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THE CESIUM LEACHING RESISTANCE OF CEMENT MATRICES FOR SECONDARY PROCESSING AND SOLIDIFICATION OF CEMENTED RADIOACTIVE WASTE MATERIALS

A. Bilodeau, C. Laviolette, J.-F. Fiset and N. Bouzoubaâ
CANMET-MMSL, Natural Resources Canada
Ottawa, Ontario, Canada

ABSTRACT

This study is part of a broader investigation on the processing and re-solidification of cemented radioactive wastes (CRW) for the production of stabilized waste materials suitable for disposal. One of the objectives of the study is to develop and assess various cementing matrices for the solidified material. The leaching resistance of those potential matrices has to be assessed. A series of tests on the leaching of cesium was performed and the results are presented in this paper.

Surrogate Cemented Waste (SCW), representative of the CRW, was reduced to a particle size suitable for mixing with cementing material (cement and other cementitious materials) and water to produce mortars. The mixture optimization program included several parameters such as the composition of the SCW, the cement-to-SCW (C/SCW) and the water-to-cementitious materials (W/C) ratios of the mortars, and the use of different types and proportions of supplementary cementing materials (SCMs). In this part of the study, the cesium leaching resistance was determined on a number of mortars of different compositions at various ages using the ANSI leach test. As an indicator of the durability, the calcium leaching resistance was also determined on selected specimens.

Reducing the water-to-cementitious materials ratio (W/CM) of the mixtures resulted in the improvement of the leaching resistance of the mortars, however, the effect of the use of SCMs was not clear. In general, the use of zeolites resulted in a relatively good performance in the leaching.

The amount of calcium leached from the mortar exposed to water, an indication of the long-term durability, was determined during the extended cesium leaching test. The calcium leaching appeared significant, however, the extended-test leachability index values for cesium indicate that the integrity of the cement matrix was not much affected by the longer exposure to water, at least not enough to affect significantly the cesium leaching resistance of the mortars.

1. INTRODUCTION

Stabilization/solidification using Portland cement has been used widely for the treatment of hazardous wastes, and this for several years. In some cases, the solidification process is relatively basic and the cemented radioactive wastes (CRW) are stored in controlled sites until further treatment, if deemed necessary, for final disposal. To be suitable for final disposal or even for very long-term storage, the CRW must meet stringent performance criteria. For instance, the leaching resistance of the material is an important parameter since some radioactive products could be leached from the CRW matrix and enter the environment if the solidified material gets in contact with water. This study is part of a broader investigation on the processing and re-solidification of CRW for the production of stabilized waste materials suitable for disposal. One of the objectives of the study is to develop and assess various cementing matrices for the solidified material. The leaching resistance of those potential matrices has to be assessed. A series of tests on the leaching of cesium was performed and the results are presented in this paper.

2. SCOPE

A separate phase of the broad investigation has dealt with the production and characterization of surrogate cemented wastes (SCW) specimens representative of the CRW but not containing any radioactive materials. The SCW material was processed and used in this study for the matrix optimization program, which includes the leaching resistance assessment.

The SCW was reduced to a particle size suitable for mixing with cementing material (cement and other cementitious materials) and water to produce mortars. The mixture optimization program included several parameters such as the composition of the SCW, the cement-to-SCW (C/SCW) and the water-to-cementitious materials (W/C) ratios of the mortars, and the use of different types and proportions of supplementary cementing materials (SCM). The use of zeolites was also investigated. The properties evaluated included, the workability, the strength and the leaching resistance. Parallel studies on the long-term durability and the microstructure were also done on selected mortars. In this part of the study, the cesium leaching resistance was determined on a number of mortars of different compositions at various ages. As an indicator of the durability, the calcium leaching resistance was also determined on selected specimens.

3. PRODUCTION OF MORTARS AND CASTING OF SPECIMENS

3.1. Materials

The mortars were made by mixing water, cement, SCMs or zeolites and crushed SCW, which act as aggregates. The procedure for producing the mortars and casting the specimens was adapted from the ASTM C109 standard procedure [1]. The different materials used for producing the mortars are described below.

3.1.1. Surrogate cemented waste (SCW)

SCW material of different compositions was produced and characterized in a separate phase of the broad investigation. Briefly, the SCW is produced by simply adding, without any mixing action, a heated solution containing several heavy metals to a known amount of Portland cement in a pail. The SCW was produced using two different cements; the general use (GU) and the high-early strength (HE) cements. Three solution-to-cement ratios, 0.21, 0.29 and 0.38, were used with each cement type, for a total of six different material compositions. Each type of material composition was made in triplicate to assess the reproducibility of the pail-making process, for a total of eighteen pails.

Following their production, the pails were simply kept at ambient room temperature and relative humidity conditions until required for characterization and processing in the various phases of the investigation. In the mixture optimization program, SCW material of the six different pail compositions were used however, for the leaching test, only one SCW composition was used at this stage. The SCW material used for the leaching studies was made with cement GU and had a solution-to-cement ratio of 0.38. Prior to the mixing program, the SCW material was crushed to the nominal sand size, smaller than 4.75 mm.

3.1.2. Portland cement

As mentioned above, two different Portland cements, the "General Use cement" (GU) and the "High Early-Strength cement" (HE), as defined by CSA [2] were used in the investigation. However, in this study, only the GU cement was used for producing the mortars. This cement is typical of the Portland cement used regularly in the concrete industry. The chemical analysis of the cement is presented in Table 1.

3.1.3. Supplementary cementing materials (SCMs)

Different supplementary cementing materials (SCMs) were used in the study: two types of fly ash, one type of ground granulated blast-furnace slag and one type of silica fume. Fly ash is a finely divided residue that results from the combustion of pulverized coal in power plants. Both an ASTM Class F (low calcium) and an ASTM Class C (high calcium) fly ash are used [3]. Ground granulated blast-furnace slag usually simply called slag, is a by-product from the production of pig iron. Silica fume, a very fine material, is a by-product of the production of metallic silicon or ferrosilicon.

