Leaching and Adsorption Modeling of Boron in Fly Ash and Nonlinear Transport Analysis

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ABSTRACT

This paper presents a mathematical model based on mass conservation which was developed to simulate boron sorption - desorption process. In the model, ion solution and re-solidification are generally path-dependent. The formulae identifies material characteristic which is examined with experimental data. This assessment method is closely linked with the DuCOM-COM3 life-span simulator for concrete and reinforced concrete. For verification, a simple one dimensional finite element was used to simulate migration of boron ion into the liquid. The model exposed a good prediction of boron leaching in de-ionized water as compared with the experimental result. Some cementitious material applied to surround the dumped fly ash can be simulated with the model for boron migration from fly ash into underground.

KEYWORDS: boron, leaching, sorption, desorption

INTRODUCTION

Fly ash is one of the sources of boron, which will be dissolved into underground water when it contact with water. Boron concentration in the soil is considered a critical level for toxicity when it exceeds a concentration of 2.5 mg/l in the soil solution. Boron ions are also adsorbed rapidly by the surface of fly ash particles. A specific problem of interest for leachable boron from fly ash is adopted as one of the harmful substances to humans and plants when it is highly concentrated in nature. A comprehensive observation is necessary to determine soluble boron from fly ash in the aqueous media. Process of sorption and de-sorption of boron ions was found less than one week as reported by Keren[1,3]. After the dissolution of ion from inside the ash particles, ionized boron is captured in liquid again as an adsorbed one which is fixed on the surface of solids including soil particles, clay and fly ash itself as reported by Goldberg[2]. Then, experimental results are needed to develop a mathematical model of boron leaching from fly ash. The requirement of mass conservation was formulated to simulate the boron release from fly ash to the natural environment.

A serial account of thermodynamic problems regarding an examination of liquid-phase equilibrium is also the substantial scope in this paper. The thermodynamic complexity of leaching is explained by coupling the irreversible ionization process with the recoverable

course of adsorption-desorption action. It means that the ion solution and re-solidification are generally path-dependent. Here, an experimental investigation is required to obtain initial boron concentration in solid and saturated ion phase. A computational approach to predict both release and capture of the boron ion is presented based upon the finite element discretization. This computational method was validated by using experimentally identified material parameters. i.e., the final adsorption capacity, dissolution capacity of leaching from solid and their intrinsic half time which represents the stability and transient process of these chemical events.

According to some previous research, boron leaching from fly ash occurs in a very short time. This process occurs without revitalization to initial solids which are analogous to the plastic evolution of yield solid of mechanics. The stability process which occurs rapidly is necessary to be observed and investigated in an ideal condition. A problem to be solved, however, is how to generate the relation between boron in solid-liquid equilibrium from the experimental result to a fundamental approach for mathematical model. The model is linked with a simulator named DuCOM-COM3 which has been developed for life-span concrete simulation and problems on calcium leaching in concrete proposed by Nakarai[6,7,8].

The contribution of this paper is to provide phenomena of liquid stability of boron migration and the resulting of boron sorption-desorption in the aqueous media through numerical analysis. Ones the model of boron migration is established, it can be developed for the ion migration for other toxic substances. Thus, the model can be applied to simulate and predict the problem in macro-scale. Obviously, it is very useful for practical application then, to simulate a long term migration of boron in nature.

EXPERIMENTAL INVESTIGATION

A class F fly ash from Sapporo, Japan, having 2.33 g/cm3 of density, Blaine's surface area of 3660 cm2/g and density of 1.931 g/ml is adopted. Its initial total boron (B_{tot}) contained in chemical composition of fly ash is 120 μgr/gr.

