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Long-term field and laboratory leaching tests of cemented radioactive wastes

Michael I. Ojovan[a]*, Galina A. Varlackova[b], Zoya I. Golubeva[b], Olga N. Burlaka[b]

[a]Immobilisation Science Laboratory, Department of Materials Science and Engineering, University of Sheffield, UK
[b]Scientific and Industrial Association ‘Radon’, 7-th Rostovsky Lane 2/14, Moscow, Russia

Abstract

Experiments with real and simulated radioactive cementitious wasteforms were set up to compare the leaching behaviour of cementitious wasteforms containing nuclear power plant operational waste in field and laboratory test conditions. Experiments revealed that the average annual ^{137}Cs leach rate in deionised water was about thirty-five times greater compared with the measured average value for the 1st year of the field test. Cumulative leached fraction of ^{137}Cs for 1st year (3.74%) was close to values reported in literature for similar laboratory experiments in deionized water, however more than two orders of magnitude higher than the 1st year leached fraction of ^{137}Cs in the repository test (0.01%). Therefore, to compare field and laboratory test results, a scaling factor is required in order to account for surface to volume factor difference, multiplied by a temperature factor and a leach rate decrease coefficient related to the ground water composition.

Keywords: Waste immobilisation; Cement; Leaching; Field tests; Laboratory tests; Long-term performance

1. Introduction

Cementation of radioactive waste has been practised for many years to immobilise low and intermediate level wastes [1-4]. Cemented radioactive wastes are characterised by good compressive strength, thermal, chemical and physical stability. Moreover the alkaline chemistry of hydraulic cements ensures low solubility for most radioactive waste radionuclides. The prominent advantages of cement immobilisation are due to the inexpensiveness and readily availability of hydraulic cements, simple and low cost processing at ambient temperature. Cement matrix acts as diffusion barrier and provides sorption and reaction sites. Cementation is suitable for sludge, liquors, emulsified organic liquids and dry solids. Most of cementation technologies utilise hydraulic cements among which ordinary Portland cement (OPC) is of most use. Phases formed during cement hydration influence its structure and properties. The most important is tobermorite gel or CSH phase, which is the main cementing component of concrete. Setting and hardening behaviour, strength and dimensional stability depend primarily on the tobermorite gel. Development of the microstructure of hydrated cement occurs after the concrete has set and continues for months (and even years) after placement. OPC is typically 95-98% hydrated after 12 months and comprises an aqueous phase, which is largely confined to filling pores less than 1μm in radius (pore water) and a heterogeneous paste matrix. Typically the phase composition of hydrated cement paste is represented by the following crystalline phases: Ettringite: $3CaO \cdot Al_2O_3 \cdot 3CaS0_4 \cdot 32H_2O$ (AFt); Monosulphate $Ca_4Al_2(OH)_{12}\ SO_4\ 6H_2O$ (AFm); Hydrogarnet $Ca_3Al_2(OH)_{12} – Ca_3Al_2Si(OH)_8$ ($C_3AH_6 – C_3ASH_4$); Portlandite $Ca(OH)_2$ (CH); and amorphous calcium silicate hydro-gel with typical Ca/Si molar ratio 1.7 ± 0.1 (CSH) [4]. Physical adsorption is a significant factor for immobilization of radionuclides by cements. In hydraulic cements basically calcium silicate hydrate gel (CSH) provides adsorption as it has a high surface area and large micropore volume [1, 4-8]. Note however that although cementation technology is typically simple the actual development of an appropriate formulation might require extended research dependent on the chemical complexity of the waste streams (see e.g. [9]).

Most of cemented radioactive wastes as low and intermediate level radioactive wastes are stored and disposed of in near-surface repositories. Performance of cementitious materials including cementitious wasteforms in these conditions is of paramount importance [10]. The particular role of the wasteform to long term safety is repository design and site dependant with typical near surface repository designs which rely on multi-barriers system [10]. Each component of an engineered barrier system (EBS) such as concrete vaults, concrete monoliths containing the waste packages immobilised by a cementitious grout will contribute to the long term safety [10-12]. The role of the cementitious wasteform can be therefore very important in ensuring the overall safety of a disposal. The experience of cement utilisation demonstrates its prominent long-term durability, e.g. modern Portland cements have been in use for ~150 years and $Ca(OH)_2$-based compositions have been successfully used in civil engineering for more than 2000 years [5]. Data obtained via both laboratory and field experiments with real cementitious wasteforms are most relevant to improve our confidence in understanding their long term behaviour [2, 13].