In the concrete industry, SCMs are materials that can be used to partly replace Portland cement. SCMs can be pozzolanic or cementitious or a combination of both. A pozzolan is defined as a siliceous and aluminous material, which in itself possesses little or no cementitious property but which will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementing properties [4]. It should be mentioned that calcium hydroxide is one of the hydration products of Portland cement. ASTM Class F fly ash and silica fume are pozzolanic materials. Cementitious SCMs are defined as non-crystalline or poorly crystalline materials similar to pozzolans but containing sufficient calcium to form compounds which possess cementing properties after interaction with water [4]. ASTM Class C fly ash and slag are considered cementitious materials. In general, in concrete, the incorporation of SCMs would lead to an enhancement in most properties as long as these materials are used in the right proportions using the adequate concrete practices. However, the physical and chemical processes associated with those materials, and responsible for improving the engineering properties of concrete are slow and therefore take a long time to manifest. Similarly, SCMs were used in this study with the intent of improving the long-term performance of the mortars. The chemical analysis of the various SCMs is presented in Table 1.

3.1.4. Zeolites

Zeolites were also used in the mortars. Zeolites are microporous aluminosilicates minerals commonly used as commercial adsorbents. These materials have the ability to selectively sort molecules based primarily on size exclusion process. They can therefore capture some ions while allowing others to pass freely and this, based on size of molecules. It is believed that the zeolites in the mortars could capture some of the cesium and thus reduce the leaching of that element from the mortar. Three different zeolites, two natural (Clinoptilolite and Chabazite) and one artificial (Molecular sieve 3A) were used in the study.

Table 1. Chemical analysis of cement and supplementary cementing materials.

	Cement GU	ASTM Class F Fly Ash	ASTM Class C Fly Ash	Slag	Silica Fume
SiO_2, %	20.0	47.9	35.8	35.7	68.6
Al_2O_3, %	4.59	25.3	18.8	10.3	3.97
Fe_2O_3, %	2.90	16.2	5.95	0.51	2.21
MgO, %	2.52	0.82	5.90	12.9	0.95
CaO, %	63.3	2.70	25.1	36.1	19.7
Na_2O, %	0.27	0.54	1.82	0.64	0.31
K_2O, %	0.96	1.88	0.48	0.59	0.75
TiO_2, %	0.27	1.35	1.45	0.69	0.16
P_2O_5, %	0.22	0.35	1.27	< 0.01	0.11
MnO, %	0.05	0.02	0.02	0.75	0.04
Cr_2O_3, %	< 0.01	0.03	0.01	< 0.01	< 0.01
V_2O_5, %	0.03	0.05	0.04	< 0.01	0.08
SO_3, %	3.62	0.87	1.60	3.67	1.06
LOI, %	2.39	1.88	0.60	1.26	1.21
C, %	0.40	1.32	0.11	0.19	1.32

3.2. Proportions of mortar mixtures

The proportions and the properties of the mortars used for the leaching test are given in Table 2. For the reference mixture and for the mixture incorporating 30% slag and 30% Class F fly ash, two different nominal W/CM ratios, 1.59 and 0.99, were used to determine the effect of that parameter on the leaching resistance. In concrete technology, lowering the W/CM ratio improves, in general, the properties of the material. The lowest nominal W/CM ratio of 0.99 was used for all the other mixtures made with SCMs or zeolites. This value of W/CM ratio would be very high for mortars made with normal sand. In this study, it was found that very high amounts of water were required to produce mortars with adequate workability, resulting in high W/CM ratios. This high water demand was probably due to the porous nature of the crushed SCW.

For each mixture, two different W/CM ratios (nominal and adjusted) are given. The adjusted W/CM ratio takes into account the un-hydrated cement content in the SCW.

Table 2. Proportions and properties of mortars used for the leaching test

Mix No.	CM/SCW	W/CM		SCMs or Zeolite	Flow, %	28-day strength, MPa
		Nominal	Adj.			
LN3	0.18	1.59	1.10	0	133	12.8
LN4	0.32	0.99	0.79	0	138	25.2
LN5	0.18	1.59	1.10	30% Slag	133	13.9
LN6	0.32	0.99	0.79	30% Slag	N.A.*	25.2
LN7	0.32	0.99	0.79	50% Slag	N.A.*	22.0
LN8	0.18	1.59	1.10	30% FA F	134	10.0
LN9	0.32	0.99	0.79	30% FA F	N.A.*	19.2
LN10	0.32	0.99	0.79	50% FA F	N.A.*	15.0
LN11	0.32	0.99	0.79	30% FA C	N.A.	23.9
LN12	0.32	0.99	0.79	50% FA C	N.A.*	24.4
LN17	0.32	0.99	0.79	7% SF	125	30.2
LN18	0.32	0.99	0.79	10% SF	119	30.4
LN19	0.32	0.99	0.79	30% Slag / 7% SF	125	27.4
LN20	0.32	0.99	0.79	30% FA F / 7% SF	136	20.8
LN21	0.32	0.99	0.79	30% FA C / 7% SF	134	27.8
LN22	0.32	0.99	0.79	10% Clino	117	27.3
LN23	0.32	0.99	0.79	10% Chabazite	109	33.3
LN24	0.32	0.99	0.79	10% Molecular Sieve	117	23.6

* Mixture too fluid to determine the flow

The procedure used for producing the SCW results in the fact that some of the cement in the pails remains un-hydrated. When the crushed SCW is mixed with additional cement and water to make mortars, this un-hydrated cement will hydrate and thus participate to the strength development of the mortar. The amount of un-hydrated cement in the pails varied considerably depending on the solution-to-cement ratio used to produce the SCW. An indirect method based on strength comparisons and specifically developed for this project was used for estimating the un-hydrated cement content of the SCW. It was estimated at 8% for the SCW used in the leaching studies.

Up to 50% of the cement was replaced by either slag or fly ashes. Such high proportions of SCMs tend to increase the workability but will, in general, lower the 28-day strength of the mortars, which was the case. Silica fume is a very fine and very reactive SCM, and should preferably be used at relatively small cement replacement levels to be efficient. In this series of mixtures, the silica fume contributed to increase the strength of the mortars. The three mixtures made with 10% zeolites achieved significantly different strengths. This is unexplained at this stage of the study.

