EVALUATION OF A RADIOACTIVE CONCRETE WASTE FORM RECOVERED FROM AN OCEAN DUMPSITE

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INTRODUCTION

Sea disposal of low-level radioactive waste began in the United States in 1946 under the licensing authority and direction of the U.S. Atomic Energy Commission. Most of the radioactive wastes were packaged in used or reconditioned 210-liter (55-gallon) mild steel drums filled with concrete so that the average package density was sufficiently greater than seawater to ensure sinking. Generally, the drums were capped with "clean" concrete rather than with the conventional metal 210-liter drum tops. It was assumed that all the contents would eventually be released since the packages were not designed or required to remain intact for sustained periods of time after descent to the ocean bottom.(1)

This practice continued until 1962 when the first commercial shallow-land disposal site was licensed in Beatty, Nevada. As land disposal operations expanded, waste processors turned to land burial and by 1970 most ocean dumping activities had been phased out. The practice stopped completely in 1970 upon the recommendations of the Federal Council on Environmental Quality, Report to the President.(2)

Recently there has been renewed interest in sea disposal of radioactive low-level wastes, both nationally and internationally, as a waste management alternative to land burial. The U.S. Environmental Protection Agency (EPA) has been designated as the responsible federal agency for establishing and administrating a permit review and evaluation program for the ocean disposal of any waste including radioactive waste.(3)

As a first step in developing effective controls on ocean dumping of low-level radioactive wastes, and to assess the effectiveness of past packaging techniques, it was necessary to determine the fate of radioactive waste packages dumped in deep sea disposal sites in past years.(4)

Between 1974-1978, a series of investigations were conducted at the major Atlantic and Pacific dumpsites by EPA, and in 1976,

the first of a series of three waste packages was retrieved from a depth of 2800 m (9200 ft.) in the Atlantic Ocean. As part of this effort, Brookhaven National Laboratories (BNL) assisted in the recovery of the waste packages and conducted studies to determine the effect of the ocean environment on the waste packages.(5)

EXPERIMENTAL

Waste Package Retrieval

On 31 July 1976, a 300-liter (80 gallon) radioactive waste package was retrieved from the Atlantic Ocean 2800-meter depth disposal site located approximately 190 km (120 miles) off the Maryland-Delaware coast. The site, situated on the upper continental rise is centered at coordinates 38^{o} 30'N, 72^{o} 06'W and occupies an area of 256 km^2.

The retrieval operation was a coordinated effort involving the R/V LULU, support ship for the deep submersible vessel ALVIN, the DSV ALVIN, and the R/V CAPE HENLOPEN, escort ship for the survey operations. At 0800, 31 July 1976, the waste package surfaced as shown in Fig. 1 and Fig. 2. Once aboard it was carefully documented photographically, sampled for corrosion products and biological growth, and finally sealed under inert atmosphere in a shipping container for transfer of the drum to Brookhaven National Laboratory (BNL) for evaluation.

Description of the Retrieved Waste Package

The waste package comprised a 300-liter mild steel drum filled with a concrete matrix waste form. According to identification markings stamped into the lower drum head, the drum was fabricated in June 1959, using 0.121 cm (0.0478 in.) nominal thickness steel. The drum was not fixed with a cover lid, however, the pertinent information was inscribed onto the exposed top surface of the concrete as shown in Fig. 2. The markings indicated that the drum was designated package 28, dated 1961, and weighed 762.8 kg (1682 lbs) at the time of disposal. The markings also indicated that the package contained cesium-137 and cobalt-60, and that the radiation dose level at the surface and at one meter was initially 40 and 3 mr/hr. respectively. The surface dose rate measured at the time of recovery ranged from 0.1 to 4.0 mr/hr with the highest reading at the open end portion of the drum that had been buried in the sediment.

After sufficient time had been allowed for drainage of seawater, the retrieved drum weighed 730 kg (1600 pounds). This is an apparent weight loss of approximately 5% since disposal. Weight loss may be attributed to three factors: (1) dissolution of calcium hydroxide (a hydration product) and some of the cement phase from the waste form, (2) erosion of the waste form, and (3) loss of water

Fig. 1. Side view of the radioactive waste package prior to being brought aboard ship.

