Cesium binding and leaching from single and binary contaminant cement–bentonite matrices

R.O. Abdel Rahman [a,*], D.H.A. Zin El Abidin [b], H. Abou-Shady [c]

[a] Hot Laboratory Center, Atomic Energy Authority of Egypt, P.O. 13759, Inshas, Cairo, Egypt
[b] Center of Nuclear Studies and Peaceful Application, Egypt
[c] Faculty of Science, Cairo University, Egypt

HIGHLIGHTS

- Cesium immobilization in cement–bentonite waste matrices was investigated.
- Cs was found as free ions in the interstitial pore fluid before and after hydration reactions.
- The pH of interstitial pore fluid was found to be dependent on the presence of benonite.
- Ettringite and CSH intermolecular channels can contribute to the physical entrapment of Cs and Sr.
- Cs release from solidified matrices is independent on the presence of Sr.

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ABSTRACT

Binding mechanisms and leaching characteristics of cesium from different cement–bentonite immobilization matrices were investigated. The effect of Sr presence as a competitive contaminant in the matrices was studied by investigating the binding and leaching mechanisms in binary contaminant matrices that contains both Cs and Sr solutions. Binding investigations aimed to trace Cs binding mechanisms by calculating the distribution of contaminant and major structural elements aqueous complexes in the mixing solution and interstitial pore fluid before the hydration reaction take place. The hydration phases development within 28 day curing period was studied and their effects on the speciation of contaminant and major structural elements were investigated. The leaching characteristics were studied by analyzing the experimental results of the long term leaching test. The results indicated that the percentage distribution of aqueous Cs and Sr complexes in their solution are independent on the presence of each other. Cs was found as free ions in the interstitial pore fluid for all the studied cases. The interstitial pore fluid pH was found to be dependent on the presence of bentonite and sodium was found as dissolved Na^{+1} ions, this might form evidence that Cs^{+1} might substitute Na^{+1} in bentonite structure. The intermolecular channels in Ettringite and CSH structures were found to contribute to the physical entrapment of Cs and Sr ions within the solidified matrices. The leaching characteristics were resulted from a combination of first-order, diffusion, dissolution and instantaneous release of contaminants mechanisms. Dissolution and instantaneous release mechanisms were found to have very low contribution to the leaching process.

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1. Introduction

Safe disposal of radioactive wastes, either in near surface or deep geological disposal facilities, aimed to efficiently isolate these wastes from the environment for sufficient periods of time to allow substantial decay of the shorter lived radionuclides and in the longer term to limit releases of the remaining long-lived radionuclides [1]. To ensure that these facilities will work as planned, regulatory bodies entailed the demonstration of their safe performance before issuing execution licenses i.e. site confirmation, construction, operation, and closure. Due to the dynamic nature of the hydrological and biological subsystems in the host environment and evolution of near-field materials, changes in the containment and mechanical performance of the disposal materials might take place. To address all these changes as a function of time, the performance assessment is conducted using modular approach in which the disposal system is divided into modules

i.e. near-field, geosphere, and biosphere [2]. The utilization of this approach allows the license applicant to update his assessment as more site-specific information is obtained [3].

The containment performance of near-field module is evaluated by predicting contaminants release rates from the disposal facility as a function of time. Releases might occur due to near-field materials evolution under different environmental conditions over long periods of times. The nature of material evolution and the releases should be identified as a part of the assessment. There are two approaches that could be used in this respect namely; conservative and realistic approaches. Conservative approach is widely adopted worldwide at which conservative assumptions are used and supplemented by following the defense in depth safety philosophy. The utilization of this approach has resulted in substantial safety margins that have served the interests of safety well over years [4]. To evaluate the containment performance of monolith waste matrix under most conservative assumptions, IAEA suggested the utilization of static long-term leaching test that is designed to simulate the disposal conditions during bathtub scenario [5,6]. Recently, the argument in the scientific committee on the switch from conservative approach to more realistic approach is receiving considerable attention. The application of the realistic approach is bounded by a clear understand of different disposal modules and their evolution over the disposal design life. So comprehensive understand of radiocontaminants binding mechanisms within the waste matrix and their transport through the engineered barriers are critical issues towards realistic assessment of the near-field module.

