THE MIGRATION OF CESIUM-137 THROUGH CEMENT FORMULATIONS APPLICABLE TO RADIOACTIVE WASTE MANAGEMENT

Mark J. Rudin and Robert R. Landolt
School of Health Sciences
Purdue University
West Lafayette, Indiana 47907

ABSTRACT

An experimental method was developed to measure the penetration of radioactivity through cementitious barrier materials applicable to radioactive waste management. The technique was used to test eighteen portland cement formulations containing three levels of cement/fly ash content (100%/0%; 85%/15%, and 60%/40%), two levels of water to cementitious solids ratio (w/s = 0.33 and 0.43) and three levels of additive (none, silica fume, and latex polymer). Each formulation was molded into a solid cement specimen containing a centered well space which served as a reservoir for the Cs-137 solution. After a predetermined time period, the Cs-137 solution was removed and a 2-cm long by 1.27-cm diameter cement core was extracted from the monolith well bottom using a diamond core drill. Each cement core was then cut into successive horizontal slices using a diamond saw blade. The Cs-137 activity in each cement slice was determined with a NaI(Tl) detector connected to a single channel analyzer.

Analysis of variance (ANOVA) and regression models were used to examine the statistical relationship between the different formulations in terms of the Cs-137 activity in the cement slices versus the migration distance as indicated by the respective slice depths. The generation of regression curves allowed the comparison between different cement formulations and their relative ability to effectively retard the migration of the Cs-137.

The results indicate that mixes incorporating 5% silica fume (EMSAC) at a w/s ratio of 0.33 are more effective at retarding Cs-137 migration compared to the other formulations tested. Those mixes exhibited high Cs-137 uptake in the slices in contact with the Cs-137 well solution and a dramatic decrease in Cs-137 activity in successive slices compared to other mixes. In addition, formulations with a w/s ratio of 0.33 consistently demonstrated better retardation of the Cs-137 compared to those formulations with a w/s ratio of 0.43. Finally, it was found that the addition of 5% latex polymer did not improve the ability of the cements to retard Cs-137 ion migration, when compared to no additive, under the curing conditions used.

INTRODUCTION

Cementitious materials are used in low level radioactive waste management in several ways, such as in remedial action, as solidification media, as engineered barriers, as concrete bunkers, and to fill void spaces in containers. If contaminated liquids are released from the waste and impact on cementitious barriers, the probability exists for eventual penetration of the barrier due to the porous network of hardened cement paste. In addition, contamination of the surface of the cementitious barrier as well as within the media pose problems for decontamination and dismantling the barrier, if such action is necessary.

The effectiveness of engineered barriers at preventing radionuclide release is a function of the cementitious mix itself as well as to the environmental stresses to which it is subjected. The objectives of this research were to develop an experimental procedure to accurately measure the migration of radioactivity through cementitious barriers and to use this technique to compare the amount of Cs-137 migration at various depths in several formulations.

MATERIALS AND METHODS

Eighteen portland cement formulations, listed in Table I, containing three levels of cement/fly ash content, two levels of water to cementitious solids ratio, and three levels of additive were tested.

Cement Mold Preparation

The experimental unit used to study the migration of the Cs^+ ion through various cement formulations consisted of a solid cylindrical cement sample containing a centered well space. The novel shape of the experimental unit warranted defining terms to describe its various parts. An individual cement specimen was referred to as a monolith. The well space, which served as a reservoir for the Cs-137 solution, was termed the monolith well. The cylindrical solid drilled from the bottom of the monolith well was called a core. Horizontal sections cut through an individual core resulted in the formation of slices.

The mold developed to cast all cement monoliths was designed to reduce stress to the cement during the demolding process. The formation of stress-induced microcracks

TABLE I

List of Cementitious Formulations.

100% cement/0% fly ash, w/s = 0.33 and w/s = 0.43
100% cement/0% fly ash + 5% EMSAC, w/s = 0.33 and w/s = 0.43
100% cement/0% fly ash + 5% latex, w/s = 0.33 and w/s = 0.43
85% cement/15% fly ash, w/s = 0.33 and 0.43
85% cement/15% fly ash + 5% EMSAC, w/s = 0.33 and w/s = 0.43
85% cement/15% fly ash + 5% latex, w/s = 0.33 and w/s = 0.43
60% cement/40% fly ash, w/s = 0.33 and w/s = 0.43
60% cement/40% fly ash + 5% EMSAC, w/s = 0.33 and w/s = 0.43
60% cement/40% fly ash + 5% latex, w/s = 0.33 and w/s = 0.43