Fig. 2. Open end of the radioactive waste package immediately after surfacing from the Atlantic 2800 meter disposal site.

by evaporation during concrete curing. Since the weight of the package was inscribed on the concrete surface, the concrete was apparently "wet" during weighing. Since hydration of the cement phase requires substantial time (hours or days), both hydration and evaporation compete during curing for water and appreciable loss of unreacted water loss due to evaporation is likely. Note however, that this is an apparent weight loss since one might question the accuracy of the initial weighing relative to the weighing after retrieval. As such, it should represent the maximum weight loss in disposal.

ANALYSES OF THE WASTE FORM

Radiography

Information supplied by the site where the waste was packaged indicated that the 300-liter (80-gallon) drum was formed by welding one half of a standard 210-liter (55-gallon) drum to the end of a full size 210-liter (55-gallon) drum to increase its overall length. The added length was necessary to accomodate a sealed metal container used to encapsulate demineralized resin or filter material containing cobalt-60. This container was centered in the 300-liter (80-gallon) mild steel drum and the surrounding space was filled with concrete containing radioactive cesium and possibly cobalt-60. The waste package was radiographed to determine the exact position of the internal vessel since knowledge of the location was necessary prior to proceeding with the concrete coring operation.

The radiographs were produced at BNL, using a 45 curie cobalt-60 source. Two series of radiographs were taken along the length of the drum; one in which the source was positioned on the drum circumference along the 180 degree longitudinal axis with the film located along the zero degree axis and a second series with the source located on the 90 degree longitudinal axis with the film along 270 degree axis. The second series, along an axis displaced 90 degrees from the first, was necessary to define the location and shape of internal items. Fiducial markers were placed on the drum to allow the subsequent positioning of one radiograph relative to another.

Interpretation of the radiographs by BNL personnel permitted the determination of the location of the inner vessel. This permitted the calculation of the maximum depth cores that could be taken at various positions without impacting the inner vessel. The radiographs indicated that the inner steel vessel was approximately 100 cm (39 inches) in length, with an outside diameter of 16 cm (6.3 inches) and a wall thickness of 0.064 cm (0.25 inches). The flanged end was located approximately 14 cm (5.5 inches) from the open end of the waste package. These values proved to be quite

close to the actual dimensions of the inner container measured after it had been removed from the concrete. In addition to the inner container, the radiographs indicated the presence of other objects, including two pipes located near the inner container. The radiographs also indicated a large indentation along the longitudinal axis of the inner container. This was later ascribed to bending of the wall of the inner container due to implosion during the descent.

Concrete Coring

Figure 3 and Fig. 4 show a schematic of the retrieved drum and the orientation system used in describing the waste package. In this system, one point on the drum circumference at the open end was arbitrarily assigned to be the zero degree reference point. Looking at the open end of the drum, an angle (θ) measured clockwise about the longitudinal axis of the drum was used to describe any radius about this axis. In taking metal samples and concrete cores, coordinates of any point in the waste form are described by (θ, x, r) where x is the distance (in inches) along the longitudinal axis from the open end concrete surface and r is the distance (in inches) along a radius from the circumferential surface towards the longitudinal axis. The diameter of the waste package, 58.2 cm (22.9 inches) is such that 2.54 cm (1.00 inch) along the circumference is equivalent to a theta (θ) of 5 degrees. Note in Fig. 3 that the sediment line is indicated for both the open and closed ends of the drum. Above these lines (as indicated by the shaded areas in the figure) the drum was buried in sediment at the time of retrieval.

After separating the 300-liter steel drum from the concrete, the waste form was cored to determine the type, quantity and distribution of contained activity in the concrete and to evaluate the integrity of the waste form. Cores were taken in incremental depths of 5 cm (2 inch) using an impregnated diamond core bit with a 5.7 cm (2.25 inch) diameter.

The coring operation was performed inside a hot cell (primarily for dust control purposes) as shown in Fig. 5. Cores were taken along the 0^{o}, 90^{o}, 180^{o}, and 270^{o} longitudinal axis as shown in Fig. 6 for the 0^{o} axis. Although individual cores could be described by the (θ, x, r) coordinates, the core holes were also designated by a letter for ease of identification. The center of any particular letter designated core hole was the same distance from the open end concrete surface (x) independent of the theta (θ) for that axis. Figure 4 gives the x distances for the letter designated core holes. Cores were described as, for example, 90C6, which indicates the core was taken along the 90^{o} longitudinal axis, from

