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1 Leaching resistance of hazardous waste cement solidification 2 after accelerated carbonation

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11
12 **Abstract:** When cement-based materials are carbonated, some of their physicochemical properties
13 are changed, which includes reductions of porosity by 20% and pH from 12-13 to 8-9. These
14 changes can enhance the retention ability of cementitious solids containing hazardous waste. This
15 research studied the effect of carbonation on the leaching resistance of hazardous waste cement
16 solidification. The finite element software COMSOL Multiphysics was used to simulate the process
17 of accelerated carbonation and the effect of carbonation on leaching. Laboratory tests were
18 conducted to validate the numerical models. Parametric studies from the numerical simulations
19 revealed that carbonation could significantly improve leaching retention capabilities of cementitious
20 solids containing hazardous wastes.

21
22 **Keywords:** Hazardous waste cement solidification, Accelerated carbonation, COMSOL
23 Multiphysics simulation, Particle leaching test, Leaching rate and cumulative leaching rate.

24 1. Introduction

25 With the rapid development of human society, the amount of hazardous waste produced from
26 our daily life has increased significantly. Since hazardous waste, among which nuclide waste
27 represents a significant fraction, poses potential threats to both public health and environment, it
28 must be safely disposed. Over the last few decades, more and more researchers have been working
29 in this area, trying to find better solutions. Due to political, economic or military reasons, the
30 number and scale of nuclear reactors have also increased rapidly worldwide over the years. In
31 France or some other developed countries, nuclear power produces 50% or more of their total
32 electricity, concurrently producing a large amount of nuclear waste that needs to be disposed safely
33 ^[1]. Nuclear waste contains a large amount of hazardous substances, most of which are in a liquefied
34 state. Before the final disposal, they must be solidified or immobilized. The cement solidification
35 method has become a commonly-used method to deal with nuclear waste because the process is
36 simple, technically proven and has good stability. However, since cement is porous, the retention
37 capacity for the internal particles needs to be improved ^[2]. One of the practical approaches to
38 improve this capacity is through a carbonation process to consolidate further the cement. This is
39 because carbonation will change the physicochemical properties of cement solids, such as producing
40 reductions of pH from alkaline to neutral and porosity by more than 20%. The process also increases
41 the strength of the cement solids. All of the above will affect the curing properties of solidification

1 [3].

2 There have been some applications and research on waste or sludge cement solidification
3 treated by carbonization technology. Fernandezbertos et al. [4] published a review on accelerated
4 carbonation for improving properties of cement-based materials. Guning et al. [5] demonstrated that
5 accelerated carbonation could enhance the curing property of cement solidification and reduce the
6 cost of disposal processes. Shen et al. [6] studied carbonation of cementitious materials in CO₂
7 geological storage conditions and published a study on particle exchange and porosity reduction
8 during carbonation. Other researchers showed that accelerated carbonation could increase the
9 impermeability and chemical consolidation of radionuclide solidification. This technology has been
10 used in the production of cement-based materials in the United States [7].

11 Most of the above investigations were based on experimental studies. Since leaching tests are
12 complex and time consuming, a real scenario test is normally not possible. Naturally, numerical
13 simulations can be used as an alternative tool to assess the properties of cement solidification. A
14 number of numerical models have been developed for heavy metal particles and radionuclides
15 leaching from porous media. Suarez et al. [10] developed a one-dimensional model to predict
16 leaching and pointed out that the effective diffusion coefficient was not constant during the process.
17 Batchelor [11] developed a theoretical leaching model of solidified waste, but its actual application
18 was limited by the lack of measured values for certain parameters. Birdsell et al. [12] developed a
19 leaching model to support groundwater pathway analysis of low-level solidified radionuclides.
20 Kamash et al. [13] developed a model of radionuclides leaching out from cement-based materials and
21 verified the model through experiments. It was found that all these models were based on simplified
22 theories that ignored many influential factors, and were almost exclusively of either a one- or
23 two-dimensional spatial domain that inevitably had limitations and resulted in inaccurate solutions
24 for a complex leaching process. Moreover, none of these models considered the effect of
25 carbonation on the leaching process. Due to the above limitations, it is not possible to apply any of
26 these models to simulate the leaching tests currently specified by industrial standards, such as
27 GB7023-2011 [16].

28 This paper attempts to develop a three-dimensional leaching model, coupled with an existing
29 carbonation model as proposed by Zha et al. [17], to accurately simulate cement solidification
30 leaching tests. The simulations include the processes before and after accelerated carbonation, and
31 are validated by carbonation experiments carried out also by the authors.

32 **2. The theoretical basis of modeling**

33 **2.1 The leaching model**

34 The leaching model is established according to the conservation of heat and mass. The flow of
35 the hazardous particles is driven by concentration and temperature gradients. There are three main
36 kinds of particle diffusion resistance: chemical fixation, mechanical seal and physical adsorption.

37 **2.1.1 Coupled heat and mass transfer model**

38 According to the laws of heat flow and the principle of energy conservation, and by ignoring
39 the influence of particle movement on energy [18], the energy conservation equation of a cement
40 material system can be written as:

$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot [\lambda \nabla T] \quad (1)$$

1 where ρc is the heat capacity and λ is the coefficient of thermal conductivity.

2 In the same way, one can deduce the equation of mass conservation shown as below:

$$\nabla \cdot [\rho D_T \nabla T + \rho D \nabla C] - \lambda' C + F = \rho \frac{\partial C}{\partial t} \quad (2)$$

3 where ρ is the density of material; D_T is the thermal diffusion coefficient; D is the effective
4 diffusion coefficient; λ' denotes a decay constant and $\lambda' = \ln 2 / T_h$; T_h is the half-life period of
5 the radionuclide; C is the nuclide mass per unit volume (g/cm^3), which is a function of position
6 coordinates and time; $C = f(x, y, z, t)$; and F is the quality of adsorption.

