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Leaching resistance of hazardous waste cement solidification after accelerated carbonation

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ABSTRACT

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

1. Introduction

With the rapid development of human society, the amount of hazardous waste produced from our daily life has increased significantly. Since hazardous waste, among which nuclide waste represents a significant fraction, poses potential threats to both public health and environment, it must be safely disposed. Over the last few decades, more and more researchers have been working in this area, trying to find better solutions. Due to political, economic or military reasons, the number and scale of nuclear reactors have also increased rapidly worldwide over the years. In France or some other developed countries, nuclear power produces 50% or more of their total electricity, concurrently producing a large amount of nuclear waste that needs to be disposed safely [1]. Nuclear waste contains a large amount of hazardous substances, most of which are in a liquefied state. Before the final disposal, they must be solidified or immobilized. The cement solidification method has become a commonly-used method to deal with nuclear waste because the process is simple, technically proven and has good stability. However, since cement is porous, the retention capacity for the internal particles needs to be improved [2]. One of the practical approaches to improve this capacity is through a carbonation process to consolidate further the cement. This is because carbonation will change the physicochemical properties of cement solids, such as producing reductions of pH from alkaline to neutral and porosity by more than 20%. The process also increases the strength of the cement solids. All of the above will affect the curing properties of solidification [3].

There have been some applications and research on waste or sludge cement solidification treated by carbonization technology. Fernandezbertos et al. [4] published a review on accelerated carbonation for improving properties of cement-based materials. Guning et al. [5] demonstrated that accelerated carbonation could enhance the curing property of cement solidification and reduce the cost of disposal processes. Shen et al. [6] studied carbonation of cementitious materials in CO_2 geological storage conditions and published a study on particle exchange and porosity reduction during carbonation. Other researchers showed that accelerated carbonation could increase the impermeability and chemical consolidation of radionuclide solidification. This technology has been used in the production of cement-based materials in the United States [7,8].

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Most of the above investigations were based on experimental studies. Since leaching tests are complex and time consuming, a real scenario test is normally not possible. Naturally, numerical simulations can be used as an alternative tool to assess the properties of cement solidification. A number of numerical models have been developed for heavy metal particles and radionuclides leaching from porous media. Suarez et al. [9] developed a one-dimensional model to predict leaching and pointed out that the effective diffusion coefficient was not constant during the process. Batchelor [10] developed a theoretical leaching model of solidified waste, but its actual application was limited by the lack of measured values for certain parameters. Birdsell et al. [11] developed a leaching model to support groundwater pathway analysis of low-level solidified radionuclides. Kamash et al. [12–14] developed a model of radionuclides leaching out from cement-based materials and verified the model through experiments. It was found that all these models were based on simplified theories that ignored many influential factors, and were almost exclusively of either a one- or two-dimensional spatial domain that inevitably had limitations and resulted in inaccurate solutions for a complex leaching process. Moreover, none of these models considered the effect of carbonation on the leaching process. Due to the above limitations, it is not possible to apply any of these models to simulate the leaching tests currently specified by industrial standards, such as GB7023-2011 [15].

This paper attempts to develop a three-dimensional leaching model, coupled with an existing carbonation model as proposed by Zha et al. [16], to accurately simulate cement solidification leaching tests. The simulations include the processes before and after accelerated carbonation, and are validated by carbonation experiments carried out also by the authors.

2. The theoretical basis of modeling

2.1. The leaching model

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

2.1.1. Coupled heat and mass transfer model

According to the laws of heat flow and the principle of energy conservation, and by ignoring the influence of particle movement on energy [17], the energy conservation equation of a cement material system can be written as:

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

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

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

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

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

Gawin [18] proposed the following equations, respectively, for effective heat capacity and effective thermal conductivity coefficients:

$$\rho c = (1-n)\rho_s c_s + nS_w\rho_w c_w + nS_g\rho_g c_g \tag{3}$$

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

where ρc is the effective heat capacity; λ is the effective thermal conductivity coefficient; ρ_w is the density of pore solution; ρ_g is the density of gas in the pores; ρ_s is the density of the solid skeleton; c_w is the heat capacity of pore solution; c_g is the heat capacity of gas in the pores; c_s is the heat capacity of the skeleton; S_w and S_g are the saturation of liquid and gas, respectively. In the simulation, S_g ranges from 0 to 1 for modeling carbonation and takes 1 for modeling leaching, where $S_g + S_w = 1$ is always satisfied; λ_0 and A_λ are the fitting parameters taking 1.67 W/(m·s) and 0.0005 K^{-1}, respectively [18]. T_r is the room temperature and is taken as 298.15 K; and D_T takes a value of 4×10^{-11} cm^2/(K·s) from experiment [17].

2.1.2. Effective diffusion coefficient of nuclides or heavy metals

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

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

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

The tortuosity factor, which depends on many properties such as water-to-cement ratio, proportion of filler in the cement, curing conditions, etc. is normally hard to determine, especially when leaching of cement hydrates and release of calcium are considered. Sanchez [20] found that there is an exponential relationship between tortuosity factor and porosity:

$$\tau = n^\eta \tag{6}$$

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

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

From Katz and Thompson [21], m is set to 2.5.

In order to introduce chemical fixation on the diffusion coefficient, we used the following equation proposed by Xue [22]:

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

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

When considering the influence of temperature on the diffusion coefficient, we followed Amey's theory [23]:

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