For long term storage and disposal waste immobilisation should be an irreversible process, which avoids release of contaminants from the matrix during storage and disposal. A key property of any wasteform is its leaching resistance, which determines how well the radionuclides of concern are retained within the wasteform in a wet environment. Estimating the rate of leaching from a matrix during disposal is a key consideration in assessing an immobilisation method. Low matrix solubility means reduced likelihood of radionuclide release. The leaching behaviour of cemented radioactive waste is important to ultimately ensure the overall safety of a storage/disposal system. Dedicated experiments are carried out to identify leaching behaviour of cementitious wasteforms and to demonstrate their acceptance for storage and disposal [10, 14-20]. Both laboratory tests [14-17] and long-term tests using conditions similar to those expected in a disposal environment are currently used [10, 18-21]. For the assessment of long term performance and safety of a near-surface disposal system, knowledge of the long term behaviour of actual radioactive wasteforms is needed. Early tests of cementitious wasteforms were started as earlier as sixties [19, 20]. Test conditions represented the most likely (water infiltration) and possible (waste repository opening and direct exposure of wasteform to environment) long-term evolution scenarios for a near-surface disposal. Later, in 1987 new field tests of cementitious wasteforms immobilising operational waste from nuclear power plants (NPP) were set up [18]. These tests comprised three cylindrical cement blocks (24 cm by 24 cm height) which were manufactured at Moscow Scientific and Industrial Association (SIA) “Radon” using Ordinary Portland Cement (OPC) and operational waste from the Kursk NPP operating a channel RBMK type reactor. The aim of this work was to compare the results of laboratory tests with those from field tests of same type cementitious wasteforms.

Leaching data are requested for assessing the long term safety of surface disposal in the present case. Note however that over a very long term, crack development and evolution might significantly affect the retention capacity and the leaching rate of cementitious wasteforms [22, 23]. Leaching beahviour of the wasteform provides data for performance assessment of a repository. Note however that leach rates might significantly evolve especially due to degradation processes and in case of environmental conditions change [24, 25].

2. Experimental

2.1. Radioactive waste characteristics

Operational radioactive waste of a channel type nuclear reactor (RBMK of Kursk NPP) was used to prepare cementitious wasteforms. Typical operational radioactive waste is in the form of evaporator concentrate with salt content ~340 g/L. Table I gives its chemical composition.

Table I. Chemical composition (in g/L) of radioactive waste.

$NaNO_3$	KNO_3	Na_2CO_3	NaCl	Na_2SO_4	$Ca_3(PO_4)_2$	$MgCO_3$	$Fe(OH)_3$
281.1	7.4	13.1	8.2	7.7	1.9	1.0	5.5

Sodium nitrate at 86 wt.% on a dry basis content is the main non-radioactive component of this waste. Caesium isotopes accounted for 97-98 % of the total waste radioactivity. Table II gives the radionuclide composition of waste immobilised in a cementitious wasteform.

Table II. Radionuclide composition (in MBq/L) of radioactive waste.

^{137}Cs	^{134}Cs	^{60}Co	^{239}Pu	^{90}Sr	$\Sigma^*\beta$ (^{137}Cs)**	$\Sigma\beta$ ($^{90}Sr+^{90}Y$)**	$\Sigma\alpha$ (^{239}Pu)**
4.1·	0.85	0.053	$5.0 \cdot 10^{-3}$	$1.5 \cdot 10^{-4}$	6.7·	4.0·	$3.0 \cdot 10^{-3}$

*Σ stands for the sum of; **radionuclides given in brackets show the source radionuclides used for calibration.

2.2. Field test samples

Cementitious wasteform samples were prepared in form of cylinders using the technological procedures and equipment used on cementation of radioactive waste [10]. The parameters of wasteforms prepared are given in Table III. Portland cement type Russian designation M-500 was used. Aqueous waste to cement ratio was 0.6 and water to cement ratio, w/c=0.43 (on wt.% basis). Calculated waste loading of the final product was 37.5 wt.%.

Table III. Characterization of wasteform samples used for long-term field tests.

Sample	Weight, kg	Contact surface, cm^2	Waste loading, wt.%	Density, g/cm^3	β_{tot}($^{90}Sr+^{90}Y$), MBq/kg	α_{tot}(^{239}Pu) Bq/kg
K-28	44.0*	5430	37.5	1.5	2.10	n.m.