within the cement matrix caused by rigorous demolding could dramatically affect the rate of Cs-137 migration through the hardened cement paste. The transport of the Cs^+ solution would no longer be governed by migration through the pore network of the paste, but rather by flow through the microcracks. A plastic cylindrical bowl with 15.5-cm top diameter, 12-cm bottom diameter, and a 9-cm height was used as the cement mold. The well space in the cement monolith was formed by the insertion of a plastic cup with a 7.5- cm diameter, 5-cm bottom diameter, and a 9.5 cm height into the cement prior to hardening. The plastic cup was held into position by a 6.6-cm diameter hole centered on a plastic lid fitted on top of the plastic bowl. The cup was inserted to a depth which resulted in a 2-cm clearance between the bottom of the cup and the bottom of the plastic bowl. The core specimens to be tested came from this 2-cm thick layer of cementitious material.

Mixing

All cement formulations were prepared in a tabletop batch mixer in accordance with ASTM specifications. The mixing procedure was as follows:

1. Premeasured amounts of cement and fly ash, if any, were added and hand mixed until thoroughly blended.
2. A premeasured amount of mixing water was added to the dry powder to achieve a particular water to cementitious solids ratio (w/s).
3. Premeasured amounts of the additive components, EMSAC or latex, if required, were added to the paste and hand-mixed until thoroughly blended. The amount of EMSAC and latex added to the formulations was 5% by weight of cement and fly ash. Since the latex polymer was approximately 50% water, the amount of water added to the latex mixes was reduced to achieve the proper water to cementitious solids ratio (w/s).
4. Mechanical mixing was started for 3 min., interrupted for 2 min., and followed by 2 min. of final mixing at a higher speed.

Monolith Casting and Curing

Upon completion of the mixing phase, the cement paste was immediately poured into the lightly oiled plastic bowls to a height of 6 cm. Each bowl containing the paste was placed on a vibrating plate for 1 min. to remove air bubbles, thereby consolidating the cement paste. Plastic lids were fitted onto the plastic bowls and the plastic cups were inserted into the paste to a predetermined depth. Once molding of the cement monoliths was complete, additional vibrating was performed to remove any air bubbles formed during cup placement. The molds were left undisturbed on a flat surface for 24 h at room temperature ranging between 68 and 70°F. At the end of this time period, the hardened cement monoliths were removed from the plastic bowls and placed in a fog room for 28 days. The fog room was maintained at 100% relative humidity and a temperature range of 73.4° +/- 3° F. The plastic cups forming the well space of each monolith were left in place for the duration of the curing period. Final demolding of the monoliths was performed at the end of the 28-d curing period. The plastic cups were detached from the monolith wells and the formulation of each monolith was labeled on its surface. The monoliths were placed in the plastic bowls used for the molds in preparation for the addition of the Cs-137 solution to their wells.

Addition of the Cs-137 Solution

The radioactivity was added to the monolith wells by pipetting 50 μL (16.8 μCi) directly into 50 mL of distilled water in the wells, giving a concentration of 0.38 μCi per mL. The monoliths were sealed within the plastic bowls with a solid plastic lid and left undisturbed on the floor of an area maintained at 65 to 68°F. The sealing of the monoliths during the migration study serves two purposes. First, the environment within an individual monolith/plastic bowl would more closely simulate conditions a cementitious structure may be exposed to underground. Second, the radiological hazard is minimized when the monolith system is sealed off from direct exposure to the surrounding environment. In the event a monolith fails to hold the Cs-137 solution, the plastic bowl would provide a secondary barrier which would effectively contain the radioactive solution. The volume of solution was maintained at 50 mL in all monoliths throughout the migration period by periodically refilling with a solution containing 0.38 μCi mL^{-1} of Cs-137.

Monolith Drilling Preparation

Three monoliths per cement formulation were chosen at random and drained of their Cs^{+} ion solution at the designated time intervals of 118 d, 210 d and 308 d. All monoliths were removed from their molds and left inverted in a laboratory hood for 24 h prior to drilling. Air drying of the monoliths facilitated the ease at which the cement was drilled.

Drilling Apparatus and Procedure

The drilling of a core from a monolith well bottom was performed with a drill press positioned inside a singly ducted glove box system. The glove box was equipped with a high efficiency particulate filter. In addition, a hand held miniature vacuum chamber with a filter was used within the glove box to provide further dust control. Constant air monitoring of the drill press operator's breathing zone was performed to ensure that dust was not escaping from the glove box into the surrounding environment. A photograph illustrating the position of the monolith just prior to drilling is shown in Fig. 1.