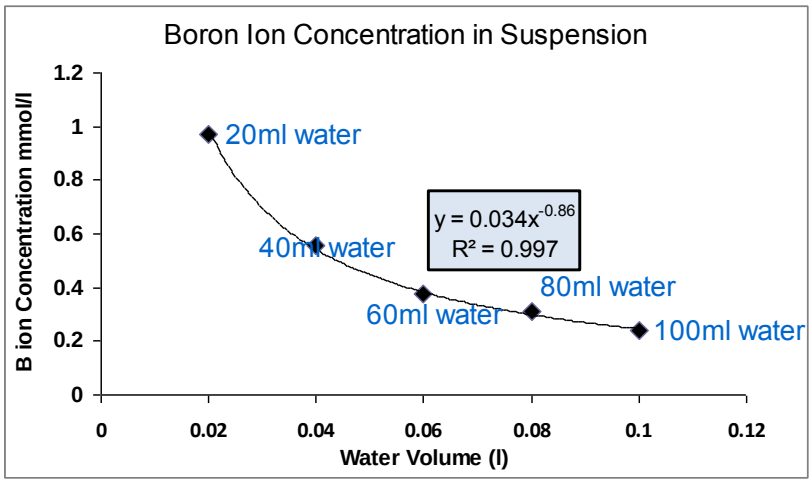


Figure 1 Boron concentration in solution

Fly ash sample of 10gr was prepared and mixed with 20ml, 40ml, 60ml, 80ml, and 100ml of distilled water. The suspension was then filtered with filter paper before ICP analysis for boron determination (B_{ion}). The result was given in Figure 1.
The experimental results shown in Figure 1 shows important information about boron released from fly ash that relation between boron concentration and the dilute solution can be expressed by the exponential equation.
From the equation obtained in Figure 1, an extrapolation is employed for obtaining boron concentration in saturated condition (B_{satu}) where the amount of water is very small. Boron ion in saturated condition is equal to 3.70mmol/l or 0.016mmol considering the volume of 10gr fly ash is 0.0043 liter with density of fly ash of 2.33gr/cm3 .Since the total boron in fly ash is a given value (120μgr/gr), then boron in solid is obtained from the reduction in the total value of boron. This process is shown in Figure 2. Finally, boron concentration in solid is 0.095mmol or equal to 22,060mmol/m^3 with density of fly ash of 2.33gr/cm^3.

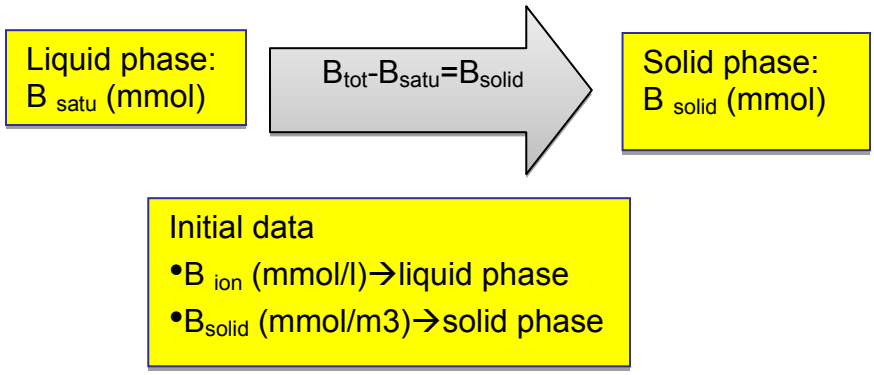


Figure 2 Intrinsic parameters

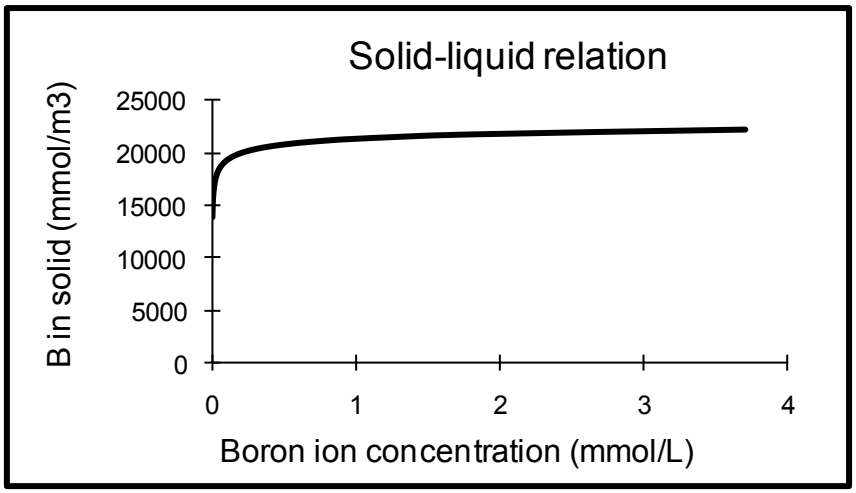


Figure 3 Solid –liquid relation of boron

Information obtained from Figure 3 was then are necessary as data input for the proposed method to simulate boron released from fly ash. Boron in solid and saturated ion has initial concentration of 22,060mmol/m^3 and 3.70mmol/l respectively. These

values may be different considering the ash varies in its composition depending upon the coal where it is mined