3.3. Casting of specimens

A number of 37 x 63-mm cylinders and two 50.8-mm cubes were cast from each mortar. The day after casting, the cube specimens were demoulded and wrapped in thin plastic sheet to prevent the drying of the specimens. Those were then placed in a plastic bag, which was sealed and stored at room temperature (23°C) until the age of 28 days when they were used for determining the compressive strength of the mortars. No external moisture was provided to the specimens and the cement hydration resulted from the moisture that was kept in the specimen (autogenous curing). Small plastic bottles with snap-on plastic cap were used as moulds for the cylinders. The cylinders were kept in the moulds for the specified number of days as curing period (autogenous curing).

4. LEACHING OF CESIUM

4.1. Test method

Leach tests were performed on the mortars to measure their ability to impede the release of species incorporated in the SCW when they become in contact with water. The selected test method is the American National Standard Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by Short-Term Test Procedure (ANSI/ANS-16.1), a procedure published by the American Nuclear Society [5].

Briefly, the procedure can be described as the following:

- Mortar specimens are immersed in demineralised water for different time intervals.
- At the end of each leach interval:
    - The specimen is transferred to a new container with fresh leachant (demineralised water).
    - The conductivity and the pH of the leachant are determined.
    - A sample of the leachant is taken for chemical analysis for determining the content of the species of interest
- The effective diffusivity (D) and the leachability index (L) are determined, after 7 days for the standard test or after 91 days for the extended test, using the following:

$$D = \pi \left[\frac{a_n / A_0}{(\Delta t)_n} \right]^2 \left[\frac{V}{S} \right]^2 T \qquad (1)$$

$$L = \frac{1}{7} \sum_{1}^{7} \left[\log(\beta / D) \right]_n \qquad (2)$$

Where:

D is the effective diffusivity (cm^2/s)

a_n is the quantity of cesium leached during the leaching interval n

A_0 is the total quantity of cesium in the specimen at the beginning of the first leaching interval

$(\Delta t)_n$ is the duration of the n'th interval, in seconds (s)

V is the volume of the specimen (cm^3)

S is the geometric surface area of the specimen (cm^2)

T is the leaching time representing the "mean time of the leaching interval"

$$\mathrm{T} = \left[\frac{1}{2}(t_n^{1/2} + t_{n-1}^{1/2})\right]^2 \qquad (3)$$

L is the leachability index

β is a defined constant (1.0 cm^2/s)

Equation 2 is given for 7 leaching intervals but can be modified for 10 leaching intervals in the extended test. The higher the value of the leachability index is, the better is the leach behaviour (less leaching) of the mortar.

The diffusivity D is calculated for each leaching interval. Equation 1 can be used only if up to 20% of the leachable species (cesium in this study) has been removed by the time t otherwise a tabular method provided in the standard has to be used.

The leaching test method specifies a standardized uniform leachant-renewal schedule. In this study, the leachate was sampled and completely replaced after cumulative leach times of 2, 7, 24, 48, 72, 96 and 168 hours for the standard 7-day test. In the extended option, three additional leach intervals of 11, 28 and 45 days were used.

The 7-day test was done after curing periods of 7, 28 and 56 days early in the study but was done only after 28 and 56 days later on. The extended test was done only on specimens at 56 days of age so that the test was performed on a more mature specimen. Testing a less mature specimen may introduce additional difficulties in the interpretation of the results since significant cement hydration and SCMs reaction may take place during the extended test and change noticeably the porosity of the mortar. For a certain number of tests, two specimens (A and B) were used per test for reproducibility purpose but most of the time only one specimen was used. From each mixture, one specimen was used for chemical analysis for determining the initial content of cesium in each specimen, assuming the mortar was a quite homogenous material.

In addition to the cesium leaching, as an indicator of the durability of the mortars, the amount of calcium leached from the specimens was determined during the extended test.

4.2. Leaching test results for Cesium

4.2.1. Effect of age and W/CM ratio

The leaching test results of the mortars incorporating SCMs and zeolites are given in Table 3. Regardless of the type of mixture, the leachability index (L) for the 7-day test (standard) ranged from 6.7 to 8.5 when the specimens were cured for 7 days, whereas it ranged from 7.4 to 8.6 and from 7.8 to 9.1 for specimens cured 28 and 56 days, respectively. The leachability index of all the mortars tested in this part of the study is higher than the minimum value of 6 required by the U.S. Regulatory Commission [5].

Although, the above results indicate that longer curing improved the leaching resistance (higher L values), this was not always the case when the data are analyzed for each type of mortars. In general, with a few exceptions, the L values increase when curing is extended from 7 to 28 days however, additional curing from 28 to 56 days does not clearly improve the leaching resistance of the mortars, and in fact, in some cases the leachability index is noticeably lower for the more mature specimens. This was unexpected and remains to be fully explained. This could simply be due to the variability of the test but another explanation could be related to the cesium concentration of the mortar pore solution. In principle, mature specimens have a denser, less porous microstructure, which should reduce their diffusion coefficient compared to specimens that had only few days of curing. On the other hand, due to the consumption of water resulting from the formation of hydration products, the concentration of cesium in the pore solution probably increases thus increasing the gradient of concentration with the leachant (pure water).

Figures 1 to 7 illustrate the relative performance of the various mixtures by showing the cumulative proportion of cesium leached as a function of the cumulative exposure time. It can be seen from the figures that in some cases more than 20% of the cesium was leached from the specimen at some point during the test. In those cases, the tabular method had to be used for calculating the leachability index of the specimens.

