Time-Dependent Modeling of Boron Leaching from Fly Ash and Adsorption to Solid

Januarti J E¹*, Maekawa K²

¹Department of Civil Engineering, Institut Teknologi Sepuluh Nopember, Indonesia
²Department of Civil Engineering, The University of Tokyo, Japan

ABSTRACT

This paper presents a mathematical modeling to simulate boron leaching from fly ash and adsorption onto solid surfaces in space and time. The mass conservation was formulated in terms of ionized boron and solidified ones, which remained in fly ash as well as being captured on the surfaces of particles. Both path-dependency of boron leaching from fly ash and path-independency of boron adsorption-desorption cycles were coherently taken into account with strong coupling. Based on the proposed formulae, material characteristic values can be experimentally identified and examined by comparing the numerical solution of boron ion concentration into the de-ionized water with the experimental facts. The model was applied to simulate boron migration into underground water in sensitivity analysis, and the critical factors were discussed.

Keywords: Boron leaching, fly ash, adsorption, desorption, diffusion.

INTRODUCTION

Leakage of rare substances from fly ash as by-product of power plants and industrial manufactures can be a trigger for environmental impact problems. Hazardous complexity caused by heavy metal leaching from fly ash has been considered in many countries since massive fly ash has been disposed in soil creating enormous progressive waste ponds. Through exposing to weather and contacting with biosphere, the toxic substances will easily transport in air and aqueous media, especially when the ground water exists near the ponds [1]. The disposal of dumped fly ash in soil foundation is one of the sources of boron accumulation, which may result in undesirable environmental consequences as boron-toxicity [2]. Boron concentration in fly ash samples widely ranges from 100 to 600 mg/kg depending upon the area concern. 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.

With respect to the experimental work on bare fly ash without solidification, 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 solid particles. This boron retention depending upon the (OH) solution is denoted by pH [3]. Therefore, The mechanism of boron ion transport incorporating experimental results in laboratory scale is a necessary to investigate the boron leaching considering fly ash-soils reaction [4].

The main issue on the macro-scale environmental problems should be simplified in laboratory scale. Then, a comprehensive observation is necessary to obtain the relation between boron in solid-liquid relation from the experimental result to a fundamental approach for mathematical model. The program so-called DuCOM-COM3 was developed in the authors group for life-span simulation and problems on calcium leaching in concrete [5].

Hence, a mathematical model based on mass conservation should be developed to simulate boron sorption - desorption process. In the model, ion solution and re-solidification are generally path-dependent. Then, a single solid-ion isotherm may not be sufficient to formulate this thermodynamic process. The first dissolution process from the coal-fired fly ash is thought to be irrecoverable accompanying the entropy increase in nature. Additionally, the subsequent sorption - desorption process after the first leaching of boron should be recoverable similar to an isothermal process of adsorbed moisture specified by BET theory. Then, the capacity term of mass conservation in terms of the leaching and adsorption can be formulated. Therefore, the primary objective of this paper is to link the thermodynamic coupled analysis system of chemo-physics of boron leaching simulation with DuCOM-COM3.

MATERIALS AND METHODS

Experiment on Solid-Ion Relation of Boron

To obtain an initial boron concentration in solid and saturated ion phase, some experimental investigations are required. A class F of fly ash having 2.33 g/cm³ of density, Blaine's surface area of 3660 cm²/gr and density of 2.33gr/cm³ adopted in this paper, was obtained from Sapporo, Japan. Its chemical composition and toxic substances are listed in Table 1 and Table 2 respectively.
Table 1. Chemical composition of source materials

<table>
<thead>
<tr>
<th>Oxide (%)</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>TiO$_2$</th>
<th>MnO</th>
<th>SO$_3$</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>59.5</td>
<td>22.84</td>
<td>6.33</td>
<td>2.44</td>
<td>0.96</td>
<td>0.02</td>
<td>1.63</td>
<td>1.14</td>
<td>0.80</td>
<td>0.21</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 2. Toxic substances in fly ash adopted

