



Processes controlling the variations of pH, alkalinity, and CO₂ partial pressure in the porewater of coal ash disposal site

Kangjoo Kim^{a,*}, Seok-Hwi Kim^a, Sung-Min Park^a, Jinsam Kim^a, Mansik Choi^b

^a Department of Environmental Engineering, Kunsan National University, Miryong-Dong, Kunsan, Jeonbuk 573-701, Republic of Korea

^b Graduate School of Analytical Science and Technology, Chungnam National University, Daejeon, 305-764, Republic of Korea

ARTICLE INFO

Article history:

Received 17 February 2010

Received in revised form 18 April 2010

Accepted 19 April 2010

Available online 28 April 2010

Keywords:

Ash weathering

Soil cover

Saline porewater

Common ion effect

Calcite precipitation

Dolomitization

ABSTRACT

Alkalinity, pH, and pCO₂ are generally regarded as the most important parameters affecting trace element leaching from coal ashes. However, little is known about how those parameters are actually regulated in the field condition. This study investigated the processes controlling those parameters by observing undisturbed porewater chemistry in a closed ash disposal site. The site is now covered with 30–50 cm thick soils according to the management scheme suggested by the Waste Management Law of Korea and our results show the important role of soil cover regulating those parameters in the shallow porewater. Without the soil cover, the shallow porewater shows low pCO₂ and alkalinity, and highly alkaline pH. In contrast, the porewater shows much higher alkalinity and near neutral pH range when the site was covered with the low permeability soils. This difference was caused by the CO₂ supply condition changes associated with the changes in infiltration rate. The geochemical modeling shows that the calcite precipitations induced by porewater aging, dolomitization, and weathering of solid phases are the main processes controlling alkalinity, pH, and pCO₂ in the deep saline porewaters. The weathering of coal ash plays the most important role decreasing the alkalinity in the deep porewater.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Several studies report that trace elements leached from coal ashes can create a potential threat to the environments [1–4]. It has been shown that the trace element leaching can be explained by geochemical processes such as precipitation/dissolution, adsorption/desorption, and redox speciation [2,3,5–7]. Since pH regulates those processes, it is generally regarded as a master variable controlling the leaching of toxic trace elements in natural environments [2]. Alkalinity and pCO₂ (log partial pressure of CO₂ in atmosphere) are also considered as important variables for prediction of trace element leaching because they define solution pH in natural conditions. Therefore, many previous studies have tried to measure or predict the element leachability as a function of pH [3,7–9], alkalinity [10], or pCO₂ [11]. However, studies mainly focusing on the processes regulating pH, alkalinity, and pCO₂ of porewaters have never been performed so far. In addition, most of the previous studies were carried out based on lab leaching experiments using fresh coal ashes. As a result, the leaching and the behavior of trace elements in the field condition are still poorly understood.

In this study, we investigated porewaters of a closed ash disposal site of a power plant, which is located on the western coast of Korea (Fig. 1a), to see how pH, alkalinity, and pCO₂ are regulated in natural conditions. The plant burns about 0.8 Mt of pulverized anthracite coals annually for production of electric power and has disposed of its coal ash into ponds formed inside of the concrete offshore dykes (Fig. 1a). Ashes are conveyed to the pond through pipelines in slurry form and seawater has been used to make the slurry because the plant is located on the seashore. The ash disposal site where this study was performed had been operated since 1983 till 1994 and is now covered with 30–50 cm thick soils (<10⁻⁵ cm s⁻¹ in hydraulic conductivity) to avoid blowing of the ashes and to reduce the amount of leachates [5]. Therefore, a precise inspection of the porewaters of the study site can also provide substantial insights into the role of soil cover on the porewater chemistry and the geochemical processes affecting pH, alkalinity, and pCO₂ by interaction between seawater and coal ash. We believe this study provides valuable insights into the variations of the leachability and the behavior of trace elements by prolonged reaction with coal ashes in the field condition.

2. Method

To collect undisturbed porewater samples, two multilevel samplers were installed: one at a site where the dumped ashes were covered with soils (OM2) and the other in the 2.5 m deep, square-

* Corresponding author. Tel.: +82 63 469 4766; fax: +82 63 469 4964.

E-mail address: kangjoo@kunsan.ac.kr (K. Kim).

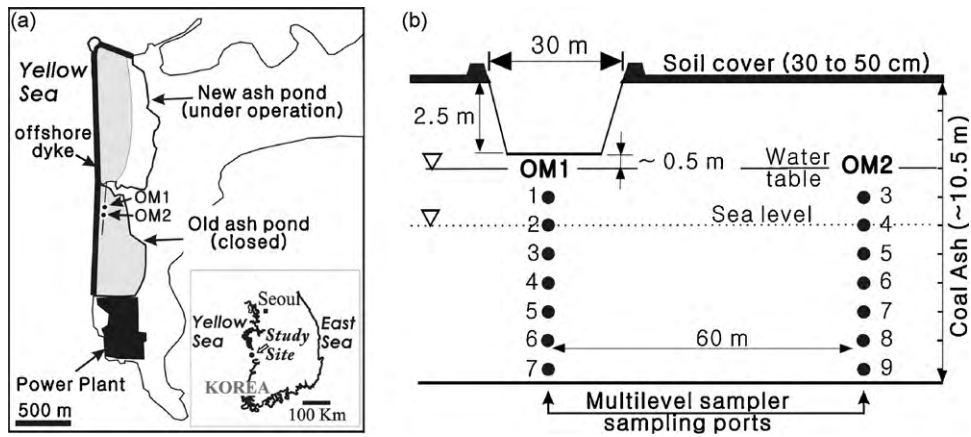


Fig. 1. Location of study site (a) and the sampling points of the multilevel samplers (b). Numbers in (b) represent sampling port ID.