*Total weight of three cylindrical samples (∅=h=24 cm);

The cementitious wasteforms in form of three cylindrical samples (∅=h=24 cm) were placed for long–term testing in a shallow-ground repository. Stainless steel trays holding cementitious wasteforms were placed at a depth of 1.7 meters which is below the soils freezing depth (0.7 m). Pure coarse sand was used to backfill the cemented blocks in the tray to facilitate infiltration of water to the blocks and to isolate them from direct contact with the host rock. The space outside the containers was filled with host loamy soil from the land surface. The stainless steel tray was supplied with a water trap and a tube for water extraction by pumping.

2.3. Field test conditions

Climatic conditions of the experimental burial site are given in Table IV. Testing conditions are summarised in Table V. Compositions of both host rock and backfill are given in Table VI. Data on ground water composition from the burial site, averaged for 4 control boreholes, are given in Table VII. The test conditions may be considered as water-saturated. Note that although in many instances unsaturated conditions are expected to prevail in real repository systems saturated conditions are often specific for a long period of time.

Table IV. Climatic characteristics of testing site.

Parameter	Season			
	Winter	Spring	Summer	Autumn
Average temperature, °C	-5.77	8.14	18.52	5.16
Average precipitation, mm	134	90	175	158

Table V. Burial site host rock parameters.

Annual average soil temperature, ^{o}C	+4.5
Depth of seasonal freezing, m	0.7
Content of clay particles, wt.%	Up to 30
Specific weight of soil, g/cm^3	2.5 - 2.7
Volume density, g/cm^3	1.9 - 2.4
Moisture, wt.%	20 - 30
Ionic-exchange complex	Ca^{+2}, Na^+, Mg^{+2}, K^+
Ion-exchange capacity, mg-eq./100g soil	25-39
Distribution coefficient for ^{137}Cs mL/g	2000
Distribution coefficient for ^{90}Sr, mL/g	300
Coefficient of filtration of coat loam layer, cm/d	0.3 - 0.8

Table VI. Burial site host rock compositions (wt.%).

Mineral	Quartz	Microcline	Albite	Illite	Smectite	Calcite	Dolomite
Soil	76.9	10.8	4.9	2.7	2.6	1.2	0.8
Sand	83.3	4.6	7.6	1.5	1.2	1.8	2.1

Table VII. Characteristics of burial site groundwater (mg/L).

Salt content	Fe^{+3}	Ca^{+2}	Mg^{+2}	Na^+	K^+	Cl^-	NO_3^-	HCO_3^-	CO_3^{-2}	SO_4^{-2}
292.47	1.16	48.74	20.91	13.11	1.26	13.17	2.30	258.03	12.57	4.73

The average pH of the burial site ground water was 7.6-7.7 and the mineralization (dry residue after water evaporation) was 600 mg/L. Meteorological observations on the site showed an average temperature 6.5 ^{o}C and 557 mm of precipitation per year. The dominant wind direction was SE-S-SW. The atmospheric precipitate composition is given in Table VIII.

Table VIII. Composition of atmospheric precipitates (mg/L).

pH	Salt content	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe	Cl^-	NO_3^-	HCO_3^-	SO_4^-	SiO_2	B
6.89	31.56	0.32	1.25	4.67	2.28	0.4	1.25	2.17	29.77	3.71	0.48	1.4

2.4. Test procedures for radioactive components

Field testing procedure used was typical for long-term field tests carried out to analyse the performance of wasteforms [13, 18, 26-28]. The water which contacted cementitious wasteforms was periodically collected and analysed. The amount of radionuclides leached from the cementitious wasteforms was quantified by measuring the volume and radioactivity of the collected water. Water sampling was performed periodically, usually twice a month (except in winter). The volume of water v_j (L) was recorded at each sampling time. Water aliquots were retained for analysis. Standard radiometrical technique was applied including measurement of the specific radioactivity of water samples a_j (Bq/L). Overall measurement errors were not higher than 10%.

The volume of groundwater, $V(t)$, collected over time t, was calculated as a sum of the volume of the individual batches (v_j) collected. The total amount of groundwater collected that had been in contact with K-28 cementitious wasteform during the 12 years of testing was $V(12\text{ y}) = 1747$ litres. The amount of radionuclides (β_{tot}) leached from the K-28 cementitious wasteform A(t) (Bq) was calculated using:

$$A(t) = \sum_j a_j v_j \ . \qquad (1)$$

Data on the volume and specific radioactivities of the groundwater batches that had been in contact with the cementitious wasteform are shown in Table IX.