<table>
<thead>
<tr>
<th>Element</th>
<th>Chrom$^{6+}$</th>
<th>Arsenic</th>
<th>Fluorine</th>
<th>Boron</th>
<th>Selenium</th>
</tr>
</thead>
<tbody>
<tr>
<td>(mg/kg)</td>
<td>0.87</td>
<td>14</td>
<td>310</td>
<td>120</td>
<td>3.7</td>
</tr>
</tbody>
</table>

Samples were digested to a liquid state. To form a suspension, 10gr sample was prepared and mixed with following distilled water: 20mL, 40mL, 60mL, 80mL, and 100mL. After stirring, the suspension was then filtered with filter paper before ICPS analysis for boron determination. The result is given in Figure 1.

![Figure 1: Boron concentration in solution about 30 minutes after fly ash contact with water](image)

The experimentally obtained results as shown in Figure 1 provide the exponential relation of the boron concentration and the dilute solution. From the equation obtained, an extrapolation was employed for obtaining boron concentration in saturated condition ($B_{satu}$) where the amount of water was very small. Boron ion in saturated condition is equal to 3.70mmol/L or 0.016mmol. Since the initial boron in fly ash is a given value (120mg/kg), then boron in solid is obtained from the reduction in the total value of boron. Finally, boron concentration in solid is 0.095mmol or equal to 22,060mmol/m$^3$. This process is shown in Figure 2. In a closed system, total boron ion in the same mass of fly ash is constant, but it may be different in formation. Figure 3 shows the concentration in some different dilution water that is derived from data in Figure 2.

![Figure 2: Intrinsic parameter obtained from experimental results](image)

![Figure 3: Concentration of boron ion in the suspension](image)
In a small amount of water, the system is dense and boron ion in the liquid form becomes saturated. When the system contains a large amount of water, boron changes its solid form to liquid. The relation between concentration of boron in solid and liquid phases can be expressed in Figure 4. This is necessary as a data input for the proposed method to simulate boron released from fly ash. Since fly ash varies in its composition depending upon the coal where it is mined, this initial concentration may be different.

![Solid-Liquid Relation](image)

**Figure 4: Solid-liquid relation of boron in suspension**

**Scheme of Thermodynamics**

The observation on experiment results has shown that boron released from fly ash reached its equilibrium time rapidly [6]. The following is two relations found from the results as solid-ionized boron when fly ash contact with water and ionized-absorbed boron followed the first relation if the contact is prolonged as illustrated in Figure 5. Then, a single solid-ion isotherm is not sufficient to formulate this path-dependent thermodynamic process. The first dissolution process from the coal-fired fly ash is irrecoverable accompanying the entropy increase in nature.

![Experimental Result of Boron Concentration](image)

**Figure 5: Boron released from fly ash in one week.**

On the other hand, the subsequent sorption - desorption process after the first leaching of boron is recoverable similar to an isothermal process of adsorbed moisture specified by BET theory. Then, the capacity term of mass conservation was formulated in terms of the leaching and adsorption.

**Mass Conservation of Boron**

In thermodynamics equilibrium, total energy and mass flow must fulfill the conservation law. The model proposed here was based on the mass conservation equation proposed for calcium leaching model [5]. The mass conservation of boron in both solid and ion phases in the system was derived in Equation (1). This equation provides total boron in solid phase, adsorbed boron ions and boron ions in the solution.

\[
\frac{\partial}{\partial t} (\phi \cdot S \cdot B_{ion}) + \frac{\partial B_{solid}}{\partial t} + \frac{\partial B_{ad}}{\partial t} - div J_{ion} = 0
\]

(1)