7 Gawin^[19] proposed the following equations, respectively, for effective heat capacity and
8 effective thermal conductivity coefficients:

$$\rho c = (1 - n)\rho_s c_s + n S_w \rho_w c_w + n S_g \rho_g c_g \quad (3)$$

$$\lambda = \lambda_0 [1 + A_\lambda (T - T_r)] \left(1 + 4 \frac{n S_w \rho_w}{(1 - n)\rho_s} \right) \quad (4)$$

9 where ρc is the effective heat capacity; λ is the effective thermal conductivity coefficient; ρ_w is
10 the density of pore solution; ρ_g is the density of gas in the pores; ρ_s is the density of the solid
11 skeleton; c_w is the heat capacity of pore solution; c_g is the heat capacity of gas in the pores; c_s is
12 the heat capacity of the skeleton; S_w and S_g are the saturation of liquid and gas, respectively. In
13 the simulation, S_g ranges from 0 to 1 for modeling carbonation and takes 1 for modelling leaching,
14 where $S_g + S_w = 1$ is always satisfied; λ_0 and A_λ are the fitting parameters taking $1.67 \text{ W}/(\text{m}\cdot\text{s})$
15 and 0.0005 K^{-1} , respectively^[19]. T_r is the room temperature and is taken as 298.15 K ; and D_T takes
16 a value of $4 \times 10^{-11} \text{ cm}^2/(\text{K}\cdot\text{s})$ from experiment^[18].

17 2.1.2 Effective diffusion coefficient of nuclides or heavy metals

18 A tortuosity factor can be defined as the relationship between diffusion coefficient and void
19 structure of a material^[20]:

$$D_{(n)} = D_0 \frac{n}{\tau} \quad (5)$$

20 where $D_{(n)}$ is the effective diffusion coefficient; D_0 is the initial diffusion coefficient in water; n
21 denote capillary porosity; and τ is the tortuosity factor that refers to the degree of hole twists and
22 turns of the porous media. It is worthwhile to mention that both n and τ are normally determined by
23 experimental tests, by which the effect of micro cracks or shrinkage on porosity should have been
24 collectively included, though these were not individually evaluated.

25 The tortuosity factor, which depends on many properties such as water-to-cement ratio,
26 proportion of filler in the cement, curing conditions, etc. is normally hard to determine, especially
27 when leaching of cement hydrates and release of calcium are considered. Sanchez^[21] found that
28 there is an exponential relationship between tortuosity factor and porosity:

$$\tau = n^\eta \quad (6)$$

29 Hence the relationship between porosity and diffusion coefficient is reduced to:

$$D_{(n)} = D_0 n^{1-\eta} = D_0 n^m \quad (7)$$

1 From Katz and Thompson^[22], m is set to 2.5.

2 In order to introduce chemical fixation on the diffusion coefficient, we used the following
3 equation proposed by Xue^[23]:

$$D_{(r)} = D_0 \cdot r \quad (8)$$

4 where $D_{(r)}$ is the diffusion coefficient considering chemical fixation ability of particles; r is the
5 ion coefficient representing the ratio of the number of free particles to the total number of particles.
6 In this paper, r is 0.7 and 0.06, respectively, for Sr and Cs nuclides.

7 When considering the influence of temperature on the diffusion coefficient, we followed
8 Amey's theory^[24]:

$$D_{(T)} = D_0 \frac{T}{T_0} e^{q\left(\frac{1}{T_0} - \frac{1}{T}\right)} \quad (9)$$

9 where $D_{(T)}$ is the particle diffusion coefficient at temperature T ; D_0 is the initial particle diffusion
10 coefficient at temperature T_0 ; T_0 normally takes 25°C; q is the constant of activity (related to
11 activation energy), which is related to water-to-cement ratio.

12 When considering the influence of cement hydration effects on the diffusion coefficient, for
13 short-term leaching, we used Kamash's theory for diffusion coefficient^[13]:

$$D(t) = D_0 \left(\frac{t_0}{t + t_0} \right)^\omega \quad (10)$$

14 where $D(t)$ is the diffusion coefficient at t ; D_0 is the initial diffusion coefficient at t_0 , t_0 is the
15 curing time of the cement block often taking the value of 28 d; ω is the diffusion attenuation factor
16 related to the properties of cement block and the leaching liquid, taking values of 1.1 and 10 for Sr
17 and Cs, respectively.

18 Eqs.(7-10) are the respective variations of the diffusion coefficient with a change of porosity,
19 ion coefficient, temperature or hydration time, representing a modification on the initial diffusion
20 coefficient D_0 . To include the effect of all the influences, the diffusion coefficient can be collectively
21 expressed as:

$$D' = D_0 \cdot n^{2.5} \cdot r \cdot \frac{T}{T_0} \cdot e^{q\left(\frac{1}{T_0} - \frac{1}{T}\right)} \cdot \left(\frac{t_0}{t_0 + t} \right)^\omega \quad (11)$$

22
23 It can be seen from the above that chemical fixation ability and diffusion attenuation determine the
24 diffusion properties of particles. In general, different particles (e.g., Sr and Cs) will have different
25 diffusion coefficients.

26

27 2.1.3 The selection of an adsorption equation

28 According to the model proposed by Suarez^[10], we adopted the linear isothermal adsorption
29 equation for the particles in cement solidification:

$$F_l = K_d C \quad (12)$$

1 where F_l is the linear isothermal adsorption concentration; K_d is the adsorption distribution
2 coefficient of a material, taking values, respectively of 150 ml/g for Sr and 15 ml/g for Cs in this
3 paper^[25]; C is the concentration of nuclide in the pore solution.