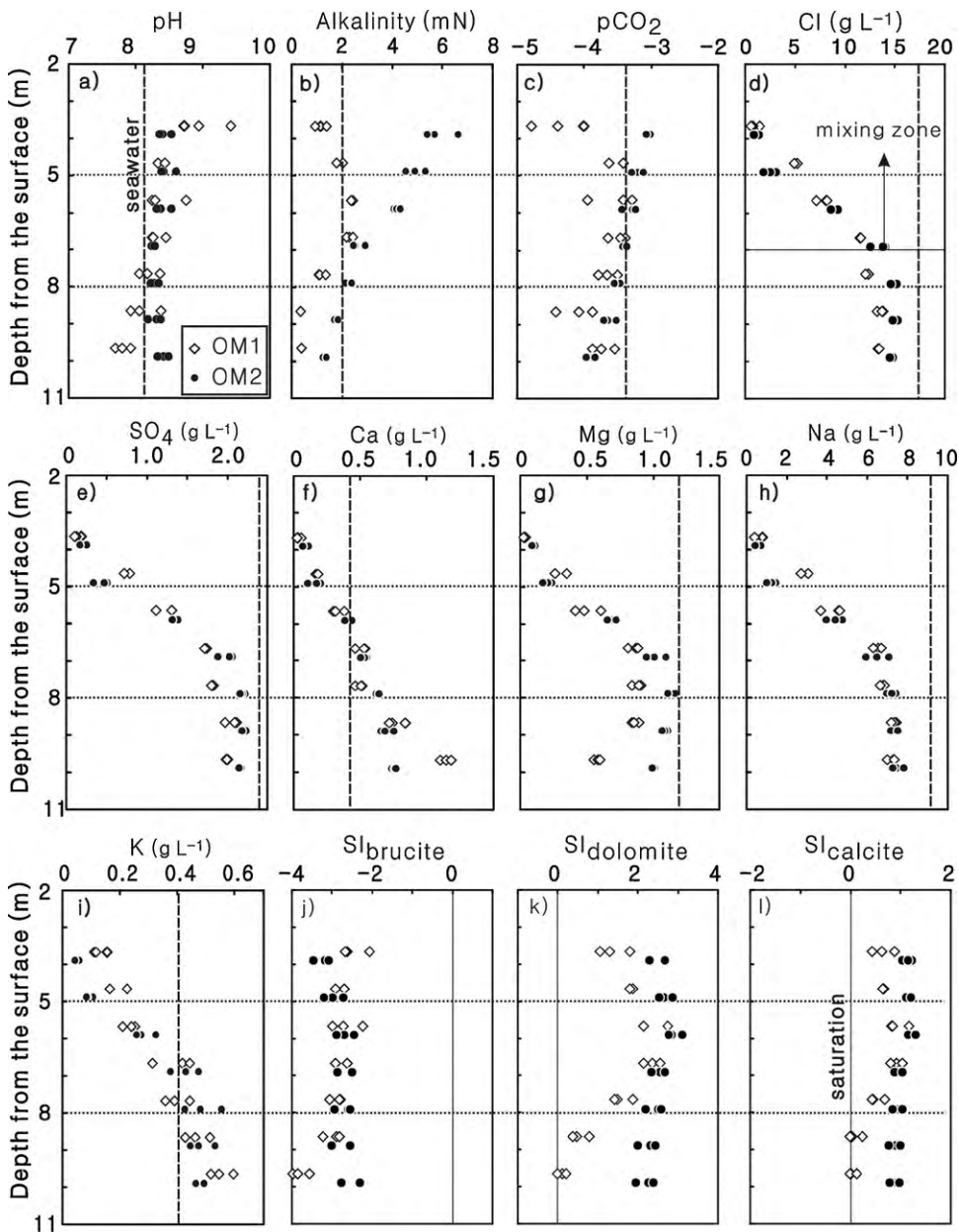


Fig. 2. Vertical distributions of various chemical parameters.

shaped excavation (OM1) (Fig. 1b). The samplers were installed with a bundle of polyethylene tubes of 3.18 mm in diameter according to the hand driven method suggested by Stites and Chamber [12]. Sampling ports of each sampler were placed at depths ranging from about 4 to about 10 m (Fig. 1b). Each port was screened with stainless steel mesh (#200). The excavation was dug in August 4–5, 2001 and the samplers were installed in August 12–15 of the same year.

Porewater samplings were carried out three times in September 15, 2001, November 10, 2001, and April 12, 2002. Samples were collected using a peristaltic pump after pumping water till the changes in temperatures, EC, and pH of the flowing water became negligible. A seawater sample was also collected directly from the sea near the study site. Temperature and pH were measured in the field using an overflowing chamber to minimize the disturbances by the contact with air. Samples for lab analysis were immediately filtered using 0.45 μm cellulose membranes. The samples for major cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and silica were acidified to $\text{pH} < 2$ with several drops of ultra-pure hydrochloric acid. Alkalinity was analyzed using Gran titration technique. Major cations were analyzed using an atomic absorption spectrophotometer, anions such as SO_4^{2-} and Cl^- using an ion chromatograph, and dissolved silica using a spectrophotometer. A computer code PHREEQC [13] was used to calculate the partial pressures of carbon dioxide as pCO_2 (log partial pressure of CO_2 in atm.) and saturation indices with respect to various mineral phases ($\text{SI}_{\text{mineral}} = \log \text{IAP} - \log \text{Ksp}$, where IAP = ion activity product, Ksp = solubility product), and to quantify geochemical processes affecting water chemistry.

