

RADIOACTIVE CEMENTITIOUS WASTE FORM BEHAVIOR UNDER LONG-TERM FIELD AND LABORATORY TEST CONDITIONS

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ABSTRACT

Control leaching experiments with laboratory cement samples containing simulated radioactive RBMK operational waste were set up to compare the leaching parameters with the field test leach data of pilot-scale cemented waste forms containing real RBMK operational waste. The aim was to gain information on reliability of field test data and to validate the leach test methods. Average annual ^{137}Cs leach rate in deionized water was about thirty times greater than the measured value for the 1st year of the repository test that may be accounted for by the lower average annual temperature in the repository, influence of leachant medium and some other factors. ^{137}Cs cumulative leached fraction (3,7% for 1 yr) was close to value reported in literature for a similar experiment in deionized water. It was more than two orders of magnitude higher than the 1st-yr leached fraction in the repository test (0,01%). In the latter case sample volume was 630 times greater and sample surface to volume ratio, S/V, was 8.6 times less. To compare the field test results with the laboratory leach test, a scaling factor S/V multiplied by a temperature factor and a leach rate decrease coefficient related to the leachant media should be taken into consideration.

INTRODUCTION

Cementitious materials are widely applied by the SIA "Radon" as a matrix for the immobilization of low- and intermediate-level radioactive waste. In 1987 orthocylindrical cement blocks (24 x 24, diameter x height, cm) were manufactured on base of Ordinary Portland Cement (OPC) and operational waste from the Kursk nuclear power plant (reactors RBMK) and placed for long-term testing in a shallow-ground repository and at an open testing site. 12-yr field test has demonstrated the ability of the OPC matrix to provide a high degree of containment for short-lived radionuclides ($^{137,134}\text{Cs}$) under shallow-ground repository conditions [1]. Corrected for decay radioactivity of the samples taken from cement block after 12yr field test was the same as the initial radioactivity of the compound within the measurement error. Control leaching experiments with laboratory prepared cement samples containing simulated operational radioactive waste rich in NaNO_3 were set up to compare the leaching parameters with the field leach test data of pilot-scale cemented waste forms and to validate the leach test methods. Laboratory samples were identical in composition, specific radioactivity, salt content, geometry and preparation technique to the cement blocks in the

shallow-ground repository. Leaching measurements were performed according to the national standard test method for determining chemical durability of solidified radioactive waste.

The aim of the experiment was to get insight into the possible reasons for the high containment properties of cement matrix with respect to the most soluble radionuclide salts such as ^{137}Cs nitrate, found out in the long-term repository leach test.

EXPERIMENT

Leaching experiments were carried out on orthocylindrical (2.8 x 2.8, D x H, mm) cement samples prepared from Portland cement M-500 and sodium nitrate solution, 340 g/L. As in the field experiment initiated in 1987, in this experiment salt solution to cement ratio was 0.6 and water to cement ratio, W/C, 0.43 (on wt.% basis). Calculated salt loading of the final product was 10.6 wt.%. For the preparation of radioactive cement samples, the NaNO_3 solution was doped with $^{137}\text{CsNO}_3$ solution to get radioactivity level of $2.1 \cdot 10^6 \text{Bq/kg}$, corresponding to the initial radioactivity of cemented waste material placed for testing in 1987. The main radioactive component of the cemented waste in the field test was ^{137}Cs (92%). Mortar mixtures were pored into steel molds and after one-day hardening were cured in a humid atmosphere for a month.

In the first leach experiment two sets of three radioactive (R) and four nonradioactive (NR) cement samples were investigated. Leach tests at room temperature (24°C) in deionized water have been ongoing for one year. Sample surfaces were completely opened to contact with water. Samples were suspended in glass beakers (NR samples) and in plastic beakers (R samples) and immersed in 140 and 300 mL of deionized water, respectively. According to the national standard leach test procedure, leachate sampling was performed after 1, 3, 7, 10, 14, 21, 28 days, then once monthly. Water was renewed at each sampling. Concentrations of ion species ($^{137}\text{Cs}^+$, Na^+ , NO_3^- , Ca^{2+}), total salts content and pH were monitored in the leachate solutions. After completion of the experiment, compression strength and porosity of the leached and intact samples were estimated and compared with the initial data.