Table IX. Radioactive contamination of groundwater contacted with the K-28 cementitious wasteform.

Average annual specific radioactivity of ground water, Bq/L, (for the nth year of exposure)					
1	2	6	10	11	12
65.8	43.1	26.7	25.3	24.8	24.9

The normalised mass loss of radionuclides, NM (g/cm^2), was obtained from:

$$NM = \frac{A(t)}{qS}, \qquad (2)$$

where $S = 5430$ cm^2 is the cementitious wasteform-water contact surface area and $q = 2.10$ kBq/g is the specific radioactivity of K-28 cementitious wasteform. The average normalised leaching rate, NR (g/cm^{2}day), was calculated using

$$NR = \frac{NM}{t} \qquad (3)$$

where t is the test duration in days. The dimensionless leached fraction of radionuclides, ϕ, from K-28 cementitious wasteform was calculated using

$$\phi = \frac{A(t)}{A(0)}, \qquad (4)$$

where A(0) = 92.4 MBq was the initial level of radioactivity in K-28 cementitious wasteform. Calculated leach parameters are given in Table X.

Table X. Leaching properties of the cementitious wasteform K-28 in field conditions.

NR, g/cm^{2}day (for the nth year of exposition)						ϕ	
1	2	6	10	11	12	1-st yr	Total
$4.8\ 10^{-6}$	$3.1\ 10^{-6}$	$1.9\ 10^{-6}$	$1.8\ 10^{-6}$	$1.8\ 10^{-6}$	$1.7\ 10^{-6}$	10^{-4}	$4\ 10^{-4}$

The repository was opened in July 1999, after a dwell of 12 years, to examine the physical condition of the waste forms, to obtain information on their alteration, and to evaluate the nature, extent and distribution of radionuclide contamination within the environment closest to the waste form (Fig. 1).

Fig. 1. Cementitious wasteforms after 12 years dwell in a near-surface testing repository.

The twelve year field test has demonstrated the ability of the OPC matrix to provide a high degree of containment for short-lived radionuclides (^{137,134}Cs) under shallow-ground repository conditions. Corrected for decay radioactivity of the samples taken from cement block after 12-yr field test was the same as the initial radioactivity of the compound within the measurement error [18, 26].

2.5. Laboratory tests

Control laboratory tests with laboratory prepared cementitious wasteform samples containing simulated operational radioactive waste rich in $NaNO_3$ were set up. These aimed 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 (with smaller sizes) and preparation technique to the cement blocks in the shallow-ground repository for field tests. Experiments were carried out on cylindrical (28 x 28, D x H, mm) cement samples prepared from OPC cement type M-500 (Russian specification) and sodium nitrate solution, 340 g/L. As in the field experiment initiated in 1987, in laboratory tests 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 $^{137}CsNO_3$ solution to the radioactivity level of 2.1·MBq/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 (accounting for 92% of total radioactivity). Mortar mixtures were pored into steel molds and after a one-day hardening they were cured in a humid atmosphere for a month.

2.6. Standard leaching tests

Leaching measurements were performed according to the national standard test method for determining chemical durability of solidified radioactive waste [29] which is a Russian national analogue of ISO testing standard [30]. In the first (standard) leach experiment two sets of three radioactive and four non-radioactive cement samples were investigated. Standard leach tests at room temperature (24 ^{o}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 (non radioactive samples) and in plastic beakers (radioactive samples) and immersed in 140 and 300 mL of deionised water, respectively. According to the national standard leach test procedure [29], leachate sampling was performed after 1, 3, 7, 10, 14, 21, 28 days, then once per month.

Deionised water was renewed at each sampling. Concentrations of ionic species ($^{137}Cs^+$, Na^+, NO_3^-, Ca^{2+}), total salts content and pH were monitored in the leachate solutions.

2.7. Non-standard leaching tests

The second leach experiment has been undertaken in groundwater from the repository site. Additional leach tests experiments were carried out to analyse the behaviour of cementitious wasteform in groundwater of an expected disposal site [31, Chapter 5.6]. Fresh groundwater was used to renew leachate at each sampling. The composition of groundwater from the repository site used in leaching experiments is shown in Table XI.