Fig. 1. Drilling Apparatus in Glove Box.

Preliminary studies indicated that diamond coated drills would penetrate the various formulations rather efficiently. Hollow, 0.5-in. diameter diamond tipped core drills produced cores 0.5 in. in diameter and approximately 0.75 in. in length. Although lubrication of the core drill with water or oil is recommended during the drilling of the cement, no lubricant was used in this work. It was felt that the introduction of water or oil into the cement during the drilling process could facilitate further Cs-137 movement through the cement pore system. However, the lifetime of an individual diamond core drill without lubrication was dramatically shortened. Only nine cores could be drilled before the diamond coating was stripped from its surface.

The procedure adopted for drilling an individual monolith was as follows:

1. The monolith was fed into the glove box and demolded.
2. The bare monolith was placed upon a thin pad of polyethylene which rested on the drill press base with the monolith well facing in an upward position.
3. Clamps were used to secure the monolith to the drill press base.
4. The diamond core drill was fastened in the chuck.
5. The handheld vacuum was turned on and the nozzle was placed in close proximity to the drilling area to collect dust dispersed during drilling.
6. The rotating core drill was lowered into the monolith well bottom. Care was taken not to drill too rapidly so the core would not prematurely break off in the core drill. Completion of the drilling occurred when the core drill exited the bottom of the monolith. It should be noted that dull or worn core drills would at times cause the cracking of the core during drilling. If this occurred, a new core drill would be inserted and the drilling process would begin again on a clean section of the monolith well bottom.
7. The drill press was turned off and the core drill containing the core was raised to its original position.
8. The core drill was removed from the chuck and the intact core was pushed out with a small steel rod.
9. The exterior of the core was wiped clean with a wire brush to remove all excess dust on its surface. The core was then placed into a marked 7-mL polyethylene vial.
10. The interior of the core drill was cleaned with a wire

brush to remove all excess dust and replaced in the chuck for further drilling.

11. The vials were then labeled as containing radioactivity and transported to the sawing apparatus.

Sawing Apparatus and Procedure

The process of sawing a core into consecutive slices was performed with a small jewelry saw positioned in a glove box. The saw utilizes a 4-in. diameter by 0.012-in. thick diamond blade rotating at 3450 rpm. For best cutting performance on hard materials such as cement, a good coolant/lubricant such as mineral seal oil is recommended by the manufacturer. Once again, a lubricant was not used during the sawing performed in this work. The absence of a lubricant during the sawing process did not appear to diminish the efficiency at which the diamond blade cut the cement cores. In fact, the original diamond blade provided quality cutting throughout the entire regimen of sawing. A picture of the sawing apparatus is shown in Fig. 2.

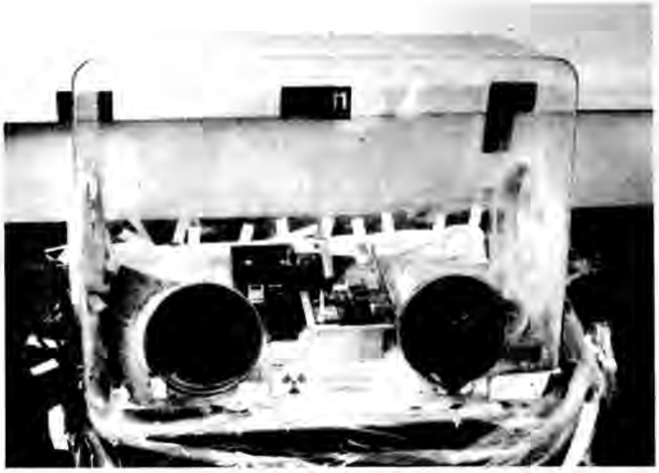

Fig. 2. Sawing Apparatus in Glove Box.

For additional radiological safety, the glove box containing the saw was placed in a laboratory hood. Negative pressure in the glove box was maintained by a pump stationed at the exterior of the laboratory hood. A glass microfibre filter was placed across the pump lines to collect dust generated during sawing which entered the pump lines.

The procedure for sawing consecutive slices from an individual plug was as follows:

1. A core was fed into the glove box via a small access port.
2. The core was marked to designate the thickness of each slice which was to be cut.
3. The core was fixed in place on a sliding tray guide with a clamp. The tray guide was engineered to allow the secured core to be fed into the rotating blade along a track. The core was fed into the blade at a constant hand pressure. The end of the core closest in proximity to the radioactive solution when intact was sliced first with consecutive slices cut thereafter.
4. Four slices were taken per core. If any of the core remained, it was considered to be the fifth slice.
5. Each slice was placed in a separate 7-mL polyethylene vial. Each vial was appropriately marked with formulation, monolith number, and slice number.
6. Each vial was counted on a NaI(Tl) scintillation counter calibrated at 0-1 MeV.
7. After counting, the thickness of each slice was measured with a micrometer.