Different matrices could be used to immobilize the radiocontaminants, i.e. cementitious, polymeric, metallic, and glass based materials. Among these matrices, cementitious materials are the most commonly used for immobilizing Low and Intermediate Level Radioactive Wastes (LILRW) [7–9]. Leachability studies were conducted to evaluate the release from these matrices concluded that lanthanides and actinides were found to be well immobilized due to their low solubility in the high pH pore fluid of the matrices. On the other hand, immobilization of alkali metals, that remain substantially soluble, is representing a continuous challenge [10–12]. Immobilization of cesium has received considerable attention due to the low sorption potential of cement towards cesium and its solubility in the cementitious matrices. Different natural and synthetic materials that have high sorption potential towards cesium were tested to check their feasibility to reduce Cs leaching from the cementitious waste matrices [6,11–17]. The assessment of the additive performance was restricted to study the contaminant performance by applying leaching tests. On the other hand, limited studies were devoted to study Cs binding by conducting batch sorption tests [18–21]. These studies investigated the sorptive behavior of hydrated calcium–silicate–aluminate systems, CEM I, CEM V, and cement without examining the effect of adding the contaminants during the hydration process. This work aims to examine and understand Cesium binding in cement–bentonite single and binary matrices, where single matrices include Cesium ions and binary matrices contain both Cesium and Strontium ions. Within this context, the studied matrices were prepared by adding the contaminants during the mixing process then the mechanical performance, contaminant binding behavior, and containment performance of these matrices were studied. The mechanical performance and containment binding behavior were investigated by studying the development of the compressive strength, and hydration phases and their effects on the aqueous complex species of contaminants and major structure elements. Finally, cesium containment performance through single and binary matrices was addressed by analyzing the long term leaching data mathematically to determine the leaching mechanisms and calculate the leaching parameters.

2. Procedures and models

2.1. Materials and preparation of immobilization matrices

Cement–bentonite matrices were prepared using varied weight percent of commercial OPC and natural bentonite, the chemical compositions of these materials are listed in Table 1 [22,23]. Bouge equations were used to calculate major unhydrated phases percentages, as follow [24,25]:

$$Tri\text{-}calcium\ silicate = 4.07CaO - 7.60SiO_2 - 6.72Al_2O_3$$
$$- 1.43Fe_2O_3 - 2.85SO_3 \qquad (1)$$

$$Di\text{-}calcium\ silicate = 2.87SiO_2 - 0.754Tri - calcium\ silicate \qquad (2)$$

$$Tri\text{-}calcium\ aluminate = 2.65Al_2O_3 - 1.69Fe_2O_3 \qquad (3)$$

$$Tetra\text{-}calcium\ aluminoferrite = 3.04Fe_2O_3 \qquad (4)$$

Cesium and strontium solutions were prepared by dissolving weighted quantity of CsCl and $SrCl_2\cdot6H_2O$ in distilled water. These solutions were used as stocks for the preparation of single and binary cement–bentonite waste matrices. Eight different matrices were prepared, as listed in Table 2, at 0.45 solution to solid ratio [22]. The matrices were prepared by placing the required amount of solids in a smooth non-absorbent surface and a crater was formed in the center, then solutions were poured into the crater for preparation of single or binary matrices. The mixing operation was performed at room temperature by continuous mixing (1500 rpm for 4 min) [11,12,26]. The pastes were then poured into cubic moulds (5 cm side length) in two approximately equal layers; each layer was compacted and passed along the surface of the moulds until homogenous specimen was obtained. After the top layer was compacted, the moulds were then vibrated to

Table 1
Chemical composition of OPC and bentonite [22].

Chemical composition	OPC	Bentonite
CaO	63	2–6
SiO$_2$	20	49–55
Al$_2$O$_3$	6.0	20–24
Fe$_2$O$_3$	2.1	2.5–6
MgO	1.5	0.5–2
Na$_2$O	0.5	1.1–2.4
K$_2$O	–	1.2–1.4
Others	6.9	–
LOI at 850 for 2 h	–	9–10
Tri-calcium silicate*	55.35	–
Di-calcium silicate*	15.88	–
Tri-calcium aluminates*	12.34	–
Tetra-calcium aluminoferrite*	6.39	–

* Un-hydrated phase determination were obtained using Bogue equations.

Table 2
Single and binary cement–bentonite matrices composition.

Matrix	Label	Solution, wt%	OPC, wt%	Bentonite, wt%
Single	Sample 0%	31% of 0.1 g/l of Cs$^+$	69	0
	Sample 5%		65.5	3.5
	Sample 10%		62	7
	Sample 15%		58.6	10.4
Binary	Sample 0%	31% of 0.1 g/l of Cs$^+$ +0.1 g/l Sr^{+2}	69	0
	Sample 5%		65.5	3.5
	Sample 10%		62	7
	Sample 15%		58.6	10.4