Coal fly ash and synthetic coal fly ash aggregates as reactive media to remove zinc from aqueous solutions

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ABSTRACT

Coal fly ash (CF) and synthetic coal fly ash aggregates (SCFAs) were evaluated as low-cost reactive media for the remediation of groundwater contaminated with Zn. The SCFAs were prepared by mixing CF, sodium silicate, and deionized (DI) water. Serial batch kinetic and static tests were conducted on both CF and SCFAs, under various conditions (i.e., pH, initial Zn concentration, reaction time, and solid dosage), using $Zn(NO_3)_2 \cdot 6H_2O$ solutions. Serial column tests were also conducted on both CF and SCFAs. The final rather than the initial pH of the solution had a greater effect on the removal of Zn. At pH > 7.0, the removal of Zn was due to precipitation, whereas at <7.0, the removal of Zn was due to adsorption onto the reactive media. The removal of Zn increased with increasing dosage of the reactive medium and decreasing initial Zn concentration. The results of the column and batch tests were comparable. Preferential flow paths were observed with CF, but not SCFA. The hydraulic conductivity of CF was more significantly decreased than that of SCFA with increasing dry density of the specimen.

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1. Introduction

Groundwater contaminated by heavy metals in industrial areas, especially abandoned mine areas has been the cause of great concern as heavy metals have a detrimental impact on humans [1,2]. Various methods have been used for the remediation of the groundwater contaminated by heavy metals. Of these methods, a permeable reactive barrier (PRB), as a passive in situ treatment method, has been increasingly used for the treatment of groundwater contaminated by various inorganic and organic chemicals due to lower operation and maintenance costs as well as external energy inputs relative to other treatment methods. The main component of the PRB is a reactive medium, which is placed in the subsurface for the removal of contaminants or the conversion of toxic into non-toxic chemicals [1,2].

Low-cost reactive media, possessing strong reactivity, high hydraulic conductivity, and long-term physical and chemical stability, are required for the PRB [1,3]. Generally, naturally abundant materials or industrial by-products are regarded as low-cost reactive media [4]. Various reactive media, such as granular zero valent iron (Fe[0]), granular activated carbon, zeolite, apatite, and limestone, are commonly used for the treatment of heavy metals contamination by precipitation, adsorption, and reduction [1,5–7]; however,

the use of these pure reactive media can result in high treatment costs. Therefore, many studies have been conducted on low-cost industrial by-products, such as foundry sand and red mud, which have comparable properties to those of pure reactive media [6–9].

One of these possible low-cost industrial by-product reactive media is coal fly ash (CF), which is produced from the burning of coal in fired power plants. In general, CF consists of mainly (SiO_2), alumina (Al_2O_3), lime (CaO), and iron oxide (Fe_2O_3), with a trace amount of unburned carbon. Even though the physical and chemical properties of CF vary depending on the mineralogy and particle size of the raw material and the type of coal burning process, many studies have shown CF to be a good reactive medium for the removal of various heavy metals (e.g., Cd, Cr, Cu, Pb, and Zn) from water systems by adsorption and precipitation. However, the adsorption capacity of CF is relatively lower than that of other potential reactive media such as granular activated carbon and zeolite. Thus several studies were conducted to improve the adsorption capacity of CF by activating it (e.g., hydrothermal synthesis of zeolite from CF) [10–18].

In addition, several studies have been conducted to evaluate the feasibility of CF as the reactive medium for the PRB for the treatment of groundwater contaminated by heavy metals [12,19]. For an appropriate reactive medium for the PRB, a high hydraulic conductivity and environmental stability are essential besides strong reactivity and low-cost. However, CF has pozzolanic characteristics, becoming cementatious on the reaction of lime (CaO) with the pozzolans (SiO_2, Al_2O_3, and Fe_2O_3) in the presence of water [20].

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Table 1
Components of CF and SCFAs

Material	Composition (wt.%)		
	Coal fly ash	Sodium silicate liquid	DI water
CF	100.0	0.0	0.0
SCFA 1	62.2	24.0	13.8
SCFA 2	60.7	31.7	7.6
SCFA 3	55.3	36.0	8.6

This cementatious material can clog pore spaces and decrease the hydraulic conductivity of the barrier when CF is used as a reactive medium in the PRB, potentially resulting in redirection of the flow paths and changes to the residence time [1,21–25].

Another key issue with the use of CF as a reactive medium in the PRB is the potential release of toxic elements from CF to the groundwater due to changes in the environmental conditions (e.g., pH and ionic strength) [1,2]. CF frequently contains trace elements, such as As, Cd, Cu, Pb, Zn, and Se, which can have environmental impacts if released (e.g., groundwater quality) [26–28].

The objective of this study was to evaluate the potential of CF and synthetic coal fly ash aggregate (SCFA) as reactive media in the PRB for the treatment of groundwater contaminated by heavy metals, especially Zn. The SCFA, which is a mixture of CF and sodium silicate, was synthesized to minimize the pozzolanic effect on the barrier, which results in a decreased hydraulic conductivity when used as the reactive medium. Batch tests were conducted on both CF and SCFA for evaluation of the removal efficiency of Zn in aqueous solutions under various conditions (i.e., pH, initial Zn concentration, reaction time, and solid dosage), as well as their suitability as reactive media when used as in situ reactive barriers for groundwater. Column tests were conducted on both CF and SCFA to evaluate of hydraulic performance and efficiency of Zn removal under more realistic flow-through conditions. Batch leaching tests were also conducted on both CF and SCFA for evaluation of the environmental feasibility with respect to environmental regulations (i.e., drinking water standards).

2. Materials and methods

2.1. Coal fly ash (CF) and synthetic coal fly ash aggregates (SCFAs)

The CF used in this study was obtained from a coal-fired power plant in Korea. The SCFA was prepared to minimize potential clogging and cementation problems associated with CF when used as a reactive medium in PRBs for the treatment of heavy metals in groundwater, with the components of the mixture shown in Table 1. Sodium silicate liquid was used as an additive to enhance the solidification and strength. The sodium silicate has been commonly used as a cementing material to increase the rate of solidification and improve strength [29]. The ratio of SiO_2 to Na_2O of the commercial sodium silicate used in this study was about 2.0 (Si:Na ratio = 135,463 mg/L:68,566 mg/L, analyzed

by Seoul National University National Center for Inter-University Facilities).

The sodium silicate liquid was mixed with deionized (DI) water in a stainless steel container, with CF then added to the DI water and sodium silicate liquid mixture. The CF, sodium silicate, and DI water was thoroughly mixed for approximately 2 min using a mechanical stirrer, after which, the mixture was placed in a Teflon mold with small holes to produce pillar samples. The diameter and height for each hole were each 3.0 mm. The mixture filled into the small holes of the Teflon mold was cured in an oven at about 100 °C for 24 h. After curing, the pillar samples were removed from the Teflon mold and then dried at room temperature 22 °C for 7 days. Detailed procedures for the syntheses of the SCFAs have been described in Hong (2008) [30].

The physical properties and chemical composition of CF and SCFAs are shown in Table 2. The specific gravity was measured following ASTM C 618 [31], with those of CF and SCFAs ranging between 2.17 and 2.41. The pH of the paste was measured on CF pastes prepared with DI water [32]. CF (12.4) had a relatively higher paste pH than those of SCFAs, ranging between 10.5 and 11.5. The specific surface area of CF was determined by the BET method (Model; ASAP 2020) at the Kyounggi technical complex. The specific surface areas of SCFAs ranged between 1.82 and 3.30 m^2/g, which were lower than that of CF (4.73 m^2/g) due to their larger particle sizes. The specific surface area of the SCFA increased with increasing CF content. The specific surface area of SCFA 1 (3.30 m^2/g) with the highest CF content was the largest of the SCFAs.

The X-ray fluorescence (XRF) results showed that CF was mainly composed of SiO_2 (53.4%), Al_2O_3 (21.0%), Fe_2O_3 (8.0%) and CaO (7.4%), and was classified as a class F fly ash in accordance with ASTM C 618-99 [31], as the SiO_2, Al_2O_3, and Fe_2O_3 content exceeded 70%. The compositions of SCFAs were comparable to those of CF, but had slightly lower CaO and higher Na_2O and SiO_2 contents due to the addition of the sodium silicate.