3. Water analysis results

The analysis results show that porewater chemistry was fairly stable over time (Fig. 2). Significant differences in pH, alkalinity, and pCO_2 were observed according to sampling depths and locations (Fig. 2a–c). At the site where the soil cover was removed (OM1), shallow porewaters show higher pH and lower alkalinity than those at the site covered with soil cover (OM2). OM1 shows continuously decreasing pH levels as depth increases while OM2 shows nearly consistent levels. Alkalinity of OM2 is highest near the water table (5.40–6.64 mN) and shows a continuously decreasing trend with

depth to a level (1.24–1.40 mN) that is even lower than that of seawater (2.01 mN). In contrast, alkalinity of OM1 porewaters shows a trend increasing from 0.93 to 1.41 mN near the water table to its maximum (2.40 mN) at about 7 m in depth and then declining to a very low level (~ 0.40 mN) at the bottom.

4. Discussion

4.1. Origin of porewater and mixing

Chloride, the conservative ionic species, shows an increasing trend with depth, indicating two different porewater origins: the seawater at the bottom and the rainwater infiltrated through the topsoil (Fig. 2d). Seawater fraction calculated based on chloride concentration was consistent (70–85%) at the depth $> \sim 7$ m. The depth range where seawater fraction was less than 65% will be referred as ‘mixing zone’ in this paper. Considering that major ions (SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , K^+) show similar vertical trends to that of chloride (Fig. 2e–i) and that they are linearly related with seawater fraction at the shallow depths (Fig. 3), mixing was the main process regulating concentrations of those ionic species within the mixing zone.

The seawater fraction observed below the mixing zone is comparable with the data obtained from the new ash pond (Fig. 1a). The pond water and the deep porewater in the new ash pond were always diluter (between 70 and 90% in seawater fraction) than the seawater due to influence of precipitation [14]. Chloride levels that were consistent but diluter than that of seawater indicate that the deep saline porewater was the one existed before the termination of ash disposal, which had reacted with coal ash for a longer time than that in the mixing zone.

4.2. Role of soil cover

The lower pH and the higher alkalinity of OM2 than those of OM1 at the shallow depth reflect the importance of soil covers. In the presence of soil cover, CO_2 gas generated by oxidation of unburned coal or dissolved organic carbon would be trapped in the unsaturated zone. As a result, the shallow porewater of OM2 showed the highest pCO_2 level in the study site (Fig. 2c). Its high

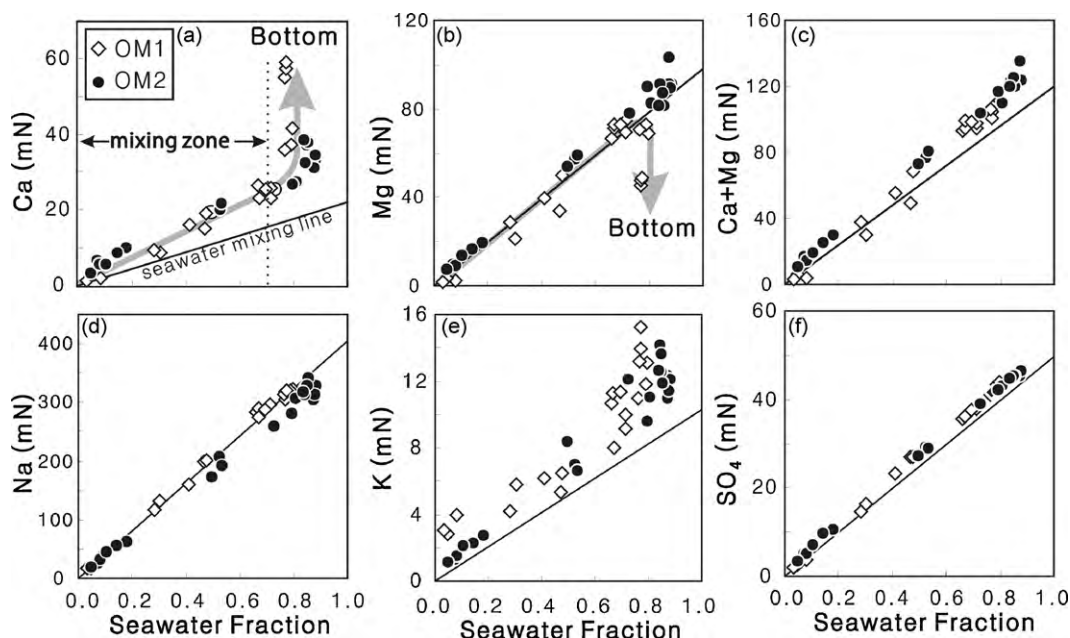


Fig. 3. Plots of various chemical parameters as a function of seawater fraction.

alkalinity is also related with the high $p\text{CO}_2$. Groundwater with higher $p\text{CO}_2$ has more capacity of dissolving solutes by lowering pH and, thus, can show the higher alkalinity when it reacts with minerals for enough time [15,16].

When the soil cover is removed, the trapped CO_2 gas underneath the soil cover would escape into the open atmosphere, resulting in lowered $p\text{CO}_2$ and increased pH levels as we observed in the shallow porewater of OM1. This may trigger carbonate precipitation and the lowered alkalinity could be caused. However, $p\text{CO}_2$ levels near the water table in OM1 are even lower than the atmospheric $p\text{CO}_2$ (-3.5 ; Fig. 2c), indicating that the CO_2 -degassing hypothesis is not plausible here.

Since the soil cover was removed in OM1 (Fig. 1b), rainwater can easily infiltrate into the ash. When the recharge rate is high, the recharged water would be soon separated from the unsaturated zone air due to the later recharged water. Under this condition, the CO_2 supply is partly limited and the $p\text{CO}_2$ of water could be reduced by slight weathering of coal ashes because mineral weathering generally converts H_2CO_3 (or HCO_3^-) into HCO_3^- (or CO_3^{2-}) in water by increasing pH, which lowers $p\text{CO}_2$ drastically in a closed system [15,16]. This would be even more significant for the precipitation-originated porewaters because the rainwater has very low dissolved CO_2 contents due to its low ionic strength and pH. For the case of OM2, however, the recharge is greatly prevented owing to the soil cover. The shallow porewater could have reacted with coal ash under a near CO_2 gas open condition for a longer time. As a result, very high alkalinity levels at the shallow depth could be caused.