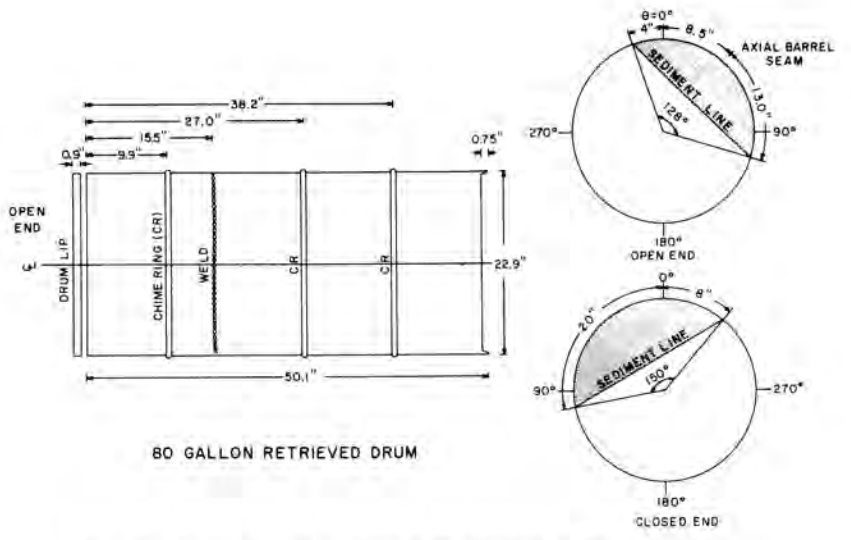

Fig. 3. Schematic of retrieved 80 gallong waste package.

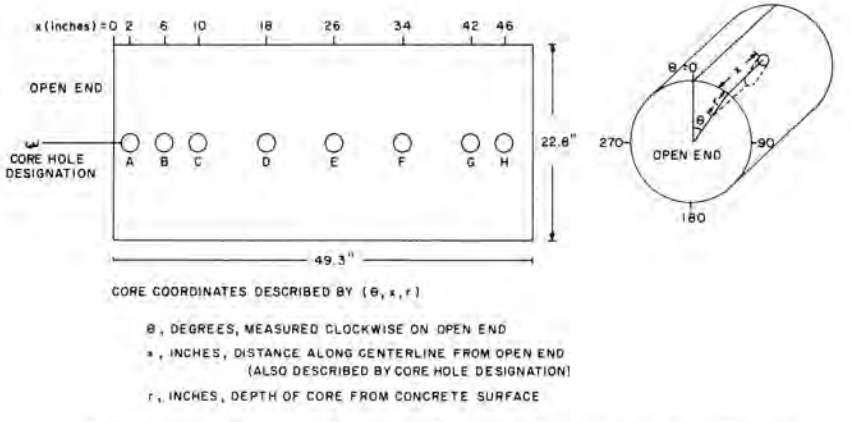

Fig. 4. Schematic of the orientation system used to describe the waste package and the letter designation of core holes.

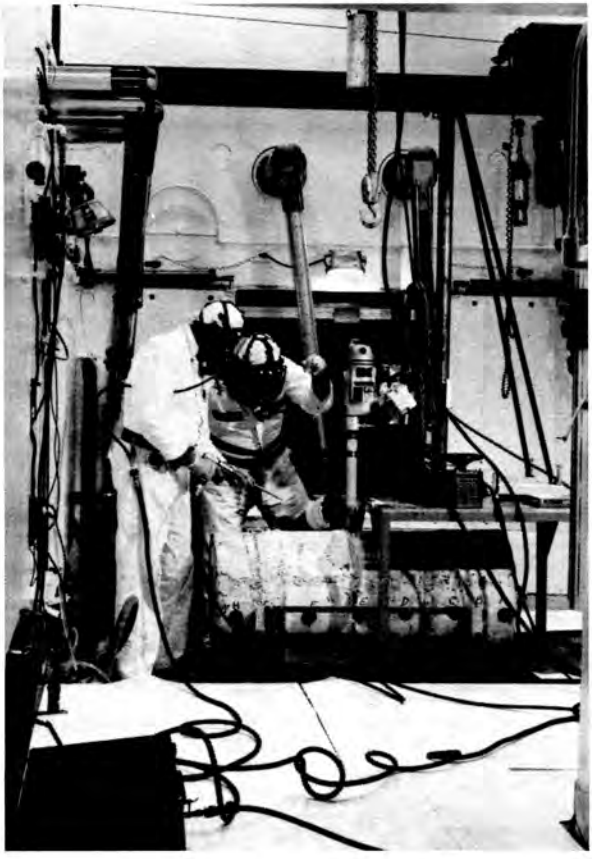

Fig. 5. Core drilling of the concrete waste form.