2.2. Batch leaching tests

2.2.1. Water leaching tests (WLTs)

WLTs were conducted on CF and SCFAs following the ASTM D 3987 procedure [30] to assess their leaching characteristics and determine their suitability for the PRB with respect to the drinking water standards (DWSs) defined by the Korea Ministry of Environment (KMOE), United States Environmental Protection Agency (U.S. EPA) and World Health Organization (WMO) [33–35].

Samples were dried at room temperature (22 °C). A 10 g sample was mixed with 0.2 L of DI water at pH 6.3 in a 0.25 L-sealed container. The mixture was then shaken in a shaking water bath, at a rate of 29 rpm (rotations/min), for 18 h at room temperature (22 °C). After mixing, the mixture was allowed to settle for 5 min, with the pH of the leachate measured immediately using a pH meter (DKK-TOA Corp., Japan). The leachate was filtered through 0.45 μm-filter paper, stored in a polyethylene bottle, and acidified with nitric acid solution to pH < 2.0 prior to the chemical analyses.

Table 2
Physical properties and chemical composition of CF and SCFAs

Material	Specific gravity	Paste pH	Specific surface[a] (m^2/g)	Chemical composition (%)							
				SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	Others	LOI[b]
CF	2.41	12.4	4.73	53.4	21.0	8.0	7.4	1.6	2.1	2.9	3.6
SCFA 1	2.22	11.5	3.30	54.7	19.7	6.1	5.5	0.4	4.0	2.1	5.2
SCFA 2	2.22	10.4	2.81	55.2	20.5	6.3	5.7	0.6	4.4	2.3	5.0
SCFA 3	2.17	10.5	1.82	54.3	20.1	6.7	6.1	0.5	3.5	2.3	4.9

[a] Measured by the BET method.
[b] Loss on ignition.

2.2.2. Toxicity characteristic leaching procedure (TCLP) tests

TCLP tests were conducted on CF and SCFAs, in accordance with U.S. EPA Method 1311 [36], to determine the leachability of the inorganic compounds presented in CF and SCFAs under strong acidic conditions (pH 3.0). The TCLP test was similar to that of the WLT, with the exception of the different extract pH (TCLP: 3.0 vs. WLT: 6.3).

Samples were dried at room temperature (22 °C). A 7 g sample was mixed with 0.14 L of acetic acid solution at a pH of 3.0 in a 0.25 L-sealed container. The mixture was then shaken in a shaking water bath, at a rate of 29 rpm (rotations/min), for 18 h at room temperature (22 °C). The pH of the leachate was measured immediately using a pH meter. The leachate was filtered through 0.45 μm-filter paper. The filtered leachate was stored in a polyethylene bottle and adjusted to pH < 2.0 by the addition of nitric acid (HNO_3) solution prior to the chemical analyses.

2.3. Batch Zn removal tests

Batch kinetic and static tests were conducted on CF and SCFAs using Zn solutions. A 1000 mg/L stock Zn solution was prepared by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ solid in DI water. Solutions with various Zn concentrations were prepared by diluting the 1000 mg/L stock Zn solution with DI water. The initial pH of the solution was adjusted with concentrated nitric acid or 1.0 M-sodium hydroxide solution.

2.3.1. Batch kinetic tests

A series of batch kinetic tests were conducted on CF, SCFA 1, SCFA 2, and SCFA 3 to determine the reaction time required to establish equilibrium conditions and the adsorption kinetics for Zn, using an initial Zn concentration of 100 mg/L, at an initial pH of 2.0. A 1 g sample of CF or SCFA was placed in a 50 mL-polypropylene copolymer centrifuge tube. The tube was then tumbled for various reaction times, ranging between 20 and 1440 min, using a rotation shaker at 30 rpm, with the leachate collected at designated sampling times (i.e., 20, 40, 60, 80, 120, 720, 1080, and 1440 min). The pH of the suspension was measured using a pH meter immediately after tumbling. The suspension was filtered through 0.45 μm-filter paper, stored in polyethylene bottle, and acidified with nitric acid solution to pH < 2.0 prior to the chemical analyses.

2.3.2. Batch static tests

Batch static tests were conducted with various CF or SCFA 1 solid concentrations ranging between 5 and 100 g/L in a 50 mL-polypropylene copolymer centrifuge tube containing initial Zn concentrations ranging between 5 and 100 mg/L. The tests were conducted at the specified initial solution pH ranging between 1.0 and 5.5.

A designated sample of CF or SCFA 1 was placed in a 50 mL-polypropylene copolymer centrifuge tube containing a 100 mg/L-Zn solution with a pH ranging between 1.0 and 5.5, adjusted by addition of concentrated nitric acid. The tube was then tumbled for 24 h using a rotation shaker at 30 rpm, and this was found to be sufficient to ensure the attainment of equilibrium in the batch kinetic tests. The final pH of the suspension was measured using a pH meter immediately after tumbling. The suspension was filtered through 0.45 μm-filter paper, stored in a polyethylene bottle, and acidified with nitric acid solution to pH < 2.0 prior to chemical analyses. The desired pH of the solution and final pH of the suspension are defined as the initial solution pH and the final pH of the solid and solution mixture (i.e., suspension), respectively. In addition, control tests, without any solid samples (i.e., CF and SCFA 1), were conducted with an initial Zn concentration of 100 mg/L at

various pHs, ranging between 2.0 and 12.0 to evaluate the effect of pH on the removal of Zn by precipitation. The pH of the solution was adjusted by addition of concentrated nitric acid or 1.0 M-sodium hydroxide solution.

2.4. Column tests

2.4.1. Column Zn removal tests

Column Zn removal tests were conducted on CF and SCFA 1 in rigid-wall glass columns for evaluation of the Zn removal efficiencies and leaching stabilities under more realistic flow-through conditions.

The material was packed into the glass column to simulate the dry density under potential field conditions (i.e., CF and SCFA 1: 0.93 g/cm^3). The rigid-wall glass column was 10 cm in height and 2.4 cm in diameter. Glass filter disks, 0.4 cm thick, were placed on the top and bottom of the material to prevent clogging during permeation. The 100 mg/L Zn solutions, at pH 2.0 and 6.2, were used as the influents, with a 2 L-mass flask used as the influent reservoir.

After placement of the specimen into the column, the influent solution was injected into the bottom of the column (i.e., upward flow), to minimize consolidation of the specimen, using a metering pump (Model QG50, USA) at a flow rate of 3 mL/min, representative of the typical hydraulic conductivity of a sand aquifer ($k \sim 1.0 \times 10^{-2}$ cm/s), assuming a hydraulic gradient of one [37].

After terminating the column test with the Zn solution, the influent Zn solution was switched to DI water to evaluate the leaching potential of the Zn adsorbed onto the reactive medium, as well as the dissolution of Zn precipitates caused by the elevated pH. Effluent samples were periodically collected during permeation. The effluent sample was collected at a given period and measured the volume to evaluate whether changes occurred in the flow rate due to precipitation during permeation. In addition, the pH and Zn concentration of the effluent samples were measured.

2.4.2. Hydraulic conductivity tests

Hydraulic conductivity tests were conducted on CF and SCFA 1, under falling-head conditions, using rigid-wall glass columns, with a diameter of 2.4 cm and a height of 10.0 cm. The material was packed into the glass column to the desired dry density ranging between 0.88 and 1.12 g/cm^3. The specimen was then permeated with DI water with an average hydraulic gradient of 11. The tests were continued until the hydraulic conductivity became steady and the volume of the inflow equaled that of the outflow.

2.5. Chemical analyses

The filtered samples from the batch and column tests were analyzed for their elements concentrations (e.g., Zn, Na, Al, Cr, and Ca) via inductivity coupled plasma-atomic emission spectrometry (ICP-AES) at the National Center for Inter-University Research Facilities, Seoul National University.