To confirm above explanation, a geochemical calculation was performed using PHREEQC. It was assumed that the shallow porewater was originated from rainwater infiltration and was initially in equilibrium with atmospheric $p\text{CO}_2$. Since the shallow porewater already showed the oversaturation with respect to calcite (Fig. 2l), its chemistry was likely to be affected by weathering of very reactive phases such as lime (CaO) or portlandite ($\text{Ca}(\text{OH})_2$) and the extreme increase of alkalinity by the dissolution of those phases was limited by calcite precipitation [16]. The lime and portlandite are frequently observed or predicted to exist in coal ash due to burning of calcite in coal at above 1000°C (i.e., lime) or due to reactions between lime and H_2O (i.e., portlandite) [17,18]. Even small presence of those phases can greatly regulate the porewater chemistry due to their high reactivity.

The calculation results show that dissolution of only $5.8\ \mu\text{mol}$ of portlandite dissolution in a liter of porewater can cause the $p\text{CO}_2$ value (about -4.4) observed in the shallow porewater of OM1 under a CO_2 -closed condition. However, the pH (7.29) was much less than the observed ones (8.72–9.42). In contrast, the dissolution of $0.5\ \text{mmol}$ portlandite (or lime) in a liter of porewater, which is required to show the observed alkalinity ($\sim 1.0\ \text{mN}$), caused the $p\text{CO}_2$ as low as -9.0 and the pH as high as 11.0. This reflects that the newly recharged porewater can show the observed $p\text{CO}_2$ and pH by reaction with ash minerals if the CO_2 supply from the unsaturated zone is only partly limited. This is also reflected in the total dissolved inorganic carbon (DIC) of the shallow porewater of OM1 (OM1-1 in Fig. 1; $0.998\ \text{mM}$), which was about 88% of that ($1.131\ \text{mM}$) under a CO_2 open condition ($p\text{CO}_2 = -3.5$, alkalinity = $1.161\ \text{mN}$). However, the soil cover effect becomes negligible as the depth increases, considering that both samplers show the similar water compositions at about 7 m in depth (Fig. 2).

4.3. Dolomitization

Ca and Mg showed different trends from that of chloride below the mixing zone (Fig. 2f and g). At this depth range, Ca level increased continuously with depth while Mg showed the declining concentration, indicating the exchange between Mg in water

and Ca in solid phase. This is evidenced by the plots of Ca, Mg, and $\text{Mg} + \text{Ca}$ as a function of seawater fraction (Fig. 3a–c), which show that the abrupt increase and decrease in Ca and Mg, respectively, below the mixing zone are exactly balanced. The similar phenomenon was also observed from the stabilized coal-waste blocks [19] and the coal fly ash [20], which had been exposed to seawater for more than 10 years. The blocks and ash particles showed depleted Ca and enriched Mg concentrations near their surfaces. The previous studies interpreted this phenomenon as a result of two reactions occurring concurrently: Ca leaching and brucite ($\text{Mg}(\text{OH})_2$) precipitation [19,20]. These two processes, however, do not necessarily induce the exact balances between the depleted Mg and the enriched Ca as we observed because those are independent processes. In addition, brucite precipitation is a doubtful process here because all the porewaters are significantly undersaturated with respect to brucite ($\text{SI}_{\text{brucite}} = -2.1$ to -4.0 ; Fig. 2j).

We think that the observed exchange is a dolomitization, a process replacing Ca in calcite by Mg dissolved in seawater. Dolomitization is generally observed in marine sediments due to high Mg concentration in seawater [15]. This is evidenced by the slow reaction, which is reflected in the facts that the exchange becomes more severe in aged porewaters among the porewaters with similar seawater fractions and that the deep porewater showed any significant changes in Ca and Mg over a period of 7 months (Fig. 2f and g). The replacement of Ca adsorbed onto the exchangeable sites is a fast process that can reach equilibrium within several hours. The significantly declined $\text{SI}_{\text{dolomite}}$ levels where the severest exchange is observed suggest that this process occurs to reach equilibrium with respect to dolomite ($\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$) as the porewater ages (Fig. 2k).

4.4. Calcite precipitation

4.4.1. Processes

Alkalinity levels even lower than that of seawater in deep saline porewaters conflict with the results of a batch experiment performed for up to 1 month using seawater and the weathered coal ashes collected from our study site [21]. This experiment showed alkalinity levels (2.10 – $2.30\ \text{mN}$) always higher than that of seawater ($2.08\ \text{mN}$). It is likely that the low alkalinity levels in deep porewaters are related with long-term processes that cannot be easily replicated in the lab experiments. Because the waters are mostly oversaturated with respect to calcite (Fig. 2l), the calcite precipitation ($\text{Ca}^{2+} + \text{CO}_3^{2-} \Rightarrow \text{CaCO}_3$) is presumed to take place slowly as the water ages. This is reflected in the deep porewaters, which showed a decreasing trend in $\text{SI}_{\text{calcite}}$ as depth increases (Fig. 2l). In addition, the generation of Ca and alkalinity ($= \text{CO}_3^{2-} + \text{HCO}_3^- + \text{OH}^- - \text{H}^+$ in equivalent) by coal ash weathering can also cause calcite precipitation by ‘common ion effect’ if the waters were saturated or oversaturated with respect to calcite. Dolomitization also can cause the same effect because it increases Ca concentration.