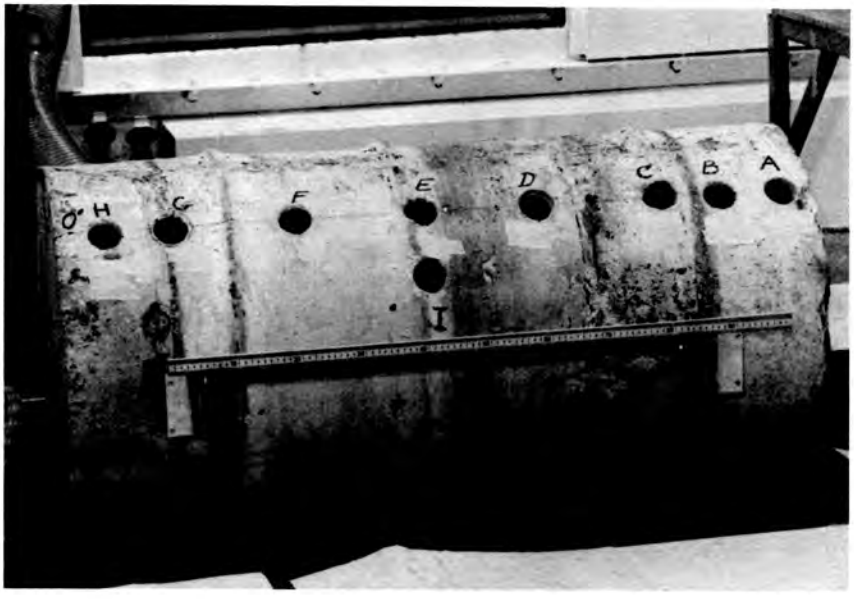

Fig. 6. Side view of the concrete waste form showing the core hole locations along the 0^{o} and 20^{o} longitudinal axis.

core hole C (x = 25 cm or 10 inches) and to a depth (r) of 15 cm (6 inches).

After core samples were taken for activity analysis and compression testing, the concrete waste form was dissected using a power chisel to free the inner steel vessel. Figure 7 shows the open end of the waste form with the upper 20 cm (8 inches) of concrete removed, exposing the inner container flanged end and the two steel pipes which traverse almost the entire length of the waste form. This figure also shows the indentation which runs the length of the inner container on the side which imploded during descent.

Radiochemical Analysis

The concrete cores for determining the radionuclide content and distribution in the waste form were dissolved in aqua regia prior to analysis. Since the concrete was composed of portland cement, sand and quartz aggregate, only the cement phase dissolved in the aqua regia. All of the activity in the cores went into solution with the cement phase. No activity remained with the aggregate or non-soluble fraction of the core.

Core dissolution samples were analyzed using an Ortec coaxial Ge(Li) detector, (Oak Ridge, Tennessee). The detector was horizontally mounted with an integral FET preamplifier whose signal was fed into an Ortec 472A spectroscopy amplifier. The detector had an efficiency of 20% with a resolution of 2 keV at 1.33 MeV. The energy spectrum was analyzed using a Tracor Northern multichannel analyzer (Tracor Northern, Middleton, Wisconsin) in the pulse height analysis mode. A hardwired peak search routine (ALI) was used for peak identification and peak area determination. Strontium-90 was measured using a low-level beta counter to determine the ingrowth of yttrium-90 after a radiochemical separation of strontium. Plutonium analysis was performed by alpha spectroscopy using a surface barrier silicon detector after radiochemical separation and electrodeposition on to a disk.

The results from the concrete coring can be considered in terms of annular volume elements. The average cesium-137 and cobalt-60 content of the concrete in annular volume elements has been determined and is shown in Table I. The thickness of these volume elements correspond to the position of core series depths, i.e., 0-5, 5-10, 10-15, and 15-19 cm (0-2, 2-4, 4-6, and 6-7.5 inches) (this final volume element has a thickness of 3.8 cm or 1.5 inches). While these elements only consider the concrete to a depth of 19 cm from the surface, this represents 88% of the drum volume, and the majority of the volume not considered was occupied by the inner steel container.

Fig. 7. View of the exposed flange end of the inner steel container.