MASS CONSERVATION OF BORON

In thermodynamics equilibrium, total energy and mass flow must fulfil the conservation law. The mass conservation of boron in both solid and ion phases in the system is derived in Equation (1). This equation provides total boron in solid phase, adsorbed boron ions and boron ions in the solution.

$$\frac{\partial}{\partial t}\left(\phi \cdot S \cdot B_{ion}\right) + \frac{\partial B_{solid}}{\partial t} + \frac{\partial B_{ad}}{\partial t} - divJ_{ion} = 0 \qquad (1)$$

where ϕ is porosity [m^3/m^3] of the composite including voids, S is degree of saturation in the voids, B_{ion} is the molar concentration of boron ions in the liquid phase [mmol/l], B_{solid} is the amount of boron in the solid phase [$mmol/m^3$], B_{ad} is the amount of adsorbed boron trapped on the micro-particle's surfaces and/or micro-pore walls [$mmol/m^3$] and J_{ion} is the flux of boron ions [$mmol/m^2$-s].

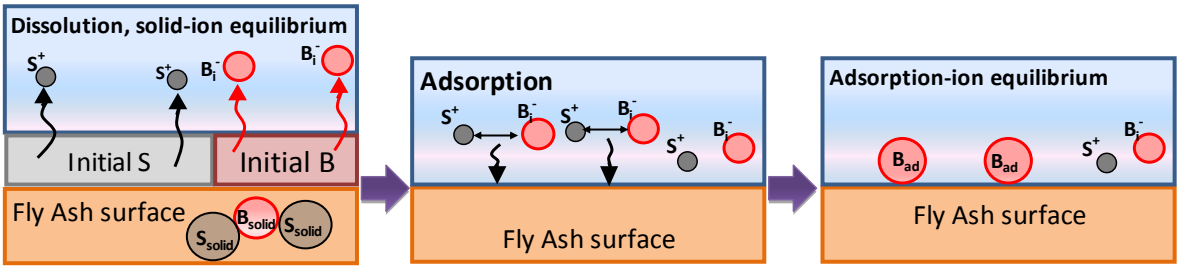


Figure 4 Sorption-desorption process of boron

The first term expresses the increasing rate in ionized boron, and the second is the one of solidified boron whose thermodynamic state is created just after being coal-fired. This term has to be negative definite (leaching) without revitalization to initial solids. The third term is to represent the boron adsorption on the micro-solid surfaces. The fourth term of the equation represents the flux term. The illustration of boron sorption - desorption is given in Figure 4. When the contaminant that contains initial boron in solid and ion phase contacts with its medium, the process of dissolution begins. Initial boron in solid phase releases its ions to reach solid-ion equilibrium at a particular leaching time. The relation between the solid and liquid phase of boron is represented as the dissolution from solid to liquid at this state. Besides the first reaction, the second reaction on boron adsorption to capture boron ions, which has been released at the first reaction, also starts to satisfy adsorption-ion equilibrium at a determined half-time. This equilibrium state represents precipitation of boron that is adsorbed by fly ash surface. Boron ions change from liquid phase to solid phase as adsorbed boron.

If the composite of unit mass may include sand and clay with fly ash for example, the third term shall cover the whole surface to adsorb boron. In this model, sorption – desorption process is assumed to be path-independent and updated rate-type formula

is thought to be valid similar to the elasticity of solid materials. As the migration of boron is possible solely in the form of ion in pore water, the fourth term represents the divergence of boron ion. The overall process is integrated in DuCOM program as illustrated in Figure 5.