4.4.2. Evaluation of the roles of the suggested processes

Based on above discussions, three processes are likely to be important in causing calcite precipitation in the deep saline waters: (i) ‘porewater aging’, the process causing calcite precipitation simply to reach an equilibrium state with calcite, (ii) coal ash weathering generating alkalinity and Ca, and (iii) dolomitization. Their contributions to the observed variations of pH, alkalinity, and $p\text{CO}_2$ below the mixing zone were assessed based on geochemical modeling for six porewater pairs ($4 \Rightarrow 5$, $5 \Rightarrow 6$, and $6 \Rightarrow 7$ for OM1 and $6 \Rightarrow 7$, $7 \Rightarrow 8$, and $8 \Rightarrow 9$ for OM2; here, each number represents sampling port ID shown in Fig. 1b). The modeling was performed using the averaged chemistry data for the three-time measurements (Table 1) with an assumption that the shallower porewater (initial water) chemically evolves into the deeper one

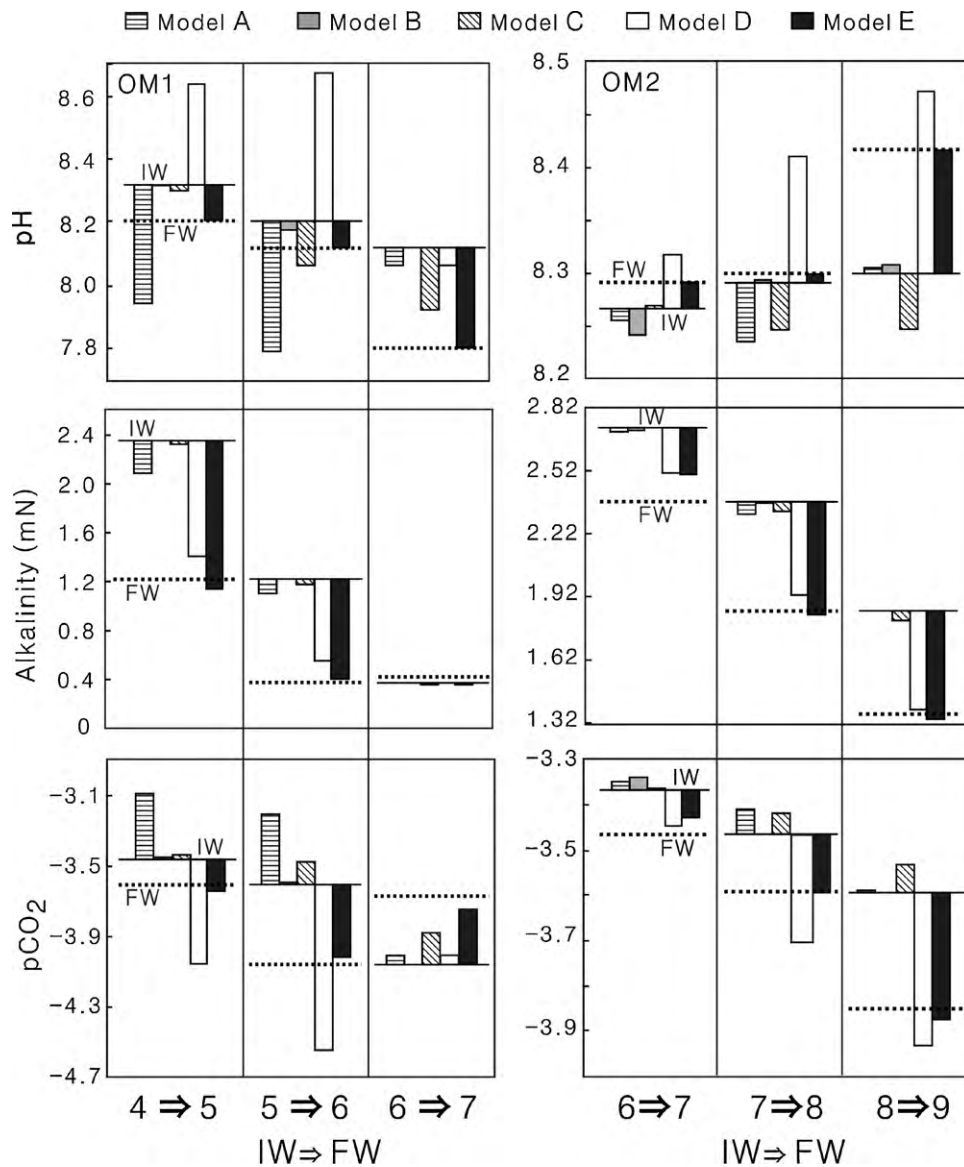


Fig. 4. Effects of various processes causing calcite precipitation on the variations of pH, alkalinity, and $p\text{CO}_2$ as the initial porewater (IW) evolves into the final water (FW). Horizontal solid lines and dotted lines represent the values for initial and final porewaters, respectively.

(final water) by the reaction with coal ash. Even though the selected porewater pairs show only a small variation in seawater fraction, the seawater mixing effect was also considered in the calculation because any changes in Ca concentration can affect the calcite precipitation.

Five separate calculations were performed to compare the effect of each process and details of the calculation are summarized in Tables 2 and 3. The porewater aging (Model A) was approximated simply by allowing calcite precipitation till the initial water shows the $\text{SI}_{\text{calcite}}$ of the final water. The seawater mixing (Model B)

Table 1
Averaged chemistry data for the porewaters used for the modeling shown in Table 2.