RESULTS AND DISCUSSION

All regression curves were plotted with square root counts per min (sqrt cpm) on the ordinate versus distance in millimeters to the end of the slices on the abscissa. The curves were plotted using a statistical software package which gave predicted values of square root counts per min as indicated at the four measured distance levels on each regression curve. The plotting system was programmed to generate least significant interval error bars at these predicted ordinate values. These uncertainty intervals provided a basis for the statistical comparison between predicted values at a particular distance level. Overlapping least significant intervals indicated that the predicted values of square root counts per min at a distance level were not significantly different.

Figure 3 is an example of the results that can be obtained using this experimental technique. It shows the migration of the Cs-137 ion through the 100% cement/0% fly ash, w/s = 0.33 mix for the three time intervals used in this study.

The mean values of Cs-137 activity exhibited statistically significant increases at the first distance level from 118 d to 308 d for all 18 formulations studied. This implies that more Cs-137 is being allowed to penetrate and more Cs-137 is being captured at this distance level as time proceeds.

Figure 4 is an example of the results that were obtained in the study of the effect of additive on the migration of Cs-137 through 0.33 w/s and 0.43 w/s at 210 days. The figure displays three additive regression curves (no additive, 5% EMSAC, and 5% Latex) at a particular cement/fly ash content. The addition of 5% EMSAC to mixes resulted in a significantly higher Cs-137 activity relative to the no additive and 5% latex mixes at the first level of distance for all

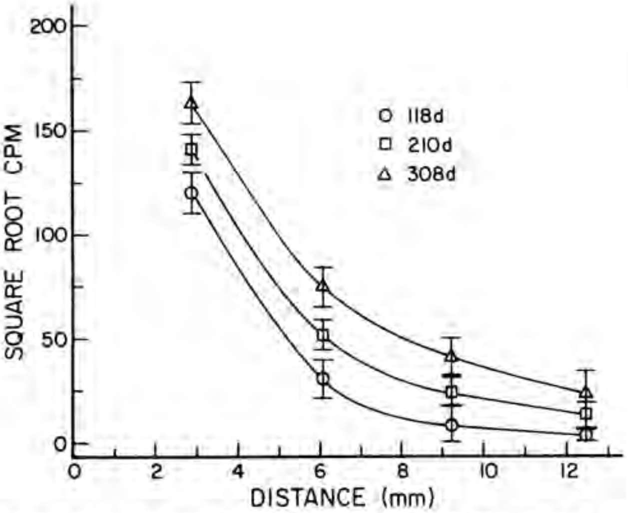

Fig. 3. Time Curves for 100% Cement/0% Flyash, w/s = 0.33.

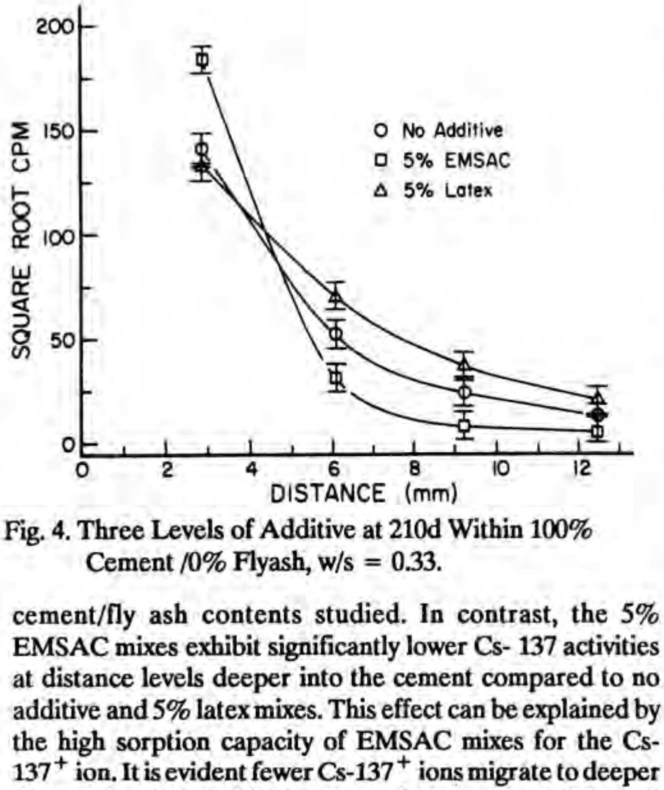

Fig. 4. Three Levels of Additive at 210d Within 100% Cement /0% Flyash, w/s = 0.33.