Where:
- \(\phi\) = porosity \([m^3/m^3]\) of the composite including voids
- \(S\) = degree of saturation in the voids
- \(B_{ion}\) = molar concentration of boron ions in the liquid phase \([\text{mmol/l}]\)
- \(B_{solid}\) = amount of boron in the solid phase \([\text{mmol/m}^3]\)
- \(B_{ad}\) = amount of adsorbed boron trapped on the micro-particle’s surfaces and/or micro-pore walls \([\text{mmol/m}^3]\)
- \(J_{ion}\) = flux of boron ions \([\text{mmol/m}^3s]\).
The first term represents the increasing rate in ionized boron when the process of dissolution begins. The second is one of the 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. This is analogous to the plastic evolution of yield solid of mechanics. Besides the first reaction, the second reaction on boron adsorption to capture boron ions, which has been released at the initial reaction, also starts to satisfy adsorption-ion relation at a determined half-time. This state represents precipitation of boron that is adsorbed by fly ash surface. Boron ions change from liquid phase to solid phase as adsorbed boron. It is to represent the boron adsorption on the micro-solid surfaces. If the composite of a unit mass may include sand and clay with fly ash, for example, the third 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. The fourth term of the equation represents the flux term. 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 6.

\[
\frac{\partial B_{\text{solid}}}{\partial t} = -\frac{k}{h_{\text{solid}}}, \quad k = B_{\text{solid}} - B_{\text{solid,eq}}(B_{\text{ion}}) > 0,
\]

\[
B_{\text{solid,eq}} = B_{\text{solid,lim}} \left( \frac{B_{\text{ion}}}{B_{\text{ion,sat}}(C_{\text{solid}})} \right)^{C_{\text{solid}}}
\]

Where:
- \(B_{\text{solid,eq}}\) = isothermal amount of solidified boron statically equilibrated with \(B_{\text{ion}}\)
- \(h_{\text{solid}}\) = intrinsic leaching time to thermodynamic equilibrium
- \(B_{\text{solid,eq}}\) = solid-ion isotherm is specified by the intrinsic solid amount of boron
- \(B_{\text{ion,sat}}\) = saturated molar concentration of boron ion
- \(C_{\text{solid}}\) = poly-nominal order parameter

Based on the experiment result, the intrinsic parameter of \(B_{\text{ion,sat}}\), \(B_{\text{solid,eq}}\), \(h_{\text{solid}}\), and \(C_{\text{solid}}\) are the input values. Equation (2) can be expressed as a relation between B solid-as in illustrated in Figure 7.

Figure 6: DuCOM Scheme for chemo-physical coupled system

Path-Dependent Relation of Intrinsic Solid and Ionized Boron (State A)

Analogous to the adsorption isotherm, the following formulation of path-dependency is assumed for leaching of intrinsic boron of solid phase into the pore water as expressed in Equation (2). Here, the condition of negative definite is given.

[Equation (2)]

Figure 7: Ionized boron model coupled with time dependent
Adsorption-Desorption Isothermal Relation (State B)

If the quasi-static process could be assumed with quasi-balanced state of the thermodynamic system of adsorbed boron and the ionized one, the value of $B_{ad}$ in Equation (1) can be expressed by a unique function of $B_{ion}$. This assumption may hold only when the process is so slow as to create perfect uniformity of boron ion in pore solution. However, the boron leaching and re-adsorption process shows some time-lag and transient process in appearance, especially when the single mixture of fly ash with water is dealt with. It implies that the initial leaching of boron from burned ash is not static but rather dynamic in nature. Then, the simple linear rate modeling of boron adsorption is explained in Equation (3).

$$\frac{\partial B_{ad}}{\partial t} = \frac{B_{ad} - B_{ad,eq}(B_{ion})}{h_{ad}},$$  

$$B_{ad,eq} = B_{ad,lim} \left( \frac{B_{ion}}{B_{ion,satu}} \right)^{C_{ad}}$$  

Where:

- $B_{ad,eq}$ = isothermal amount of adsorbed boron statically equilibrated with $B_{ion}$
- $h_{ad}$ = intrinsic e-half time on the way to the state of thermodynamic equilibrium
- $B_{ad,eq}$ = maximum possible adsorption of boron
- $B_{ion,satu}$ = saturated molar concentration of boron ion
- $C_{ad}$ = polynomial order parameter

In this model, the static isotherm of equilibrium is formulated by $B_{ad,eq}$ in the composite, $B_{ion,satu}$ and $C_{ad}$. These three values are material constants to be input in the analysis. 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 Equation (4). If the ion concentration is kept constant, the exact solution by integrating the differential is given as in Equation (4).

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

When $t = h_{ad}$ gives the elapsed time to (1/e) convergence to the static equilibrium of the thermodynamic system, then, the value of $h_{ad}$ can be inversely identical or roughly found 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,

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

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 (3) can be express as a relation between B adsorption-ion as illustrated in Figure 8.

![Figure 8: De-sorption of boron model coupled with time dependent](image)

**RESULTS AND DISCUSSION**

**Model Verification**

Experiment of mixing fly ash and distilled water was conducted again for the model verification. The same material and method used in the experiment to obtain two intrinsic parameter: $B_{solid,eq}$ and $B_{ion,satu}$ was applied. A 10g fly ash in a plastic container containing 40 mL water was analyzed for boron concentration for one to five days. Boron ion concentration in suspension was then determined with ICPAS. The same material was
used for analysis with DuCOM, which was simulated as a single element.

The result from analysis needs to be fitted with the experimental result. Inversed identification is necessary to obtain three parameters as half time of dissolution \( (h_{\text{solid}}) \) half time of adsorption \( (h_{\text{ads}}) \) and maximum adsorption of boron \( (B_{\text{ads}}) \). Here a constant value of 0.2 is set for \( C_{\text{ad}} \) and \( C_{\text{solid}} \).

Then, fitting model with the experimental results detects some intrinsic parameters as illustrated in Figure 9. As shown in the result, precipitation occurred during the first leaching and simulated by the model as 95% of maximum initial boron in solid was adsorbed in fly ash. Boron dissolved in a half day after 40 gr fly ash contact with 40 mL water. Boron ions were adsorbed in 1.2 days after fly ash contact with water. Based on this initial data, this phenomenon in the aqueous system can be also reasonably simulated with the proposed model.

![Figure 9: Inversed identification for adsorption parameters](image)

Here, the fitting model was applied for another two experimental results for comparison. Figure 10 shows that boron dissolved in one day, and boron ions were adsorbed in three days after fly ash contact with water when 70 gr fly ash was mixed with 1000 mL water. In the last case, adsorbed boron was about 68% of initial boron in solid.

![Figure 10: Analysis and experiment comparison with 70gr fly ash in 1000mL water](image)

**Sensitivity Analysis on the Influence of Medium**

To investigate the influence that nature condition can stimulate migration of boron, sensitivity analysis was performed using the proposed model. The targets of the analysis were the fly ash as a source of the contaminant was located in three different condition of biosphere. Migration of boron ion in medium having various material properties was considered. Fly ash was surrounded by sand having a unit weight of 1000 kg/m\(^3\). Then, the same contaminant was surrounded by water. Finally, the ash was covered by mortars having water to cement ratio of 35% with thickness of 50 cm and exposed to water. The model is described as in Figure 11. Here, ion diffusivity was set different for each medium. Diffusion coefficient for ions transport \( (D_{\text{ion}}) \) due to the convection current generated by hydraulic pressure gradients should be set to a value higher than the one used for free water in the cementitious material [7].
Figure 1: The material model for simulation on the influence of media

Figure 12 shows the boron ion concentration at the observed point in 200 days. Boron ion concentration changed 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 at the observed point. The different boron ion diffusion in water and in the sand will result in boron ion migrates in distinctive rate. It means that the increase of ion diffusivity accelerates the leaching.
Sensitivity Analysis on Diffusion of Boron ion Associated with Boron Adsorption Capacity of the Medium