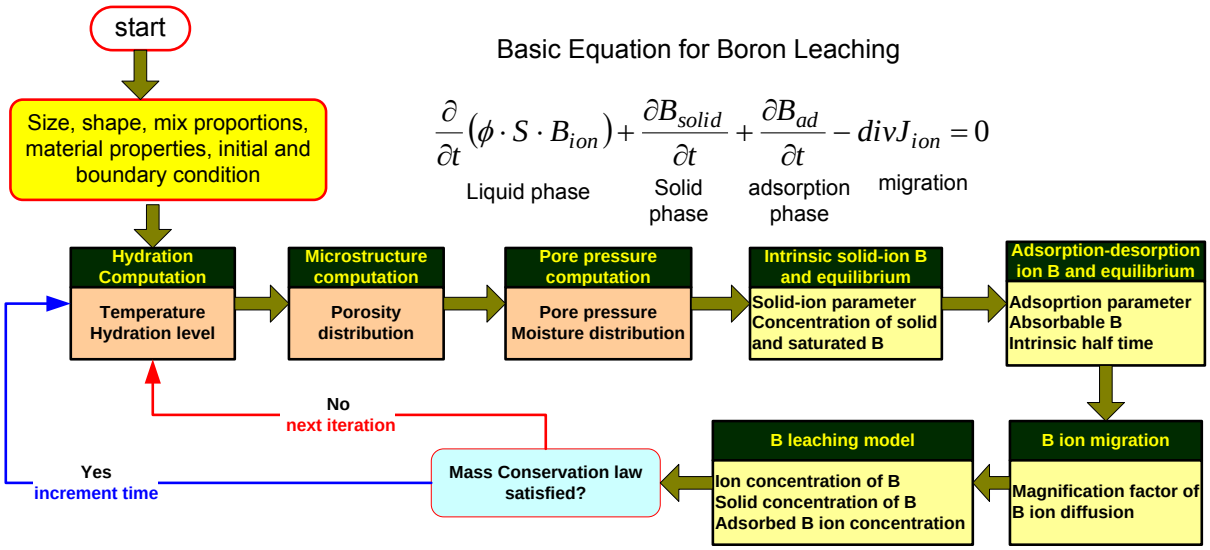


Figure 5 DuCOM Scheme for chemo-physical coupled system

EQUILIBRIUM OF INTRINSIC SOLID AND IONIZED BORON

The following formulation of path-dependency as expressed in Equation (2) is assumed for leaching of intrinsic boron of solid phase into the pore water.

$$\frac{\partial B_{solid}}{\partial t} = -\frac{k}{h_{solid}}, \quad k = B_{solid} - B_{solid,eq}(B_{ion}) > 0,$$
$$B_{solid,eq} = B_{solid,\lim} \cdot \left(\frac{B_{ion}}{B_{ion.satu}} \right)^{C_{solid}} \tag{2}$$

where $B_{solid,eq}$ is the isothermal amount of solidified boron statically equilibrated with B_{ion}, h_{solid} is the intrinsic leaching time to thermodynamic equilibrium. The solid-ion isotherm is specified by the intrinsic solid amount of boron ($B_{solid,eq}$), the saturated molar concentration of boron ion ($B_{ion,satu}$) and the poly-nominal order parameter (C_{solid}).

Based on the experiment result, the intrinsic parameter of $B_{ion\ satu}$, B_{solid}, , h_{solid}, and C_{solid} are the input values. Equation (2) can be express as relation between B solid-ion coupled with time dependent as illustrated in Figure 6.

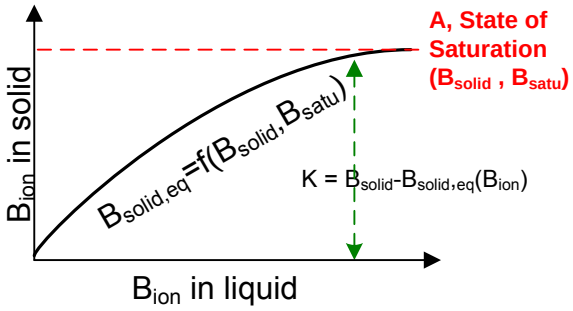


Figure 6 Ionized boron model

ADSORPTION-DESORPTION ISOTHERMAL EQUILIBRIUM

Experimental observation shows the boron leaching and re-adsorption process occurs rapidly , so Equation (3) explains the simple linear rate modeling of boron adsorption.