3. Results and discussion

3.1. Batch leaching tests

The WLTs and TCLP tests were conducted on CF and SCFAs to assess environmental risks when used as reactive media. The procedures for the WLTs and TCLP tests were similar, with the exception of different pH of the leaching media (WLT: pH 6.3, TCLP: pH 3.1). The concentrations of the elements in the leachate from the WLTs and TCLP tests are summarized in Table 3, along with the drinking water standards (DWSs) defined by KMOE, U.S. EPA, and WHO

Table 3
Results of leachate concentrations from the WLT and TCLP tests

Element	Drinking water standards (μg/L)			Leachate concentration (μg/L)							
	KMOE[a]	U.S. EPA[b]	WHO[c]	WLT (initial pH 6.3)				TCLP (initial pH 3.1)			
				CF	SCFA 1	SCFA 2	SCFA 3	CF	SCFA 1	SCFA 2	SCFA 3
pH	5.8–8.5	6.5–8.5	NS	12.0	11.8	11.7	12.0	5.6	4.9	4.9	5.1
Na	NS	NS	200000.0	3820.0	**500600.0**	**561400.0**	**639900.0**	4470.0	**550200.0**	**667500.0**	**745600.0**
Ca	NS	NS	NS	380300.0	6460.0	6570.0	3610.0	869200.0	12500.0	16500.0	8900.0
As	50.0	10.0	10.0	4.1	**31.0**	**12.2**	**17.0**	**269.2**	**40.9**	**20.4**	**20.6**
Cd	5.0	5.0	3.0	0.8	0.2	0.2	0.2	3.5	0.2	0.2	0.2
Cr[d]	50.0[d]	100.0[e]	50.0[d]	**134.0**	**57.10**	43.4	**52.9**	**332.9**	**51.7**	**55.1**	**50.1**
Cu	1000.0	1300.0	2000.0	3.2	1.9	3.9	2.7	11.4	23.6	10.1	5.0
Mn	300.0	50.0	500.0	0.2	0.7	0.7	0.6	**735.7**	10.5	8.1	3.7
Ni	NS	20	20.0	29.7	<0.1	<0.1	<0.1	**97.5**	1.8	2.3	1.1
Pb	50.0	150.0	10.0	0.1	<0.1	<0.1	<0.1	0.2	5.0	3.3	3.3
Se	10.0	50.0	10.0	**61.6**	**41.3**	**38.3**	**44.0**	**78.9**	**34.5**	**40.7**	**41.6**
Zn	1000.0	5000.0	3000.0	26.3	20.1	6.7	5.7	59.6	54.2	17.5	13.2

[a] Drinking water standards defined by Korea Ministry of Environment [32].
[b] Drinking water standards defined by U.S. Environmental Protection Agency [33].
[c] Drinking water standards defined by World Health Organization [34].
[d] Cr^{6+} concentration.
[e] Total Cr concentration, numbers in bold exceed the DWSs of KMOE, NS represents no standards defined, <represents below detection limit.

[33–35]. For all the elements analyzed, the DWSs of the WHO were more conservative than those of the other DWSs, with the exception of Zn. Any concentration exceeding those specified in the DWSs are shown in bolds.

For the WLTs, the pH of the leachates for all materials (i.e., CF and SCFAs) increased from 6.3 to approximately 12.0 after mixing. The concentrations of Cr (134.0 μg/L) and Se (61.6 μg/L) for the CF were higher than the DWSs of all the regulatory agencies. However, these results were comparable to those reported by Bin-Shafique et al. [38] when conducting WLTs on various CFs (Cr: 59.0–123.2 μg/L, Se: 18.0–82.0 μg/L). Conversely, the Cr concentrations for the SCFAs slightly exceeded the DWS of KMOE, but fell below the DWS of the U.S. EPA. The Cr concentrations from the WLTs and DWSs of the U.S. EPA are given as the total Cr concentrations, whereas the Cr concentration of the DWSs of the KMOE represents the Cr^{6+} concentration. The Se concentrations for all materials exceeded the DWSs of the KMOE, but the SCFAs had lower Se concentration than the DWSs of the U.S. EPA. The As concentrations for the SCFAs exceeded the DWSs of the U.S. EPA and WHO, but were below the DWSs of the KMOE. The Na concentrations for the SCFAs exceeded the DWSs of the WHO as sodium silicate had been added to the SCFAs. Some studies indicate that a high concentration of Na may cause negative impacts on human such as an increase in blood pressure if taken for very long period [39]. However, the WHO standard is based on its esthetic effects (i.e., taste) and no requirement for Na exists in the DWSs of the KMOE and U.S. EPA.

For the TCLP tests of the leaching medium with a pH of 3.1, the pH of the leachates for all materials increased slightly (4.9–5.6). In general, the concentrations of all elements analyzed increased with decreasing pH of the leaching medium from 6.3 (WLT) to 3.1 (TCLP test). Of the elements analyzed, the As, Cr, Mn, and Se concentrations for the CF exceeded the DWSs of the KMOE. Conversely, only the Cr and Se concentrations for the SCFAs exceeded the DWSs of the KMOE, but this was only modest. Moreover, the Cr and Se concentrations for SCFAs were below the DWSs of the U.S. EPA.

The results of the batch leaching tests indicate that the SCFAs may pose less environmental risks than the CF, even though none of the materials tested completely satisfied any of the DWSs used in this study. In addition, the environmental risk may decrease when the materials are used as reactive media, which are placed below the groundwater table, due to dilution effects.

3.2. Batch Zn removal tests

3.2.1. Batch kinetic tests

A series of batch kinetic tests were conducted on CF, SCFA 1, SCFA 2, and SCFA 3 to determine the adsorption kinetics and time to attain equilibrium for Zn at an initial pH of 2. Batch kinetic tests were conducted only at an initial pH of 2 to mimic acid mine drainage conditions because when the initial pH was higher than 2, the final pHs became higher than 7 within 30 min, resulting in approximately complete removal of the Zn from the solutions due to precipitation (explained later). The results of the batch kinetic tests are shown in Fig. 1. The removal of Zn represents the percentage of Zn removed in the batch kinetic tests to that of the initial Zn concentration in the solution.

The removal of Zn increased with increasing reaction time. For CF, the greatest removal of Zn occurred within 2 h, but then became stable thereafter (i.e., 100% Zn removal). Conversely, the removal of Zn for the SCFAs increased gradually with increasing reaction time. Of the SCFAs, SCFA 3, with a lower fraction of CF, gave the greatest removal of Zn for a given time, but the Zn was completely removed from solution after 24 h, with the exception of SCFA 1, with the highest fraction of CF. The removals of Zn after 6 h of reaction were approximately 70 and 35% for SCFA 1 and SCFA 2, respectively, but then increased to 100% for both after 24 h. However, for SCFA 1, the removal of Zn gradually increased to about 23% after 6 h, but then only slightly increased to 30%, after 24 h. More rapid removal of Zn for CF than SCFAs is probably due to higher the specific surface area of CF ($4.73 m^2/g$) compared with SCFAs ($1.82–3.30 m^2/g$). In addition, the Zn may be delivered more rapidly to the adsorption surface of CF than SCFAs because SCFAs are porous aggregates [11].

From the batch kinetic tests, the removal of Zn was shown to be directly related to the final suspension pH, as shown in previous studies [13,14]. The final suspension pH increased, and then stabilized with increasing reaction time. For CF, the final suspension pH increased by approximately 10 units after 30 min, but became stable at pH 10 after 2 h; whereas, for SCFA 2 and SCFA 3, the final suspension pHs were less than 7 after 6 h of reaction time, but increased by approximately 11 unit. For SCFA 1, even after 24 h, the final suspension pH did not increase to much more than 7.0, indicating no significant precipitation of Zn ions, which were precipitated at pH > 7.0 [41]. An increase in pH is generally attributed to the lime (CaO), organic materials, and leached base metals [38].
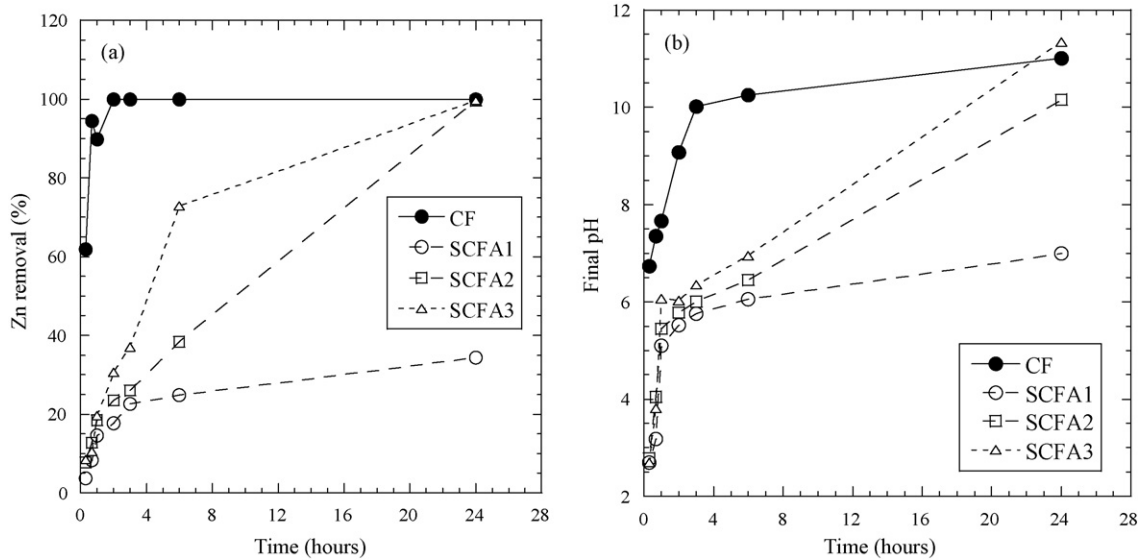
Fig. 1. The removal of Zn (a) and final pH (b) as a function of time for CF and SCFAs at the initial solution pH of 2.0.

