LILW BITUMINIZATION PROGRAMMME AT SIA "RADON": WASTE FORM PERFORMANCE

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ABSTRACT

Waste blocks were prepared in bituminization plants on base of NPP-operational and other liquid wastes of low and intermediate level activity and tested under laboratory and wet near-surface disposal conditions. Leach rates of radioactive and non radioactive waste components and depth of radionuclide penetration into the host loamy soil were estimated. Bituminized waste seems to occupy a middle position between cemented and vitrified waste forms in terms of radionuclide retention ability. However, properties of bitumen as a waste matrix are not fully understood for modelling the waste form behavior over the required time period of several hundred years.

INTRODUCTION

Waste matrix is considered the first and the most important barrier to radionuclide release in a multi-barrier waste disposal concepts. SIA 'Radon' has been investigating three main types of matrixes for low and intermediate level waste (LILW) conditioning for over two decades (1). Cemented, bituminized and vitrified waste blocks were produced in industrial and pilot scale facilities and disposed of at the testing area consisting of an open testing site and experimental shallow-ground repositories. Bitumen has been used as a matrix material for encapsulating liquid radwaste (sludges from evaporation or precipitation, ets.) since 1968. (Two industrial bituminization plants started operation in 1974 and 1978: a continuous, two-stage-type installation of high capacity and the rotary thin film evaporator/mixer, resp.). Three types of bitumen were used in the laboratory and field experiments (Table I).

Table I. Fractional compositions and standard physical properties of bitumens.

Type of bitumen		BN-II	BN-III	BN-IV
Fractions, wt %	oils (aliphatic hydrocarbons)	55.5	54.5	50.0
	resins	17.5	15.0	11.0
	asphaltenes	27.0	30.5	39.0
Depth of the hardening zone at 25°C, mm		81-120	41-80	21-40
Softening temperature, °C		40	45	70
Ignition temperature (in an open crucible), °C		200	200	230

This paper presents results from laboratory and long-term field tests performed on samples/blocks of bituminized waste.

EXPERIMENT

Short Term Laboratory Tests

The scope of laboratory work involved research of interactions in systems: waste form - water: (the impact of waste loading level, bitumen type, and of admictures on radionuclide leach properties of bituminized waste) and water - soil (the influence of waste form on soil properties) and estimation of waste product radiation stability.

Leach resistance was measured according to E.D.Hespe (2) on samples with waste loading 30, 35, 40, 50, and 60 %. Two leach stages were identified. At the initial stage of high leach rates (on the order of $1{\cdot}10^{-1}$ to $1{\cdot}10^{-3}$ cm/day), the dissolution of salts from the outer layer of the waste product occurs, it takes 15-50 days. At this stage, the leach rate rapidly decreases with time. The next stage is characterized by slow decrease in leach rate to values of about $8{\cdot}10^{-5}$ cm/day (for waste loading up to ~40 %). This is indicative of a diffusion mechanism of the waste components release. Normalized leach rates of waste macrocomponents are somewhat higher than those of the radionuclides (after 15 days). Some leach trends were revealed for elements and species encountered in wastes. Cations and anions may be arranged in order of decreasing leach rate as follows: $Na^{+}> NO_3^{-}>K^{+}>Cs^{+}>Ca^{2+}>Mg^{2+}> Cl^{-}>SO_4^{2-}$.

Rates of radionuclide release from bitumen compound increase with the rise in waste loading. For waste loadings of up to 25-30 wt.%, only slow growth in radionuclide leach rates was observed. For more high levels of waste content, this growth is more pronounced as a concequence of pore formation bringing to enchanced ingress of water to the interior of bitumen compound. Waste loading of 50 wt.% is considered a threshold level.

Waste samples prepared on base of the soft bitumen BN-II proved to be the most leach resistant. Samples on base of BN-IV, characterized by high content of asphaltens, displayed the worst leach resistance properties.