$$\frac{\partial B_{ad}}{\partial t} = -\frac{B_{ad} - B_{ad,eq}(B_{ion})}{h_{ad}}, \qquad B_{ad,eq} = B_{ad,\lim} \cdot \left(\frac{B_{ion}}{B_{ion.satu}} \right)^{C_{ad}} \tag{3}$$

where $B_{ad,eq}$ is the isothermal amount of adsorbed boron statically equilibrated with B_{ion}, h_{ad} is the intrinsic e-half time on the way to the state of thermodynamic equilibrium. The rate of adsorption is assumed to be linear-proportional to the difference between the updated adsorbed boron and the statically equilibrated one, which is specified by the equation of state as follows. In this modeling, the static isotherm of equilibrium is formulated by the maximum possible adsorption of boron ($B_{ad,eq}$) in the composite, the saturated molar concentration of boron ion ($B_{ion,satu}$) and the polynominal order parameter (C_{ad}). These three values are material constants to be input in analysis.

the exact solution by integrating the differential is given as in Equation (4) where the ion concentration is kept constant.

$$B_{ad} - B_{ad,eq} = \left(B_{ad} - B_{ad,eq}\right)\Big|_{t=0} \cdot \exp\left(-\frac{t}{h_{ad}}\right) \tag{4}$$

Where t=h_{ad} gives the halftime to (1/*e*) convergence to the static equilibrium of the thermodynamic system. Then, the value of h_{ad} can be inversely identical from the experimental data.

Provided that the quasi-static equilibrium process is assumed with so dynamically quick convergence to the static state of equilibrium, the value of B_{ad} coincides with $B_{ad,eq}$ without any delay and is expressed as,

$$\frac{\partial B_{ad}}{\partial t} = \frac{dB_{ad,eq}(B_{ion})}{dB_{ion}} \cdot \frac{\partial B_{ad}}{\partial t} = \frac{B_{ad,\lim}}{B_{ion.satu}} \left(\frac{B_{ion}}{B_{ion.satu}} \right)^{C_{ad}-1} \cdot \frac{\partial B_{ad}}{\partial t} \quad (5)$$

Similar to solid-ion relation, the experiment result is required to obtain the intrinsic parameter of $B_{ion\ satu}$, B_{ad}, h_{ad}, and C_{ad} are the input values. Equation (5-3) can be express as relation between B adsorption-ion as illustrated in Figure 7.

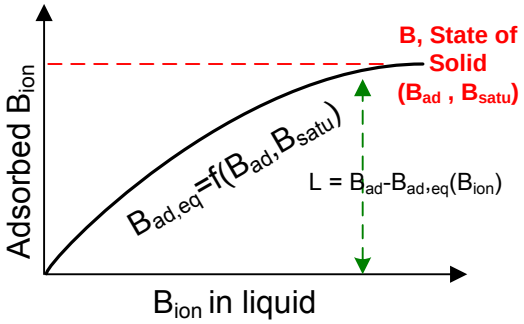


Figure 7 De-sorption of boron model coupled with time dependent

RESULT AND VERIFICATION

Experiment series of mixing fly ash and distilled water for obtaining boron ion concentration were validated again for inversed identification. Material condition used in the model was the same as in the experiment. Since the nature condition is considered, this model is subjected to normal temperature at 20^{o}C. In the experimental investigation, fly ash having the same properties was adopted. A 70gr fly ash in a plastic container containing 1 l liter water is analyzed with ICPS for boron concentration in day 1, 2, 3, 4, and 5. The same material was used for analysis with DuCOM which is simulated as single element in Figure 8.