To investigate the effect of the final suspension pH on the removal of Zn in the batch kinetic tests, a series of batch tests were conducted under various final pH conditions. The pH of the solution was set at the specified final pH by the addition of HNO_3 or NaOH solutions. As control tests, no solids (i.e., CF or SCFAs) were used in the batch test, where the removal of Zn occurred mainly due to precipitation. The removals of Zn as a function of the final solution pH without solids and final suspension pH with solids in the batch tests are shown in Fig. 2.

In the control tests without solids, the precipitation of Zn began at pH higher than around 6, and increased significantly with increasing pH. In the batch tests with solids (i.e., CF and SCFA 1), the Zn ions were removed by approximately 20%, even pH less than 7. For pH higher than 7, the removals of Zn in the batch tests with the CF and SCFA 1 were approximately 20% higher than those in the control tests. The results of the tests indicate that for pH < 6.0, Zn ions were removed from the batch tests with solids due only

to adsorption (about 20% Zn removal). Adsorption of Zn ions onto fly ash may be attributed to the electrostatic attraction because fly ash has negative surface charge. This can be caused by some components of the fly ash; e.g., SiO_2, Al_2O_3, and Fe_2O_3. The point of zero charges referred to as the isoelectric point for SiO_2, Al_2O_3, and Fe_2O_3 are 2.0, 6.7, and 8.5, respectively [40,41]. Accordingly, most Zn ions are adsorbed onto SiO_2 rather than Al_2O_3 and Fe_2O_3 at a pH < 6.0. On the other hand, at pH > 7.0, Zn ions were removed from the batch tests with solids as a result of adsorption and precipitation [11–14,40]. At pH < 7.0, the removal of Zn was approximately twice as high for SCFA 1 (~20%) than for CF (~10%), indicating that SCFA 1 has a higher adsorption capacity. This higher adsorption capacity may be attributed to the presence of zeolites and calcium silicate hydrates on SCFA 1. Some zeolites may be formed by conversion of CF during the synthesis of SCFA 1. Zeolites converted from CF can have a higher sorption capacity than CF [17,18]. Zn ions also can be adsorbed in the interlayer sites of calcium silicate hydrates, which are formed by reaction of silicates and calcium oxides, resulting in an increase in the adsorption capacity [42].
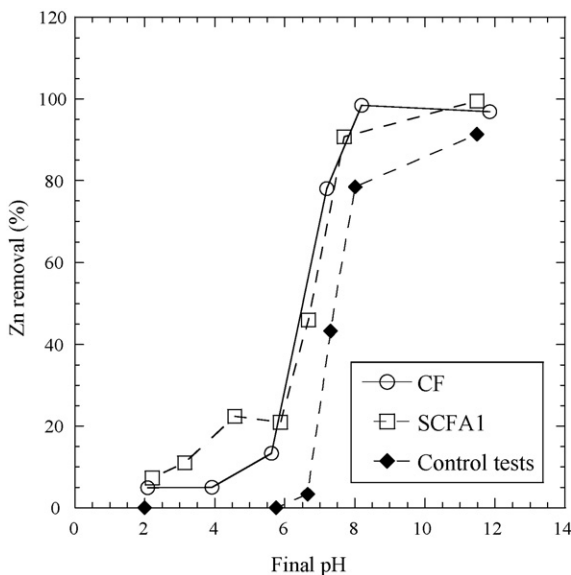
3.2.2. Batch static tests

A series of batch static tests were conducted on CF and SCFA 1 to investigate how the initial and final solution pH, reactive media dosage and initial Zn concentration affected the removal of Zn from the solutions. Of the SCFAs, only SCFA 1 was used in the batch static tests to evaluate a conservative material with respect to its efficiency, as SCFA 1 showed less Zn removal characteristics in the batch kinetic tests (Fig. 1).

3.2.2.1. Effect of pH. A series of batch static tests were conducted on CF and SCFA 1 using the 100 mg/L $Zn(NO_3)_2$ solution with various initial pH, ranging from 1.0 to 5.5. In general, the removal of Zn increased with increasing initial pH, with almost complete Zn removal (~100%) at pH > 2.0, regardless of the materials, as shown in Fig. 3(a). The final solution pH increased significantly from 2.0 to 7.0 on increasing the initial solution pH from 1.0 and 2.0 (Fig. 3(b)), indicating that adsorption caused the removal of Zn with the initial pH range of 1.0–2.0. A gradual increase in the final solution pH occurred from 8.0 to 12.0 when the initial solution pH was increased from 2.0 to 5.5 (Fig. 3(b)), indicating that the removal of Zn occurred due to precipitation of Zn at initial pH between 2.0 and 5.5 [11].
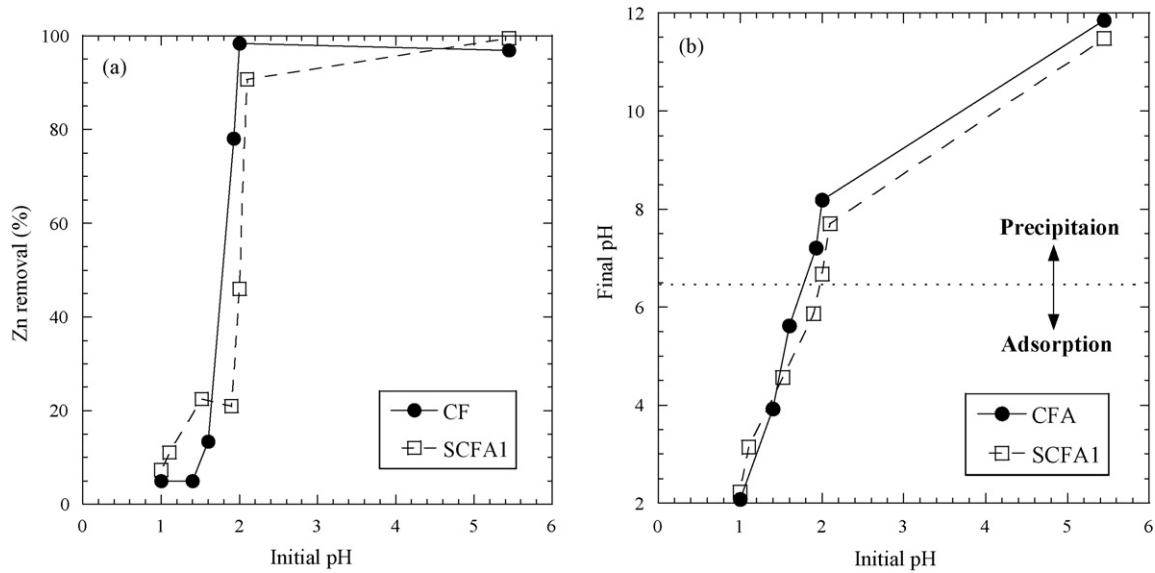

Fig. 2. The removal of Zn as a function of the final solution pH from the batch tests.

Fig. 3. The removal of Zn (a) and final suspension pH (b) as a function of the initial solution pH for CF and SCFA 1 from the batch tests.

As shown in Fig. 3, the Zn was removed from the solutions predominantly by adsorption at a final pH < 6.5 (∼30%), whereas the Zn was removed from the solutions predominantly by precipitation at a final pH > 6.5, regardless of the materials. These results suggest that both CF and SCFA 1 can be used as reactive media for the removal of Zn ions from solutions with an initial pH of less than 2.0, but the removal efficiencies were only modest (∼25%). Conversely, for solutions with a pH higher than 3.0, the Zn ions can be completely removed by both adsorption and precipitation when CF and SCFA 1 are used as reactive media.