4 However, when it came to the choice of adsorption equation of metal ions dissolved in pore
5 solution, a Langmuir linear adsorption isotherm was employed. It was shown experimentally, that
6 Langmuir's equation described the absorption process more accurately when the pH of cement is
7 greater than 9:

$$F_e = \frac{S_m K_L C}{1 + K_L C} \quad (13)$$

8 where F_e is the amount of sorbate adsorbed at equilibrium; S_m is the maximum monolayer
9 adsorption constant (243 $\mu\text{eq/g}$ for Sr and 332 $\mu\text{eq/g}$ for Cs, respectively in this paper); K_L is
10 Langmuir adsorption distribution coefficient, taking values of 8.3 ml/g for Sr and 1.9 ml/g for Cs,
11 respectively^[26]. In general, temperature has an impact on absorption. However, on the basis of the
12 authors' best knowledge, there are no published results on the relationship between absorption and
13 temperature that can be used in the simulations. We used the adsorption constant that was obtained
14 from experimental tests carried out under the room temperature^[13]. In principal absorption will be
15 reduced with increase of temperature there exists a limiting absorption^[27] even as temperature is
16 increased further.

17 When cement solids are not carbonated, their pH is greater than 9 and a Langmuir isothermal
18 adsorption equation should be chosen. Otherwise, for the fully carbonated zone, the pH is less than
19 9 and the linear isothermal one should be used instead.

20 2.1.4 Index of leaching behavior

21 This study mainly focused on hazard waste cement solids containing nuclides. For nuclides, the
22 Chinese standard test method for leachability of low and intermediate level solidified radioactive
23 waste forms (GB/T 7023-2011) was followed. According to GB/T 7023-2011^[16], the measurements
24 of leaching resistance of cement solidification are leaching rate R_n and accumulative leaching rate
25 P_t . The leaching rate measures the speed and trend of leaching and the accumulative leaching rate is
26 directly related to the degree of leaching. The R_n and P_t are calculated, respectively, as below:

$$R_n = \frac{a_n/A_0}{(S/V)(\Delta t)_n} \quad (14a)$$

$$P_t = \frac{\sum a_n/A_0}{S/V} \quad (14b)$$

27 where a_n is the leaching quality in the n_{th} leaching cycle; A_0 is the initial leaching quality of the
28 components; S is the contact surface area between the test block and leaching liquid; V is the
29 volume of the test block; $(\Delta t)_n$ is the number of days in the n_{th} leaching cycle.

2.2 The theoretical basis of the carbonation model

2.2.1 Governing equation

With a pressure greater than 7.29 MPa and a temperature higher than 31.26 °C, the process of carbonation will be accelerated and the state of carbon dioxide is called supercritical, at which the carbon dioxide has the viscosity and diffusion coefficient close to a gas while the density is close to that of a liquid. Under these conditions, it will be easier for carbon dioxide to penetrate into a porous media like cement and take part in carbonation reactions.

In this paper, we use a carbonation model that is different from the commonly-used one established by Saetta^[28] for natural carbonation. We use solubility instead of concentration of CO₂ in the pore water, since supercritical carbonation takes place in an environment where there is always sufficient CO₂ in the pores of cement solids to keep the pore water constantly in a saturated state. Then, we utilize the following PDEs consisting of Darcy's law (Eq.15a), the conservation equation of energy (Eq. 15b), conservation of mass (Eq.15c), the reaction rate equation (Eq.15d) and the concentration equation of carbon dioxide (Eq.15e)^[17]:

$$\vec{u}_\alpha = -\frac{kk_{r\alpha}}{\mu_\alpha}(\Delta P_\alpha - \rho_\alpha \vec{g}) \quad (15a)$$

$$\rho c \frac{\partial T}{\partial t} = \nabla \cdot (\lambda \nabla T) - (C_g \rho_g \vec{u}_g + C_w \rho_w \vec{u}_w) \nabla T \quad (15b)$$

$$\frac{\partial(nS_\alpha \rho_\alpha)}{\partial t} + \nabla \cdot (\rho_\alpha \vec{u}_\alpha) = q_\alpha \quad (15c)$$

$$\frac{\partial R_c}{\partial t} = \alpha_1 f_1(h) f_2(g_v) f_3(R_c) f_4(T) \quad (15d)$$

$$\frac{\partial m_{CO_2}}{\partial t} = \frac{\partial g}{\partial t} \quad (15e)$$

where \vec{u}_α is the Darcy flow velocity of component α ; k is the intrinsic permeability of the material, which is related to its porosity; $k_{r\alpha}$ is the relative permeability of component α ; μ_α is the dynamic viscosity of component α ; P_α is the pressure of component α ; ρ_α is the density of component α ; \vec{g} is the acceleration of gravity, which is ignored in our model; q_α is the change of the source term caused by chemical reaction or precipitation of component α ; λ is the equivalent thermal conductivity coefficient of the material; ρc is the equivalent heat capacity of the material; g is the concentration of carbon dioxide in the pore solution; and m_{CO_2} is the solubility of carbon dioxide in the pore liquid, which is related to pressure and temperature^[29].

The five equations (15a-15e) are coupled PDEs with five variables, including degree of carbonation R_c , pressure of gas P_g , pressure of water P_w , concentration of carbon dioxide in pore solution g and temperature T , that are the governing equations of supercritical carbonation.