The other leaching experiment have been undertaken in groundwater from the repository site and in deionized water for control. Fresh groundwater was used to renew leachant at each sampling. Three other leachant media have also been used to assess the impact of $\text{Ca}(\text{OH})_2$, NaHCO_3 and sodium silicates on the OPC-based waste form leaching behavior. Leachants are characterized in Table I. The chemistry of groundwater from the repository site is shown in Table II. Presented are the average annual values for four control boreholes.

Table I. Experiment 2 with radioactive cement samples. Leachant chemistry.

Leachant medium	$\text{Ca}(\text{OH})_2$ + deionized water	NaHCO_3 + deionized water	Water glass + deionized water	Ground water
Concentration	1 g CaO/L	$1.8 \cdot 10^{-2} \text{M/L}$	5 g/L	average. salt content 267 mg/L

Table II. Chemistry of groundwater from the repository site, mg/L.

pH	7.54
Salt content	267.01
Ca ⁺²	49.46
Mg ⁺²	21.22
Na ⁺	12.72
K ⁺	1.36
Cl ⁻	10.31
NO ₃ ⁻	2.44
HCO ₃ ⁻	259.76
SO ₄ ⁻²	9.15

In this experiment cement samples were identical to the samples used in the 1st experiment and were prepared from the same cement and NaNO₃ batches. The tests were set at room temperature in sealed polyethylene containers. Leachant volume in each case was 300 mL. Concentrations of ion species (¹³⁷Cs⁺, Na⁺, NO₃⁻, Ca²⁺), total salts content and pH were monitored in the leachate solutions.

Concentrations of radioactivity and Na⁺, NO₃⁻, Ca²⁺, total salts content and pH were also measured in every fresh sample of groundwater.

RESULTS AND DISCUSSION

Results of the leaching test in deionized water for the samples 'NR' and 'R' are summarized in Figs. 1, 2 and in Table III. In Fig. 1 the average of fourplicate and triplicate test results for cumulative leached fractions of ion species are shown as functions of time. Figure 2 illustrates the corresponding time dependencies of the average leach rates for the cation species ¹³⁷Cs⁺, Na⁺ and Ca²⁺ in 'R' samples.

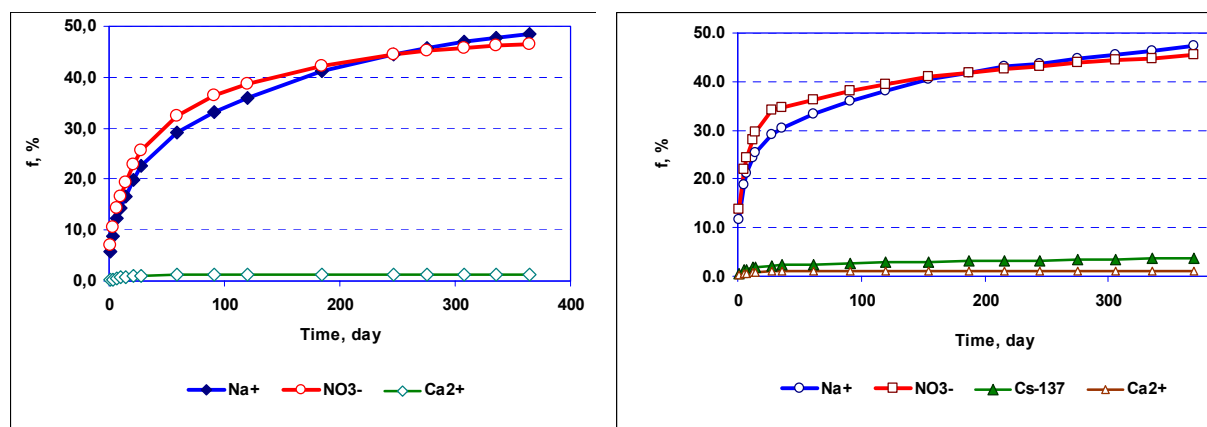


Fig. 1. Time-dependent variations in cumulative leached fractions of ion species for the laboratory leach tests of nonradioactive (left) and radioactive cement samples containing simulated NaNO₃-rich waste.