Table XI. Chemical composition of groundwater used in leaching experiments, mg/L.

pH	Salt content	Ca^{+2}	Mg^{+2}	Na^+	K^+	Cl^-	NO_3^-	HCO_3^-	SO_4^{-2}
7.54	267.01	49.46	21.22	12.72	1.36	10.31	2.44	259.76	9.15

In addition to that, three complex leaching media have also been used to assess the impact of $Ca(OH)_2$, $NaHCO_3$ and sodium silicates on the OPC-based wasteform leaching behaviour. The leachate solutions used in addition to deionised water for the second set of experiments with radioactive cementitious wasteform samples are characterized in Table XII.

Table XII. Chemical composition of leaching media used in addition to deionised water.

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

*e.g. 1.5 g/L.

These tests were set at room temperature in sealed polyethylene containers. Leach solution volume in each case was 300 mL. Concentrations of ion species ($^{137}Cs^+$, Na^+, NO_3^-, Ca^{2+}), total salts content and pH were monitored in the leachate solutions. Concentrations of radioactivity (β_{tot}) and Na^+, NO_3^-, Ca^{2+}, total salts content and pH were also measured in every fresh sample of groundwater. Same procedures were used as for the tests with deionized water (see above).

2.8. Leach rates for ionic species

The normalized leaching rate of a non-radioactive specie (i), NR_i (g/cm^2day), was calculated using the expression:

$$NR_i = \frac{c_i V}{f_i S t} \quad (5)$$

where c_i (g/L) is the concentration of specie i in the leaching solution, V (L) is the leaching solution volume, S (cm^2) is the surface area of the wasteform in contact with the leaching solution, t is the test duration in days, and f_i is the mass fraction of specie i in the wasteform:

$$f_i = \frac{M_i}{M_0}, \qquad (6)$$

M_i (g) is the mass of specie i in the cementitious wasteform and M_0 (g) is the total mass of the wasteform.

The dimensionless leached fraction of ionic species, ϕ_i, from cementitious wasteform was calculated using expression

$$\phi_i = \frac{c_i V}{M_i} \qquad (7)$$

2.9. ^{60}Co irradiation tests

An additional factor which could affect leach rates from large-scale cement blocks is self-irradiation of samples due to natural decay of waste radionuclides [10, 32]. The effects of irradiation were studied using non-radioactive cementitious wasteform samples after a hardening period of 1 year. Irradiation facility RHM-Gamma-20 was used with ^{60}Co sources. Cumulative dose used was 10^6 Gy for all samples irradiated which is expected to be not higher than the waste lifetime absorbed radiation dose. Dose rate applied was not inducing a significant temperature rise in the sample and the radiolysis hydrogen production rate was enough low and did not cause any damage of samples able to result in experimental artefacts.

3. Testing results

The results of standard leaching tests in deionized water for radioactive and non-radioactive samples are summarized in Figures 2 and 3. Figure 2 shows the average of four-plicate and triplicate test results for cumulative leached fractions of radionuclides and of ion species as functions of time.

