritiated water batch, but they were immersed in water for the first time at successive one week intervals in the order stated. It would appear that the older samples with a higher percentage of bound water should have a lower loss rate which is the case for all except the T-14 curve, for which no explanation is offered.

Figure 4

Comparative Release of Tritium from Uncoated Tritiated Cement Paste Blocks Immersed in Water



In later attempts to provide asphalt coatings of greater thickness, three cement paste block samples were dipped for very brief periods in steep asphalt which was heated to about 150°C. The samples were air-dried for 15 seconds between dippings. Coating weights which resulted varied from 40 to 45 g. These samples were prepared only recently and the loss or release data available at this time for a typical sample are shown in Table 2.

Three samples were placed in paper cartons and surrounded with steep asphalt to provide a 2.5-cm thick coating at top and bottom and a circumferential coating thickness of about 1.9 cm. These "cast"

Table 2

Release Rates of Tritium
Through an Asphalt Coating

Immersion Time, Days	"Dipped" Block Cumulative % Tritium Released	"Cast" Block Cumulative % Tritium Released
7	0.08	0.0040
14	0.17	0.0061
21	0.26	0.0075
28	0.36	0.0086
35	0.48	--
42	0.60	--
56	0.80	--

blocks were immersed in 1500 ml of distilled water and early data indicate that this thick coating is very effective in containing the tritium, with release rates essentially zero as indicated in Table 2. Coatings of 2.5 cm of asphalt would be neither difficult to apply nor prohibitive in cost. Beeswax or paraffin of similar thickness may well be as effective and will be tested, but they would be much more expensive to use in actual practice. A similar argument can be used with respect to polyethylene.

Four samples were encased in sealed polyethylene bags and from 0.08 to 0.7 percent of the tritium was released during the first week. Though much heavier polyethylene, which is being tested, may prove as satisfactory as the thick asphalt, it is unlikely that the cost of the polyethelene will compare favorably in the near future.

The chemical and physical characteristics of the matrix have a major role in control of the variation in release rate. Loss from a matrix other than cement is shown in the plot of the special asphalt samples in Figure 2. These special samples, TL-2, TL-3 and TL-4, were prepared by slaking quicklime with tritiated water in stoichiometric amounts and mixing this lime with steep asphalt. The matrix in this case is the much less porous asphalt which contains no readily evaporable water and which appears to lose tritium at a much more uniform rate throughout the period than the uncoated cement paste blocks.

Conclusions

Though the study is in its early stages, it has shown that a tritiated water-cement paste mixture provides a solid from which the tritium is released readily into an air or water environment. Several coatings have been investigated, which, in sufficient thickness, act as a reasonably effective barrier to the loss of moisture and the release of tritium. These materials, asphalt, paraffin and beeswax, are relatively common and the first two mentioned are available in large quantities at reasonable cost. For large accelerators, power reactors or fuel reprocessing plants, the cost of tritium disposal with this process would be minor even with very expensive coatings.

Continued investigation may uncover more effective coating materials or, ideally, a compound into which tritium may be incorporated in a nonlabile form by chemical reaction with dilute tritiated water. A thorough, more sustained study is necessary and it is hoped that this paper will stimulate other efforts along this line.

ACKNOWLEDGMENTS

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