2.2.2 Initial values and boundary conditions

In order to solve the above PDEs, one needs to measure the initial values and boundary conditions. The initial values of the five independent variables are imposed as shown below:

$$R_c = R_{c0} = 0, P_g = P_{g0}, P_w = P_{w0}, g = g_0 = 0 \text{ and } T = T_0$$

The boundary conditions on the insulated boundaries, including the pressure of carbon dioxide P_g , the pressure of the liquid P_w and the temperature T , satisfy the following equations:

$$1 \quad \vec{n} \cdot \nabla P_g = 0, \quad \vec{n} \cdot \nabla P_w = 0 \quad \text{and} \quad \vec{n} \cdot \nabla T = 0$$

2 On the inflow boundary, the pressure of carbon dioxide P_g , the pressure of the liquid in the pore P_w
3 and the temperature T on the boundary are shown as below:

$$4 \quad P_g = P_{g,sur}, \quad P_w = P_{w,sur} \quad \text{and} \quad T = T_{sur}$$

5 **2.3 Relation between degree of carbonation and porosity**

6 Through the introduction of the theories of accelerated carbonation and leaching processes, we
7 know that in the process of leaching, porosity directly affects the diffusion coefficient of the
8 particles. In order to evaluate leaching, how carbonation changes porosity is essential. In this study,
9 we used the relationship proposed by Kwan and Song^[30] as shown below:

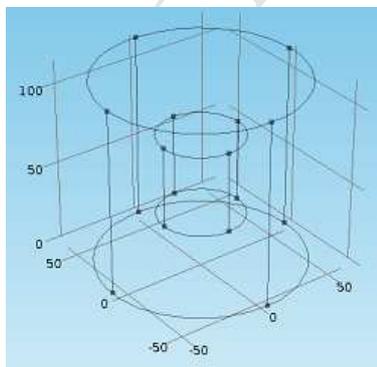
$$10 \quad n = f(R_c) = \begin{cases} n_0(1 - 0.5R_c) & 0 \leq R_c \leq 0.4 \\ 0.8n_0 & 0.4 \leq R_c \leq 1 \end{cases} \quad (16)$$

11 where n_0 is the initial value of capillary porosity before accelerated carbonation, taken as $0.13^{[31]}$ in
12 this paper. R_c is the degree of carbonation defined as $R_c = c/c_{max}$; c and c_{max} are the current and the
13 maximum amount of calcium carbonates, respectively.

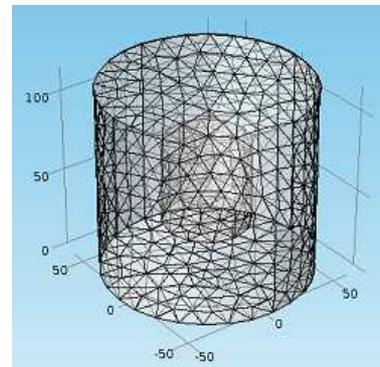
14 **3. Coupled model of carbonation and leaching**

15 FEM simulations were conducted using COMSOL, as virtual tests, for cement blocks in the
16 containers filled with deionized water during the test time. Following the guidelines in GB/T
17 7023-2011, we replaced the leach liquid at the 1st, 3rd, 7th, 10th, 14th, 21st, 28th, 35th and 42nd
18 days. The replaced water was tested for leaching and cumulative leaching rates. The model is shown
19 in Fig.1(a). According to GB/T 7023-2011, the chosen size of the cement block is $\phi 50 \text{ mm} \times 50 \text{ mm}$,
20 and the size of the leaching container is $\phi 120 \text{ mm} \times 150 \text{ mm}$. The height of the liquid inside the
21 container is 106.2 mm and the total volume of the leaching liquid is 1.2 L.

22 Boundary layer meshes were used at the boundary of the cement block and automatic
23 tetrahedron meshing in other parts. The total number of elements is 12158. The FE-meshes are
24 shown in Fig.1(b). In order to detect the concentration of waste particles in the leaching liquid, we
25 added 40 numerical probes uniformly distributed in the solution to record the liquid concentration.



(a) Model geometry



(b) Model meshing

Fig. 1 Test unit diagram

26 However, in order to calculate the required measurements continuously throughout the

1 carbonation and then the leaching processes using the same model, the simulations consisted of the
2 following two steps to decouple the processes of carbonation and leaching. The first step was to
3 simulate supercritical carbonation. We set the diffusion coefficient of internal particles as
4 infinitesimal to achieve the effect of carbonation without any leaching. The second step was for
5 leaching assuming that the carbonation process had completed. We then used the desired diffusion
6 coefficient of the particles and set the velocity of carbonation to zero to start leaching without
7 carbonation.

8 Following the guidelines in GB/T 7023-2011, the simulation included two processes within
9 each of the leaching phases. The first process was the normal leaching process for evaluating
10 leaching resistance, during which the flux at the boundary of the container was set to zero to prevent
11 any particles from leaching out of the container. The second process was for the moment of
12 replacing the leaching solution prior to the next leaching phase. To do this, both the flux of the
13 container and the diffusion coefficient of the particles in the leaching liquid were set to a large
14 number to allow fast deionization and achieve zero ion concentration of the leaching liquid. During
15 the leaching process, the cement block and leaching liquid were modelled as the same material with
16 different diffusion coefficients that are much greater in the leaching liquid than in the cement block,
17 in order to simulate particles leaching from the waste solids into the leaching liquid.

18 The simulation of the leaching process of the particles, Sr, was carried out for two different
19 conditions imposed on the cement blocks, i.e., the carbonation condition shown in Fig.2 before
20 leaching and the leaching process without applying supercritical carbonation.