3.2.2.2. Effect of initial Zn concentrations. A series of batch tests were conducted on both CF and SCFA 1 with various initial Zn concentrations, ranging from 20 to 120 mg/L and under specific pH conditions, ranging from 5.2 to 6.8. The Zn was removed from the solutions under pH conditions between 5.2 and 6.8 mainly due to adsorption. The removal of Zn as a function of the initial Zn concentration is shown in Fig. 4. In general, the removal of Zn decreased on increasing the initial Zn concentration with both CF and SCFA 1, as shown in previous studies [11–14]. The removal of Zn with SCFA 1 was higher than that with CF for a given initial Zn concentration. These results suggest that SCFA 1 has a higher adsorption capacity than CF, which increases with decreasing initial Zn concentration.

3.2.2.3. Effect of reactive media dosage. A series of batch static tests were conducted on CF and SCFA 1 using 100 mg/L Zn(NO$_3$)$_2$ suspension with various solids concentrations, ranging from 5 to 100 g/L under uncontrolled and controlled pH conditions to investigate the effects of the dosage of reactive media on the removal of Zn under various pH conditions. The effects of the dosage of reactive media under uncontrolled (final pH: 2.0–12.0) and controlled pH conditions (final pH: 5.5–7.3) are shown in Figs. 5 and 6, respectively. The "uncontrolled" pH condition indicates that the pH of suspension that contains CF or SCFA 1 was not adjusted to the specific pH (5.5–7.3), whereas the "controlled" pH condition indicates that the pH of the suspension was adjusted to the specific pH by adding HNO$_3$ solution.

Under uncontrolled pH conditions (2.0–12.0), the removal of Zn increased, but then became constant with increasing solids concen-

tration, regardless of the materials, but significant increased with CF for solids concentrations ranging from 10 to 50 g/L (Fig. 5(a)). The final pH increased significantly, to about pH 12.0, and then became stable with increasing concentrations of both CF and SCFA 1 (Fig. 5(b)). The change in the final pH strongly affects the tendency for the removal of Zn, as shown in Fig. 2. The increase in the pH was more significant with CF than SCFA 1 for solids concentrations ranging from 10 to 50 g/L. For example, at a solids concentration of 20 g/L, the final pH and Zn removal for CF were about 8.0 and 99%, respectively, whereas those for SCFA 1 were about 6.0 and 20%, respectively. The difference in the removals of Zn for the same solids concentration might have been caused by the difference in final pH for the materials. These results suggest that CF can increase suspension pH than SCFA 1, resulting in a higher Zn removal capacity due to the precipitation of Zn. The higher increase in suspension pH for CF is probably because CF has higher CaO and MgO (Table 2). Bin-
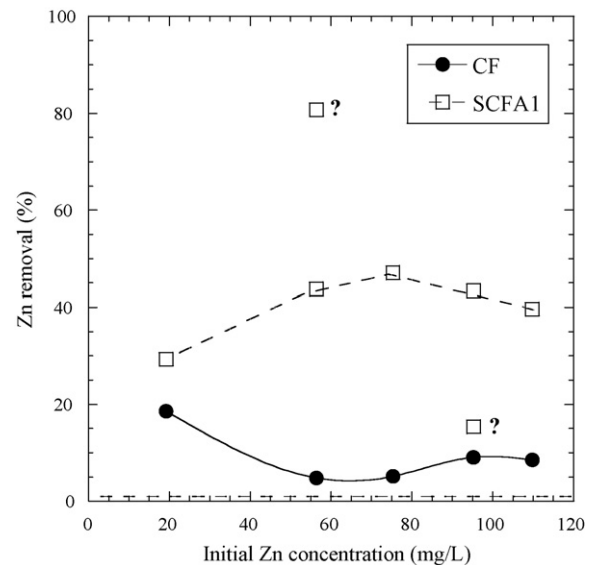

Fig. 4. The removal of Zn as a function of the initial Zn concentration from the batch tests. Outliers marked with "?".
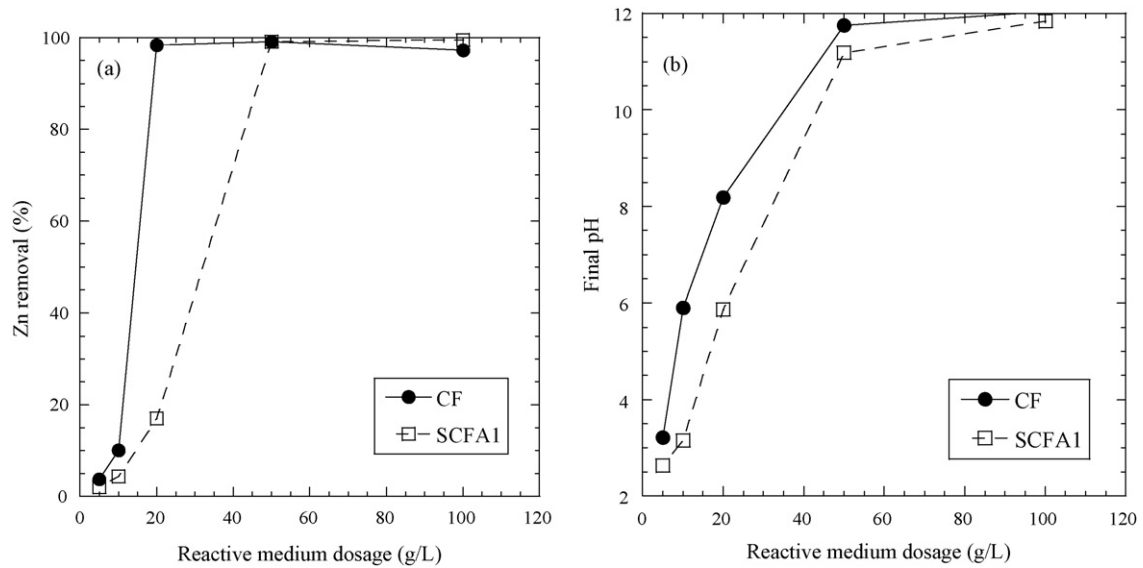
Fig. 5. The removal of Zn (a) and final suspension pH (b) as a function of the dosage of reactive medium under uncontrolled final pH conditions (pH 2.0–12.0).

Shafique et al. [38] suggests that the fly ash having higher content of CaO can increase more suspension pH.

Under controlled pH conditions (5.5–7.3), the removal of Zn generally increased with increasing concentrations of both CF and SCFA 1 (Fig. 6). For CF, the removal of Zn increased from 15 to 30% as the solid concentration increased from 20 to 100 g/L. These results indicate that CF had an adsorption capacity ranging between 0.2 and 0.8 mg/g. The adsorption capacity of CF for Zn is comparable to that reported by other studies (0.07–2.8 mg/g) [13–15]. However, the increase in the removal of Zn was more significant with the SCFA 1 than CF. SCFA 1 gave approximately 2–4 times higher removal of Zn than CF with solids concentrations ranging between 20 and 100 g/L. These results suggest that SCFA 1 has a higher adsorption capacity than CF, as adsorption dominates under pH conditions between 5.5 and 7.3. The higher adsorption capacity of SCFA 1 may be attributed to the presence of zeolites and calcium silicate hydrate which may be components of SCFA 1.

3.3. Column tests

A series of column tests (i.e., Zn removal and hydraulic conductivity tests) were conducted on CF and SCFA 1 in fixed-wall columns. For the Zn removal tests, the specimens were permeated with 1000 mg/L of $Zn(NO_3)_2$ solutions with different pHs (2.0 and 6.3) for the evaluation of the Zn removal efficiency under flow-through conditions. After 1000 pore volumes of flow (PVF) had passed through the specimens, the influent Zn solution was switched to DI water to evaluate the potential desorption of the Zn adsorbed onto the reactive media or the dissolution of Zn precipitates (i.e., column leaching tests). For the hydraulic conductivity tests, the specimens with various dry densities were placed in fixed-wall columns.

