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Strontium release from wollastonite-based brushite cement paste under semi-dynamic leaching conditions

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1. Introduction

During the decommissioning of old nuclear facilities, cleaning operations can produce aqueous waste streams mainly contaminated by cesium and strontium. Various treatments are usually applied, such as evaporation, co-precipitation and filtration, or sorption onto ion exchange materials. The objective is to concentrate radioactivity and reduce the volume of waste to be disposed of. Low-level and intermediate-level radioactive wastes are usually encapsulated in a cement-based matrix before being sent to disposal. This conditioning step aims at avoiding any dispersion of the waste, facilitating handling and transportation operations, and limiting the release of hazardous elements that can be a threat to human health and environment. Portland cement and blastfurnace slag cement are widely used to design cement-based matrices. These binders can be easily supplied, are compatible with aqueous waste, and, after hydration, generally exhibit good mechanical strength, stability over time, and high alkalinity which allows precipitating, and thus confining, many radionuclides such as actinides ([1], [2]). However, limited retention of key radionuclides such as ¹³⁷Cs and ⁹⁰Sr can be an issue with these binders ([3], [4]). This work is focused on ⁹⁰Sr, a high-energy β -emitter showing similarity to calcium and thus attaching easily to bone. The objective is to assess the potential of a phosphate binder as an alternative to Portland cement for strontium retention.

Wollastonite-based brushite cement (WBC) is prepared by mixing wollastonite, a natural meta-silicate mineral (CaSiO_3), with a solution containing phosphoric acid, boron and metallic cations (Al^{3+} , Zn^{2+} ...). Wollastonite reacts through dissolution/precipitation, leading to the formation of a multiphase material containing brushite, amorphous calcium aluminophosphate, amorphous silica, and residual wollastonite [5]. Brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) is well-known to exhibit a flexible structure, making it possible to substitute strontium for calcium [6]. As compared to other phosphate binders, WBC has also the advantage of being cost-effective thanks to its raw materials and its preparation at room temperature.

In the present study, the American Nuclear Society ANS/ANSI-16.1 test procedure was used to measure strontium release from a wollastonite-based brushite cement paste and calculate the corresponding effective diffusion coefficients and leachability indices (LI). The results were then compared to those achieved with conventional binders.

2. Experimental

2.1. Materials and preparation of immobilization matrix

The WBC matrix was prepared using a commercial binder provided by Sulitec. The wollastonite powder (specific surface area: $1.2 \text{ m}^2/\text{g}$, $d_{10} = 2.8 \text{ }\mu\text{m}$, $d_{50} = 15.2 \text{ }\mu\text{m}$, $d_{90} = 48.3 \text{ }\mu\text{m}$) was slightly carbonated: it contained 98.4 wt% CaSiO_3 and 1.6 wt.% CaCO_3 . The mixing solution was a phosphoric acid solution ($[\text{P}] = 9.3 \text{ mol/L}$), containing metal cations ($[\text{Al}^{3+}] = 1.3 \text{ mol/L}$, $[\text{Zn}^{2+}] = 1.3 \text{ mol/L}$) and borax (0.15 mol/L).

The cement paste was prepared by mixing these two components at a liquid-to-solid weight ratio of 1.25 for 5 min. Stable strontium was used as a surrogate for its radionuclide and was added as $\text{Sr}(\text{NO}_3)_2$

(Merck, >99% purity) to the mixing solution ($[\text{Sr}^{2+}] = 1 \text{ g/L}$). Sr-doped cement paste was cast into a polypropylene cylindrical container which was tightly sealed and cured for 28 days at room temperature.

The XRD pattern of Sr-doped cement paste is presented in Fig. 5. The paste contained brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) [7] and residual wollastonite (CaSiO_3). Quartz, an impurity present in the wollastonite powder, was also evidenced. Meanwhile, there was no new crystalline phase related to the addition of strontium in the cement matrix.