As expected, reducing the nominal W/CM ratio from 1.59 to 0.99 (adjusted from 1.10 to 0.79) clearly improved the leaching resistance of the mortars (Figures 1 and 2), the only exception being the fly ash mortar specimens tested at 7 days

4.2.2. Effect of the use of SCMs

The relative performance of the mortars incorporating different proportions of SCM in the standard 7-day test is illustrated in Figures 3 to 5. The effect of the use of SCMs on the performance of the mortars in the leaching test is not clear. It depends on the type and proportion of SCMs used and on the age of the specimen when it is tested. In general, with a few exception, compared to the reference mortars, both the slag and the Class F fly ash mortars seems to perform better, especially when tested at later ages. In fact, the mortar specimen incorporating 50% slag showed the highest resistance to cesium leaching in this series of experiments with an L value of 9.1. Compared to the reference mortar, the use of Class C fly ash resulted in lower L values at 7 days, higher values at 28 days, and significantly lower values at 56 days (Table 3). In the case of silica fume and of ternary blends, the performance of the mortars is slightly better at 7 days but lower at both 28 and 56 days compared to that of the reference mixture

The reason for using SCMs in mortars was their tendency to refine the pore structure of the cement matrix, which would contribute to reduce the mobility of the cesium ions in the mortars. However, slag and fly ash (both Class F and Class C) reacts at a slower pace than Portland cement and thus the benefits of using these materials were expected to occur at later ages. It was not really the case in this experiment except for slag, to some extent. It is possible that 56 days of age was still too early to get full benefit of using these materials. Additional tests would be required to confirm this.

Silica fume is a very fine and reactive pozzolan that is known to refine considerably the pore structure of a cement matrix even at relatively early ages. Therefore, it was expected that silica fume would have contributed to improve noticeably the leaching resistance of the mortars. The use of silica fume did not meet expectations, and the age of testing should not be a major factor in this case. In general, the leaching test results are difficult to interpret as for the effect of the use of SCMs and, as it was the case for the effect of the age of specimens, this could be related to the opposite effects of two factors, the refinement of the pore structure and the increase of the cesium concentration in the pore solution. Additional tests will be required to draw proper conclusions on the potential benefits of using SCMs in mortars.

Table 3. Results of the leach test for mortars incorporating SCMs or zeolites

Mix No	W/CM Nominal	W/CM Adj.	SCMs or Zeolite	L, 7-day test 7 d (A)	L, 7-day test 7 d (B)	L, 7-day test 28 d	L, 7-day test 56 d	L, 91-day test 56 d
LN3	1.59	1.10	0	7.1	6.7	7.8	7.8	N.A.
LN4	0.99	0.79	0	7.8	7.8	8.0	8.4	N.A.
LN5	1.59	1.10	30% Slag	7.5	7.3	8.0*	8.2	N.A.
LN6	0.99	0.79	30% Slag	7.7	7.6	8.6*	8.6	N.A.
LN7	0.99	0.79	50% Slag	8.1	8.0	8.8*	9.1	N.A.
LN8	1.59	1.10	30% FA F	7.7	7.8*	8.4	7.9	7.8
LN9	0.99	0.79	30% FA F	7.6	7.8	8.5	8.0	7.9
LN10	0.99	0.79	50% FA F	7.8*	7.7*	8.5	8.4	8.3
LN11	0.99	0.79	30% FA C	7.2	7.5	8.3	7.8	7.7
LN12	0.99	0.79	50% FA C	7.1	7.4	8.4	7.8	7.8
LN17	0.99	0.79	7% SF	7.9	8.0	N.A.	7.8	7.8
LN18	0.99	0.79	10% SF	8.1	8.0	7.7	7.9	7.8
LN19	0.99	0.79	30% Slag / 7% SF	8.2	8.5	7.7	8.2	8.1
LN20	0.99	0.79	30% FA F / 7% SF	N.A.	N.A.	7.4	8.0	8.0
LN21	0.99	0.79	30% FA C / 7% SF	N.A.	N.A.	7.5	8.2	8.1
LN22	0.99	0.79	10% Clino	N.A.	N.A.	8.3	8.1	8.1
LN23	0.99	0.79	10% Chabazite	N.A.	N.A.	8.5	8.5	8.4
LN24	0.99	0.79	10% Molec. Sieve	N.A.	N.A.	7.8	7.8	7.7

* Average of less than 7 intervals (missing data)
N.A.: Data not available.

The results on the extended 91-day test showed L values similar to those of the 7-day test (Table 3). This would indicate that the integrity of the cement matrix was not much affected by the prolonged exposure to water, at least not enough to affect the cesium leaching resistance of the mortars. Figure 5 illustrates the relative performance of the mortars incorporating various percentages of SCMs in the extended leaching test. It shows that the cumulative proportion of cesium leached ranged from about 40 to 60%, which appears considerable.

As far as the relative performance of the various SCMs, the mixture incorporating 50% Class F fly ash performed the best, followed by mortars incorporating ternary blends (slag or fly ash with silica fume). Unfortunately, the extended test was not performed on the reference nor on the mortars incorporating slag.

4.2.3. Effect of the use of zeolites

The use of 10% Clino and especially 10% Chabazite zeolites resulted in a relatively good performance in the leaching test with leachability index values similar to, or higher than that of the reference mortar (Table 3 and Figure 6). On the other hand, the mortar incorporating 10% Molecular Sieve zeolites did not perform quite as well as the reference mixture.

As it was the case for the mortars incorporating SCMs, the results in the extended test of the mortars incorporating zeolites were similar to those of the standard test (Table 3 and Figure 7). In this study, during the mixing process, the zeolites were added to the mixture at the same time as the other ingredients. A modified sequence of addition of the ingredients that would allow additional contact time between the cesium ions in solution and the zeolites before the addition of cement could possibly improve the performance of the mixtures incorporatin zeolite. More research is required to confirm this.