3.3.1. Column Zn removal tests

The removal of Zn, effluent pH, and flow rate as functions of the PVF, with an initial permeant pH of 2.0 are shown in Fig. 7. In gen-
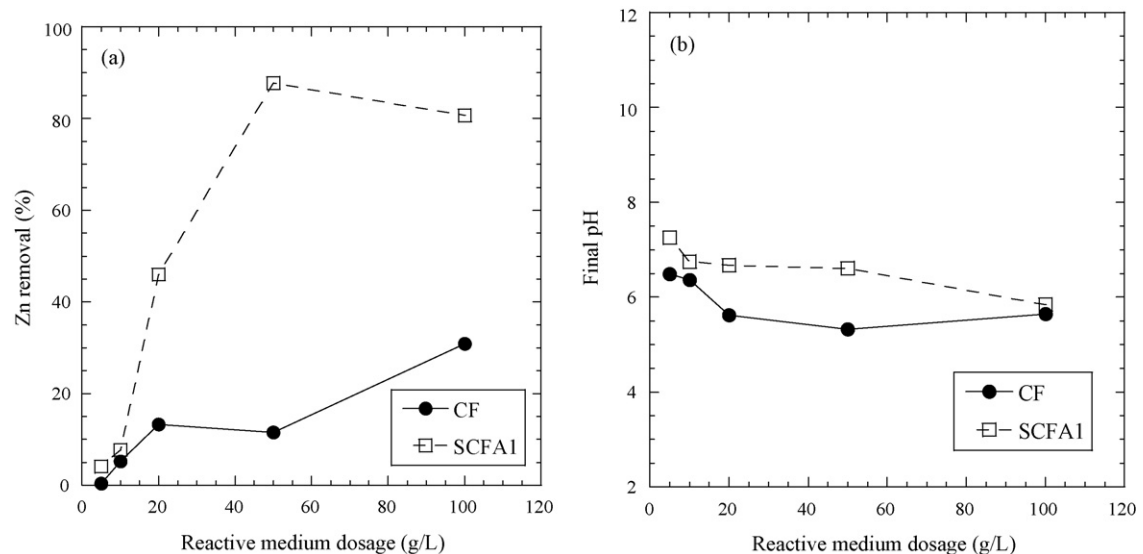

Fig. 6. The removal of Zn (a) and final suspension pH (b) as a function of the dosage of reactive medium under controlled final pH conditions (pH 5.5–7.3).
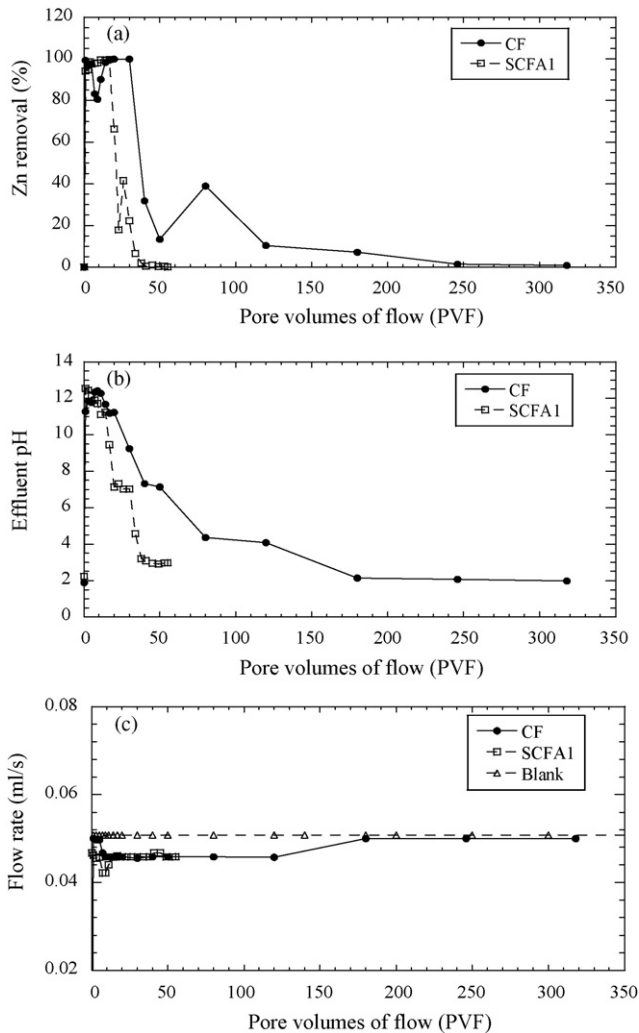
Fig. 7. The removal of Zn (a), effluent pH (b) and flow rate (c) as functions of the PVF obtained from the column tests, with an initial influent pH of 2.0.
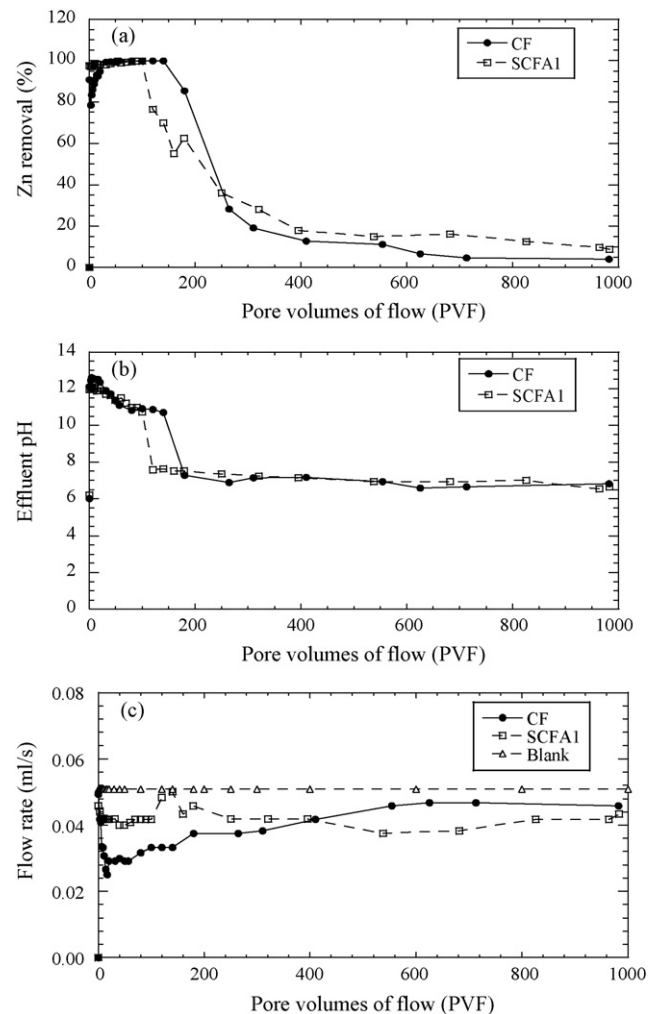

Fig. 8. The removal of Zn (a), effluent pH (b) and flow rate (c) as functions of the PVF obtained from the column tests, with an initial influent pH of 6.0.

eral, for both CF and SCFA 1, the complete removal of Zn occurred within approximately 20–40 PVF, but decreased significantly with increasing PVF. The removal of Zn with CF was more persistent than with SCFA 1. For CF, the complete removal of Zn occurred until approximately 40 PVF had passed, but then gradually decreased to 0% after 240 PVF, whereas for SCFA 1, the complete removal of Zn occurred until 20 PVF had passed, but then decreased significantly to 0% thereafter.

The temporal behavior of the effluent pH was comparable to that of the removal of Zn obtained from the column Zn removal tests. For CF, the effluent pH initially reached approximately 12.0 within 20 PVF, but then gradually decreased to 2.0 thereafter. Conversely, for SCFA 1, the effluent pH initially reached approximately 12.0 within 20 PVF, but then significantly decreased to 2.0 after about 40 PVF. These results indicate that the change in the removal of Zn was directly related to the change in the effluent pH, as Zn ions can be precipitated at pH > 7.0 [6,43]. In addition, these results suggest that CF has a higher buffering capacity than SCFA 1, resulting in a higher removal of Zn at a given PVF due to precipitation, which is consistent with the results obtained from the batch static tests (Fig. 3). At any given PVF, the removal of Zn and effluent pH obtained from CF were higher than those obtained from SCFA 1.

The removal of Zn, effluent pH, and flow rate as functions of the PVF when an initial permeant pH was 6.3 are shown in Fig. 8. The

results were comparable to those obtained from the column test with an initial permeant pH of 2.0, but more persistent removal of Zn occurred in the column test with an initial permeant pH of 6.3. With an initial permeant pH of 6.3, the complete removal of Zn was observed within approximately 200 PVF; the removal of Zn significantly decreased with increasing PVF. Similarly, the effluent pH increased to approximately 12.0 and was constant within 200 PVF. After 200 PVF, the effluent pH significantly decreased to about 7.0. Consequently, the removal of Zn was attributed to the increasing pH of the pore water in the specimens.

