

**ДРУШТВО ЗА ЗАШТИТУ ОД ЗРАЧЕЊА
СРБИЈЕ И ЦРНЕ ГОРЕ**



ЗБОРНИК РАДОВА

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COMPARATIVE STUDY OF JAPANAISE AND SERBIAN BENTONITE IN CEMENT- ION EXCHANGE RESINS-BENTONITE CLAY COMPOSITION

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ABSTRACT

To assess the safety of disposal of radioactive waste material in cement, curing conditions and time of leaching radionuclides ¹³⁷Cs have been studied. Leaching tests in cement-ion exchange resins-bentonite matrix, were carried out in accordance with a method recommended by IAEA. Curing conditions and curing time prior to commencing the leaching test are critically important in leach studies since the extent of hydration of the cement materials determines how much hydration product develops and whether it is available to block the pore network, thereby reducing leaching. Incremental leaching rates $R_n(\text{cm/d})$ of ¹³⁷Cs from cement-ion exchange resins-bentonite matrix after 60 days were measured. In this paper we compared two bentonite clay as sorption component, from Japan and Serbia. The results presented in this paper are examples of results obtained in a 30-year concrete testing project which will influence the design of the engineer trenches system for future central Serbian radioactive waste disposal center.

1. Introduction

Cement-waste matrix characteristics

The objectives of immobilization are to convert the waste into forms which are:

- leach resistant, so that the release of radionuclides will be slow even in contact with flowing water,
- mechanically, physically and chemically stable for handling, transport and disposal.

Although cement has several unfavorable characteristics as a solidifying material, i.e. low volume reduction and relatively high leachability, it possesses many practical advantages: good mechanical characteristics, low cost, easy operation and radiation and thermal stability. It is generally assumed that the cement leachability of ¹³⁷Cs and other radionuclides can be reduced by adding minerals like bentonite and zeolite. Bentonite is a type of clay mineral formed by the earth from volcanic ash and lava deposited on the bottoms of seas and lakes. Bentonite is an [absorbent aluminium phyllosilicate](#), essentially impure [clay](#) consisting mostly of [montmorillonite](#). There are different types of bentonite, each named after the respective dominant [element](#), such as [potassium](#) (K), [sodium](#) (Na), [calcium](#) (Ca), and [aluminum](#) (Al). The montmorillonite crystals of bentonite have a specific structure that provides various useful sorption characteristics. Bentonite is one of the most promising candidates for use as a buffer material in the disposal systems for nuclear waste, because of its ability to retard the movement of radionuclides by adsorption. Bentonite is characterized by a low hydraulic conductivity and excellent adsorption capacity for cationic radionuclides, but is generally ineffective in adsorbing anionic contaminants. Natural zeolites were the first material to be used in ion exchange process. In addition to being ion exchangers, natural, mineral inorganic materials can also act as adsorbents. Bentonite clay, (montmorillonit), had empirical

formula: $(\text{Na,Ca})_0,3(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n(\text{H}_2\text{O})$, (43% SiO_2 ; 19% Al_2O_3 ; 4% Fe_2O_3 ; 2,6% MgO , 36 % H_2O and 3,3% CaO).

The spent Ion exchange resin has active groups in the form of electrically charged sites. At these sites ions of opposite charge are attached but may be replaced by other ions depending on their relative concentrations and affinities for the sites. Spent cation exchange resins containing ^{60}Co and represent a major portion of the solid radioactive waste in nuclear technology [1,2,3,4,5]. Cement is used as a solidification material for the storage of intermediate-level radioactive waste. However, the retention of radionuclides, especially cesium, in the cement matrix is negligible. The sorption of cesium on cement is low and diffusivity of cesium in the hydrated cement is high. Only when the cement is mixed with a material having a significant sorption capacity, normally bead or powdered ion exchange resins, is the leachability of cesium and cobalt from the cement matrix low enough to be acceptable.

Although cement has several unfavorable characteristics as a solidifying material, i.e. low volume reduction and relatively high leachability, it possesses many practical advantages: good mechanical characteristics, low cost, easy operation and radiation and thermal stability [7,8,9].

It is generally assumed that the cement leachability of ^{137}Cs and other radionuclides can be reduced by adding minerals like bentonite, vermiculite and clinoptilolite.