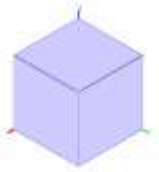


Figure 8 Analysis model for a single element

The result from analysis was fitted with the experimental results to obtain half time of disolusion ($h_{solid,}$) half time of adsorption (h_{ads}) and maximum adsorption of boron (B_{ads})

Then, fitting model with the experimental results detects some intrinsic parameters as illustrated in Figure 9. As shown by the experimental result, precipitation occurred during the first leaching and simulated by the model as 68% of maximum solid boron is adsorbed in fly ash. Boron dissolves in 1 day after fly ash contact with water and boron ions are adsorbed in 3 days after fly ash contact with water. Base on this initial data, this

phenomenon in the aqueous system can be also reasonably simulated with the proposed model.

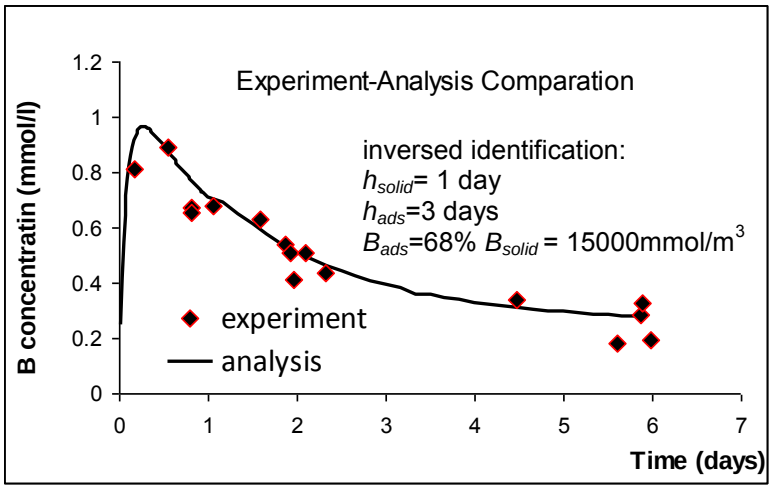
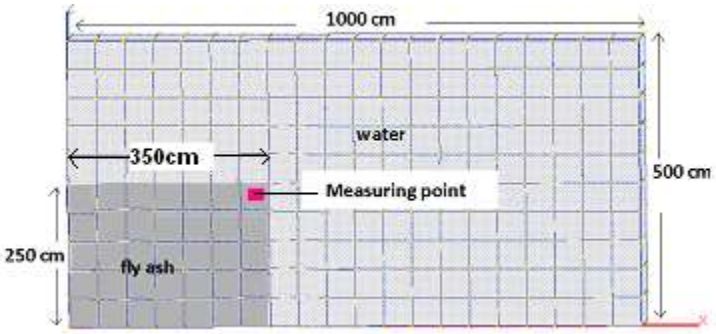


Figure 9 Fitting the model with the experimental results for adsorption parameters

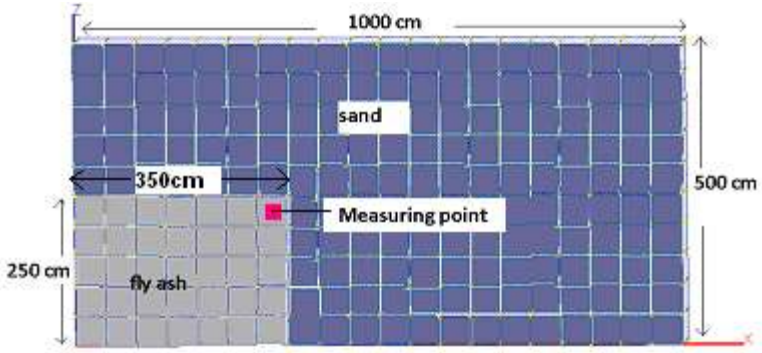
The experimental evidence to evaluate the boron ion adsorption in soil can be provided since the model that is linked with DuCOM simuator can accommodate the composite material such as sand, soils and clay minerals.