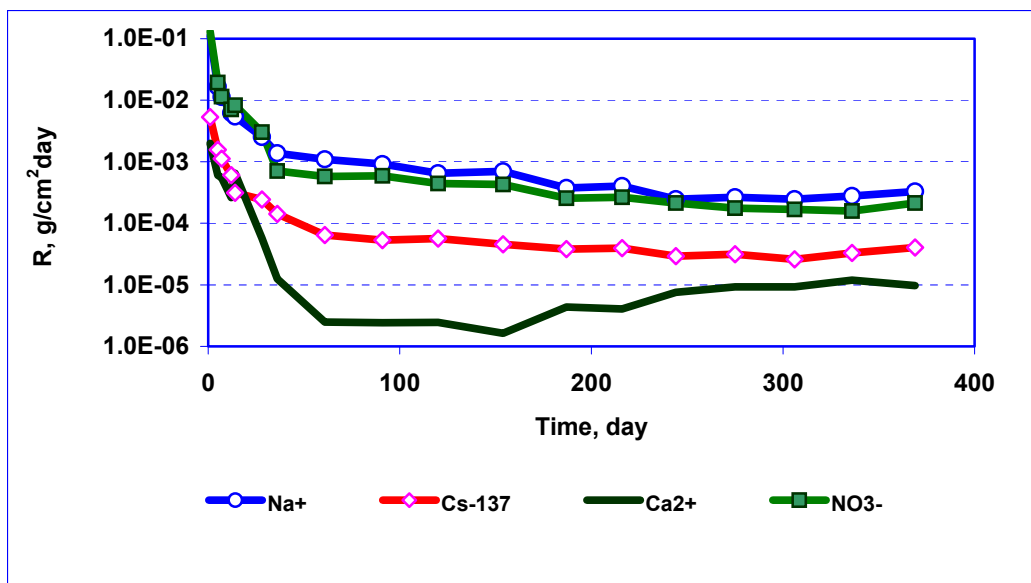


Fig. 2. Average leach rates of $^{137}\text{Cs}^+$, Na^+ , Ca^{2+} and NO_3^- from cement samples containing simulated operational radioactive waste rich in NaNO_3 , as the functions of time.

Leaching data for the 1st year of the field test are also given in Table 3. Ion species leach rates reached its ‘saturation’ levels after about three months of the laboratory experiments. Therefore the corresponding ‘saturation’ values R_{sat} are given in Table 1 along with the average annual values R_{av} for the leach rates of ^{137}Cs , Na^+ and NO_3^- in the laboratory and field tests.

Table III. Average annual (R_{av}) and “saturation” (R_{sat}) leach rates of ion species measured in the laboratory (R samples) and field tests.

	$^{137}\text{Cs}^+$			Na^+			NO_3^-		
	R_{av} , β_{tot} , g/cm ² day	R_{sat} , g/cm ² day	f, %	R_{av} , g/cm ² day	R_{sat} , g/cm ² day	f, %	R_{av} , g/cm ² day	R_{sat} , g/cm ² day	f, %
Field test	$4.8 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$	0.01	$7.3 \cdot 10^{-3}$	$6.7 \cdot 10^{-5}$	3.9	$1.1 \cdot 10^{-3}$	$2.3 \cdot 10^{-5}$	3.4
Laboratory test	$1.7 \cdot 10^{-4}$	$3.2 \cdot 10^{-5}$	3.7	$2.6 \cdot 10^{-3}$	$3.9 \cdot 10^{-4}$	47.4	$2.8 \cdot 10^{-3}$	$2.6 \cdot 10^{-4}$	45.6