It was found that waste components leaching from the bitumen compound into the loamy soil (host rock of a repository site) depends on soil humidity. So, radionuclide leach rates increased by a factor of about eight with the increase in loamy soil humidity from 5 to 30 %. Other changes in physical, physico-chemical and physico-mechanical properties of argillaceous ground caused the increase of Sr and Cs migration rates by a factor of 10-14.

γ-ray irradiator unit PXM-20 was used for radiation stability estimations. 39 samples of bituminized waste were prepared. 12 of them were irradiated at dose rate of 10^4 Gy/h, absorbed doses were 10^3, 10^4, 10^5, and 10^6 Gy. 12 samples were exposed to dose of 10^3 Gy at dose rates from 2 to $3{\cdot}10^3$ Gy/h. 12 and 3 reference samples were stored at 43 ^{o}C and at room temperature, resp. Absorbed doses of up to 10^6 Gy at various dose rates had no effect on leach resistance of the test samples.

Long Term Field Tests

Parallel with the laboratory studies on bitumen samples containing real radwastes or simulators, field experiments are ongoing to address issue of how effective waste bitumen matrix is as a part of engeniered barrier system. Long-term behavior of bituminized waste under near-surface repository conditions is much dependent on equilibrium in the system soil - water - bitumen waste form. Two groups of factors affecting the longevity of bitumen waste products may be distinguished: *intrinsic factors* including conditioned product quality (homogeneity, water content, etc.), type of bitumen used, admixture presence, waste content and its composition, ets.; and *external factors*, such as the ambient temperature, sorption properties of the soil, leachant chemistry, water flow rate, etc..

*Waste characterization***.** Real NPP-operational (Kursk NPP) and decontamination wastes generated in the facility itself ('Radon') were used. The principal radioactive waste components were ^{137}Cs, ^{134}Cs, ^{90}Sr, and ^{60}Co (Tables II-III).

Table II. Specific radioactivity of liquid wastes, Bq/l

Waste	$\Sigma\beta\ ^{90}Sr + ^{90}Y$	$\Sigma\alpha\ ^{239}Pu$
Radon	$(1.32\text{-}1.78)\cdot 10^6$	
Kursk NPP	$4.0\cdot 10^6$	$3.0\cdot 10^3$

Table III. Radionuclide compositions of radioactive wastes, %

Waste	^{137}Cs	^{134}Cs	^{60}Co	^{90}Sr	^{239}Pu
Radon	80	+	+	8	+
Kursk NPP	81.87	16.97	1.06	0.003	0.1

Radwastes represented low alkaline solutions with nitrates of alkaline and alkaline-earth metals as dominating non radioactive components (up to 87 wt.% of the total salt content). So, waste from Kursk NPP (reactor RBMK) was characterized by salt content of about 350 g/l, of them natrium nitrate constituted approximately 86 %.

Institutional wastes (RW) are characterized by variable chemical and radionuclide compositions. Radiometric data are available for waste blocks (see Table V).

*Matrix material characterization***.** Free types of commercial paving and construction oil bitumen were used: BN-II, BN-III, BN-IV. Fractional compositions and some physical parameters are given in Table I. Admixture of K-Ni ferrocyanide was used as a leach retarder in certain samples.

*Bituminization process and waste blocks characteristics***.** Waste blocks were produced in the bituminization plant of SIA 'Radon'. Before solidification, liquid wastes were concentrated in evaporator/dryer to about 60 wt % dry matter. Preheated waste sludge and bitumen were fed into evaporator/mixer. The temperature at the casting stage did not exceed 135 °C. Hot mixtures were poured into moulding cars or into carbon steel containers with the wall thickness of 1.5-2-2.5 mm. Containers for open site tests were of a few litres or few tens of litres in volume with the upper part open for contact of solidified waste and atmosphere. The main parameters of the waste blocks tested are given in Table IV.