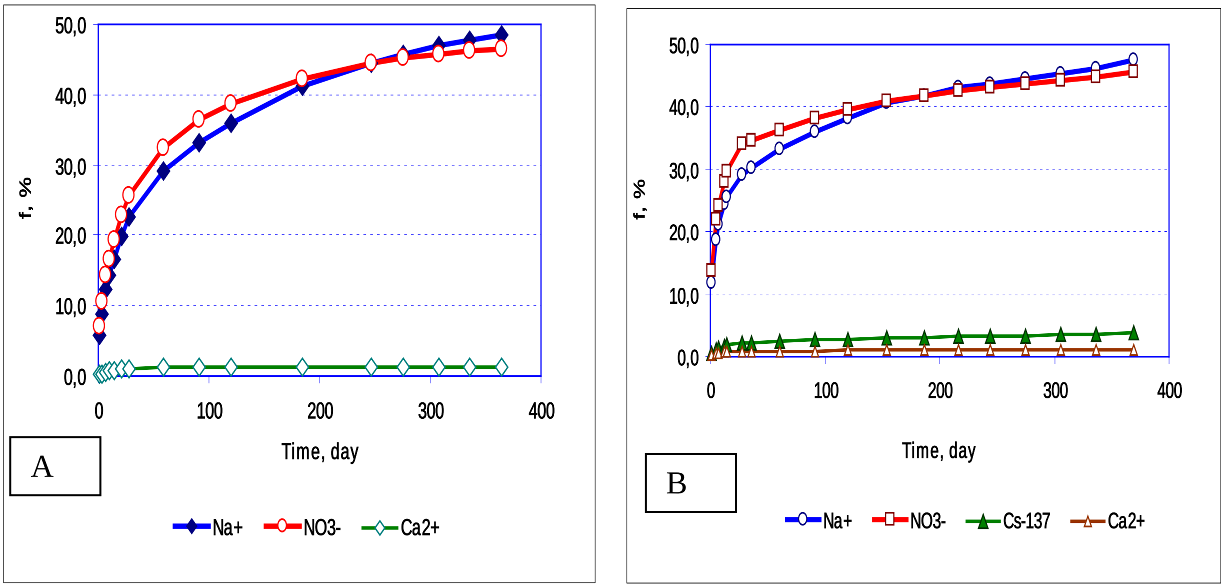

Figure 2. Time-dependent variations in cumulative leached fractions of ion species $f_i(\%)=\phi_i$ 100% for the laboratory leach tests of non-radioactive (A) and radioactive (B) cementitious wasteform samples containing simulated $NaNO_3$-rich waste.

Figure 3 illustrates the corresponding time dependencies of the average leach rates for the cationic species ${}^{137}Cs^+$, Na^+ and Ca^{2+} in radioactive samples.

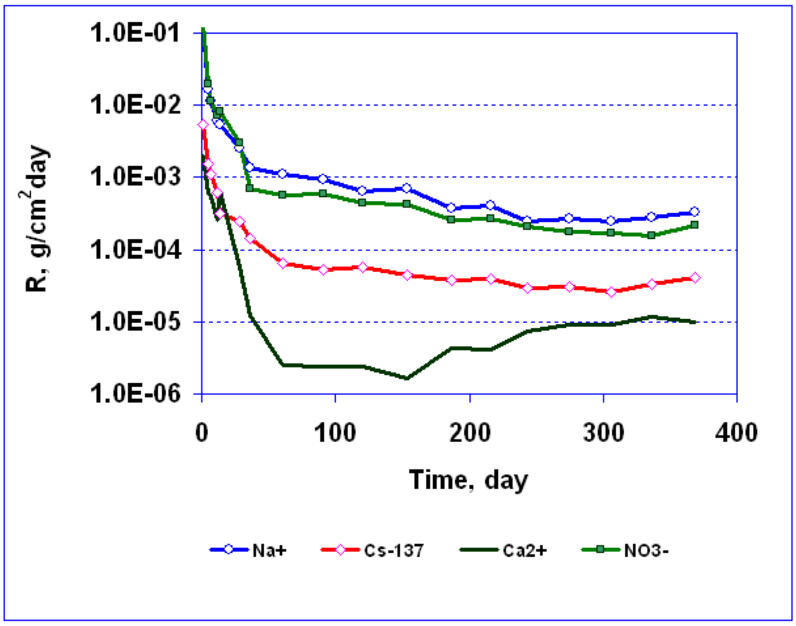

Figure 3. Average normalised leach rates (in this figure R=NR) of $^{137}Cs^+$, Na^+, Ca^{2+} and NO_3^- from cementitious wasteform samples containing simulated operational radioactive waste rich in $NaNO_3$ as a function of time.

Leaching data for the 1st year of both field and laboratory tests are given in Table XIII.

Table XIII. Average annual normalised leach rates (NR) of radioactive and ionic species from field and standard laboratory (radioactive samples) tests.

Specie	$^{137}Cs^+$		Na^+		NO_3^-	
Parameter	NR, g/cm^2day	ϕ	NR, g/cm^2day	ϕ	NR, g/cm^2day	ϕ
Field test	$4.8 \cdot 10^{-6}$	10^{-4}	$7.3 \cdot 10^{-3}$	$3.9\ 10^{-2}$	$1.1 \cdot 10^{-3}$	$3.4\ 10^{-2}$
Laboratory test	$1.7 \cdot 10^{-4}$	0.037	$2.6 \cdot 10^{-3}$	0.474	$2.8 \cdot 10^{-3}$	0.456

To estimate leach solution-related constituent of the ^{137}Cs leach rate decrease for the field test, the corresponding non-standard laboratory leaching experiment have been undertaken in groundwater from the repository site and additional leach media. The results of non-standard leaching tests (average of duplicate tests) for ^{137}Cs are shown in Figure 4.