Leaching curves of Na^+ showed good correlation with the corresponding curves for NO_3^- . The results indicate that sodium nitrate dissolution proceeds at a high rate during first months of the laboratory leach test. As a result, nearly half of the salt loading dissolved during the 1-year experiment. Average annual and ‘saturation’ leach rates of $^{137}\text{Cs}^+$ were about an order of magnitude lower than those for Na^+ and NO_3^- .

Sodium nitrate dissolution has led to an increase in porosity of the cement matrix and to decrease in its mechanical strength. After completion of the experiment, the average porosity of NR and R samples reached 50.2% and 53.1%, respectively. The corresponding intact samples had the porosity 41.4% and 45.2%. The average compression strength of NR and R samples after the leach test was above the acceptable level of 5 MPa, however in some cases it was lower.

^{137}Cs cumulative leached fraction (3,7% for 1 year) was about 1.9 times higher than a value reported in literature (~2%) for a similar experiment with orthocylindrical samples, $H=D=4.5$ cm, in 300 ml of deionized water [2]. However, in the latter case in samples preparation $^{137}\text{CsCl}$ -doped distilled water was used without salt loading. Besides, a water-to-cement ratio of 0.36 provided high cement density, 2.145 g/cm^3 , and a lower porosity of 22%.

'Saturation' ^{137}Cs leach rate in the laboratory experiment was about thirty times greater than the measured 'saturation' value for the 1st year of the repository test that mainly may be accounted for by much lower average annual temperature in the repository (the temperature interval 4° to 14°C) and effect of leachant chemistry. ^{137}Cs cumulative leached fraction (3,7% for 1 yr) was more than two orders of magnitude higher than the 1st-yr leached fraction in the repository site test (0,01%). In the latter case sample volume was 630 times greater and sample surface to volume ratio, S/V , was 8.6 times less. According to [3], the sample surface to the volume activity coefficient $S/V=8.6$ (scaling factor) should be considered to allow comparison of the ^{137}Cs leaching results of the two waste forms.

To compare the field test results with the laboratory leach test, the scaling factor $S/V = 8.6$ multiplied by the temperature and leachant-related factors of the leach rate decrease should be taken into consideration.

To estimate leachant-related constituent of the ^{137}Cs leach rate decrease for the field test, the corresponding laboratory leaching experiment have been undertaken in groundwater from the repository site and in deionized water for control. Other leachant media have also been used to assess the impact of certain components ($\text{Ca}(\text{OH})_2$, NaHCO_3 , sodium silicates) on the OPC-based waste form leaching behavior. Presented here are results on ^{137}Cs leaching. The average of duplicate test results are shown in Fig. 3.