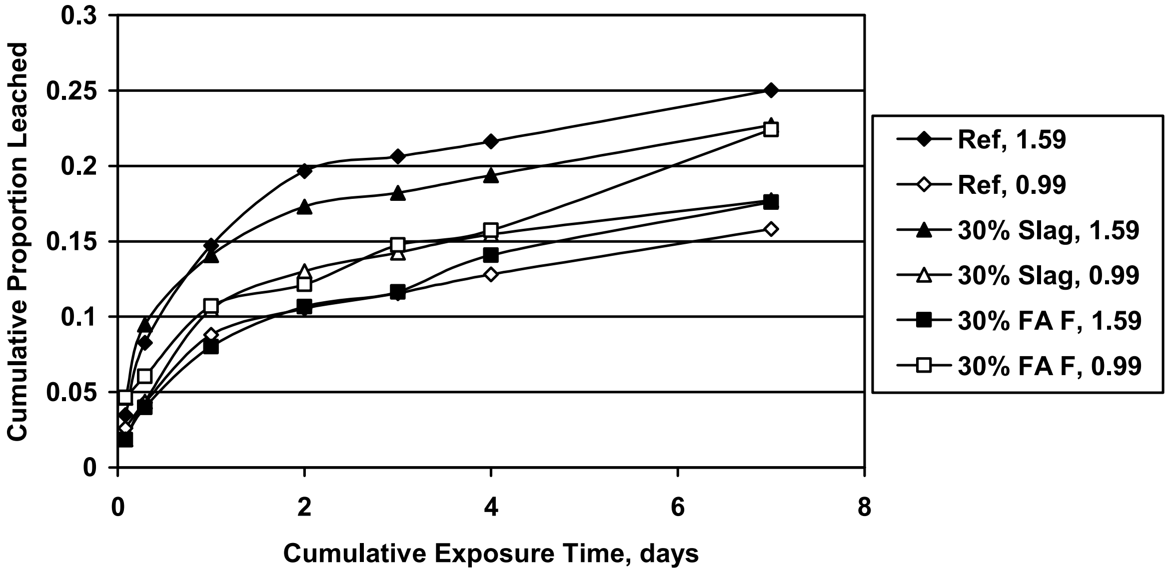

Figure 1. Cumulative proportion of Cesium leached in the standard test (7 days) from specimens tested at 7 days: effect of W/CM ratio.

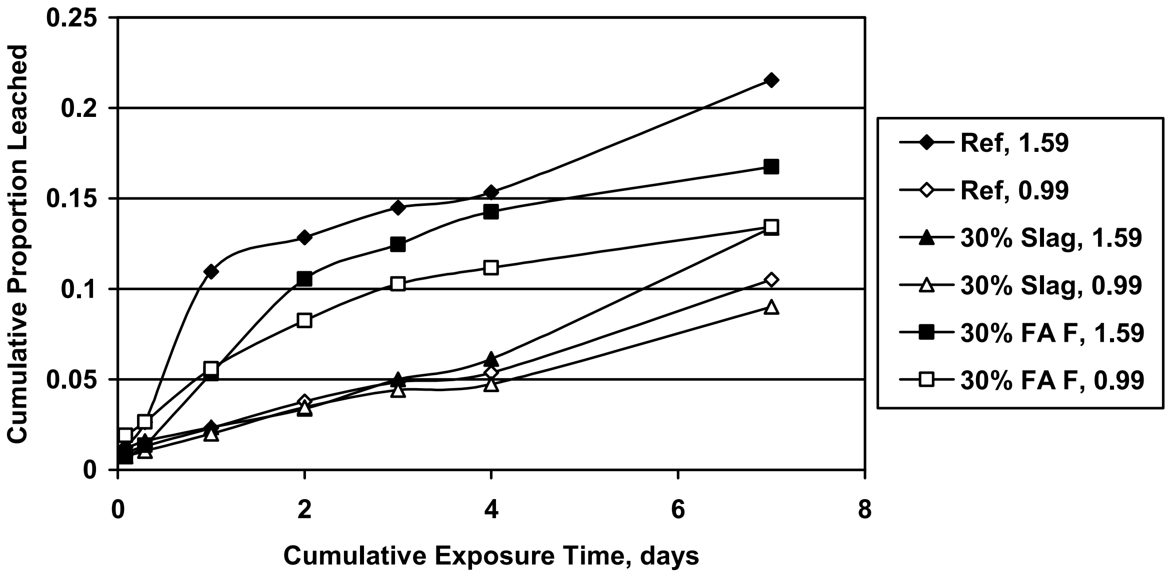

Figure 2. Cumulative proportion of Cesium leached in the standard test (7 days) from specimens tested at 56 days: effect of W/CM ratio.

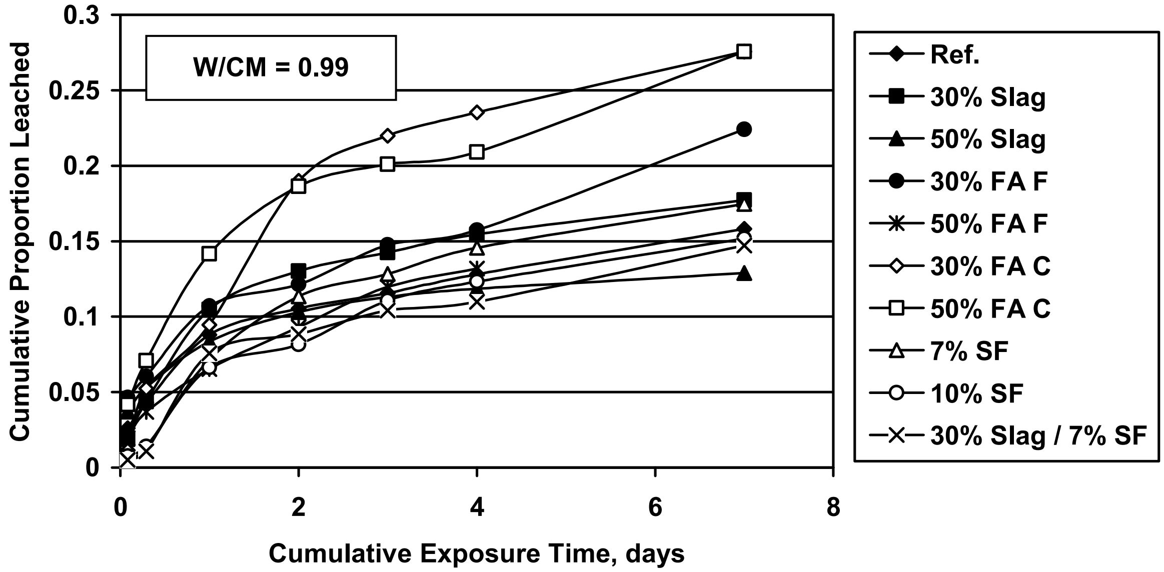

Figure 3 - Cumulative proportion of Cesium leached in the standard test (7 days) from specimens tested at 7 days: effect of SCMs.