Table IV. Some initial parameters of the waste-bitumen blocks

Sample	Waste type	Bitumen type	Weight, kg	Contact surface area, cm^2	Waste loading, %	Specific β-activity, Bq/kg	Specific α-activity, Bq/kg
Pr-11	Kursk NPP	BN-IV	21.0	1225	30.7	$3.29 \cdot 10^6$	$3.89 \cdot 10^2$
K-27	Kursk NPP	BN-IV	310.2	27700	30.7	$3.29 \cdot 10^6$	$3.89 \cdot 10^2$
Pr-10	Radon	BNK-II	4.3	900	31	$4.81 \cdot 10^7$	$6.66 \cdot 10^4$
K-4	Radon	BN-III	708.0	43585	27.7	$7.96 \cdot 10^5$	
K-5	Radon	BN-IV	750.0	48350	27.3	$8.33 \cdot 10^5$	
K-6	Radon	BN-II	2023		44.2	$1.76 \cdot 10^6$	

*Testing site description***.** The testing site consists of an open site and two isolated shallow ground repositories. The total area is approximately 1200 m^2. Complete description of the testing sites is given elsewhere [1, 4].

*Methods and techniques***.** Long-term testing of waste forms is being performed mainly through the monitoring of contamination of contact water (precipitation, groundwater) and soil. Water samples are routinely collected, usually twice a month, for chemical, radiochemical and radiometric analyses. The same analyses have been applied to soil drill cores obtained through drilling the soil surrounding waste blocks.

RESULTS AND DISCUSSION

*Precipitation and groundwater contamination***.** Radionuclide leach rates were determined for samples which differed in waste loading, type of bitumen used, isotope composition of the initial waste, and by the presence of leach retarder. Some leach curves are given in Figures 1-3.

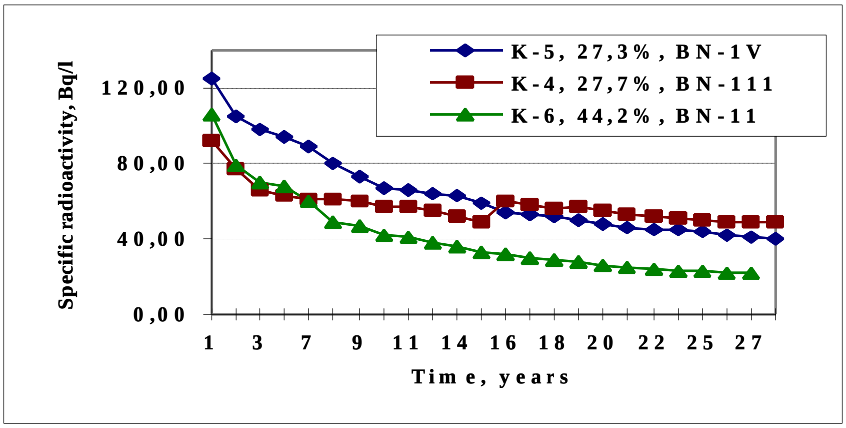

Fig. 1. Variations of annual means for radioactivity concentration in groundwater contacting bitumen blocks K-4, K-5 and K-6.

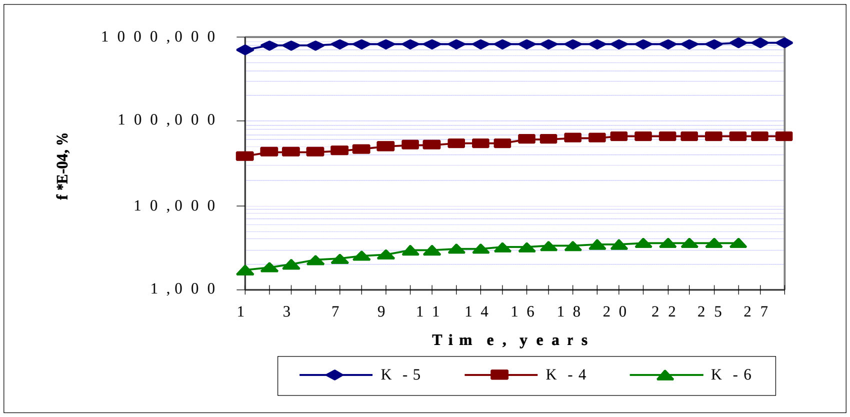

Fig 2. Leached radioactivity fractions as functions of time for bitumen blocks K-4, K-5 and K-6. Near-surface repository site.