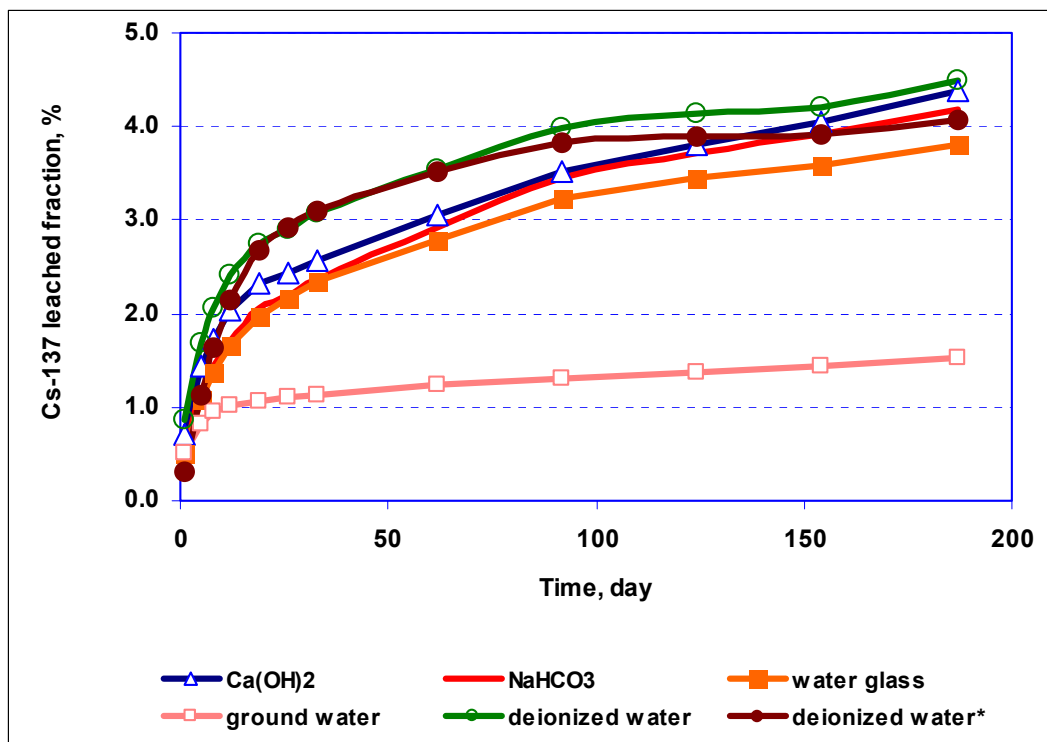


Fig. 3. Time-dependent variations in ^{137}Cs cumulative leached fractions for the laboratory leach tests of cement samples containing simulated NaNO_3 -rich radioactive waste, performed in various leachant media.

The experiment has shown that the groundwater from the repository site is the least active medium of the five in regard to ^{137}Cs leaching. The next in leaching activity is the water glass medium. Hydrocarbonate and calcium hydroxide solutions have proved to be much less effective in suppressing ^{137}Cs leaching. As expected, deionized water has the most pronounced effect on ^{137}Cs leach rate. It is known that deionized water may enhance the cement matrix dissolution rate as compared with the groundwater of moderate hardness. The estimated value of the leachant-related factor effecting the leach rate decrease in the repository test is ~ 4 .

One more factor affecting leach rates from large-scale cement blocks may be hundreds times greater gamma-radiation fields compared with laboratory tests. The impact of cement hardening time on leach rates is also of interest. In the 2nd ongoing experiment radioactive cement samples with prolonged hardening period of 1 year and nonradioactive cement samples subjected (L) and not subjected (M) to gamma ray irradiation (10^6Gy) are also being tested. All of them are the intact samples from the 1st experiment. Storage period before testing was 1 year.

From Fig. 3 no sufficient differences could be detected in ^{137}Cs leaching behavior of samples exposed to deionized water after 1 month and after 1 year (index*) of hardening during first three months of the leach test, whereupon samples with prolonged hardening period demonstrate some decrease in ^{137}Cs leach rate.

The average of duplicate test results for nonradioactive samples 'L' and 'M' are shown in Fig. 4.