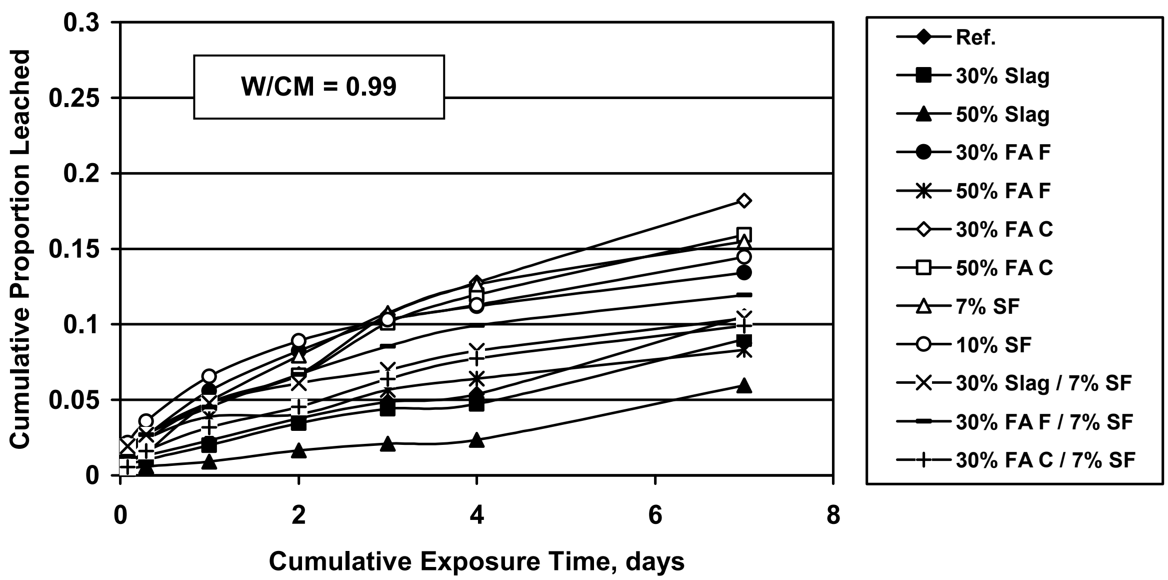

Figure 4 - Cumulative proportion of Cesium leached in the standard test (7 days) from specimens tested at 56 days: effect of SCMs.

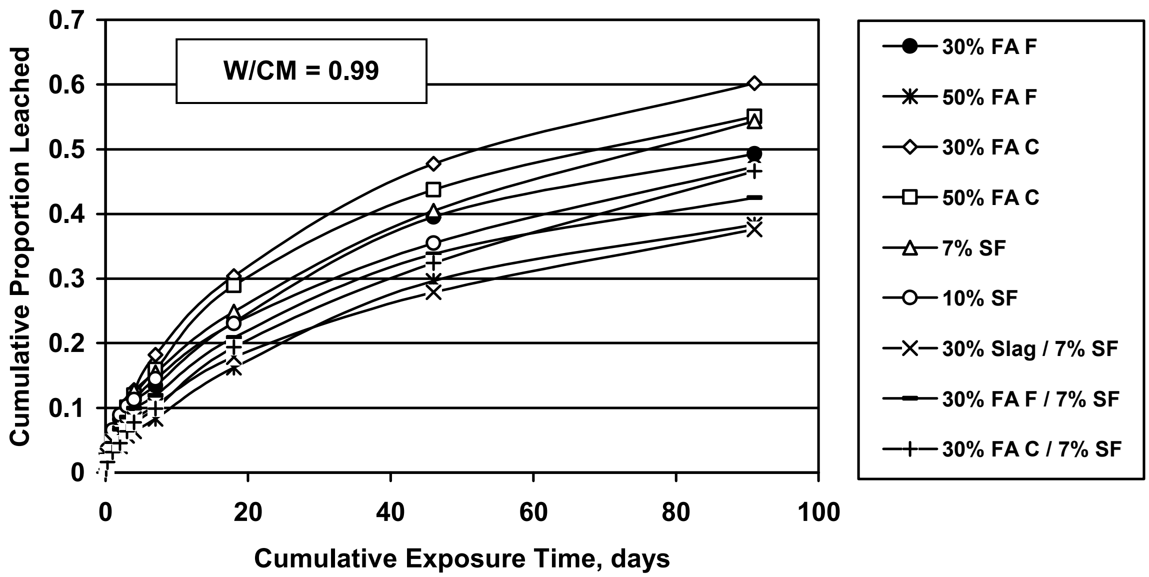

Figure 5 - Cumulative proportion of Cesium leached in the extended test (91 days) from specimens tested at 56 days: effect of SCMs.