MODEL SIMULATION

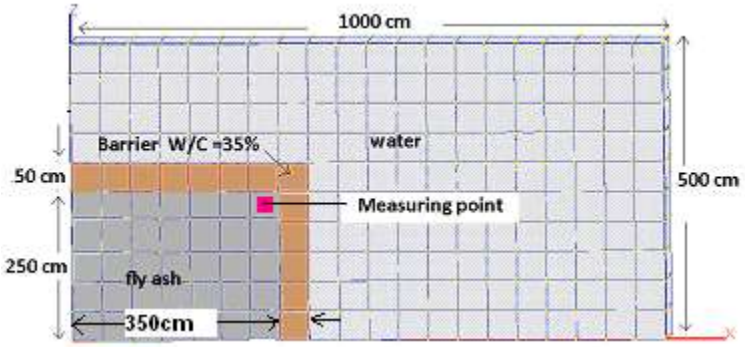
The model can accommodate the analysis considering the effect of nature that influences boron transport. Here, a sensitivity analysis was performed using fly ash as a source of the contaminant which was located in three different condition of biosphere. First, fly ash was surrounded by water. Then, the same contaminant was surrounded by sand having a unit weight of 1000 kg/m^3. Finally, the ash was covered by mortars having W/C of 35% and exposed to water. The model is described as in Figure 10 which the input data is listed in Table1.



(a) Fly ash is exposed to water.



(b) Fly ash in the sand



(c) Fly ash inside a barrier with W/C of 35% is exposed to water.

Figure 10 The material model for simulation on the influence of media

Table1 Input data for the simulation targets

Intrinsic Parameters	Fly ash	Barrier	Water	Sand
B_{solid} (mmol/m^3)	50	0	0	0
B_{satu} (mmol/l)	2.5	0	0	0
C_{solid} (day)	0.2	0.2	0.2	0.2
h_{solid}	1	1	1	1
B_{ad} (mmol/m^3)	0	0	0	0
C_{ad}	0.2	0.2	0.2	0.2
h_{ad} (day)	2	2	2	2
Ion diffusivity	500	10	500	100

Figure 11 shows the boron ion concentration at measuring point in 200 days. The result in Figure 11 indicates boron ion decreased at a prolonged time in all media. The decrease of boron ion rate in water is faster than in sand. However, when a barrier is set to prevent boron leaching, boron ions are concentrated in measuring point. The different boron ion diffusion in water and in the sand will result in boron ion migrates in different rate. It means that the increase of diffusivity accelerates the leaching. Some illustrations of boron ion concentration at day 200 are presented in three dimensional contours in Figure 12.

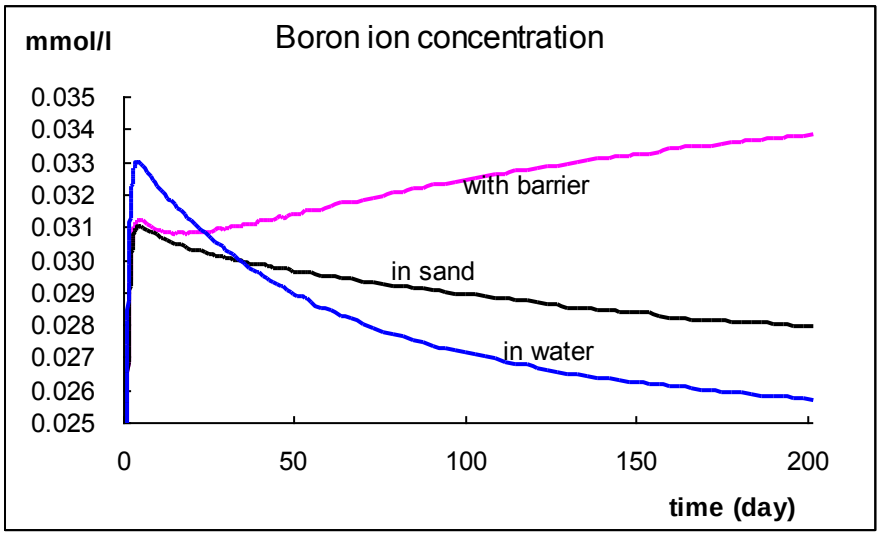


Figure 11 Boron ions released from fly ash exposed to different medium.