TABLE I. Cesium-137 and Cobalt-60 Content in Annular Volumes of the Concrete Waste Form as a Function of Depth

		Cesium-137		Cobalt-60	
Core depth, cm	Volume, cm^3	Average Conc., Ci/g concrete	Content, Ci	Average Conc., Ci/g concrete	Content, Ci
0-5	1.07×10^5	2.02×10^{-11}	4.78×10^{-6}	3.37×10^{-12}	7.97×10^{-7}
5-10	8.63×10^4	1.54×10^{-10}	2.94×10^{-5}	5.10×10^{-12}	9.73×10^{-7}
10-15	6.60×10^4	5.83×10^{-10}	8.50×10^{-5}	3.72×10^{-12}	5.43×10^{-7}
15-19	3.62×10^4	5.32×10^{-10}	4.26×10^{-5}	3.05×10^{-12}	2.44×10^{-7}
Total	2.96×10^5		1.62×10^{-4}		2.56×10^{-6}

Average concrete density = 2.21 g/cm^3

An average volume weighted cesium-137 activity concentration of 2.48×10^{-10} curies/gram was measured to a depth of 19 cm. The cesium-137 concentrations levels were largest in the 0° and 270° core orientations. Since the density of the concrete waste form (neglecting the inner concrete) is 2.21 g/cm^3, the sum of the concrete annular masses is 6.52×10^5 g, resulting in a total cesium-137 content of 1.62×10^{-4} curies at the time of analysis. This number could be related to the original cesium-137 content of the waste form (considering decay) to determine the radionuclide release during disposal if the total initially contained activity were known. However, if the original activity distribution was homogeneous and the inner container released no activity, an estimate of the minimum cesium-137 release can be made. This is accomplished by noting that the activity concentration increases from the outside to a depth of 10 cm and that for the 10-15 cm and 15-19 cm depth cores, the average activity concentration is approximately equal with a volume weighted average of 5.65×10^{-10} curies/gram. As such, leaching can be assumed to have removed activity only from the outer 10 cm of the waste form while the constant activity concentration at core depths of 10-19 cm represents the initial waste form concentration after decay. Using a decay time of 15 years from waste form disposal to analysis, cesium-137 decays to 70.5% of its original quantity ($t_{\frac{1}{2}}$ = 30.2 years). This suggests an initial homogeneous activity concentration of 7.97×10^{-10} curies/gram or a total waste form activity of 5.20×10^{-4} curies of cesium-137 at the time of disposal. The calculated loss of activity (corrected to the time of disposal) from the outer two volume elements to produce an activity concentration of 7.97×10^{-10} curies/gram is 2.92×10^{-4} curies. The waste form is calculated to have lost 2.92×10^{-4} curies of cesium-137 from a total content of 5.20×10^{-4} curies (both corrected to the time of disposal). This corresponds to a release of 56.2% of the cesium-137 contained at the time of disposal. The calculated bulk leach rate, L_B, of the waste form is 2.38×10^{-3} g/(cm^2-day) where L_B is defined by:

$$L_B = \frac{\Sigma a_n}{A_o} \times \frac{m}{S \cdot t}$$

where $\frac{\Sigma a_n}{A_o}$ = cumulative fraction release of the species of interest (corrected to the time of disposal)

m = waste form mass, g

s = external geometric surface area, cm^2

t = cumulative time since disposal, days

This calculated leach rate for cesium is lower than that observed for leaching of concrete specimens in the laboratory.[6] This is consistant, however, with the fact that only a relatively small surface area of the waste form was in direct contact with seawater in disposal in addition to other effects imposed by the disposal environment (temperature, salinity, etc).

Cobalt-60 ($t_{\frac{1}{2}}$ = 5.3 years) was found to be present in approximately equal concentrations for all orientations and core depths, as shown in Table 1. This may be attributed to the low leach rate in concrete or to the cobalt-60 retentive capabilities of the cement matrix. The total cobalt-60 curie content at the time of analysis was calculated at 2.56×10^{-6}. This value, corrected to the time of disposal (15 years) estimates an original cobalt-60 activity content of 1.84×10^{-5}Ci.

Cesium-134 ($t_{\frac{1}{2}}$ = 2.1 years) was present in concentrations below 10^{-12}curies/gram cement in most cores. It was measured above this level only in the 0° and 270° orientations and primarily in 10-15 cm depth cores. Since the time of disposal the cesium-134 has gone through approximately seven half-lives. With no loss due to leaching, only 0.64% of the initially contained quantity could be present at the time of analysis.