Curing time is critically important in leach studies since the extent of cement hydration determines how much hydration products develops and whether it is available to block the pore network ,thereby reducing leaching: The aim of this work is to describe leaching rate functional dependence of the cement curing time [8].

2. Materials, Methods and Experimental Conditions and Results

The cement specimens were prepared from construction cement which is basically a standard Portland cement, Portland cement, PC-20-Z-45 MPa. The cement was mixed with saturated wet cation exchange resins,(100gr. of dry resins +100 gr. of water containing ^{137}Cs) and two bentonite clay, from Srebia, A, and from Japan, B. (63% SiO_2 ; 18% Al_2O_3 ; 4% Fe_2O_3 ; 2,6% MgO and 3,3% CaO). The mixtures of components were cast into 50 mm diameter cylindrical molds with a height of 50 mm, which were then sealed and cured for 30 and 60 days prior to the leaching experiments. More than 100 different formulations of mortar form were examined to optimize their mechanical and sorption properties. In this paper we discuss twelve representative formulations. Grout composition formulas are shown in Table1.

Samples for leachability determination were prepared according to the IAEA standard Procedure“(Hespe,1971)”[6]. All prepared samples, were stored in laboratory at ambient temperature (25 ± 3 °C) for 30 and 60 days curing time. Leachant was exchanged and analyzed for radioactivity after:1,7,14, 28 and 60days. After each leaching period the radioactivity in the leachant was measured using EG&G- ORTEC spectrometry system and software.The volume of the leachant in every leaching period was 200 cm^3 .

The results are expressed by incremental leaching rates $R_n(\text{cm/d})$.

$$R_n = \frac{\sum a_n V}{A_0 S} \frac{1}{\sum t} \text{ (cm/d)} \quad (1)$$

where : a_n - the radioactivity of leached constituent during each leaching interval (Bq), A_0 - the specific radioactivity initially present in the specimen (Bq), S - the exposed surface area of the specimen (cm^2), V - the sample volume (cm^3), t - the duration of the leaching period, 180 (d).

Table1. Grout Composition (calculated as grams for 1000 cm^3 of mixtures)

Materials (g)	M ₁	M ₂	M ₃	M ₄	M ₅	M ₆	M ₇	M ₈	M ₉	M ₁₀	M ₁₁	M ₁₂
cation exc. Resines (g)	360	345	330	310	290	270	360	345	330	310	290	270
Portland cement (g)	130	132	133	1350	136	137	1300	132	133	135	136	137
Water (ml)	260	280	290	300	310	330	260	280	290	300	310	330
Bentonite clay, A (g)	13	41	66	13,5	42	68	-	-	-	-	-	-
)	(3)	(5*)	(1*)	(3*)	(5*)						
Bentonite clay, B (g)	-	-	-	-	-	-	13	41	66	13,5	42	68
							(1*)	(3*)	(5*)	(1*)	(3*)	(5*)
Initial activity A_0 (Bq ¹³⁷ Cs per sample)	7.0·10 ⁷											

Table 2, Table 3, Table 4, Table 5, Table 6, and Table 7, presents" Effect of curing time on the leach rate of ¹³⁷Cs from cement-waste matrix", for different grout composition and different bentonite.

Table 2. Effect of curing time on the Incremental leaching rate of ¹³⁷ Cs from cement, Sample M₁ and M₇ (same composition except bentonite, 13g.)

Cumulative time leached (days)	Incremental leaching rates R _n (cm/d) M ₁		Incremental leaching rates R _n (cm/d) M ₇	
	30 days cured	60 days cured	30 days cured	60 days cured
1	6.21 · 10 ⁻⁶	6.41 · 10 ⁻⁶	6.35 · 10 ⁻⁶	6.61 · 10 ⁻⁶
7	6.31 · 10 ⁻⁶	6.51 · 10 ⁻⁶	6.42 · 10 ⁻⁶	6.58 · 10 ⁻⁶
14	7.40 · 10 ⁻⁶	7.59 · 10 ⁻⁶	7.52 · 10 ⁻⁶	7.63 · 10 ⁻⁶
28	8.20 · 10 ⁻⁶	8.50 · 10 ⁻⁶	8.66 · 10 ⁻⁶	8.70 · 10 ⁻⁶
60	9.00 · 10 ⁻⁶	9.60 · 10 ⁻⁶	9.46 · 10 ⁻⁶	9.90 · 10 ⁻⁶

Table 3. Effect of curing time on the Incremental leaching rate of ¹³⁷ Cs from cement, Sample M₂ and M₈ (same composition except bentonite, from Srebia, A, and from Japan, B 42g.)