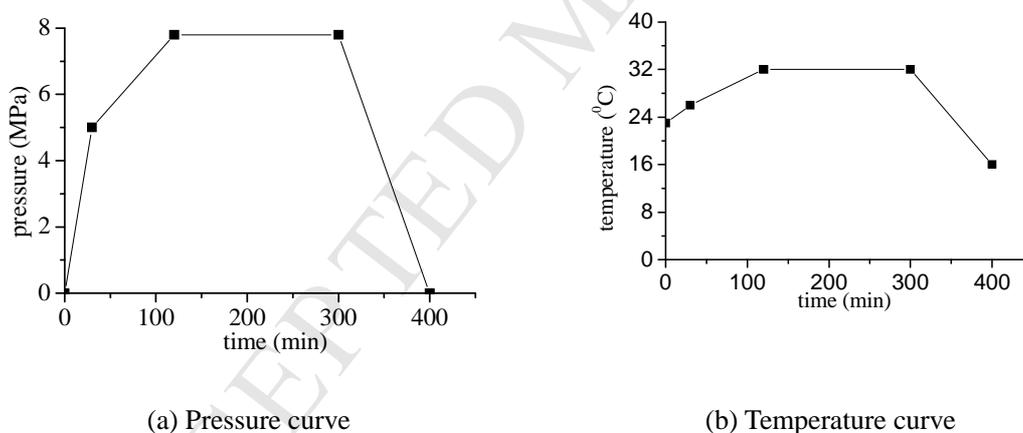


Fig.2 Supercritical carbonation condition

21 The predicted degree of carbonation R_c from the simulation is shown in Fig.3 under the
22 supercritical conditions shown in Fig. 2, where a scale of 1 indicates that full carbonation has
23 occurred. A close examination of the results shows that the carbonation depth is about 1 mm and
24 the transition zone is about 13 mm. The 3D carbonation results for the same cement block under
25 natural conditions (0.1 MPa and 25 °C) for 4 h are shown in Fig.4, in which there is virtually no
26 sign of carbonation.

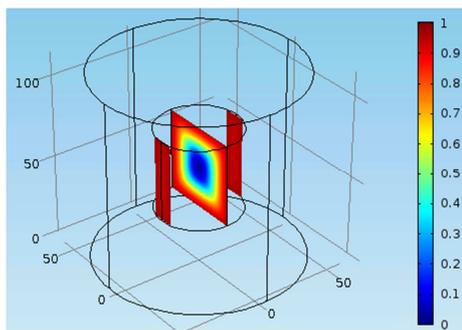


Fig.3 Degree of carbonation (supercritical)

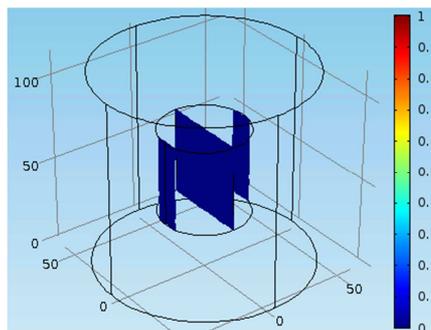


Fig.4 Degree of carbonation (natural)

- 1 The simulated concentrations of Sr in the leaching solution under the above two conditions
- 2 taken before replacing the leaching liquid are shown in Fig.5, from which the leaching rates are
- 3 calculated and presented in Fig. 6.