Porewater ID	OM1				OM2			
	4	5	6	7	6	7	8	9
Temperature	18.0	18.8	20.0	19.7	19.7	17.3	17.4	17.8
pH	8.32	8.20	8.12	7.81	8.27	8.29	8.30	8.41
Alkalinity (mN)	2.366	1.221	0.365	0.409	2.720	2.366	1.835	1.370
$p\text{CO}_2$	-3.48	-3.63	-4.08	-3.69	-3.37	-3.47	-3.60	-3.85
Ca^{2+} (mM)	12.9	12.7	19.6	29.3	13.6	16.4	18.0	19.5
Cl^- (mM)	334	354	393	387	389	433	437	425
K^+ (mM)	10.2	10.4	12.3	14.5	11.2	12.9	12.7	12.7
Mg^{2+} (mM)	35.8	37.0	36.3	24.3	42.8	47.6	46.0	42.1
Na^+ (mM)	289	301	327	322	290	323	332	338
SO_4^{2-} (mM)	18.4	19.3	22	21.3	21.3	23.4	23.8	23.1
$\text{SI}_{\text{calcite}}$	0.928	0.532	0.112	0.059	0.965	0.950	0.888	0.888
Seawater fraction (%)	66.0	70.0	77.8	76.5	76.9	85.7	86.5	84.2

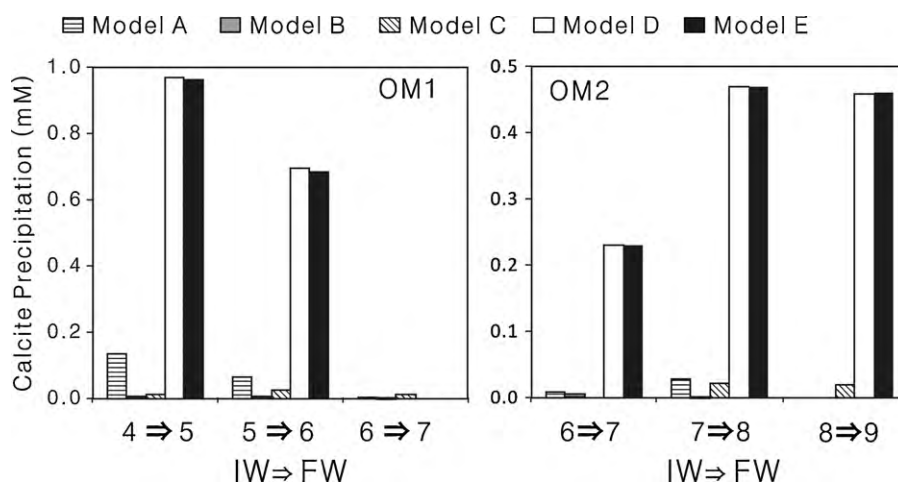


Fig. 5. Amounts of calcite precipitation calculated from each model.

Table 2

Descriptions on the methods used to estimate the roles of various processes inducing calcite precipitation as the shallow porewater (initial water; IW) evolves into the deeper one (final water; FW).

Model (process)	Methods
Model A (porewater aging)	IW was allowed to precipitate calcite till it shows the SI_{calcite} of FW
Model B (mixing)	$\Delta Ca_{\text{mixing}}$ and $\Delta Mg_{\text{mixing}}$ calculated as follows were added into IW in forms of $CaCl_2$ and $MgCl_2$, respectively $\Delta Mg_{\text{mixing}} = (SF^{\text{FW}} - SF^{\text{IW}}) \times Mg^{\text{seawater}}$ $\Delta Ca_{\text{mixing}} = (SF^{\text{FW}} - SF^{\text{IW}}) \times Ca^{\text{seawater}}$ SI_{calcite} of IW was maintained
Model C (dolomitization)	$\Delta Mg_{\text{dolomitization}}$ and $\Delta Ca_{\text{dolomitization}}$ calculated as follows are added into IW in forms of Ca^{2+} and Mg^{2+} , respectively $\Delta Mg_{\text{dolomitization}} = Mg^{\text{FW}} - Mg^{\text{IW}} - Mg_{\text{mixing}}$ $\Delta Ca_{\text{dolomitization}} = -\Delta Mg_{\text{dolomitization}}$ SI_{calcite} of IW was maintained
Model D (weathering)	The same $Ca(OH)_2$ as that estimated from Step 2 of Model E was added into IW SI_{calcite} of IW was maintained
Model E (all above)	Step 1: $CaCl_2$, $MgCl_2$, Ca^{2+} , and Mg^{2+} used for Model B and Model C, were added into IW Step 2: Allowed $Ca(OH)_2$ to dissolve till the water reaches pH of FW SI_{calcite} was maintained to that of FW in all steps

ΔCa (or Mg)_{process}: Ca (or Mg) concentration increased by the given 'process' during the evolution.

Ca (or Mg)_{water} and SF^{water} : Ca (or Mg) concentration and seawater fraction in the given 'water'.

Table 3

A summary of the input conditions of each model applied to the initial porewater.

	Operations	OM1 (IW → FW)			OM2 (IW → FW)		
		4 → 5	5 → 6	6 → 7	6 → 7	7 → 8	8 → 9
Model A	Equilibrated SI_{calcite}^a	0.532	0.112	0.059	0.950	0.888	0.888
Model B	Equilibrated SI_{calcite}^b	0.928	0.532	0.112	0.965	0.950	0.888
	$CaCl_2$ addition	0.46	0.89	-0.15	1.01	0.09	-0.28
	$MgCl_2$ addition	2.01	3.94	-0.65	4.45	0.41	-1.21
Model C	Equilibrated SI_{calcite}^b	0.928	0.532	0.112	0.965	0.950	0.888
	Ca^{2+} addition	0.84	4.65	11.38	-0.32	2.00	2.66
	Mg^{2+} addition	-0.84	-4.65	-11.38	0.32	-2.00	-2.66
Model D	Equilibrated SI_{calcite}^b	0.928	0.532	0.112	0.965	0.950	0.888
	$Ca(OH)_2$ dissolution	0.50	0.36	-0.0017	0.12	0.24	0.24
Model E	Equilibrated SI_{calcite}^a	0.532	0.112	0.059	0.950	0.888	0.888
	$CaCl_2$ addition	0.46	0.89	-0.15	1.01	0.09	-0.28
	$MgCl_2$ addition	2.01	3.94	-0.65	4.45	0.41	-1.21
	Ca^{2+} addition	0.84	4.65	11.38	-0.32	2.00	2.66
	Mg^{2+} addition	-0.84	-4.65	-11.38	0.32	-2.00	-2.66
	$Ca(OH)_2$ dissolution	0.50	0.36	-0.0017	0.12	0.24	0.24

Units are all mM except for SI_{calcite} .