The removal of Zn with CF was more persistent than SCFA 1, but a more significant decrease in the removal of Zn occurred in the column test with CF than SCFA 1. For CF, the removal of Zn remained constant (100%) until 150 PVF had passed, but significantly decreased to approximately 20% at 300 PVF. After 300 PVF, the removal of Zn gradually decreased to 5% by the end of the test (1000 PVF). Conversely, for SCFA 1, the complete removal of Zn occurred until 100 PVF, but then gradually decreased to approximately 20% at 400 PVF. After 400 PVF, the removal of Zn remained approximately constant at 20% by the end of the test (1000 PVF). The effluent pHs between 200 and 1000 PVF were between 7.4 and 6.6 for both tests (i.e., CF and SCFA 1), which might result in no precipitation. This result suggests that SCFA 1 may have a higher adsorptive capacity than CF, but CF actually has a higher buffering
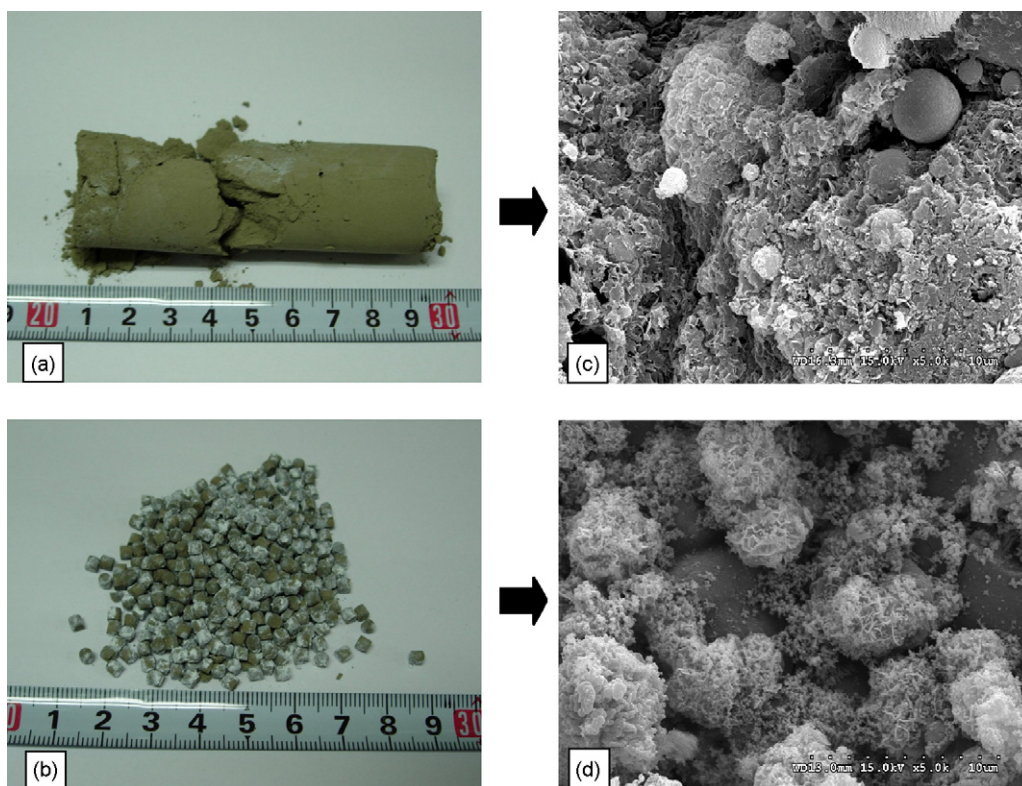
Fig. 9. Photographs of CF (a) and SCFA 1 (b) specimens, showing precipitates; scanning electron microscope (SEM) images of CF (c) and SCFA 1 (d) specimens obtained after termination of the column tests.

capacity than SCFA 1, which results in greater precipitation. This result is comparable to that from the batch sorption tests.

In the column Zn removal tests at influent pHs of 2.0 and 6.3, white precipitates were observed in the specimens, regardless of the materials (photos regarding precipitates Fig. 9). The precipitates probably clogged the pore space, resulting in a decrease in flow rate. To evaluate the temporal consistency of the flow rate, a control column test was conducted without any specimen. As shown in Fig. 7(c), the flow rates obtained from column tests with the specimens varied with time. For both CF and SCFA 1, the flow rates initially decreased, but then became constant. A more significant decrease in the flow rate occurred in the column test with CF than with SCFA 1. The decrease in the flow rate might have been caused by a reduction of the pore space, probably due to precipitation. The CF specimen had a smaller particle size than that of the SCFA 1 specimen, which probably resulted in a smaller pore size to flow. As a result, the precipitates caused by the elevated pH can clog the flow path in the CF specimen more significantly than in the SCFA 1 specimen, resulting in the significantly decreased flow rate. However, the flow rate with CF gradually increased with increasing PVF, but became constant at a flow rate of 0.05 mL/s after 100 PVF, which was comparable to the flow rate in the control test. The increase in the flow rate was probably due to the formation of preferential flow paths due to cementation and precipitation in the specimen [2,12].

To evaluate the preferential flow-through the specimens, rhodamine WT dye was added to the influent after termination of the column tests with an influent pH of 6.3. The rhodamine WT dye was used because it readily stains flow paths bright red. Permeation with dye showed dye staining of continuous fractures in the CF specimen; whereas, dye staining occurred across the SCFA 1 specimen [31]. These results indicate that the preferential flow

paths were not evident in the SCFA 1 specimen, but were present in the CF specimen. The preferential flow paths in the CF specimen might have caused the earlier breakthrough of Zn than in the SCFA 1 specimen, as Zn ions are delivered more rapidly via preferential flow paths.

3.3.2. Column leaching test

After attainment of equilibrium in the column Zn removal tests, the influent was switched from the $Zn(NO_3)_2$ solution (pH 6.0) to DI water (pH 5.5), and the stability of Zn ions precipitated or adsorbed in the specimen assessed. The effluent Zn concentration and pH as functions of the PVF from the column leaching test at an initial influent pH of 6.0 are shown in Fig. 10. In general, for both the CF and SCFA 1 specimens, only a little Zn was detected in the effluent solutions. For the CF specimen, the initial Zn concentration was 44 mg/L after switching the influent to DI water, but then decreased to 0 mg/L after 2 PVF. After 2 PVF, no Zn was detected until the test was terminated (1000 PVF). The initial elevated Zn concentration might have been caused by residual Zn ions in pore water of the specimen. For SCFA 1, almost no Zn was detected in the effluent during the test period (1000 PVF). These results indicate that no dissolution or desorption of Zn occurred from the precipitates or specimens.

For the CF specimen, effluent pH gradually increased from 6.0 to 10.0 until 50–100 PVF had passed through the specimen. After that, effluent pH remained constant until the test was terminated (1000 PVF). For the SCFA 1 specimen, effluent pH remained constant between 9.0 and 10.0 during a given test period. The high pH (9.0–10.0) for both specimens may have been caused by the slight dissolution of carbonate or hydroxide ion precipitates [44,45]. However, no significant increase of the Zn concentration in the effluent occurred due to dissolution.
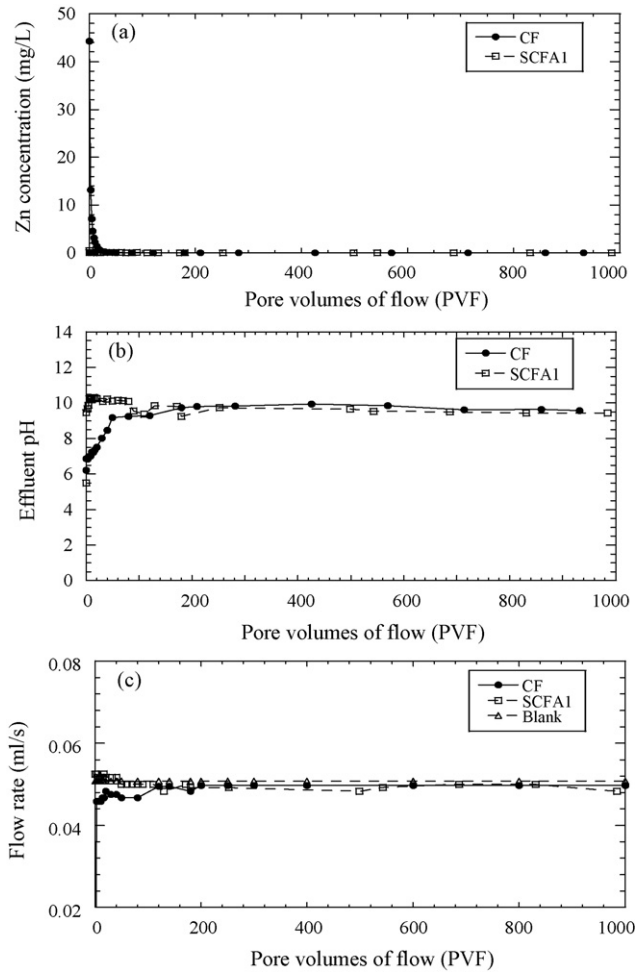
Fig. 10. The Zn concentration (a), effluent pH (b) and flow rate (c) as functions of the PVF obtained from the column leaching tests, using DI water, on the specimens permeated with 100 ppm $Zn(NO_3)_2$ solution, with an initial pH of 6.0.