cement/fly ash contents studied. In contrast, the 5% EMSAC mixes exhibit significantly lower Cs- 137 activities at distance levels deeper into the cement compared to no additive and 5% latex mixes. This effect can be explained by the high sorption capacity of EMSAC mixes for the Cs-137^+ ion. It is evident fewer Cs-137^+ ions migrate to deeper distance levels in EMSAC mixes, relative to no additive and latex mixes, due to their initial adsorption in the first distance level.

The effect of w/s ratio on the migration of Cs-137 is shown in Fig. 5. The figure displays two regression curves corresponding to a water content level (w/s = 0.33 or w/s = 0.43) performed on data sampled at the 210-d time level. In this particular mix and in almost all other cases and at almost all distance levels, the w/s = 0.43 regression curves

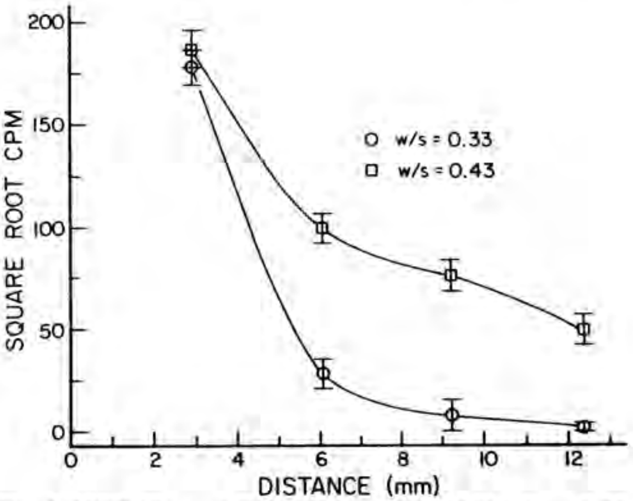

Fig. 5. 100% Cement /0% Flyash + EMSAC, w/s = 0.33 and w/s = 0.43.

show a significantly higher Cs-137 activity at each distance level than the w/s = 0.33 regression curves. It is evident that a lower w/s ratio results in a lower in Cs-137 initial penetration and eventual migration. This result is felt to be related to the fact that the number of large capillary pores in a hardened cement paste is reduced as the w/s ratio of the mix is decreased. This reduction of the larger pores would cause the flow of pore solutions to be controlled by the gel pore network of the paste. Since ion transport through the gel pore network is a slow process, the overall permeability of the paste would be reduced for the lower w/s formulation.

The results of this study also indicated, though somewhat inconclusively, that an increase in fly ash content, at both water cement ratios tested, increases the permeability of the formulation to the Cs-137 ion, regardless of the additive. The results also showed that the ability of latex mixes to retard Cs- 137 migration was similar to that observed in the mixes with no additive. However, it is felt that a true assessment of the ability of latex-modified cements to retard Cs-137 migration may not have been obtained in this research due to an improper curing regimen. Although optimum properties of latex cements are obtained by curing for 28 d at 80-90% relative humidity, all monoliths, including the latex formulations, were cured for 28 d at 100% relative humidity. The 100% relative humidity was used because the introduction the additional treatment factor of relative humidity would have created an extremely complex experimental and statistical design.

In summary, this report describes a novel method for obtaining sections of cementitious samples which can be analyzed to determine the penetration of radioactivity into the media. Analysis of variance (ANOVA) and regression models were used to examine the statistical relationship between the Cs-137 activity in the cement slices versus the migration distance as indicated by the respective slice depths. The Cs-137 ion was shown to penetrate various cementitious material to a depth of at least 12 mm, and the contamination level at a given depth continued to increase with time during the 308 day time period used in the study.

The statistical approach which was employed in this study allowed a clear indication that certain combinations of these treatment factors were able to retard Cs-137 migration better than other combinations and should be considered as prospective cementitious barriers at future LLW disposal sites. Based on the results obtained in this study, a formulation designed to have the most effective retardation of Cs-137 migration should have a low water to cementitious solids ratio and should contain a silica fume additive. Further work needs to be performed to elucidate the usefulness of fly ash and latex incorporation into cementitious barriers.