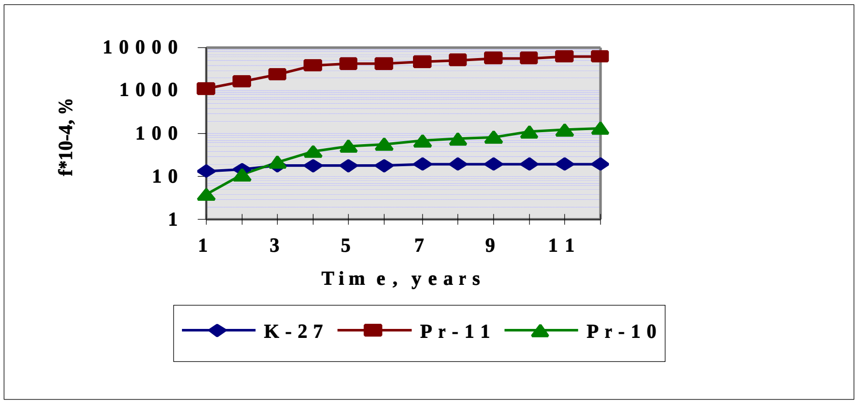

Fig. 3. Radioctivity fractions leached by precipitation and groundwater from waste blocks as functions of time. Pr-11 (open site) and K-27 (repository) are analogues. Pr-10 contains K-Ni ferrocianide admixture.

^{137}Cs was the main radioactive contaminant of contacting water (up to 96 % of the total leached radioactivity). Therefore, radioactivity release rates were strongly affected by the presence of ferrocianide admixture (see Pr-10 in Fig. 3), especially for waste loadings ≥ 50 %. Data generated from laboratory, open-site and repository tests showed that leach behavior of the waste product is notably dependent on type of bitumen used. Soft bitumen (BN-II) is the best as a waste matrix in terms of leach resistivity. The major part of leached radioactivity, 75 to 86 %, released from waste blocks during the first year of the testing period. Leach parameters of samples are given in Table V.

Table V. Leach parameters of bituminized waste blocks

Test conditions		Open area		Burials			
Parameter	Time, years	Pr-10	Pr-11	K-27	K-4	K-5	K-6
Specific radioactivity, Bq/l	1	26.74	1310	32.43	91.73	125.11	106.11
	12	92.80	696	10.72	56.91	66.08	41.29
	24	62.73	-	-	50.47	44.52	23.45
Leaching rate, $g/cm^2 \cdot day$	1	$1.02\bullet10^{-7}$	$7.29\bullet10^{-5}$	$7.11\bullet10^{-7}$	$2.19\bullet10^{-6}$	$4.10\bullet10^{-5}$	$1.85\bullet10^{-7}$
	12	$2.63\bullet10^{-7}$	$4.56\bullet10^{-5}$	$1.32\bullet10^{-7}$	$8.66\bullet10^{-7}$	$1.52\bullet10^{-5}$	$5.94\bullet10^{-8}$
	24	$2.57\bullet10^{-7}$	-	-	$4.92\bullet10^{-7}$	$8.07\bullet10^{-6}$	$3.43\bullet10^{-8}$
f, %	1	0.0004	0.11	0.001	0.004	0.070	0.0002
	12	0.01	0.64	0.002	0.005	0.082	0.0003
	24	0.02	-	-	0.007	0.084	0.0004

For comparison, radionuclide leach parameters for cemented, bituminized and vitrified waste forms containing the same Kursk NPP radwaste (reactor RBMK) are listed in Table VI.

Table VI. Leaching properties of waste forms. Open testing site.