2.2. Leaching Test

Leaching tests were carried out according to ANSI/ANS-16.1 specification [8]. The test was performed at room temperature by immersing the specimen for 90 days in ultrapure water used as the leachant. The leachate was replaced with fresh water nine times over a period of 3 months (2h, 7h, 24h, 48h, 5d, 7d, 14d, 45d, 90d) in order to limit accumulation of dissolved species. The ratio of the leachant volume to the external geometric surface area of the specimen was set to 2 cm instead of 10 cm as recommended in the specification. Decreasing the volume of solution increased the concentration of strontium in the leachates, which was more easily detected (a first attempt with a ratio of 10 cm led to Sr concentrations in solution below the detection limit (1 ppb) of the ICP-AES method used. The counterpart was a higher composition change of the leachant between two renewals. Strontium ions released in solution were analysed using ICP-AES.

The cumulative fraction of strontium leached (CFL) was determined as follows:

$$CFL = \frac{\sum A_n}{A_0} \quad (\text{Eq. 1})$$

where A_n [g] is the amount of strontium released from the specimen during leaching interval n and A_0 [g] is its initial amount in the specimen.

At the end of the test, mineralogical and microstructural characterizations of the specimen were performed using XRD and SEM-EDS.

The cement paste was characterized by XRD (PANALYTICAL X'PERT PRO) diffractometer before and after the leaching test. The samples were finely ground at a particle size below 80 μm before being analysed using the Debye-Scherrer configuration (transmission mode). They were introduced in Lindeman tubes ($\Phi = 0.7 \text{ mm}$) and mounted on a spinning goniometric head during measurement to reduce the preferred orientation effect. Data were recorded by using copper radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature in the 2θ range $5\text{--}70^\circ$ with a step size of 0.013° for a total counting time of 2 h.

SEM observations (FEI Inspect S50, high vacuum mode, acceleration voltage of 15 kV, current intensity of 50 nA, working distance of 9.7 mm) were also carried out after the leaching test. A polished section was prepared by impregnating the cement paste (in which hydration was stopped by soaking into isopropanol and gently drying at 20°C and 23% R.H.) with an epoxy resin (EPO-TEK 301) under vacuum. The sample was then polished using several diamond grades (down to 1 μm) and carbon coated using a carbon evaporator (Quorum Q150TE). Elemental mapping was performed by X-ray microanalysis (high vacuum mode, Bruker X-flash SDD detector (10 mm^2)) on a cross section including the leached surface and the sound core.

3. Results and discussion

3.1. Cumulative fraction release of strontium

The cumulative fraction of strontium leached from WBC sample (CFL) is shown in Fig. 1. Strontium ions were rapidly released from the cement paste within the first 7 days. The leaching rate then decreased. The CFL of Sr reached a value of 1.22×10^{-3} (corresponding to the leaching of $\sim 0.12\%$ Sr initially present in the specimen) at the end of the test, which is much lower than data reported for Portland Cement paste ($\sim 5 \times 10^{-2}$ for a cement paste with a water-to-cement ratio of 0.5) [9].

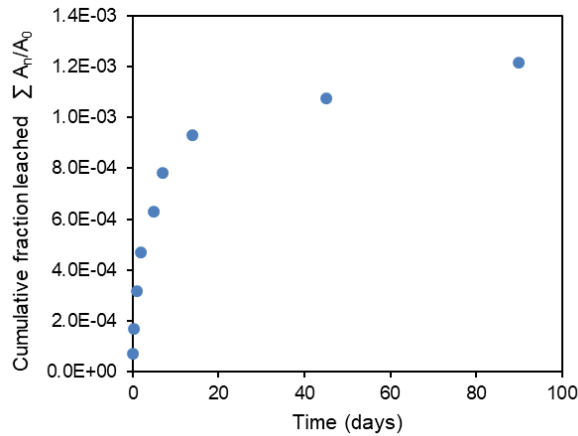


Fig. 1. Cumulative fraction of strontium leached from WBC paste.

The pH of the leachates was measured after each renewal (Fig. 2). It exhibited limited changes over the test period, with values remaining within the range 6.5 and 7.5.

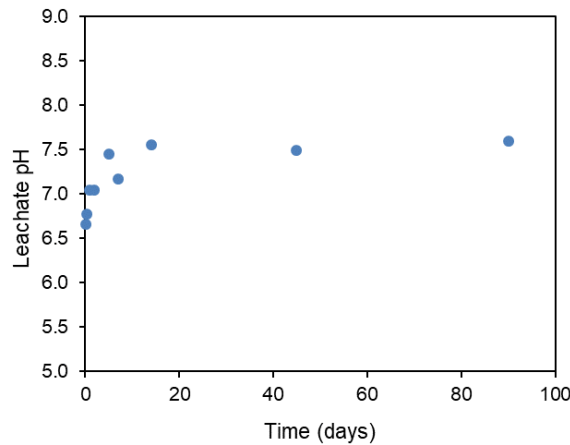


Fig. 2. pH evolution of the leachates.