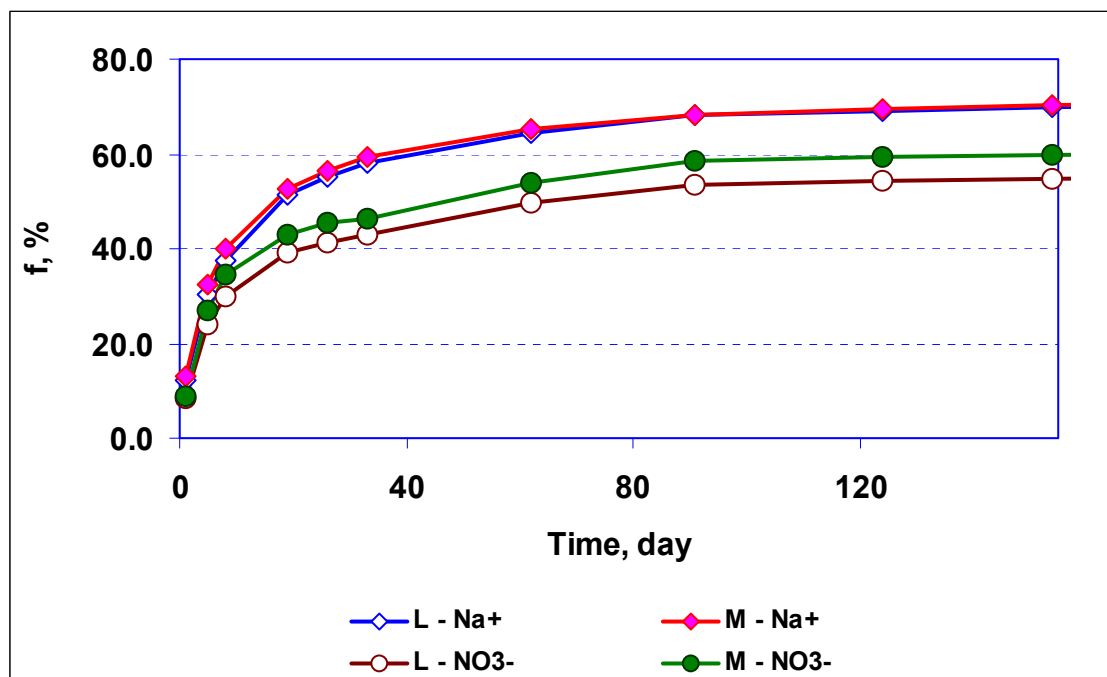


Fig. 4. Cumulative leached fractions of Na^+ and NO_3^- measured in the laboratory leach test of nonradioactive cement samples subjected (L) and not subjected (M) to gamma ray irradiation 10^6Gy .

For 154 days of the test the cumulative leached fractions and R_{sat} of Na^+ were essentially the same: 69.9% and 70.1%; $2.26 \cdot 10^{-4}$ and $2.27 \cdot 10^{-4}$ $\text{g}/\text{cm}^2\text{day}$, respectively for 'L' and 'M'. Leached fraction and leach rate R_{sat} of NO_3^- were less in the case of irradiated samples, respectively 54.7% and 59.9%; $1.43 \cdot 10^{-4}$ and $1.75 \cdot 10^{-4}$ $\text{g}/\text{cm}^2\text{day}$, possibly due to partial radiolytic decomposition of NO_3^- in samples 'L'.

CONCLUSIONS

Standard laboratory leach tests of composite cement samples containing simulated NaNO_3 -rich radioactive waste have been performed to compare the results with the field test data. High leach rates were found for sodium and nitrate at the initial stages of the leach test. Nearly half of the initial salt content dissolved during the 1-year leach test. The release of sodium nitrate has led to about 10% increase in porosity and to a decrease in mechanical strength to values which in several cases were below the level of 5 MPa.

Despite rapid dissolution of the salt component of the cement/ NaNO_3 compound accompanied by the increase in porosity up to levels exceeding 50%, ^{137}Cs leach rates during 1 year period were on average an order of magnitude lower than for Na^+ and NO_3^- . On the contrary, they were significantly higher than for a cement matrix - forming component Ca^{2+} .

Ongoing laboratory experiment in different leachant media have shown that groundwater from the repository site is essentially more effective in suppressing ^{137}Cs release from the cement compound as compared with deionized water. The possible reason may be the partial healing of capillary pores and cracks.

Considering the temperature and leachant-related factors leading together to more than tenfold decrease in ^{137}Cs leach rate in the field test and taking into account the scaling factor $S/V = 8.6$ for the repository test, the calculated value for ^{137}Cs leached fraction for the repository test conditions will be two order of magnitude lower than found in the laboratory test and close to the field test result of 0.01%.

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