Waste matrix	Initial radioactivity, Bq/kg		Leach rate, g/cm^2 day		Leach factor, cm^2/day	
	β-activity	α-activity	after 1 year	after 8 years	after 1 year	after 8 years
Glass	$3.89\cdot10^{6}$	$1.4\cdot10^{4}$	$8.61\cdot10^{-7}$	$3.72\cdot10^{-7}$	$6.03\cdot10^{-12}$	$1.78\cdot10^{-11}$
Bitumen	$3.29\cdot10^{6}$	$3.89\cdot10^{2}$	$8.06\cdot10^{-5}$	$5.38\cdot10^{-5}$	$2.50\cdot10^{-8}$	$8.03\cdot10^{-10}$
Cement	$2.2\cdot10^{6}$		$1.51\cdot10^{-4}$	$9.28\cdot10^{-5}$ (after 6 years)*	$5.11\cdot10^{-6}$	$2.67\cdot10^{-6}$ (after 6 years)*

* 6 years - cement blocks survival time at the open site

As can be seen, rates of radionuclide release from bituminized waste are two orders of magnitude higher then those of vitrified waste, however they fulfil in most cases the reasonable demands on safe disposal. Cemented blocks failed after 6-year exposure, whereas, visually, bituminized blocks remain almost intact till now. Leach data for bituminized samples prepared from the same source mixture (see Fig. 3) and tested under open site and repository conditions indicate the essentially better leaching behavior of bituminized waste throughout the near-surface disposal testing. So, the data of Table VI may be considered as conservative estimates of the radionuclide containment properties of waste forms tested.

As a result of interaction of groundwater\precipitation and bitumen compound, other changes in the chemistry of the leachate water occur. Results of long-term groundwater chemistry monitoring are provided in Table VII.

Table VII. Leachate groundwater chemistry data, mg/l.

	Time, years	K-27	K-4	K-5	K-6	Initial data
pH	1	8.03	7.54	7.54	7.39	7.69
	12	8.08	7.85	7.67	7.66	
	27	-	8.09	7.96	8.09	
TDS	1	845	1430	4131	7250	261
	12	646	1772	3632	3193	
	27	-	1790	3202	1980	
Na^+	1	186	293	1134	1603	19,6
	12	167	402	934	546	
	27	-	469	833	452	
Ca^{2+}	1	54				39,8
	12	40	42	49	52	
	27	-	24	39	31	
NO_3^-	1	174	841	2626	1935	3,2
	12	37	534	1829	330	
	27	-	427	1521	164	
HCO_3^-	1	505				230
	12	542	1349	766	622	
	27	-	970	653	753	

Salinity of the contact groundwater increased from 0.9 to 11 g per litre. The initial Ca-hydrocarbonaceous type of groundwater changed into HCO_3^- - NO_3^- - Na^+. Initial porewater chemistry, represented by HCO_3^- - Ca^{2+-} - Na^+ with salinity of 0.07 g/l, changed to NO_3^- - HCO_3^- - Ca^{2+} - Na^+ after contact with bitumen blocks. Porewater salinity reached 0.5 g/l

*Host rock contamination***.** Two samples S-I and S-II with waste loading 29 % and 5 %; specific radioactivity $6.66 \cdot 10^5$ Bq/kg and $1.85 \cdot 10^7$ Bq/kg; 500 kg and 300 kg in weight, resp., had been placed directly into bore pits. The space around waste blocks in the pits had been filled by a host loamy soil. So, waste matrix was the only barrier to radionuclide release into the environment. On expiry of 11 years, measurements of soil contamination have been carried out. Maximum soil radioactivity was registered underneath the waste blocks and reached $2.81 \cdot 10^4$ Bq/kg for S-I and $2.66 \cdot 10^6$ Bq/kg for S-II. Doubled background values for the disposal site host rock, $1.85 \cdot 10^3$ Bq/kg, were observed at a maximum distance of 40 cm below S-I and 26 cm below S-II. Hence, the average annual rates of radionuclide migration were estimated to be approximately 3.6 cm/yr and 2.4 cm/yr, resp.. They indicate the salt content of bituminized products may have a stronger effect on radioactivity release and soil contamination compared with the radioactivity concentration in these products (due to competition of Na+ and Cs+ ions for absorption and cation-exchange sites of the soil). Results show quite a good radionuclide containment properties of bitumen matrix as well as host rock of the disposal site.