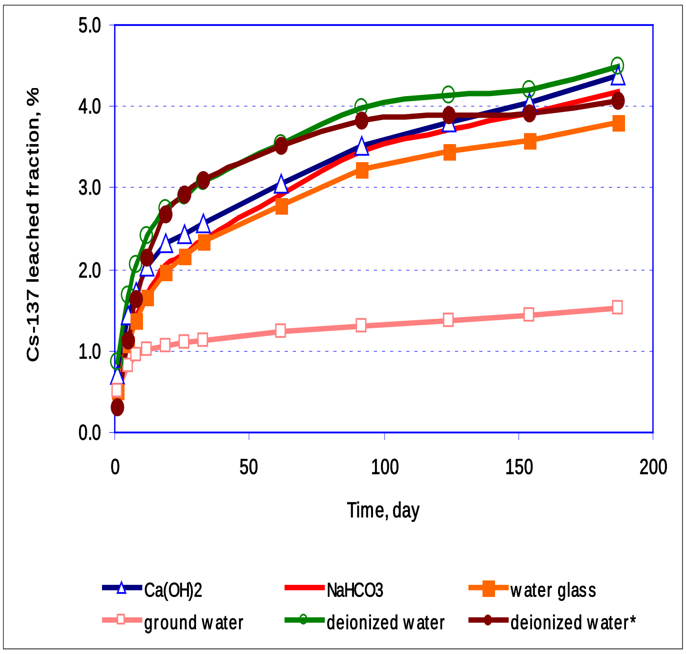

Figure 4. Time-dependent variations in ^{137}Cs cumulative leached fractions f(%)=ϕ 100% for the laboratory leach tests of cementitious wasteform samples containing simulated $NaNO_3$-rich radioactive waste performed in various leach solution media.

The average of duplicate test results for non-radioactive samples irradiated (L) and non-irradiated (M) are shown in Figure 5.

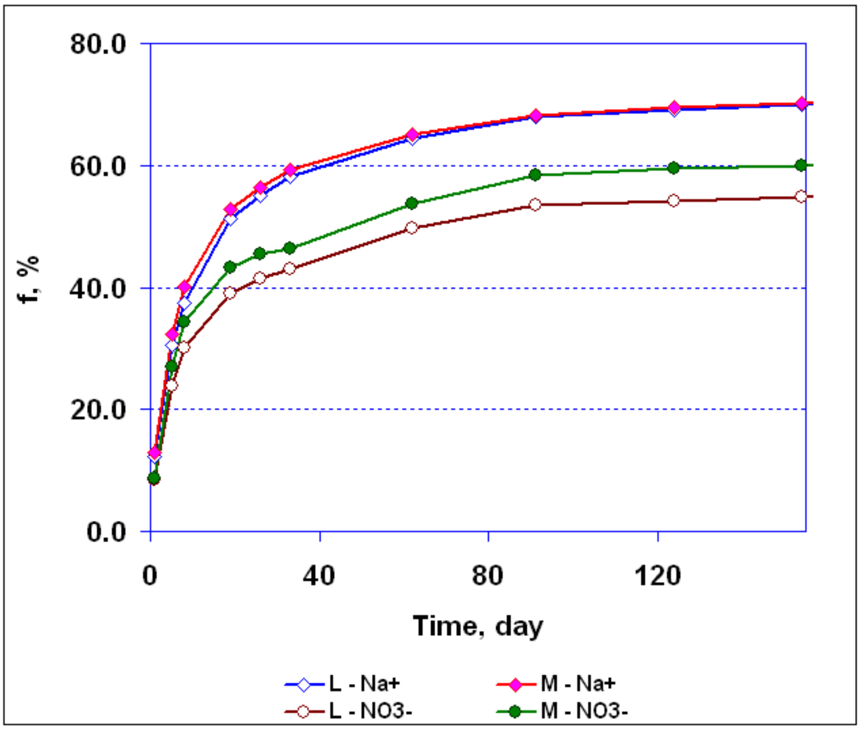

Figure 5. Cumulative leached fractions of Na^+ and NO_3^- measured in the laboratory leach test of non-radioactive cementitious wasteform samples subjected (L) and not subjected (M) to ^{60}Co gamma irradiation. The cumulative dose was 10^6Gy.

