Curing time effect on the fraction of ^{137}Cs from cement–ion exchange resins–bentonite clay composition

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To assess the safety of disposal of radioactive waste material in cement, curing conditions and time of leaching radionuclides ^{137}Cs 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(cm/d) of ^{137}Cs from cement–ion exchange resins–bentonite matrix after 240 days were measured. 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 storing center.
Keywords: cement, radioactive waste, radionuclide, leaching, concrete

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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 ^{137}Cs and other radionuclides can be reduced by adding minerals like bentonite and zeolite.

The 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 [5]. Cement is used as a solidification material for the storage of intermediate-level radioactive waste [1, 4]. However, the retention of radionuclides, especially cesium, in the cement matrix is negligible [6, 5, 7]. 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 (Torstenfeld at al, 1988). 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 hidratation determines how much hidratation products develops and whether it is available to block the pore network, thereby reducing leaching (Glasser at al, 1882). The aim of this work is to describe leaching rate functional dependence of the cement curing time.

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, (100 gr. of dry resins +100 gr. of water containing ^{137}Cs) and bentonite clay (63% SiO_2 ; 18% Al_2O_3 ; 4% Fe_2O_3; 2,6% MgO and 3,3% CaO). The mixtures 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 then 100 different formulations of mortar form were examined to optimize their mechanical and sorption properties. In this paper we discuss three representative formulations. Grout composition formulas are shown in Table 1.

Materials (g)	M_1	M_2	M_3
Cation exc. resines (g)	360	300	270
Portland cement (g)	1300	1360	1315
Water (ml)	260	280	300
Bentonite clay (g)	15 (1,1*)	41 (3*)	66 (5*)
Initial activity A_o (Bq ^{137}Cs per sample)	$8{,}0 \times 10^7$	$8{,}0 \times 10^7$	$8{,}0 \times 10^7$

* *% of cement*

Table 1. Grout Composition (calculated as grams for 1000 cm³ of mixtures)
1. táblázat Habarcs-összetétel (a keverék 1000 cm³-ére számítva, grammban kifejezve)

Samples for leachability determination were prepared according to the IAEA standard procedure [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, 2, 3, 4, 5, 6, 7 days, and thereafter every week for six months. 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(cm/d)

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

where: a_n – the radioactivity of leached constituent during each leaching interval (Bq), A_o – 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).

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

Cumulative time leached (days)	Incremental leaching rates R_n(cm/d)	
	30 days cured	60 days cured
1–10	$2{,}61 \times 10^{-6}$	$1{,}35 \times 10^{-6}$
10–30	$3{,}41 \times 10^{-6}$	$3{,}22 \times 10^{-6}$
30–100	$6{,}30 \times 10^{-6}$	$6{,}00 \times 10^{-6}$
100–240	$8{,}00 \times 10^{-6}$	$7{,}46 \times 10^{-6}$

Table 2. Effect of curing time on the Incremental leaching rate of ^{137}Cs from cement, Sample M_1
2. táblázat A tárolási idő hatása a cementből kilúgozódó ^{137}Cs mennyiségének növekedésére, M_1 minta

Cumulative time leached (days)	Incremental leaching rates R_n(cm/d)	
	30 days cured	60 days cured
1–10	$2{,}34 \times 10^{-6}$	$2{,}30 \times 10^{-6}$
10–30	$2{,}47 \times 10^{-6}$	$2{,}20 \times 10^{-6}$
30–100	$5{,}30 \times 10^{-6}$	$5{,}10 \times 10^{-6}$
100–240	$7{,}00 \times 10^{-6}$	$6{,}50 \times 10^{-6}$

Table 3. Effect of curing time on the Incremental leaching rate of ^{137}Cs from cement, Sample M_2
3. táblázat A tárolási idő hatása a cementből kilúgozódó ^{137}Cs mennyiségének növekedésére, M_2 minta

Cumulative time leached (days)	Incremental leaching rates R_n(cm/d)	
	30 days cured	60 days cured
1–10	$6{,}04 \times 10^{-7}$	$5{,}90 \times 10^{-7}$
10–30	$1{,}42 \times 10^{-6}$	$1{,}10 \times 10^{-6}$
30–100	$4{,}30 \times 10^{-6}$	$3{,}00 \times 10^{-6}$
100–240	$6{,}00 \times 10^{-6}$	$5{,}83 \times 10^{-6}$

Table 4. Effect of curing time on the Incremental leaching rate of ^{60}Co from cement, Sample M_3
4. táblázat A tárolási idő hatása a cementből kilúgozódó ^{137}Cs mennyiségének növekedésére, M_3 minta

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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A kezelési időtartam hatása a cement–ioncserélő-gyanta–bentonitagyag keverékből származó ^{137}Cs frakcióra

A radioaktív hulladék anyagok cementes közegben történő tárolása biztonságának felmérése érdekében tanulmányoztuk a ^{137}Cs radionuklid kilúgozódási időtartamát. A cement–ioncserélő-gyanta–bentonitagyag keverék kilúgozási vizsgálatát az IAEA által ajánlott módszerrel végeztük. A kilúgozási vizsgálat előtti tárolási feltételek és tárolási idő kritikus jelentőségű, mivel a cement anyag hidratációjának mértéke határozza meg, mennyi hidratációs termék keletkezik, és áll rendelkezésre a pórusszerkezet eltöméséhez, ami egyúttal a kilúgozódást is csökkenti. Megmértük a 240 napig tárolt cement–ioncserélő-gyanta–bentonitagyag keverékből a ^{137}Cs kilúgozódási sebességét, az R_n(cm/nap) értékeket. A jelen tanulmányban bemutatott eredmények egy 30 évig tárolt beton vizsgálati eredményeit tükrözik, és ezeket felhasználjuk majd a jövőben létesítendő közép-szerbiai radioaktív hulladéktároló központ vízelvezető-árok rendszerének a tervezésénél.

Kulcsszavak: cement, radioaktív hulladék, radionuklid, kilúgozódás, beton