SOME TRENDS IN RADIOACTIVE WASTE FORM BEHAVIOR REVEALED IN LONG-TERM FIELD TESTS

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ABSTRACT

Results from long-term field tests with borosilicate glass, cement and bitumen waste forms containing actual intermediate-level radioactive waste are summarised and discussed in the paper. Leaching behaviour of the waste forms was evaluated by monitoring the contamination of contacting water. Measured leach rates of the three waste-form materials were in a narrow range in shallow subsurface repositories, but varied in a wide range at an open testing site owing to weathering of bitumen and cement materials. The repositories were opened after 12-year testing for visual examination, sampling and analysis. All retrieved waste forms were in good physical condition. The study has not revealed any negative changes in the waste glass. Some ageing processes were detected in cement and bitumen waste forms, which can positively (bitumen) or negatively (cement) affect physical and containment properties of these waste materials. It has been established that a significant proportion of the radioactive inventory in the bitumen waste form became associated with the bitumen phase. Phase separation of this radioactive bitumen has shown, than the asphaltene fraction is responsible for the major part of the radioactivity retained by the bitumen.

INTRODUCTION

For the assessment of long term performance and safety of a near-surface disposal system, knowledge of the long term behaviour of actual radioactive waste forms is needed. Field testing of the three most widely used waste form materials has been conducted at the SIA 'Radon' since 1987 [1-5]. Cement, bitumen and borosilicate glass blocks containing intermediate level NPP-operational waste were manufactured and placed at an open testing site and in experimental shallow-ground repositories. Test conditions represented the most likely (water infiltration) and possible (waste form denudation) long-term evolution scenarios for a near-surface disposal. In the paper, results from the 12-yr testing period are summarised.

EXPERIMENT

Field experiments with radioactive waste forms were described in detail elsewhere [1-5]. Blocks of solidified waste for the open site and repository tests were manufactured from the same initial mix for each waste form type that allowed a comparison of radionuclide leach rates and releases to be made for the repository and open site test conditions. Rich in sodium nitrate (86 wt.% of dry solids) NPP-operational waste was incorporated in cement, bitumen and borosilicate glass. Concentrations of radioactive and non-radioactive constituents in the waste forms were not measured, but were considered to be close to the concentrations as batches. These radioactivity levels as well as waste loading were rather close for the three waste form types (Table I).

In the repository tests, deep stainless steel containers holding the blocks of solidified waste were placed at a depth of about 1.5-2 meters. A backfill of pure coarse sand was used to fill the remaining free container space.

Table I. Characterization of waste form samples used for long-term testing

Matrix	Sample	Test conditions	Weight kg	Contact area, cm^2	Waste loading wt.%	Den-sity g/cm^3	β_{tot}($^{90}Sr+^{90}Y$), Bq/kg	α_{tot}(^{239}Pu) Bq/kg	Test duration, years
Cement	PZ-87 K-28	open site Repository	16.3 44.0*	2262 5430	37.5 37.5	1.5	$2.10{\cdot}10^6$ $2.10{\cdot}10^6$		6**** 12
Bitu-men	PR-11 K-27	open site Repository	29.5** 310.2	1242 27700	30.7 30.7	1.1	$3.29{\cdot}10^6$ $3.29{\cdot}10^6$	$3.89{\cdot}10^2$ $3.89{\cdot}10^2$	12 12
Glass	BS-10 K-26	open site Repository	37.8 190***	1120 2052	35.0 35.0	2.46	$3.89{\cdot}10^6$ $3.74{\cdot}10^6$	$1.40{\cdot}10^4$ $1.30{\cdot}10^4$	12 12

*Total weight of three orthocylindrical samples (∅=h=24 cm); **sample in the form of obelisk (h=30, 25x25, 35x35) in a container; *** net weight of six blocks in six carbon steel containers of rectangular form (20x25x42cm); **** survival time.

The burial pits were filled by soil to the land surface. To provide free infiltration of water to the test any lids did not cover blocks containers. Contact water was periodically collected and analysed. The repositories were opened in July 1999, after a lapse 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. After completion of sampling, the repositories were filled up and the experiment continued.

RESULTS AND DISCUSSION

Waste Forms Leaching Behaviour

Average annual radioactivity concentrations in water that contacted with the waste forms are given in Table II. Information is also provided on the total volume of contact water that had been pumped out of each repository or collected into containers at the open site. Fig. 1 illustrates the changes in water radioactivity with time. Calculated leach parameters are given in Table III.