Test cores contained less than 2.4×10^{-12} curies/gram strontium-90 (limit of detection) and 6.7×10^{-13} curies/gram plutonium-239. These values should be evaluated relative to background fallout levels.

Concrete Integrity

Concrete cores were taken to evaluate the integrity of the concrete as measured by its compressive strength using ASTM Standard C 39-72, "Method of Test for Compressive Strength of Cylindrical Concrete Specimens." A Soiltest CT-710 compressive tester (Soiltest, Inc., Evanston, Illinois) was used to make the compression strength measurements. The compressive strengths of the cores tested averaged 120 kg/cm^2 (1,700 psi). These cores had a diameter of 4.39 cm (1.73 inches) and varied in length from 6.88-9.09 cm (2.71-3.58 inches). The sample diameter is less than the minimum diameter typically used for concrete compression testing. Core drilled samples for construction material compression strength verification typically use larger core diameters (7.6-15 cm). Small sample diameter can lead to misleading low compression strength values as the drilling operation may introduce substantial imperfections such as surface microcracking, especially when water cooling and flushing is not employed during coring. Also, small specimens are sensitive to the maximum size of the aggregate.

The concrete was also tested using a CT-320 impact test hammer (Soiltest, Evanston, Illinois). With this method, a weighted hammer is impacted against the concrete surface and the hammer rebound measured. This rebound is directly related to the compression strength. Rebound is expressed in terms of compression strength by the use of conversion tables. Available conversion tables are applicable to ordinary construction concrete. For other types of concrete (that differ appreciably in composition in terms of type and quantity of aggregate, cement and water), one must first establish the relationship between rebound and compression strength to derive an appropriate conversion table. Applying this method and construction concrete conversion tables to the concrete waste form, an average compression strength of 220 kg/cm^2 (4,100 psi) was obtained which is representative of construction grade concrete. As such, it is assumed the core samples used in actual compression testing were adversely affected during the coring operation. Note however, that it was not possible to construct a conversion table for this concrete since the actual composition is now known.

It is difficult to estimate if the strength of the concrete has decreased as a result of ocean disposal since no control exists for comparison purposes. Certainly, the concrete exhibits good integrity in that it has a reasonably high compression strength and does not indicate appreciable mechanical degradation such as exfoliation or cracking. The only visually observed degradation consisted of a small amount of cement phase dissolution or erosion near the open end of the waste form which exposed some aggregate. This aggregate, however, remained bound to the cement matrix.

The concrete waste form will lose integrity as the cement phase dissolves or the waste form is eroded. The maximum weight loss that could be ascribed to cement phase dissolution (hydrated silicate and aluminate compounds and calcium hydroxide) is 5% after fifteen years (0.33%/yr) in disposal. As mentioned previously, water loss during concrete curing or inaccuracy of the initial weighing may have contributed substantially to this apparent weight loss. Assuming a constant 0.33%/yr waste form weight loss due to cement phase dissolution or erosion, a period of 300 years would be required for the waste form to completely disintegrate. The dissolution rate is likely to decrease substantially with time as the relatively soluble calcium hydroxide is removed leaving the less soluble hydrated calcium silicate and aluminate compounds which bind the sand and aggregate together and are the primary contributors to concrete integrity. In fact, the dissolution of calcium hydroxide alone could account for the majority of a 5% waste form weight loss. Conversely, although a substantial decrease in the rate of weight loss is expected as relatively soluble products are removed, some increase above this low rate may occur as the waste container corrodes away.

CONCLUSIONS

Little dissolution of the concrete waste form in the ocean environment occurred as evidenced by a maximum waste package weight loss of approximately 5%. Water loss through evaporation during curing and dissolution of calcium hydroxide in disposal or inaccuracy of the initial weighing are believed to be responsible for the apparent weight loss. A conservative estimate that assumes a constant 0.33%/yr weight loss due solely to cement-phase dissolution predicts that it would require a minimum of 300 years in this environment before the concrete waste form would lose its integrity.

The measured compression strength of the concrete waste form is in the range expected for concrete formulations. This indicates the absence of appreciable attack which is also supported by the observation that negligible deterioration of the waste form surface has occurred.

The concrete waste form contained Cs-137, Cs-134 and Co-60. Based on the assumed initial Cs-137 distribution in the waste form, a bulk leach rate for this radionuclide of 2.4×10^{-3} g/(cm^2-day) was calculated. This corresponds to an average fractional activity loss rate of 3.7×10^{-2} per year (neglecting decay).

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