3. Discussion

Leaching curves of Na^+ demonstrate good correlation with the corresponding curves for NO_3^- (Fig. 2). The results indicate that sodium nitrate dissolution proceeds at a high rate during first months of the leach test. As a result, nearly half of the salt loading dissolved during the 1-year experiment. Leach rates of $^{137}Cs^+$, Na^+ and NO_3^- reached very close almost 'saturation' levels ($3.2 \cdot 10^{-5}$, $3.9 \cdot 10^{-4}$ and $2.6 \cdot 10^{-4}$ g/cm^{2}d, respectively) after seven months of the leach test (Fig. 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 both non-radioactive and radioactive samples reached 50.2% and 53.1%, respectively. The corresponding intact samples had the porosity 41.4% and 45.2%. The porosity P (%) was found using the expression $P = (1 - \rho_a / \rho_t) \cdot 100\%$, where the real density of wasteform ρ_t (g/cm^3) was measured using the water-displacement method with a picnometer and the average density ρ_a (g/cm^3) using the hydrostatic weighing [19, 20]. Note that the average compression strength of samples both before and after the leaching tests was above the acceptable level which in Russian Federation is 5 MPa [33].

^{137}Cs cumulative leached fraction (3,74% for 1 year) was about 1.9 times higher than a value reported in literature (~2%) for a similar experiment with cylindrical samples, H=D= 4.5 cm, in 300 ml of deionized water [34]. However, in the latter case in samples preparation $^{137}CsCl$-doped distilled water was used without additional 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% compared our samples.

^{137}Cs leach rate in the laboratory experiment was about thirty-five times greater than the measured value for the 1st year of the repository test (Table XIII). That can mainly be accounted for by much lower average annual temperature in the repository (the temperature interval 4 to 14 °C compared room temperature of 24 °C) and effect of leach solution chemistry. It is however very difficult to assess numerically this impact as the activation energies are unknown. ^{137}Cs cumulative leached fraction (3,74% for 1 yr) was more then 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 smaller. According to [35], 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 leach solution-related factors of the leach rate decrease should be taken into consideration [10].

Non-standard leaching tests (Fig. 4) have 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 [1, 4-8]. The estimated value of the leach solution-related factor affecting the leach rate decrease in the repository test is ~4.

As for the affect of irradiation no sufficient differences can be seen in the leaching behaviour (Fig. 5). Although for 154 days of leaching test the cumulative leached fractions of Na^+ and NO_3^- were several percent less in the case of irradiated samples, the leach rates at the 'saturation' stage were essentially the same: for Ca^{2+}, Na^+ and NO_3^-(in g/cm^{2}day) $6.3 \cdot 10^{-7}$, $2.1 \cdot 10^{-5}$, $1.5 \cdot 10^{-5}$, and $8.9 \cdot 10^{-7}$, $2.1 \cdot 10^{-5}$, $1.4 \cdot 10^{-5}$, respectively for the irradiated and not irradiated samples.

4. Conclusions

Standard laboratory leaching tests of cementitious wasteform 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 laboratory leaching test. Nearly half of the initial nitrate 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 lower values.

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 leaching rates in the first 6-month period were on average an order of magnitude lower than for Na^+ and NO_3^-. On the contrary, they were nearly two orders of magnitude higher than for a cement matrix - forming component Ca^{2+}. Note that Cs leaching is not solubility limited and weakly sorbed on cement hydrated phases whereas the behaviour of Ca (which is constitutive of cement phases) is partly controlled by its limited solubility. This might explained the different behaviour of Cs compared Ca.

In the laboratory test, leach rates of $^{137}Cs^+$, Na^+ and NO_3^- reached the same (~10^{-5} g/cm^{2}day) saturation level at the same time – after 7 months of the experiment. We can suppose that NO_3^- diffusion rate, the lowest among the three, may be a factor limiting caesium and sodium nitrates leaching from cement matrix at the later stages.

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 deionised water. The possible reason may be the partial healing of capillary pores and cracks. Carbonation is a well known process which could lead to clogging of pores and/or formation of a protective calcite layer resulting in a decrease of the leaching rate [36, 37]. Although surface analyses of the leached samples were not carried out in this work they could support one or the other hypotheses and help identifying the leaching determining processes e.g. carbonation and/or secondary phase formation with silicates.

Considering the temperature and leach solution-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 only 0.01%. Radionuclide contamination of the groundwater in contact with the cementitious wasteform in field conditions (Table IX) is however well below the exemption levels [38]. Moreover because of a diminishing trend in the water contamination due to a gradual decrease of the radionuclide leaching rate (Fig. 3) with time lower levels of contamination can be expected.

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