3.2. Modelling the leaching behaviour of strontium from WBC: evaluation of the Effective Diffusion Coefficient (D_e) and Leachability Index (LI)

According to the literature, leaching from cementitious materials can result from three main processes: surface exchange phenomena, diffusion and dissolution mechanisms [10]. Mathematical models have been built to describe these processes. They are briefly presented hereafter.

a- Surface wash-off

A first-order reaction model is often used to describe the kinetics of exchange between the surface of the cement matrix and the leaching solution. The surface exchange rate is given by Eq. 2 ([11],[12]):

$$\frac{dQ}{dt} = kQ \quad (\text{Eq. 2})$$

where Q is the amount of soluble radionuclide in the cement matrix (mg/g) and k is a rate constant (s^{-1}). The cumulative fraction leached (CFL) then checks Eq. 3.

$$CFL(t) = \frac{\Sigma A_n}{A_0} = Q_0 (1 - \exp(kt)) \quad (\text{Eq. 3})$$

where Q_0 is the initial amount of soluble radionuclide in the cement matrix (mg/g).

According to Coté et Constable [10], the surface processes dominate the leaching at short values of time.

b- Bulk diffusion model

Since a cementitious material may be described as a porous solid with water-filled pores, the transport of species by diffusion in the pore network can be expected to play an important role in the leaching process.

The diffusion mechanism can in general be described by Fick's second law in semi-infinite medium [10]:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \quad (\text{Eq. 4})$$

where C is the concentration of radionuclide and D_e is the effective diffusion coefficient (cm^2/s).

If the surface concentration is maintained at zero for $t > 0$, a solution to Fick's second law can be calculated and the cumulative fraction leached checks Eq. 5 [10]:

$$CFL(t) = \frac{\Sigma A_n}{A_0} = 2 \left(\frac{S}{V} \right) \sqrt{\frac{D_e t}{\pi}} \quad (\text{Eq. 5})$$

where S/V is the geometrical surface area-to-volume ratio of the specimen.

The effective diffusion coefficient (D_e) can then be calculated according to Eq. 6.

$$D_e = \pi \left(\frac{p V}{2 S} \right)^2 \quad (\text{Eq. 6})$$

where p is the slope of the plot of CFL versus $\sqrt{t}$.

c- Dissolution model

When the species being released are major components of the material, structural breakdown of the cement matrix can occur. This process is referred to as corrosion or dissolution. The kinetics of dissolution can be described by a network dissolution velocity U , defined as the volume of solid being dissolved per unit time and surface area [10] (Eq. 7)

$$U(t) = U_0 \left(1 - \frac{C(t)}{C_{sat}} \right) \quad (\text{Eq. 7})$$

where U_0 is the maximum network dissolution velocity and C_{sat} is the saturation concentration in the aqueous solution. For the simple case where $C_{sat} \gg C(t)$, $U(t) = U_0$, and an expression for the cumulative fraction leached is given by Eq. 8 ([10], [12]).

$$CFL(t) = \frac{\Sigma A_n}{A_0} = \frac{S}{V} U_0 t \quad (\text{Eq. 8})$$

d- Semi-empirical modelling

Côté et Constable (1987) have proposed a semi-empirical kinetic model taking into account the contributions of surface-wash off, diffusion and dissolution mechanisms [10]. This model combines three time-dependent terms for the cumulative fraction leached, describing respectively the kinetics of exchange between the surface of the sample and the leaching solution, the transport of species by diffusion within the porous matrix and matrix dissolution (Eq. 9).

$$CFL(t) = k_1(1 - e^{-k_2 t}) + k_3 t^{1/2} + k_4 t \quad (\text{Eq. 9})$$

In order to point out the processes governing leaching of strontium from WBC paste samples, regression analysis was carried out using Eq. 9 on the experimental CFL data. Note that several assumptions were used to derive the leaching models leading to Eq. 9.