Table II. Contamination of water in contact with the waste forms

Waste matrix	Sample	Test conditions	Average annual specific radioactivity of water, Bq/L (for the n^{th} year of exposure)						Total water volume, L
			1	2	6	10	11	12	
Cement	PZ-87 K-28	Open site Repository	2328 65.8	1676 43.1	1551 26.7	- 25.3	- 24.8	- 24.9	444 1747
Bitumen	PR-11 K-27	Open site Repository	1310 32.4	1190 21.9	833 15.7	696 11.7	694 10.7	683 10.2	735 1439
Glass	Bs-10 K-26	Open site Repository	40.3 20.4	27.3 18.5	16.9 13.0	15.2 10.9	14.8 10.4	14.0 10.0	800 937

Table III. Leaching properties of the waste forms

Matrix	Sample	Leach rate, g/cm²day (for the n[th] year of exposition)						Leached radioactivity fraction, %	
		1	2	6	10	11	12	1-st yr	Total
Cement	PZ-87	$1.8*10^{-4}$	$1.2*10^{-4}$	$1.1*10^{-4}$	-	-	-	0.43	2.02
	K-28	$4.8*10^{-6}$	$3.1*10^{-6}$	$1.9*10^{-6}$	$1.8*10^{-6}$	$1.8*10^{-6}$	$1.7*10^{-6}$	0.01	0.04
Bitumen	PR-11	$7.3*10^{-5}$	$6.3*10^{-5}$	$5.7*10^{-5}$	$4.4*10^{-5}$	$4.6*10^{-5}$	$4.4*10^{-5}$	0.11	0.65
	K-27	$7.1*10^{-7}$	$4.6*10^{-7}$	$2.2*10^{-7}$	$1.5*10^{-7}$	$1.3*10^{-7}$	$1.2*10^{-7}$	0.001	0.002
Glass	BS-10	$3.0*10^{-6}$	$1.9*10^{-6}$	$1.3*10^{-6}$	$1.1*10^{-6}$	$1.1*10^{-6}$	$1.0*10^{-6}$	0.002	0.007
	K-26	$1.3*10^{-6}$	$1.2*10^{-6}$	$8.5*10^{-7}$	$6.9*10^{-7}$	$6.6*10^{-7}$	$6.4*10^{-7}$	0.0004	0.001

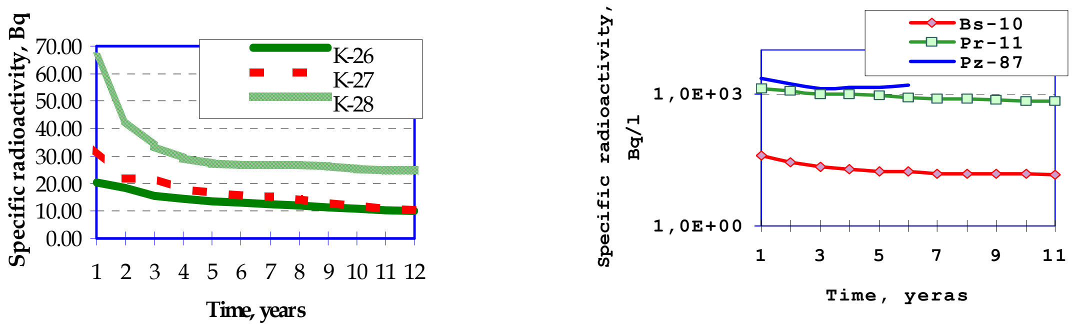

Fig. 1. Specific radioactivity of groundwater (left-hand) and rainfall water (right-hand) in contact with the glass (K-26, BS-10), bitumen (K-27, PR-11) and cement (K-28, PZ-87) waste blocks.

As expected, waste glass was the most leach-resistant in the open-site tests. Visually the bitumen block PR-11 showed no defects (e.g. formation and propagation of cracks) at any stage of the 12yr open-site experiment, but the surface had lost its lustre. Weathering of the bitumen material caused the leach rate to increase greatly (more then two orders of magnitude as compared with the bitumen-based material in the repository). Leach rates were up-to 44 times higher then those for the glass block BS-10. Extensive degradation of cemented waste form (PZ-87) occurred in the open-site experiment. Enhanced radionuclide leaching and block failure after 6-year exposure was observed.

In the repository tests, a drop in radioactivity of groundwater in contact with the bitumen block to levels only slightly higher than those for the waste glass was observed and this pattern was maintained throughout the experiment. Because the available for leaching surface area of the bitumen block was much greater than that of the waste glass[1], the radioactivity leach rates of the bitumen waste form were calculated to be at the lowest level throughout the experiment (Table III). Estimated radioactivity leach rates of the cement-based waste form were only 2-3 times higher then those calculated for the waste glass. For all three tested waste forms, radioactivity leach rates appeared to approach a steady-state values after about a decade of storage under repository conditions.

Thus, calculated leach rates were in a narrow range for all waste forms when tested in the repositories, and in a wide range when tested at the open site owing to different waste form resistance to weathering. However, leach rates fulfil the reasonable demands on safe near-surface disposal of LILW[2] provided that the possibility of weathering the cement-based waste forms is eliminated.

Waste Form Alterations

Leach tests with cement, bitumen and glass waste forms placed in shallow subsurface burials did not reveal significant differences in the leaching behaviour of the tested waste forms. These differences are of minor importance when relatively short institutional control periods of tens years or a few hundred years are implied. For longer storage periods, other factors affecting waste form physical and containment properties may be of growing importance. For ageing study, samples of waste form materials were taken from the blocks during the burials opening in 1999. The analyses are not yet completed. However, the available results may illustrate some trends in alteration processes in the waste forms.