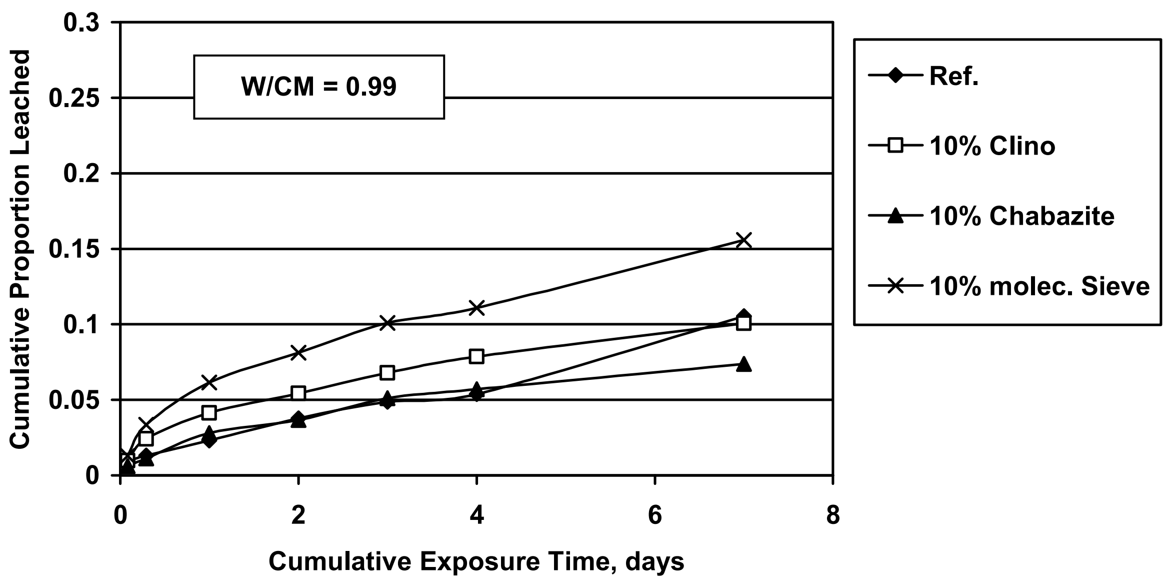

Figure 6 - Cumulative proportion of Cesium leached in the standard test (7 days) from specimens tested at 56 days: effect of zeolites.

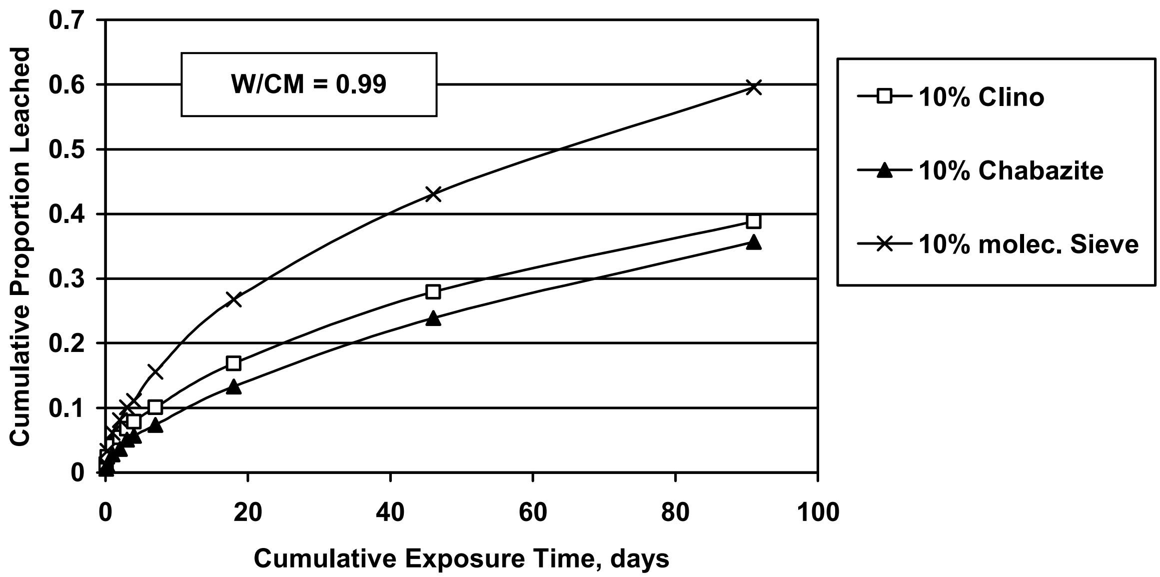

Figure 7 - Cumulative proportion of Cesium leached in the extended test (91 days) from specimens tested at 56 days: effect of zeolites.

4.3. Calcium leaching

One durability concern is the effect of the long-term exposure to water on the mortar, and one way to measure it, is to determine the amount of calcium leached during the cesium leaching test. This was done on some of the specimens in the extended leach test.

Figures 8 and 9 show the cumulative amount of calcium leached from some of the mortars as a function of the time of exposure during the extended leach test. The amounts of calcium leached (≈ 600 to 850 mg) do not appear negligible but it is too soon to conclude on the long-term durability of the mortars when exposed to water. For all the specimens tested, the rate of leaching is faster at early stages in the test and then, it decreases progressively.

It is difficult to compare the calcium leaching resistance of the different mortars since the initial calcium content in the specimens depends on the mortars composition. For instance, mixtures incorporating 30 and 50% fly ash, especially Class F fly ash contain significantly less calcium than the mixtures made with 7 or 10% silica fume as replacement for cement. More important though is the solubility of the calcium present in the mortars, which depends on the relative proportion of the different hydration products incorporating calcium. For instance, portlandite (calcium hydroxide) is much more soluble than calcium silicate hydrates. The pozzolanic reaction consumes portlandite, therefore, the amount of soluble calcium should decrease with time in mixtures incorporating highly pozzolanic SCMs such as Class F fly ash and silica fume.

The results show that the mortars incorporating Class C fly ash or 30% Class F fly ash had the highest amount of calcium leached. The mixtures incorporating 7 and 10% silica fume showed a bit less leaching than the above mixtures in spite of larger initial amount of calcium (less cement replaced). When combined with other SCMs, silica fume seemed to reduce the amount of calcium leached from the mortar specimens.

The mixture incorporating 50% Class F fly ash, due to the combined effect of reduced initial calcium content and pozzolanic reaction had noticeably lower amount of calcium leaching than the other fly ash mixtures.

The mixtures incorporating Clino zeolites showed significantly more calcium leaching than the mortars made with Chabazite and Molecular Sieve zeolites. This is unexplained at this stage.

As mentioned before, the leachability index values obtained for cesium in the extended test, indicate that the calcium leaching do not seem to have affected significantly the integrity of the cement matrix. It appears that for the duration of the extended test, the calcium leaching was only a surface phenomenon.