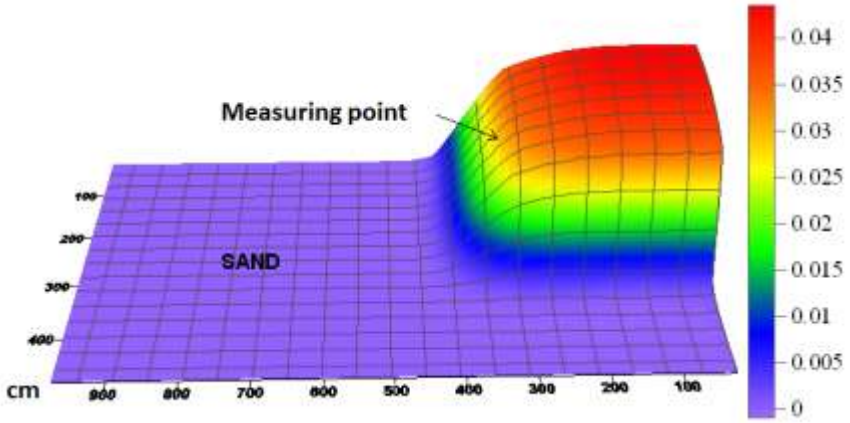


Figure 12(a) In sand

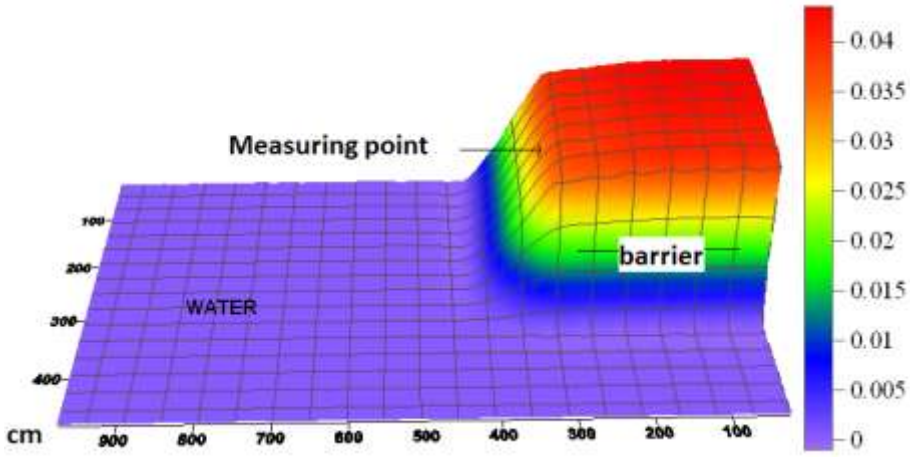


Figure 12(b) In water with barrier

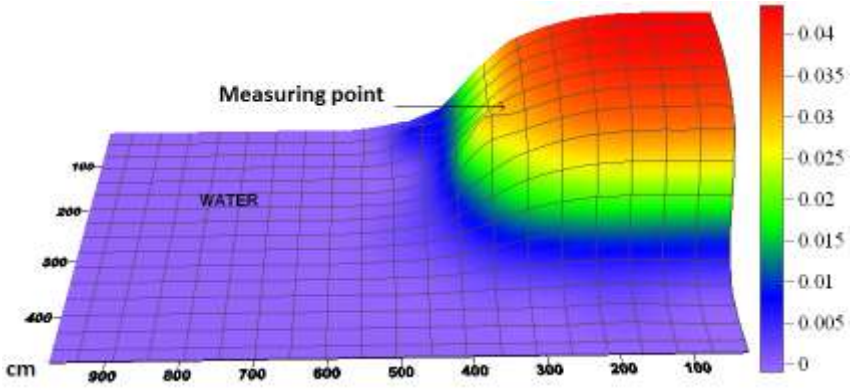


Figure 12(c) In water without barrier

Figure 12 Boron ion concentration contour in different medium

CONCLUSIONS

The proposed model can be a powerful tool to simulate boron migration in various media. It is also clarified that the proposed test can deal with the overall adsorption-desorption process of cement-soil mixtures. This versatility is regarded as the critical point since the method is intended to be employed to the aqueous underground environment. The model shows that in dense media, boron ion migrates slower than in porous media. When a barrier system is introduced, boron ion is retained in the contaminant area. Boron leaching in time based on different adsorption capacity of media and the variation of ion diffusion in different media can be also predicted. The higher the capacity of media to boron the more boron ion leaching from the contaminant can be shown by the proposed model.

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