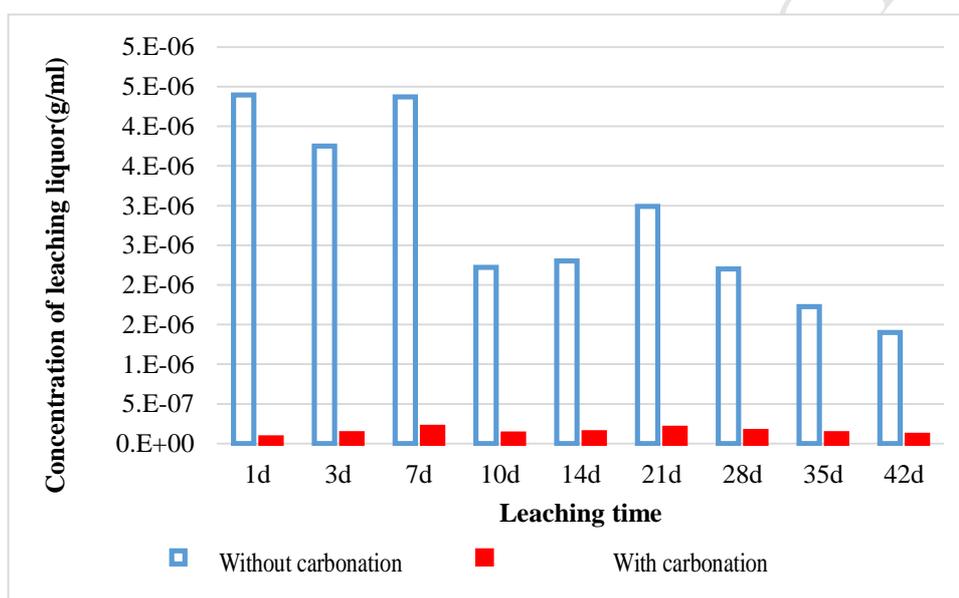


Fig.5 Concentration of leaching solution

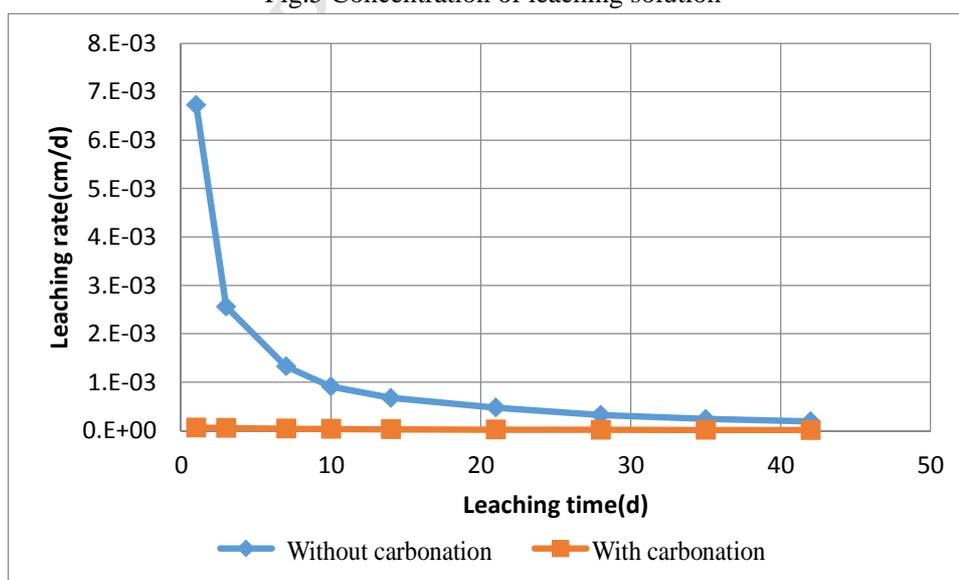


Fig.6. Leaching rate curve

It is worthwhile to mention that the above model did not include the leaching effects of cement hydrates on the overall leaching process, though to some extent some of the effects might have been partially included due to the use of various material constants obtained from the leaching tests of other researchers. Detailed analyses of the release of the hydrates will be the subject of future studies.

1 4. Experiment

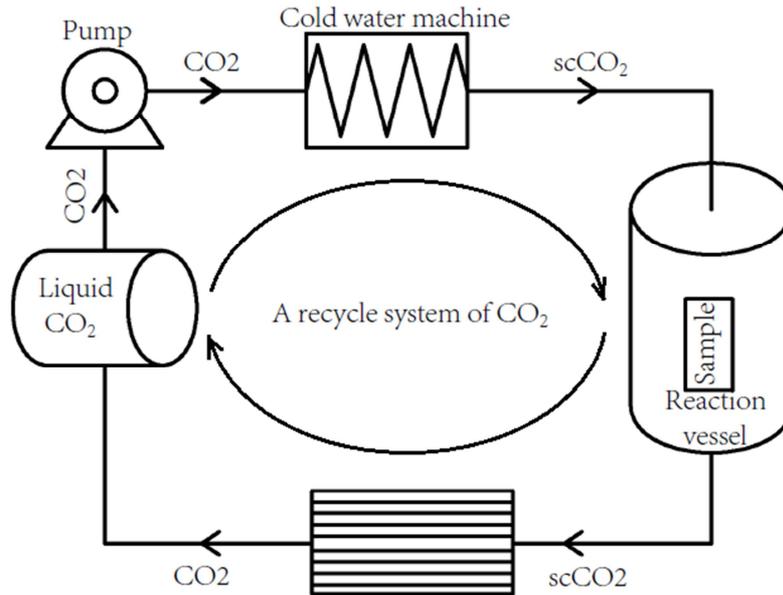
2 To verify the numerical model, 12 test blocks, which contain either Cs or Sr (the mass ratio of
3 these elements is about 0.58) with a water-to-cement ratio of 0.37 by mass, were made for
4 laboratory tests. All the blocks had the same dimensions as those used in the simulation. They were
5 equally divided into four groups, two of which had added Sr and the others had added Cs. Within
6 the groups with the same added chemicals, one group was carbonated while the other was not.
7 Average leaching rates were taken from each of the groups and are compared in this Section. The
8 specifications of the group of blocks are shown in Table 1.

9 Table 1. Leaching test samples

| Chemicals added | Sample number | Leaching temperature (°C) | Carbonation |
|-------------------|--------------------|---------------------------|-------------|
| Strontium nitrate | Sr-7, Sr-10, Sr-12 | 25 | No |
| | Sr-1, Sr-2, Sr-6 | 25 | Yes |
| Cesium chloride | Cs-5, Cs-6, Cs-14 | 25 | No |
| | Cs-2, Cs-4, Cs-10 | 25 | Yes |

10 4.1 Carbonation experiment

11 The procedure of the carbonation experiment is shown in Fig.7. Gaseous carbon dioxide
12 flowing out from the gas cylinders turns into a supercritical state after flowing through the high
13 pressure air pump and the temperature adjusting machine. The supercritical carbon dioxide then
14 flows into the reaction vessel and takes part in carbonation with the test blocks. Finally, the
15 remaining carbon dioxide flows through a switching equipment back to the gas cylinders. This
16 experiment is conducted in a closed loop system, so that we can recycle the remaining carbon
17 dioxide.



1
2

Fig.7. Design schedule and procedure of accelerated carbonation

3 The carbonation condition is the same as shown in Fig.2. After carbonation, a block was cut to
4 show the internal section. The carbonation depth was measured using phenolphthalein, by which the
5 fully carbonated area did not exhibit a red color. The measured carbonation depth is shown in Fig.8,
6 where the carbonated depths in eight random locations were measured. The measured average was 1
7 mm and was consistent with the simulation results from the previous Section.



Fig.8 Carbonation depth

8 In order to estimate the amount of carbon dioxide absorbed by the test block during the process
9 of carbonation, the mass of the blocks was measured before and after carbonation, so that the
10 percentage of mass increase were calculated as shown in Table 2.