Fig. 11. The distribution of Zn species as a function of pH, as simulated by PHREEQC ($Zn(NO_3)_2$, $I = 1 \times 10^{-3}$ M).

In general, at a given dry density, the CF specimen had a lower hydraulic conductivity than the SCFA 1 specimen. For example, the hydraulic conductivities of the CF and SCFA 1 specimens at a dry density of $0.9\,g/cm^3$, which is the same density as used for the column Zn removal tests, were 1.0×10^{-1} and $1.0\,cm/s$, respectively. In addition, at a dry density of $1.0\,g/cm^3$, the hydraulic conductivity of the CF specimen was approximately two orders of magnitude lower than that of the SCFA 1 specimen (i.e., SCFA 1: 1.0×10^{-1} cm/s, CF: 1.0×10^{-3} cm/s).

The hydraulic conductivity of the CF specimen was more significantly decreased than that of the SCFA 1 specimen with increasing the dry density. For the SCFA 1 specimen, the hydraulic conductivity decreased by approximately an order of magnitude, as the dry density of the specimen increased from 0.9 to $1.05\,g/cm^3$. Conversely, for the CF specimen, the hydraulic conductivity decreased by approximately four orders of magnitude, as the dry density of the specimen increased from 0.9 to $1.1\,g/cm^3$.

3.3.3. Identification of the precipitates

The precipitates obtained from the column Zn removal tests were analyzed using an X-ray diffractometer (XRD) to identify the mineralogical phases of the precipitates. Additional control column tests were conducted without a reactive medium, using DI water and 100 mg/L $Zn(NO_3)_2$ solution at pH 11.0. The precipitates obtained from the additional column tests were also analyzed using XRD. The XRD analyses were conducted at the Korea Basic Science Institute.

The XRD results showed that the precipitates consisted of mainly zinc oxide (ZnO) with both the CF and SCFA 1 column tests. In addition, the precipitates obtained from the control tests also primarily consisted of zinc oxide (ZnO), regardless of the permeant [31]. The XRD results were comparable to those obtained from geochemical modeling performed by PHREEQC, the equilibrium geochemical computer code [46]. The geochemical modeling indicates that Zn ions precipitate in $Zn(NO_3)_2$ solutions as zinc oxide (ZnO) with the pH range 8.0–14.0, as shown in Fig. 11.

3.3.4. Hydraulic conductivity tests

Hydraulic conductivity tests were conducted on CF and SCFA 1 in fixed-wall glass columns using the falling-head test method. The hydraulic conductivities of the CF and SCFA 1 specimens as a function of the dry density of the specimen are shown in Fig. 12.
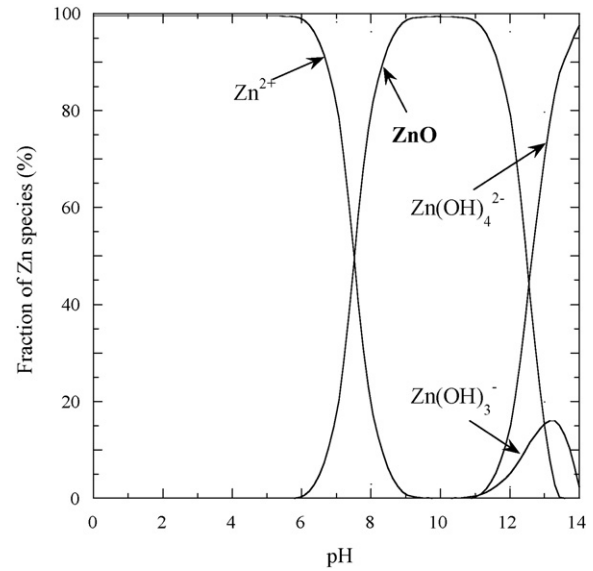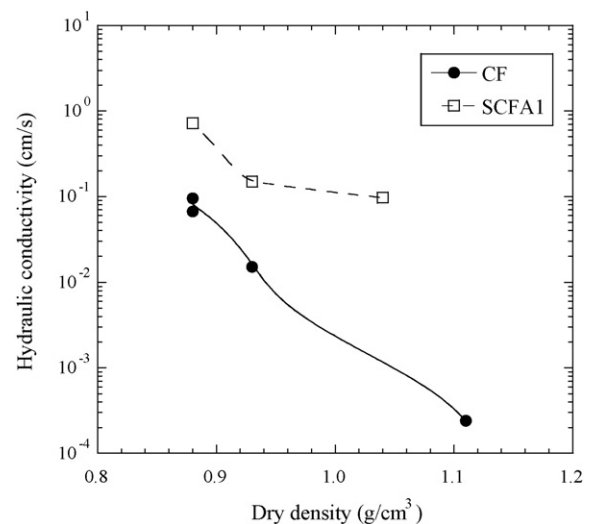

Fig. 12. Hydraulic conductivities of CF and SCFA specimens as a function of the specimen dry density.

These results indicate that for CF, an increase in the dry density in the barrier is required to increase the removal efficiency, which can result in a significant decrease in the hydraulic conductivity. The decrease in hydraulic conductivity may cause redirection of the flow paths and changes in the residence time [1,22–25]. However, for SCFA, the effect of the dry density on the hydraulic conductivity might be insignificant.

4. Conclusions

The removal of Zn increased with increasing reaction time. The removal of Zn with CF occurred earlier than that with SCFA. However, Zn was mostly removed within 6 h, regardless of materials tested. The final suspension pH had a greater effect on the removal of Zn than the initial solution pH. At pH > 7.0, the removal of Zn was mainly attributed to precipitation of Zn oxide, whereas at <7.0, this mainly occurred due to adsorption onto the reactive media. The removal of Zn increased with increasing dosage of the reactive medium and decreases in the initial Zn concentration.

The results obtained from the column tests were comparable to those from the batch tests. In general, for both CF and SCFA 1, the complete removals of Zn occurred within approximately 20–40 PVF, and significantly decreased with increasing PVF. The temporal behavior of effluent pH was comparable to that of the removal of Zn obtained from the column Zn removal tests. White precipitates were observed in the specimens in the column Zn removal tests at influent pHs of 2.0 and 6.3, regardless of the materials. The results of the XRD analyses and geochemical modeling indicate that the precipitates mainly consisted of zinc oxide (ZnO). Preferential flow paths were observed in the column test with CF, whereas no preferential flow paths were observed in the column test with SCFA, indicating that earlier breakthrough may have occurred in the column test with CF with the same dry density. The hydraulic conductivity of CF was more significantly decreased than that of SCFA with increasing dry density of the specimen. This result indicates that SCFA may maintain a higher hydraulic conductivity than CF with increasing the dosage of the reactive medium to increase the removal of Zn.

Even though CF and SCFAs have strong capacities for the removal of Zn from water by adsorption and precipitation, several issues, such as an elevated pH of the effluent and variable leaching characteristics of the materials which may pose negative environmental impacts, need to be evaluated and resolved for their use as reactive media below the groundwater table. In addition, SCFA may be more costly than CF because of additional processes required to produce aggregates in order to improve the hydraulic performance.

Acknowledgements

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