1. Leaching should take place in a time-invariant chemical environment. In the present study, the leaching solution was periodically renewed in order to limit accumulation of released species and its pH showed limited variation during the test.
2. The solid is semi-infinite. According to ANS/ANSI 16.1 specification, a semi-infinite geometry is applicable to finite geometry specimens if the cumulative fraction leached is less than 20%. In the present study, the cumulative fraction of strontium leached was less than 1% (~0.12%) at the end of the test.
3. A zero surface concentration of strontium is maintained. The Sr concentrations measured in the leachates were small (less than 20 ppb). The leachant renewal frequency was sufficiently high to approximate the boundary condition of zero surface concentration.

As a first approach, these assumptions were thus considered as satisfied during the study.

The optimized values of the model parameters are given in Table 1. The quality of the fit was excellent ($r^2_a = 0.992$). Constant k_4 was not significantly different from zero at a confidence level of 95%, meaning that two processes predominated: surface wash-off and diffusion. The model was thus simplified by omitting the third term in equation 9 and parameters k_1 , k_2 and k_3 were recalculated.

Table 1: Coefficients from the regression analysis of CFL data.

Model		Value	Standard Error	t-Value	Prob > t (%)
$CFL(t) = k_1(1 - e^{-k_2 t}) + k_3 t^{1/2} + k_4 t$ $r^2_{\text{adjusted}} = 0.992$	k_1	4.04×10^{-4}	1.17×10^{-4}	3.45	*
	k_2	4.92×10^{-1}	1.25×10^{-1}	3.93	**
	k_3	1.59×10^{-4}	4.50×10^{-5}	3.54	*
	k_4	-7.94×10^{-6}	3.67×10^{-6}	-2.16	7.4
$CFL(t) = k_1(1 - e^{-k_2 t}) + k_3 t^{1/2}$ $r^2_{\text{adjusted}} = 0.988$	k_1	6.48×10^{-4}	6.25×10^{-5}	10.37	***
	k_2	4.27×10^{-1}	8.20×10^{-2}	5.20	**
	k_3	6.20×10^{-5}	9.53×10^{-6}	6.50	***

Probability: *** < 0.1%; ** 0.1 – 1 %, * 1-5 %

Fig. 3. compares the regression line to the observed data. As expected, surface wash-off predominated during the first day of leaching, and diffusion was dominant afterwards.

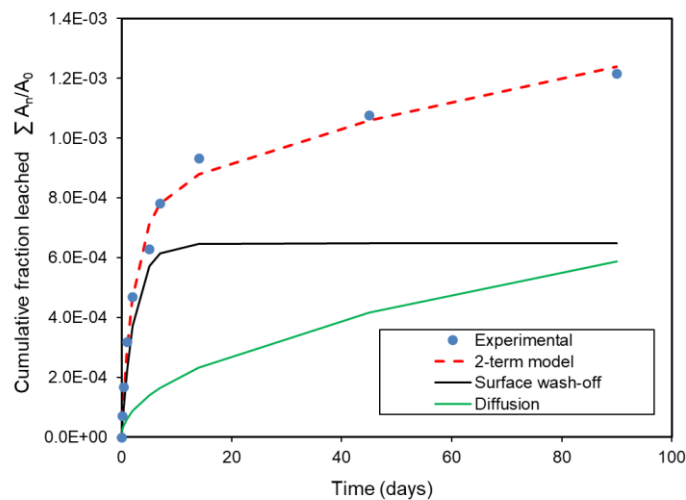


Fig. 3. Fitting of CFL data using a 2-term model taking into account surface wash-off and diffusion in the pore solution ($CFL(t) = k_1(1 - e^{-k_2 t}) + k_3 t^{1/2}$)

The effective diffusion coefficient D_e was derived from constant k_3 (Eq. 10). Its value ($4.8 \times 10^{-15} \pm 1.6 \times 10^{-15} \text{ cm}^2/\text{s}$) was at least 3 orders of magnitude smaller than those reported for Portland cement-based materials (ranging from 10^{-8} to $10^{-12} \text{ cm}^2/\text{s}$, depending on the matrix formulation, test methodology and concentration of strontium used) [8, 9, 14, 16] (Table 2). The WBC paste and a fly ash-based geopolymer [8] showed similar Sr confining properties. The best performances were reported for a magnesium potassium phosphate-based material [15]. Note however that the effective diffusion coefficient depends on the pore network of the material. The paste elaborated in this work had a very high liquid-to-solid ratio (1.25, instead of 0.45 for the magnesium potassium phosphate cement-based material). Decreasing this solid-to-liquid ratio should thus improve further the retention of strontium.