No changes in the waste glass structure (except for a structure of a thin surface layer) could be detected by the X-ray analysis. On the other hand, marked changes in some physical and chemical properties of the cement and bitumen waste forms were observed.

Considerable effort was required to break off the samples (especially the bottom one) from the retrieved cement waste form. However, very low compression strength (~1 MPa) was measured on the three prepared specimens. The material could be characterised as fragile. When broken for grinding, it consisted of very hard granules and pieces. These observations and XRD spectra suggest that re-crystallisation may be the possible reason for the deterioration of physical properties of the cement-based material.

Study of the bitumen waste material has shown that it became harder and more thermostable after 12-year storage under wet repository conditions. Penetration depth could not be measured, it was essentially nil for standard test conditions (standard test needle, 100g load, $25^{o}C$). Inhomogeneous distribution of radionuclides and salts was found. To estimate the distribution from top to bottom, a corner sample 15 cm in height was analysed. One vertical and three horizontal (upper, middle and lower) 2-3 mm thick sections were cut off from the sample. Radioactivity levels correlated with the salts content except for the lower section (Table IV).

Table IV. Radiometric and γ-spectrometric analyses for the horizontal* and vertical sections of the 'corner' bitumen sample, Bq/kg.

Section	β_{tot} (^{137}Cs)	β_{tot} ($^{90}Sr+^{90}Y$)	^{137}Cs	^{134}Cs	^{60}Co	Salts, wt.%
Vertical	$1.34\cdot10^{6}$	$1.00\cdot10^{6}$	$1.70\cdot10^{6}$	$6.20\cdot10^{3}$	$4.00\cdot10^{3}$	7.75
Upper*	$2.20\cdot10^{6}$	$1.50\cdot10^{6}$	$2.20\cdot10^{6}$	-	-	7.25
Middle*	$2.40\cdot10^{6}$	$1.70\cdot10^{6}$	$2.60\cdot10^{6}$	-	-	13.50
Lower*	$1.50\cdot10^{6}$	$0.93\cdot10^{6}$	$1.37\cdot10^{6}$	$5.30\cdot10^{3}$	$4.50\cdot10^{3}$	14.30

The specific radioactivity of the extracted bitumen was found to be nearly the same as the radioactivity of the extracted salts. In some cases it was even higher. The results show evidence for bonding/association of radioactive metal ions (^{137}Cs) with bitumen.

To study the nature of the bitumen radioactivity, bitumen samples free of radioactive waste salts were further separated into fractions of asphaltenes, saturated hydrocarbons and aromatic hydrocarbons. Results are given in Table V.

Table V. Fractional composition of the extracted bitumen samples, wt.%.

Sections of the 'corner' bitumen sample	Asphaltenes	Saturated hydrocarbons	Aromatic hydrocarbons
Vertical	43.2	30	25
Upper, horizontal	51.2	26	19
Middle, horizontal	44.3	32	21
Lower, horizontal	45.4	30	22

A noticeable increase in asphaltene fraction content, 4 to 10 wt.%, was detected. Radiometric and γ-spectrometric analyses of the bitumen fractions have shown that nearly all of the bitumen radioactivity is associated with the asphaltene fraction. Saturated hydrocarbons could retain only trace amounts of the radioactivity. Since essentially all of the bitumen radioactivity is found in the asphaltene fraction, the ageing of bitumen can have some beneficial effect on its containment properties.

CONCLUSIONS

Results from long term field tests with actual radioactive waste forms (cement, bitumen and borosilicate glass) are summarised. Test conditions represented the most likely (water infiltration) and possible (waste form denudation) long-term evolution scenarios for a near-surface disposal.

Measured leach rates of the three waste form types varied within a narrow range in the repository tests, and in a wide range in the open site tests owing to weathering of the bitumen and cement waste forms. Radioactivity leach rates appeared to approach a steady-state values after about a decade of testing. Borosilicate waste glass was the most leach resistant in both test conditions. Leach parameters closely approximating those of the waste glass were measured for the bitumen waste material in the repository test. However, a more then forty-fold increase in the leach rate of bitumen waste form was observed at the open site due to surface corrosion. No visible waste forms degradation or crack formation was observed in the experiments, excepting the cement block at the open site, which failed after 6-yr exposure.

The study has not revealed any negative changes in the waste glass. Some ageing processes were detected in cement and bitumen waste forms, which can positively (bitumen) or negatively (cement) affect physical and containment properties of these waste materials. It has been established that a significant proportion of the radioactive inventory in the bitumen waste form became associated with the bitumen phase. Phase separation of this radioactive bitumen has shown than the asphaltene fraction is responsible for the major part of the radioactivity retained by the bitumen matrix of the bitumen waste form.

FOOTNOTES

[1]Only the top open surface area of six glass blocks in the repository K-26 was taken into account in the leach rate calculations.

[2] According to waste acceptance criteria in Russia, regulatory limits for leaching rate are: for cement and bitumen waste forms, $<10^{-3}$ g/cm^{2}day (^{137}Cs, ^{90}Sr); for HLW phosphate glass, 10^{-5}-10^{-6} g/cm^{2}day (^{137}Cs).

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