11

Table 2 Mass increase percentage

| Sample number | Mass before carbonation (g) | Mass after carbonation (g) | Mass increase percentage (%) | Average mass increase percentage (%) |
|---------------|-----------------------------|----------------------------|------------------------------|--------------------------------------|
| Cs-2 | 193.86 | 199.57 | 2.914 | 2.946 |
| Cs-4 | 193.07 | 198.34 | 2.694 | |

| | | | |
|-------|--------|--------|-------|
| Cs-10 | 193.86 | 199.57 | 2.914 |
| Cs-5 | 192.06 | 197.97 | 3.036 |
| Cs-6 | 194.20 | 200.27 | 3.096 |
| Cs-14 | 194.07 | 200.12 | 3.087 |
| Sr-1 | 193.95 | 199.50 | 2.866 |
| Sr-2 | 193.90 | 198.18 | 2.207 |
| Sr-6 | 194.31 | 198.91 | 2.367 |
| Sr-11 | 194.19 | 202.86 | 4.465 |
| Sr-14 | 193.42 | 201.65 | 4.255 |
| Sr-15 | 195.44 | 202.85 | 3.791 |

3.333

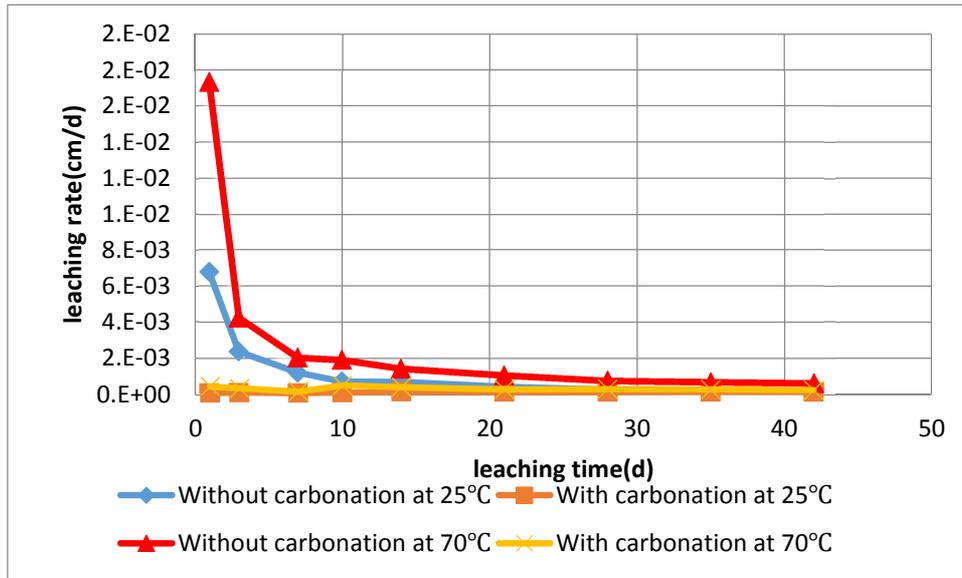
1 From Table 2, it can be seen that the blocks with added chemicals have an approximate mass
2 increase ratio of about 3 %.

3 **4.2 Leaching test**

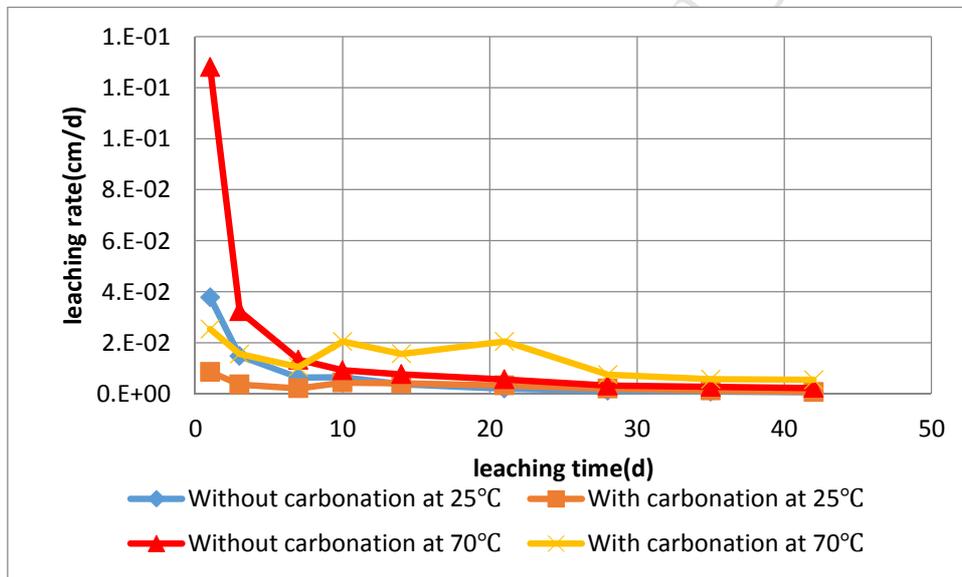
4 To evaluate the effect of carbonation on leaching, the pairs of groups (Table 1) containing the
5 same added chemicals were tested and compared for leaching, giving us the results for blocks with
6 and without carbonation. The test blocks were produced from ordinary Portland cement and the
7 water was deionized by an ultra-pure water machine.

8 The leaching temperature was controlled at 25 °C in the oven. The leaching solution at ages of
9 1, 3, 7, 10, 14, 21, 28, 35 and 42 d were replaced and measured for ion concentrations that were
10 used to calculate the leaching rates of the cement blocks. The measured average leaching rates of Sr
11 and Cs from the blocks with and without carbonation are shown in Fig.9, respectively. Similar tests
12 were also carried out at 70 °C and the respective results are shown also in Fig.9.