$$D_e = \pi \left(\frac{k_3 V}{2 S} \right)^2 \quad (\text{Eq. 10})$$

According to ANSI specification, the leachability Index (LI), defined by (Eq. 11), can be used to evaluate the efficiency of nuclide encapsulation in the matrix and rank materials immobilization performances.

$$LI = \log \left(\frac{\beta}{D_e} \right) \quad (\text{Eq. 11})$$

where β is a defined constant ($1.0 \text{ cm}^2/\text{s}$).

The LI value of the WBC paste ($LI = 14.3 \pm 0.2$) largely exceeded the minimum threshold value ($LI = 6$) recommended by the US Nuclear Regulatory Commission for the disposal of radioactive wastes [8].

Table 2. Summary of D_e and LI of strontium reported in previous studies.

Reference	Test method	Cement matrix	$D_e \text{ (cm}^2/\text{s)}$	LI
This work	ANSI/ANS-16.1	Wollastonite-based brushite cement	4.4×10^{-15}	14.3
(Goo et al., 2021) [13]	ANSI/ANS-16.1	Portland cement paste W/C = 0.4	7.6×10^{-11}	10.5
(Jang et al., 2016) [9]	ANSI/ANS-16.1	Portland cement paste W/C = 0.5	3.3×10^{-10}	9.8
		Fly ash-based geopolymer (paste) L/S = 0.5	6.8×10^{-15}	14.4
(Pyo et al., 2021) [14]	ANSI/ANS-16.1	Magnesium potassium phosphate cement (paste) MgO/KH ₂ PO ₄ = 1.5 (mol. ratio) H ₂ O/ KH ₂ PO ₄ = 5 (mol. ratio) W/C = 0.45	2.8×10^{-17}	15.6
(Matsuzuru & Ito, 1977) [15]	IAEA (radioactive ⁹⁰ Sr)	Portland cement paste W/C = 0.4	$1.4 - 4.5 \times 10^{-12}$	-
(El-Kamash et al., 2006) [16]	IAEA (radioactive ⁹⁰ Sr)	Portland cement paste W/C = 0.35	5.4×10^{-8}	7.3
		Portland cement with zeolite A (paste) W/C = 0.35	3.8×10^{-8}	7.4

3.3. Microstructural and mineralogical characterizations of the solidified cement paste after the leaching test

WBC paste was characterized by SEM-EDS at the end of the leaching test. Observation of a polished cross section of the sample showed a depletion of Ca and P near the leached surface over a depth close to 100 μm (Fig. 4)).