Cumulative time leached (days)	Incremental leaching rates R _n (cm/d) M ₂		Incremental leaching rates R _n (cm/d) M ₈	
	30 days cured	60 days cured	30 days cured	60 days cured
1	4.60 · 10 ⁻⁶	4.69 · 10 ⁻⁶	4.85 · 10 ⁻⁶	4.65 · 10 ⁻⁶
7	5.42 · 10 ⁻⁶	5.51 · 10 ⁻⁶	5.23 · 10 ⁻⁶	5.42 · 10 ⁻⁶
14	5.63 · 10 ⁻⁶	5.80 · 10 ⁻⁶	5.60 · 10 ⁻⁶	5.73 · 10 ⁻⁶
28	6.30 · 10 ⁻⁶	7.30 · 10 ⁻⁶	6.16 · 10 ⁻⁶	7.06 · 10 ⁻⁶
60	7.40 · 10 ⁻⁶	8.00 · 10 ⁻⁶	6.48 · 10 ⁻⁶	7.36 · 10 ⁻⁶

Table 4. Effect of curing time on the Incremental leaching rate of ^{137}Cs from cement, Sample M_3 and M_9 (same composition except bentonite, from Srebia, A, and from Japan, B 66g.)

Cumulative time leached (days)	Incremental leaching rates $R_n(\text{cm/d})$ M_3		Incremental leaching rates $R_n(\text{cm/d})$ M_9	
	30 days cured	60 days cured	30 days cured	60 days cured
1	$1.32 \cdot 10^{-6}$	$1.37 \cdot 10^{-6}$	$2.63 \cdot 10^{-6}$	$2.83 \cdot 10^{-6}$
7	$2.20 \cdot 10^{-6}$	$2.28 \cdot 10^{-6}$	$2.89 \cdot 10^{-6}$	$2.95 \cdot 10^{-6}$
14	$2.50 \cdot 10^{-6}$	$2.60 \cdot 10^{-6}$	$3.16 \cdot 10^{-6}$	$3.32 \cdot 10^{-6}$
28	$3.15 \cdot 10^{-6}$	$3.30 \cdot 10^{-6}$	$3.29 \cdot 10^{-6}$	$3.44 \cdot 10^{-6}$
60	$3.23 \cdot 10^{-6}$	$3.43 \cdot 10^{-6}$	$3.63 \cdot 10^{-6}$	$3.76 \cdot 10^{-6}$

Table 5. Effect of curing time on the Incremental leaching rate of ^{137}Cs from cement, Sample M_4 and M_{10} (same composition except bentonite, from Srebia, A, and from Japan, B 13,5g.)

Cumulative time leached (days)	Incremental leaching rates $R_n(\text{cm/d})$ M_4		Incremental leaching rates $R_n(\text{cm/d})$ M_{10}	
	30 days cured	60 days cured	30 days cured	60 days cured
1	$6.36 \cdot 10^{-6}$	$6.62 \cdot 10^{-6}$	$6.24 \cdot 10^{-6}$	$6.45 \cdot 10^{-6}$
7	$6.45 \cdot 10^{-6}$	$6.59 \cdot 10^{-6}$	$6.33 \cdot 10^{-6}$	$6.54 \cdot 10^{-6}$
14	$7.52 \cdot 10^{-6}$	$7.65 \cdot 10^{-6}$	$7.42 \cdot 10^{-6}$	$7.62 \cdot 10^{-6}$
28	$8.68 \cdot 10^{-6}$	$8.74 \cdot 10^{-6}$	$8.23 \cdot 10^{-6}$	$8.54 \cdot 10^{-6}$
60	$9.49 \cdot 10^{-6}$	$9.93 \cdot 10^{-6}$	$9.30 \cdot 10^{-6}$	$9.63 \cdot 10^{-6}$

Table 6. Effect of curing time on the Incremental leaching rate of ¹³⁷Cs from cement, Sample M₅ and M₁₁ (same composition except bentonite, from Srebia, A, and from Japan, B 42g.)