Boron content in fly ash, diffusivity of ion and the capacity of a medium to absorb boron ion play an important role for soluble boron released from fly ash. To simulate the ion transport in different compacted media, again, the diffusivity of boron ion were studied. Sand, a medium with unit weight of fine aggregate of 1000 kg/m$^3$ was adopted as the adsorbent. Boron ion migrated through water exists in the system and driven by a concentration gradient. In a compacted barrier as in mortar or concrete, ion migrates at given diffusion in the molecular pathway in capillary pores where in a larger size pore ions transport in a greater pathway. Therefore, migration of boron ion in greater pores ie sand has larger diffusivity. In the analysis, some initial values of the diffusion coefficient (D) were given in the data input. The higher this coefficient is input, the larger pores are existing in the medium.

In the analysis, the performance of sand was simulated with variation of the diffusion coefficient from a given value of 1 to 500, which was given in the data input. Higher diffusivity means larger pores to exist in the sand. The capacity of sand to absorb boron denoted by $B_{ad}$ in data input was also varied in the range of 0% to 20% of $B_{solid}$. The higher value of $B_{ad}$ means the more sand can absorb ion from fly ash after dissolution. In Figure 13, observed point 1 represents the contaminant where the initial boron was given. Observed point 2 and observed point 3 represent the adsorbent, where boron ions will transport at the elapsed leaching time.

Figure 14 shows the analytical result for ion concentration at point 1 in logarithmic scale of leaching time. Boron ions spread rapidly in the looser media given by curves with the higher diffusion coefficients (D) in the graph. At one week after fly ash contact with the adsorbent, boron ion was concentrated due to higher diffusion that promotes the ability of boron to transport in the contaminant. As the elapsed time of leaching increasing, boron ion migrated out from fly ash to the adsorbent lead by the diffusivity of ion. Boron ion concentration decreased as diffusion increases and the capacity of sand to adsorb ion also increased.
Figure 14: Boron ion concentration at point 1

Figure 15 illustrates the result at point 2. At looser sand, boron ion migrates faster. In Figure 16, at one week, boron ion transported to the sand was not promoted by the ability of sand to absorb the ion. However, prolonging the contact time will lead boron ions to migrate out from fly ash, passing this point, and spread to the adsorbent (in one year and five years contour). In 150 years, boron ions spread due to the ion diffusivity and higher capacity of sand to adsorb ion.

Figure 15: Boron ion concentration at point 2

Figure 16: Contour of boron ion concentration at point 2
There was no boron ion found at point 3 at one week of boron leaching. Figure 17 shows ion concentration at the observed point 3 increasing after one year. At the looser sand, boron ion in the adsorbent system was higher. In Figure 18, after five years, boron ions migrated to the sand promoted by the ion diffusivity and the ability of sand to absorb ions. Up to 150 years, boron ions were found spreading in the adsorbent due to the ion diffusivity.

CONCLUSIONS

Leaching of boron ion from fly ash was simulated using a mathematical model based on mass conservation. In the model, soluble boron in solution and precipitated of ion were generally path-dependent. Migration of boron ion from fly ash in the aqueous system presented in the proposed model had a good agreement result with the experimental result. The result also implied that adsorption and de-sorption mechanism of boron leaching from fly ash was a more dynamic in nature rather than the static process. In the isothermal condition, the equilibrium was rapidly changed from dynamically convergence to the static state.

The influence of a medium, where the fly ash has contact with, was also investigated. In the proposed model, the acceleration of leaching in related with diffusivity of boron ion was given for each medium. Adsorption capacity also plays an important role for boron migration from the contaminant to the system. Boron leaching from fly ash was also time dependent. The proposed model revealed that longer fly ash contact with water caused boron ions spread to the medium.

REFERENCES