PREDICTION OF LONG TERM BEHAVIOUR

Lets assume that the mechanism or radionuclide leaching will remain the same over all time of storage. The mechanism we will suppose after some initial period of time (less than 1 year) to be governed by the diffusion of radionuclides. Therefore one can consider that the leached radioactivity fraction consists of two terms:

$$f=f_0+f_1,$$

where f_0 is the leached radioactivity fraction due to initial dissolution processes, and f_1 is given by formula:

$$f_1=(S/V)[\Sigma q_{0i}(D_i/\lambda_i)\Phi(\sqrt{\lambda_i t})]/\Sigma q_{0i},$$

where S is the interface surface, V is the volume of waste block, q_{0i} is the initial specific radioactivity of i-th radionuclide in the block, D_i is the diffusion coefficient, $\Phi(\sqrt{\lambda_i t})$ is the error integral, t is time.

In the Fig.4 it is shown the prediction of the leaching behaviour of a block (K-27) during its storage for 300 years. We took herein f_0 from experimental data after one year of storage f_0=0.00138%. The experimental data can be seen in the beginning of the plot.

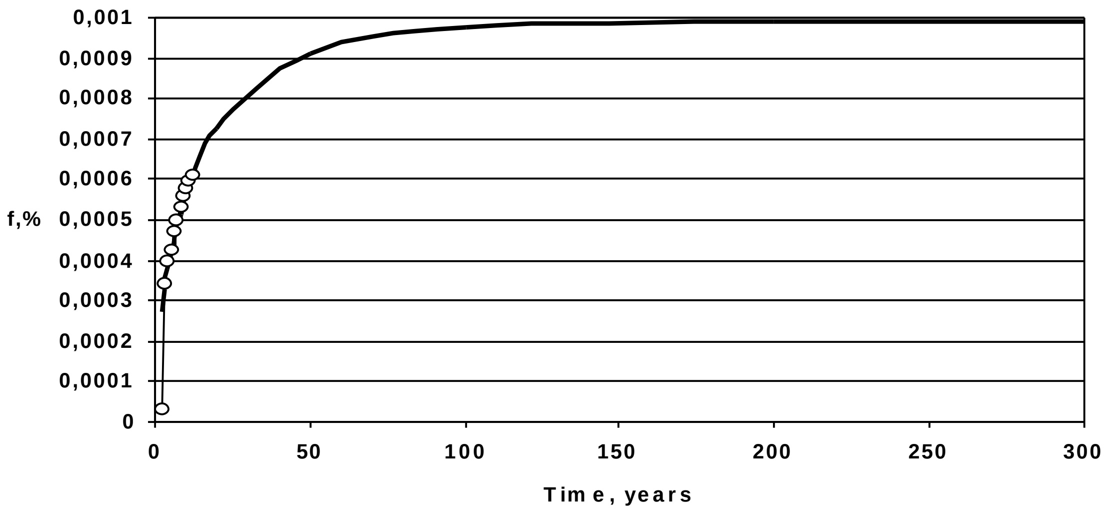

Fig.4. The leached radioactivity fraction of a block of bituminized radioactive waste (f_1).

One can see that the total (and maximum) leached radioactivity fraction will reach by time the value $f_{max} = f_0 + 0.001\% = 0.00238\%$.

CONClUSION

Bitumen may be considered a suitable host material for immobilizing certain low-level-activity wastes (first of all, with poor moisture absorption in a dry state) for the placement in a near-surface repository which design implies the introduction of several engineered barriers.

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