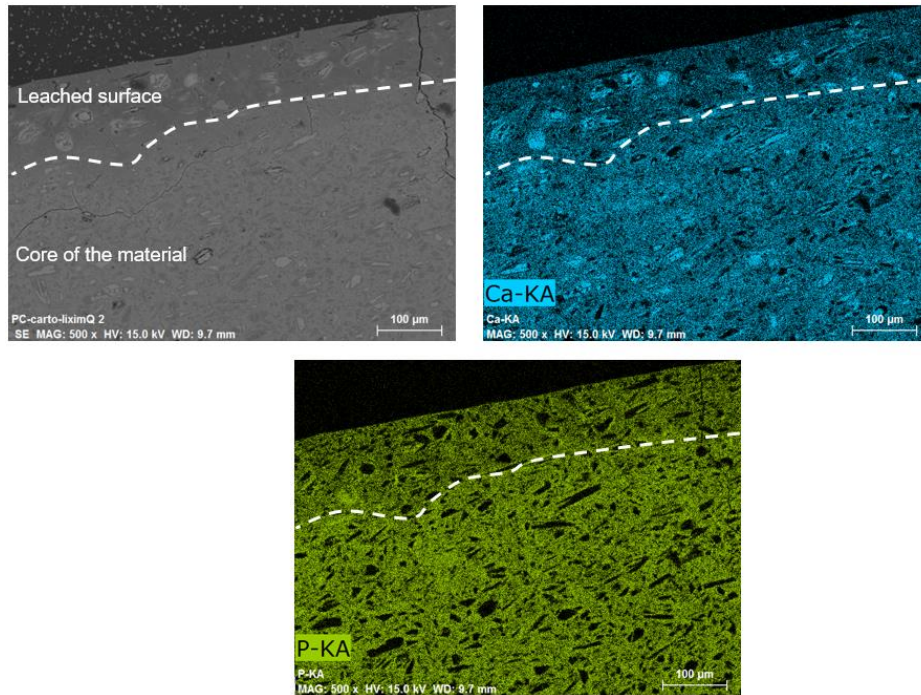


Fig. 4. Scanning electron micrograph (BSE, 15kV, WD: 9.7 mm) of Sr-doped specimen after the leaching test and elemental mapping of Ca and P.

The exposed surface, which still exhibited good cohesion, was scrapped off and the collected powder was analysed using X-ray diffraction (Fig. 5). A decrease in the brushite content was evidenced near the surface whereas the core of the sample exhibited the same phase assemblage as that of the paste before leaching. A diffuse halo was clearly evidenced after ninety days of leaching, compatible with the presence of (possibly) two amorphous phases in the surface region of the WBC paste. These signatures could correspond to amorphous silica and amorphous calcium aluminophosphate phase, the proportions of which increased in the leached surface after partial dissolution of brushite. Moreover, the XRD-pattern of the exposed surface showed the presence of new large diffraction peaks that seemed to correspond to the formation of nano-crystalline hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$).

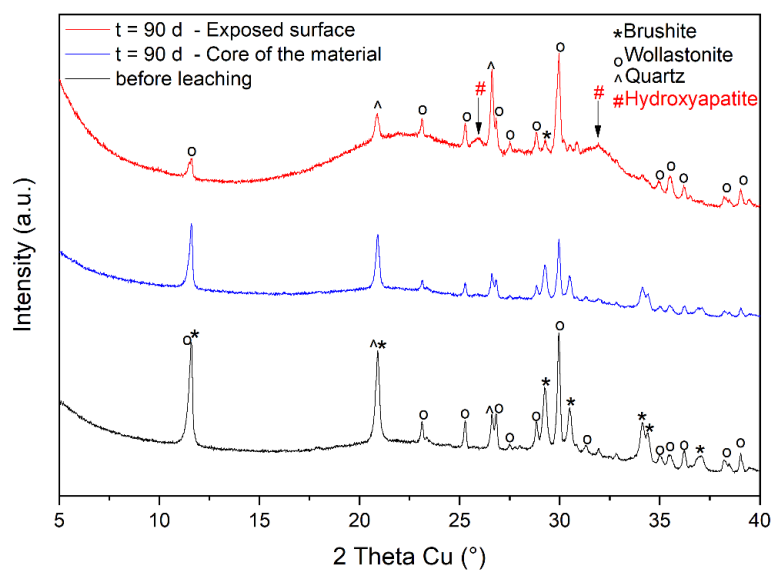


Fig. 5. X-ray diffraction patterns of the paste sample before (black), and after the leaching test (surface – red – and sound core –blue). Red XRD pattern: strong decrease of Bragg lines of brushite and increase of diffusion halos of the amorphous phases

Conclusion

This work evaluated the leaching behavior of strontium from a wollastonite-based brushite cement (WBC) paste following the ANSI/ANS-16.1 procedure and led to the following conclusions.

1. The cumulative fraction of strontium leached (CFL) at the end of the test was less than 0.2%.
2. Different models were tested to depict the CFL evolution with time. Good fit of the experimental data was obtained when two leaching mechanisms were taken into account: surface wash-off, which predominated during the first day, and diffusion in the pore network.
3. The effective diffusion coefficient mean value D_e of Sr was estimated to be as low as $4.8 \times 10^{-15} \text{ cm}^2/\text{s}$, which is at least 3 orders of magnitude smaller than typical values reported for Portland cement pastes. WBC-based materials are thus good candidates for Sr encapsulation.
4. Characterization of the leached solid showed a zonation process, involving partial dissolution of brushite and precipitation of nano-crystalline hydroxyapatite near the surface.

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