IW, initial porewater; FW, final porewater.

^a SI_{calcite} of the final porewater.

^b SI_{calcite} of the initial porewater.

was approximated by introducing CaCl_2 and MgCl_2 , the amounts of which were equivalent to the differences in seawater fraction (SF) between the final and the initial waters ($\text{SF}^{\text{FW}} - \text{SF}^{\text{IW}}$). To approximate dolomitization (Model C), Mg and Ca concentrations increased by dolomitization ($\Delta\text{Mg}_{\text{dolomitization}}$, $\Delta\text{Ca}_{\text{dolomitization}}$) were introduced into the initial water as free ionic forms (Mg^{2+} , Ca^{2+}). For this, $\Delta\text{Mg}_{\text{dolomitization}}$ was calculated first by subtracting the concentration increased by mixing ($\Delta\text{Mg}_{\text{mixing}}$) from the difference between the final and initial waters ($\text{Mg}^{\text{FW}} - \text{Mg}^{\text{IW}}$), and then the negative amount of $\Delta\text{Mg}_{\text{dolomitization}}$ was attributed as $\Delta\text{Ca}_{\text{dolomitization}}$. The coal ash weathering generating Ca and alkalinity (Model D) was approximated by the dissolution of $\text{Ca}(\text{OH})_2$ [22]. The amount of $\text{Ca}(\text{OH})_2$ dissolution in Model D was adopted from the result of Model E. Model E was performed considering all the processes using the same methods used in the previous models. But, $\text{Ca}(\text{OH})_2$ was allowed to dissolve till the initial water show the pH of the final water. The final amount of $\text{Ca}(\text{OH})_2$ obtained from Model E was used for Model D. $\text{SI}_{\text{calcite}}$ values for Models B, C, and D were set to the values of initial waters to evaluate the effect of each process. In contrast, $\text{SI}_{\text{calcite}}$ values of Model E were set to the values of final waters.

The calculation results show a good agreement with the observed alkalinity and pCO_2 of the final waters when all the processes were considered at the same time (Model E in Fig. 4), indicating that most of the variations in pH, alkalinity, and pCO_2 can be explained by the processes considered in this study. Results show that the simple calcite precipitation has an effect of reducing pH and alkalinity, and raising pCO_2 . This is shown in the results of Model A, which always show the lower pH and alkalinity, and the higher pCO_2 than those of the initial waters (Fig. 4). The calcite precipitation by dolomitization causes the similar effect to that of porewater aging (Model B). In contrast, the water shows the decreasing alkalinity and pCO_2 , and the increasing pH when mineral weathering induces calcite precipitation (Model D). The opposite result of Model D for $6 \Rightarrow 7$ of OM1 (Fig. 4) was associated with the negative dissolution of $\text{Ca}(\text{OH})_2$ (Table 3).

Model D generally shows the alkalinity values very close to the observed ones of the final waters and explains the most of the calcite precipitation occurring during the porewater evolution (Figs. 4 and 5). The calcite precipitations by Model C were negligible or much smaller than those by mineral weathering even between the porewaters where Ca concentrations are significantly increased by dolomitization (e.g., $5 \Rightarrow 6$, and $6 \Rightarrow 7$ of OM1; see Table 3) because pH is also decreased by dolomitization. The decrease in pH increases the dissolution capacity and, thus, the mineral precipitation is largely suppressed [15]. Calcite precipitations by porewater aging were also small relative to the mineral weathering effect owing to the same reason, leading to a conclusion that the decreases in alkalinity by the reaction with coal ash are caused mostly by the weathering-induced calcite precipitation.

No individual process could derive the pH and pCO_2 values similar to those of final waters, indicating that these parameters are sensitive to all the processes except seawater mixing. The effect of mixing was generally minor or negligible because the calculations were performed for the porewaters with small differences in seawater fraction. In overall, porewater aging and dolomitization play a role reducing the drastic pH and pCO_2 changes that can be caused by mineral weathering.

5. Conclusions

The results of this study show that pH, pCO_2 , and alkalinity of shallow porewater are very sensitive to the soil cover. Under a condition without soil cover, the shallow porewater showed pH as high as 9.43 because the infiltration of rainwater limits the CO_2 supply from the unsaturated zone. The increase in alkalinity was also lim-

ited by calcite saturation; as a result, the shallow porewater showed very low alkalinity. In the presence of soil cover, the porewater can react with minerals under a CO_2 open condition and the pCO_2 was high due to the CO_2 gas trapped underneath the soil cover, resulting in the lower pH. Alkalinity, which buffers pH, was also high because the lowered pH increased the mineral-dissolution capacity. Leaching experiments of previous studies have shown that the release of trace elements from coal ash is normally high in alkaline or acidic pH ranges and low in neutral ranges [5–7]. In this regard, covering the coal ash disposal site with low permeability soils, which is normally mandatory in many countries, is desirable to prevent the drastic increase of pH in the porewater of alkaline coal ash disposal sites.

Alkalinity of the saline porewaters in the depth range where the effect of soil cover was insignificant showed a continuously decreasing trend as the residence time increases and the alkalinity at the deepest part was even lower than that of seawater. This phenomenon was caused mostly by coal ash weathering, which is opposite to the general effect of mineral weathering. It is well known that mineral weathering normally increases alkalinity [23,24]. However, our study shows that further weathering of coal ashes under a condition of calcite saturation induces calcite precipitation by common ion effect and the decrease in alkalinity is observed. The pH and the pCO_2 of the saline water are regulated in a manner that the increase in pH and the decrease in pCO_2 by mineral weathering are suppressed by the calcite precipitations induced by porewater aging and dolomitization. This result also suggests that dolomitization can play an important role in regulating pH and pCO_2 in saline porewaters and, therefore, it also needs to be considered in predicting leaching and behaviors of trace elements in the coastal disposal sites.