13 Fig.9 shows all the measured leaching rates of the blocks listed in Table 1 against leaching time
14 and two different temperatures. Fig.9 (a) and (b) are, respectively, for leaching of Sr and Cs. From
15 Fig.9 (a), we can see that the leaching rates of Sr are all reduced significantly due to carbonation.
16 This mainly attributes to the fact that carbonation improves the compactness of cement
17 solidification resulting in a positive effect on retention of the internal particles. However, from
18 Fig.9(b), an increase of leaching rate of Cs after carbonation occurs between day 5 and day 25 at
19 70 °C. The reasons for this are not clear from the tests. More tests and long term leaching tests
20 lasting several years are needed for further study.



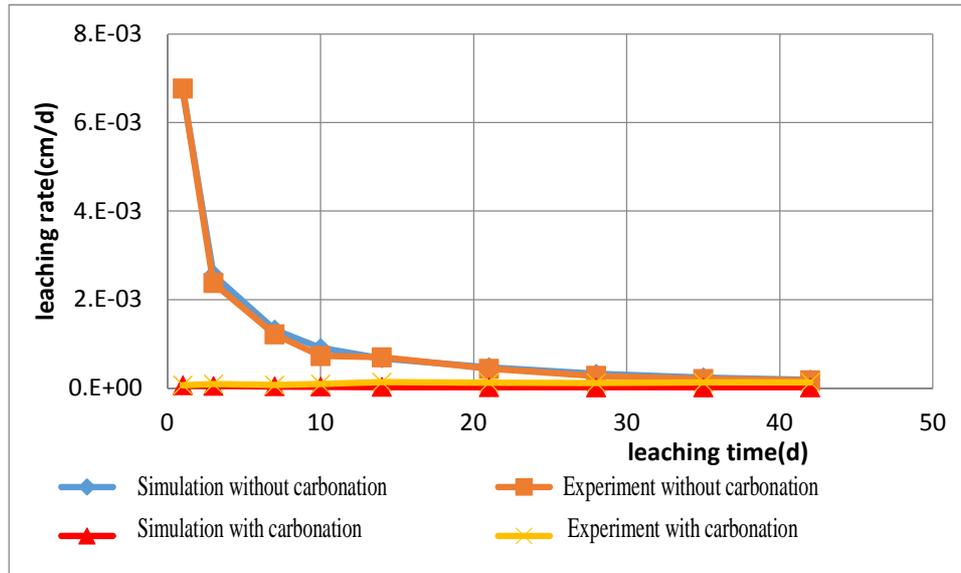
a) Leaching rate of Sr



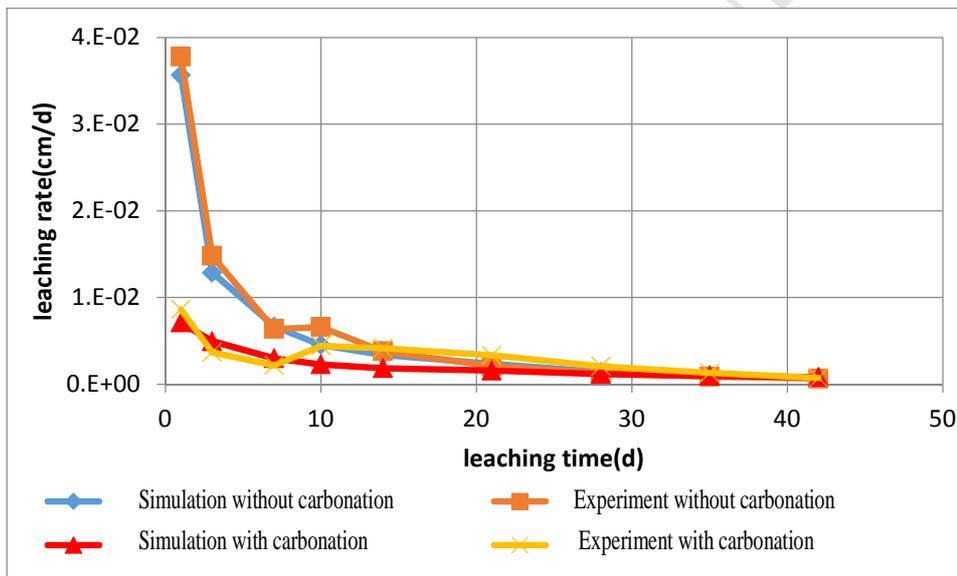
b) Leaching rate of Cs

Fig.9. Leaching rate from experiments

In order to validate the numerical models, Fig.10 presents comparisons between the experimental and the simulation results of Sr and Cs leaching at 25 °C. The comparisons show that the numerical models developed in this paper can accurately predict the process of leaching.



(a) Leaching rate of Sr



(b) Leaching rate of Cs

Fig.10 Comparisons of experimental and simulation results

1 5. Conclusion

2 A three-dimensional model of particles leaching from cement solids has been developed in this
 3 paper. The effects of temperature, time, chemical consolidation, properties of cement can all be
 4 taken into account by this model.

5 Both carbonation and leaching tests were conducted in this research, which have shown that
 6 accelerated or supercritical carbonation can reduce the leaching rate and effectively improve the
 7 impermeability of cement solidification.

8 The experimental tests were also used to validate the developed three-dimensional leaching

1 model. The satisfactory comparisons suggested that the combined carbonation and leaching model
2 developed here can accurately simulate the processes of leaching tests with or without supercritical
3 carbonation.

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Highlights

- We developed a multi- physics and –phase model for supercritical carbonation and leaching of cement based materials.
- We conducted experiments to validate the model.
- We investigated the impact of carbonation on the retention capacity of cement.
- We studied the effect of various physical properties on the leaching process of Sr and Cs ions.