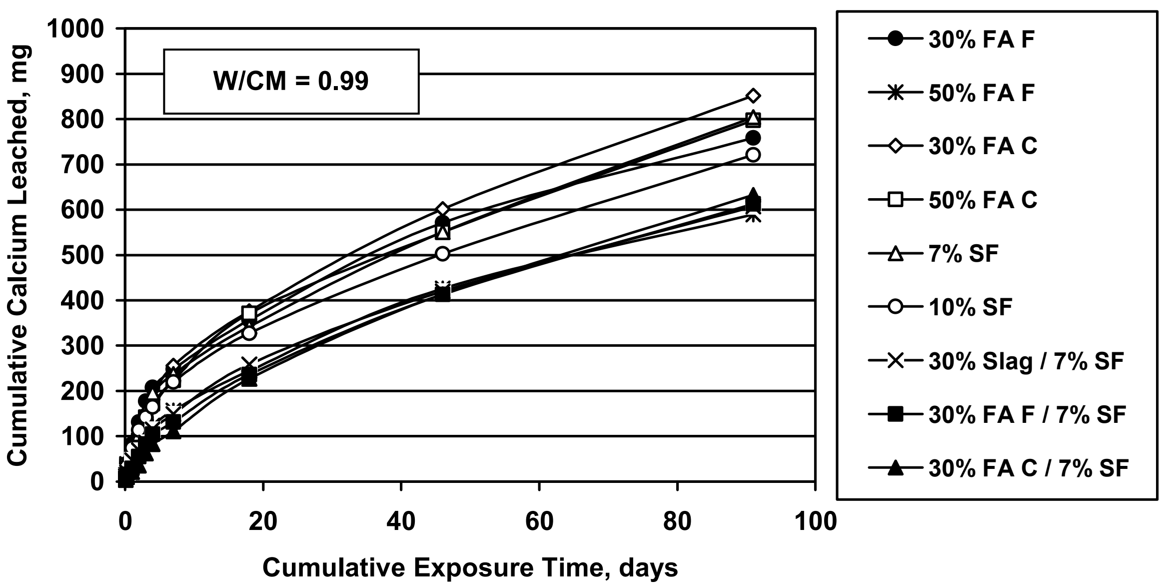

Figure 8 - Calcium leaching of the specimens tested at 56 days in the extended test (91 days): effect of SCMs.

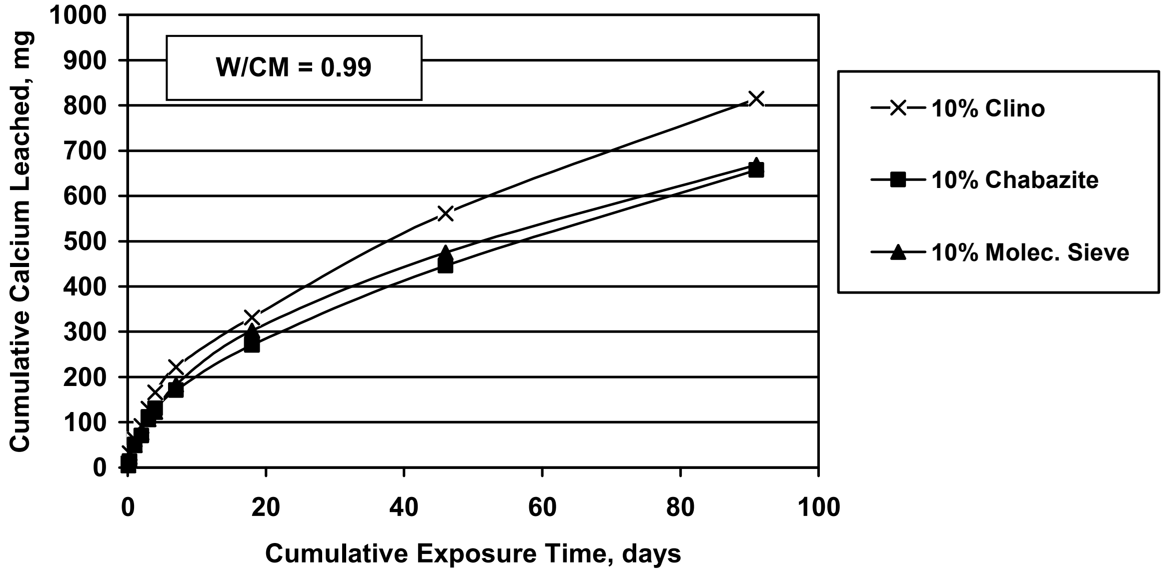

Figure 9 - Calcium leaching of the specimens tested at 56 days in the extended test (91 days): effect of zeolites.

5. CONCLUSION

The ANSI leach test was performed for cesium on mortars incorporating various proportions of SCMs and zeolites, and the standard 7-day test results showed that for all the mixtures, the leachability index (L) was significantly higher than the minimum value of 6 required by the U.S. Regulatory Commission.

Reducing the water-to-cementitious materials ratio (W/CM) of the mixtures results in a clear improvement of the leaching resistance of the mortars.

The effect of the use of SCMs on the performance of the mortars in the cesium leaching test is not clear. It depends on the type and proportion of SCMs used and on the age of the specimen at the time of testing. Additional tests will be required to draw proper conclusions on the potential benefits of using SCMs in mortars for leaching resistance.

The use of 10% Clino and especially 10% Chabazite zeolites resulted in a relatively good performance in the leaching test with L values similar to, or slightly higher than that of the reference mortar. On the other hand, the mortar incorporating 10% Molecular Sieve zeolites did not perform as well as the reference mixture.

The amount of calcium leached from the mortar exposed to water, an indication of the long-term durability, was determined during the extended cesium leaching test. The calcium leaching appeared significant, however, the extended test cesium leachability index values indicate that the integrity of the cement matrix was not much affected by the longer exposure to water, at least not enough to affect significantly the cesium leaching resistance of the mortars.

6. REFERENCES

[1.] ASTM International, "Annual book of ASTM standards 2006 – Vol. 04.01: Cement; Lime; Gypsum", 2006.

[2.] Canadian Standard Association, "Cementitious materials compendium A 3000-08", 2008, 218 p.

[3.] ASTM International, "Annual book of ASTM standards 2006 – Vol. 04.02: Concrete and Aggregates", 2006.

[4.] Malhotra, V.M. and Mehta, P.K., "Pozzolanic and cementitious materials", *Gordon and Breach Publishers*, 1996, 191 p.

[5.] American Nuclear Society, "American national standard measurement of the leachability of solidified low-level radioactive wastes by a short-term test procedure - ANSI/ANS-16.1-2003", *American Nuclear Society*, 2003, 33 p.