Cumulative time leached (days)	Incremental leaching rates R _n (cm/d) M ₅		Incremental leaching rates R _n (cm/d) M ₁₁	
	30 days cured	60 days cured	30 days cured	60 days cured
1	4.45 · 10 ⁻⁶	4.55 · 10 ⁻⁶	4.30 · 10 ⁻⁶	4.29 · 10 ⁻⁶
7	5.33 · 10 ⁻⁶	5.43 · 10 ⁻⁶	5.27 · 10 ⁻⁶	5.37 · 10 ⁻⁶
14	5.70 · 10 ⁻⁶	5.73 · 10 ⁻⁶	5.63 · 10 ⁻⁶	5.70 · 10 ⁻⁶
28	6.26 · 10 ⁻⁶	7.06 · 10 ⁻⁶	6.23 · 10 ⁻⁶	6.50 · 10 ⁻⁶
60	6.58 · 10 ⁻⁶	7.38 · 10 ⁻⁶	6.41 · 10 ⁻⁶	6.20 · 10 ⁻⁶

Table 7. Effect of curing time on the Incremental leaching rate of ¹³⁷Cs from cement, Sample M₆ and M₁₂ (same composition except bentonite, from Srebia, A, and from Japan, B 68g.)

Cumulative time leached (days)	Incremental leaching rates R _n (cm/d) M ₆		Incremental leaching rates R _n (cm/d) M ₁₂	
	30 days cured	60 days cured	30 days cured	60 days cured
1	2.61 · 10 ⁻⁶	2.80 · 10 ⁻⁶	1.35 · 10 ⁻⁶	1.40 · 10 ⁻⁶
7	2.84 · 10 ⁻⁶	2.94 · 10 ⁻⁶	2.22 · 10 ⁻⁶	2.32 · 10 ⁻⁶
14	3.10 · 10 ⁻⁶	3.30 · 10 ⁻⁶	2.60 · 10 ⁻⁶	2.70 · 10 ⁻⁶
28	3.25 · 10 ⁻⁶	3.40 · 10 ⁻⁶	3.10 · 10 ⁻⁶	3.33 · 10 ⁻⁶
60	3.60 · 10 ⁻⁶	3.73 · 10 ⁻⁶	3.28 · 10 ⁻⁶	3.53 · 10 ⁻⁶

3. Conclusion

All results exhibit practically the same general characteristics. An enhanced initial period of leaching occurs during the first 25-30 days or so, followed by a distinct reduction in the leach rate which is broadly maintained up to the long period of leaching. The leach behaviour of cement-mortar materials can be explained as a combination of two processes; surface wash-off, which is not diffusion controlled, followed by a static diffusion stage. Enhanced initial period of leaching can be explained in terms of a rapid equilibrium being established between spaces present in the surface pores of the Portland cement and ions in solution in the leachant; hence the term wash-off. It is this second stage which is controlled by diffusion and which dominates the long-term leaching behaviour of the material. Under these circumstances the effect of increased curing time on the diffusion coefficient becomes apparent.

In this paper we also prove that increasing amount of bentonite cause a significant reduction in the leaching rate, because of bentonite good sorption characteristics and ion selectivity.

Results presented in this paper are examples of results obtained in a 30-year concrete testing project which will influence the design of the engineer trenches system for future central Serbian radioactive waste storing center.

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POREDENJE JAPANSKIH I SRPSKIH BENTONITA U KOMPOZICIJI CEMENT-JONOIZMENJIVAČKA SMOLA- BENTONITNA GLINA

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SAŽETAK

Da bi se procenila bezbednost odlaganje radioaktivnog otpadnog materijala u cementu, proučavan je stepen izluživanja radionuklida ^{137}Cs . Testovi izluživanja radjeni su za kompoziciju cementa-jonoizmenjivačke smole i bentonita i sprovedene su u skladu sa postupkom preporučenog od IAEA. Vreme sušenja pre otpočinjanja ličing testa je od suštinske važnosti u studijama izluživanja, jer uticaj hidratacije cementa određuje koliko se hidratacija proizvoda razvija i da li je od uticaja na blokadu pora, čime se smanjuje curenje radionuklida iz matriksa . U ovom radu poredjena su dva bentonita kao sorpcione komponente, iz Japana i Srbije . Rezultati prikazani u ovom radu su primeri rezultata 30-godišnjeg projekta sistema inženjerskih rovova za buduće srpsko centralno odlagalište radioaktivnog otpada.