Acknowledgments

This study was financially supported by the National Research Foundation of Korea (#2009-0080708). We thank Seong-Ku Yeo for his field and lab assistances.

References

- [1] D.C. Adriano, A.L. Page, A.A. Elseewi, A.C. Chang, I. Straughan, Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: a review, *J. Environ. Qual.* 9 (1980) 333–344.
- [2] L.E. Eary, D. Rai, S.V. Mattigod, C.C. Ainsworth, Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues. II. Review of the minor elements, *J. Environ. Qual.* 19 (1990) 202–214.
- [3] J. Jankowski, C.R. Ward, D. French, S. Groves, Mobility of trace elements from selected Australian fly ashes and its potential impact on aquatic ecosystems, *Fuel* 85 (2006) 243–256.
- [4] T. Praharaj, S.P. Swain, M.A. Powell, B.R. Hart, S. Tripathy, Delineation of ground-water contamination around an ash pond: geochemical and GIS approach, *Environ. Int.* 27 (2002) 631–638.
- [5] K. Kim, S.M. Park, J. Kim, S.H. Kim, Y. Kim, J.T. Moon, G.S. Hwang, W.S. Cha, Arsenic concentration in porewater of an alkaline coal ash disposal site: roles of siderite precipitation/dissolution and soil cover, *Chemosphere* 77 (2009) 222–227.
- [6] T.L. Theis, J.L. Wirth, Sorptive behavior of trace metals on fly ash in aqueous systems, *Environ. Sci. Technol.* 11 (1977) 1096–1100.
- [7] E.E. Van der Hoek, R.N.J. Comans, Modeling arsenic and selenium leaching from acidic fly ash by sorption on iron (hydr)oxide in the fly ash matrix, *Environ. Sci. Technol.* 30 (1996) 517–523.
- [8] A.G. Kim, G. Kazonich, M. Dahlberg, Relative solubility of cations in class F fly ash, *Environ. Sci. Technol.* 37 (2003) 4507–4511.
- [9] J.J. Dijkstra, H.A. Van der Sloot, R.N.J. Comans, The leaching of major and trace elements from MSWI bottom ash as a function of pH and time, *Appl. Geochem.* 21 (2006) 335–351.
- [10] A.G. Kim, The effect of alkalinity of class F PC fly ash on metal release, *Fuel* 85 (2006) 1403–1410.
- [11] C. Kersch, S.P. Oritz, G.F. Woerlee, G.J. Witkamp, Leachability of metals from fly ash: leaching tests before and after extraction with supercritical CO_2 and extractants, *Hydrometallurgy* 72 (2005) 119–127.
- [12] W. Stites, L.W. Chambers, A method for installing miniature multilevel sampling wells, *Ground Water* 29 (1991) 430–432.

- [13] D.L. Parkhurst, C.A.J. Appelo, User's Guide to PHREEQC (version 2)—A Computer Program for Speciation, Batch-Reaction, One-dimensional Transport, and Inverse Geochemical Calculations, USGS Water-Resources Investigations Report 99-4259, 1999.
- [14] S.K. Yeo, Geochemical interaction between pulverized coal ash and seawater: a case study on an ash pond of Seocheon Power Plant, Master Thesis, Kunsan National University, Kunsan, Korea, 2002.
- [15] J.I. Drever, *Geochemistry of Natural Waters: The Surface and Groundwater Environments*, 3rd ed., Prentice-Hall Inc., Englewood Cliffs, NJ, 1997.
- [16] K. Kim, D.H. Jeong, Y. Kim, Y.K. Koh, S.H. Kim, E. Park, The geochemical evolution of very dilute CO₂-rich water in Chungcheong Province, Korea: processes and pathways, *Geofluids* 8 (2008) 3–15.
- [17] X. Querol, J.L.F. Turiel, A.L. Soler, The behaviour of mineral matter during combustion of Spanish subbituminous and brown coals, *Miner. Magn.* 58 (1994) 119–133.
- [18] S. Khanra, D. Mallick, S.N. Dutta, S.K. Chaudhuri, Studies on the phase mineralogy and leaching characteristics of coal fly ash, *Water Air Soil Pollut.* 107 (1998) 251–275.
- [19] D.E. Hockley, H.A. van der Sloot, Long-term processes in stabilized coal-waste blocks exposed to seawater, *Environ. Sci. Technol.* 25 (1991) 1408–1414.
- [20] Y. Bami, B. Herut, A. Shemesh, H. Cohen, Surface chemical characteristics of coal fly ash particles after interaction with seawater under natural deep sea conditions, *Environ. Sci. Technol.* 33 (1999) 276–281.
- [21] S.M. Park, A study on leaching behavior of elements by geochemical interactions between coal ash and seawater, Master Thesis, Kunsan National University, Kunsan, Korea, 2003.
- [22] K. Kim, N. Rajmohan, H.J. Kim, S.H. Kim, G.S. Hwang, S.T. Yun, B. Gu, M.J. Cho, S.H. Lee, Evaluation of geochemical processes affecting groundwater chemistry based on mass balance approach: a case study in Namwon, Korea, *Geochem. J.* 39 (2005) 357–369.
- [23] K. Kim, Long term disturbance of groundwater chemistry following well installation, *Ground Water* 41 (2003) 780–789.
- [24] K. Kim, H.J. Kim, B.Y. Choi, S.H. Kim, K.H. Park, E. Park, D.C. Koh, S.T. Yun, Fe and Mn levels regulated by agricultural activities in alluvial groundwaters underneath a flooded paddy field, *Appl. Geochem.* 23 (2008) 44–57.