

Remediation of heavy metal contaminated groundwater originated from abandoned mine using lime and calcium carbonate

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Abstract

Column and pilot scale experiments for a chemical treatment involving the use of coagulants to remediate heavy metal contaminated groundwater were performed. Granulated lime ($\text{Ca}(\text{OH})_2$) and calcium carbonate (CaCO_3) were used as coagulants and contaminated groundwater obtained at an abandoned Fe-mine in Korea was used for the experiments. The main removal mechanism of heavy metals in the experiments was “sweep precipitation” by coagulation. Using granulated lime as a coagulant in the column experiment, more than 98% of As and Ni were removed from artificially contaminated water. When granulated calcium carbonate was used in the artificially contaminated water, the removal efficiencies of Ni and Zn were more than 97%, but As removal efficiency was lower than 50%. For the continuous column experiment with mixed lime and calcium carbonate at a 1:1 (v/v) ratio, almost all As was removed and more than 98% of Ni was removed. For pilot scale experiments (acryl tank: 34 cm in length and 24 cm in diameter), the removal efficiencies of As and Cd were above 96% for 150 l groundwater treatment and their accumulated removal capacities linearly maintained. This suggests that coagulants could treat more than 22 times greater groundwater volume compared with the volume of coagulants used.

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1. Introduction

In Korea, there exist about 2500 mines, including 900 metals mines, 380 coal mines, and 1200 nonmetallic mines [1]. More than 80% of these mines are now closed and they have been a long term source of environmental pollution. In particular, mining and refining facilities at abandoned metal mines have been left in ruin, and mine tailing and ore rock waste were scattered without control. These mine tailings and rock waste result in serious contamination of farmland soils and the water systems around abandoned mines, and adversely affect crop growth and human health [2,3].

The O/R (oxidation and reduction) process of mine tailings and ore wastes generates ARD (acid rock drainage), which leaches out large amounts of heavy metals and arsenic, threatening the quality of groundwater and surface water [4–8]. Con-

centrations of heavy metals and arsenic in groundwater at many abandoned mines in Korea are much higher than the groundwater tolerance limit. The development of remediation processes for heavy metal contaminated groundwater is thus necessary. However, research in this area is lagging behind relative to that concerning surface water treatment processes [9–12]. Chemical processes have been widely applied to surface wastewater treatment. Chemical treatment to remove heavy metals includes several mechanisms such as coagulation, co-precipitation, and entrapment [13–16]. Sweep co-precipitation by coagulants is one of the main mechanisms utilized in current remediation processes, and it results in the formation of metal-hydroxide and carbonate [17–20]. By using coagulants such as Fe-, Al-, and Ca-salts, heavy metal ions in groundwater are changed to insoluble precipitates, or to sweep precipitates induced by enmeshment of floc particles [21–25]. Incorporation of heavy metal ion into the crystal lattice of other precipitating solid phases also occurs with the coagulation process [26,27].

To date, chemical processes for groundwater treatment have not been widely applied. However, the use of iron and aluminum

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salts to remove heavy metals from groundwater has been studied recently and the development of a purification system for contaminated groundwater by using coagulants is in progress [12,28,29].

In this research, a chemical treatment using lime and calcium carbonate was investigated in terms of its capacity to remove heavy metals and arsenic from contaminated groundwater originating from an abandoned mine. Lime and calcium carbonate as coagulants are much more economical than other coagulants such as Al- and Fe-salts, and their use is considered a pro-environmental process because their toxicities are much lower than those of other coagulants. The main removal mechanism of lime and calcium carbonate is the formation of insoluble precipitates separated from the water, or the sweep precipitation of heavy metals induced by the enmeshment of Ca-floc particles. Results of this study will provide meaningful information for future application of chemical treatment processes to the remediation of heavy metal contaminated groundwater.

2. Experimental method

2.1. Continuous column experiment with artificially contaminated water

Continuous column experiments with coagulants were performed in order to investigate the efficiency of the chemical treatment process. Granulated calcium carbonate and lime (purchased from Hanil Co., Korea) were used as coagulants for the experiments. Table 1 shows the results of XRF analysis for lime and calcium carbonate used in this study. A glass column including capping plates, valves, and tube (purchased from Kontes Glass Company, USA) was used (15 cm in length and 4.8 cm in diameter). Lime and calcium carbonate granules were sieved at 5–7 mm in diameter and packed in the column. One column was filled with granulated calcium carbonate (CaCO_3) at 10 cm thickness and a second column was packed with granulated lime ($\text{Ca}(\text{OH})_2$) at 10 cm thickness (Fig. 1(a) and (b)). A third column was packed with both lime and calcium carbonate at a 1:1 volume ratio (Fig. 1(c)). The bottom 5 cm of the third column was packed with lime and calcium carbonate was added to the lime at 5 cm thickness (weight: 225.3 g). The artificially contaminated water was made from deionized water, adding standard solutions of heavy metals and arsenic. Artificial water was titrated to 506 $\mu\text{g/l}$ of As, 260 $\mu\text{g/l}$ of Ni, and 2315 $\mu\text{g/l}$ of Zn, a range of 2–10 times higher than the Korean groundwater tolerance limit (As: 50 $\mu\text{g/l}$). The pH of contaminated water was controlled at 8 using 1N of NaOH solution (similar to pH of real groundwa-

ter at Dalcheon mine). The artificially contaminated water was injected into the bottom of the column at a constant velocity (2 ml/min) and the treated water was drained from the top of the column. Water samples were taken from the top of the column every 4 h and analyzed on an ICP-MS (PerkinElmer, Elan 6100) to investigate the removal efficiency of heavy metals for the three column experiments. About 11–15 l of artificial water (160–220 pore volumes of lime packed column) were flushed for each column experiment.

2.2. Continuous column experiment with contaminated groundwater

The physical and bio-chemical properties of groundwater are quite different from those of artificially contaminated water. To consider the effect of real groundwater on the removal efficiency, heavy metal contaminated groundwater was sampled from an extraction well at Dalcheon abandoned mine, Korea. Dalcheon abandoned mine is located at Dalcheon dong, Ulsan, Korea. Following activation by the Japanese in 1906, Dalcheon mine produced about 40 000 tonnes of iron ore and some serpentines until activity for iron ore finished in June 1993 and that for serpentine in February 2003. About 15 000 tonnes of mine tailings were buried around the mine pit, seriously contaminating the soil, groundwater, and surface water in the vicinity of the mine. In 2003, soil investigation for Dalcheon mine area was performed by the Ulsan city government. The findings indicated that concentrations of arsenic, zinc, and nickel exceeded the Korea Soil Pollution Warning Limit (KSPWL). The results also revealed arsenic, mainly in the form of arsenopyrite (FeAsS) in ore and tailings, as the main pollutant for soil and groundwater at the Dalcheon mine area [30]. A private construction company had plans to build a large apartment complex at the Dalcheon mine area in 2006 and mine tailings and contaminated groundwater were required to be properly treated before development of the site. The heavy metal concentration distribution of soil and groundwater at the site is related to its geographical characteristics. The iron ore mineralized zone, which was located in the central area of the site was filled by several soil layers to a depth of 50 m, and most of the mine tailings were buried around the zone.

Groundwater at Dalcheon mine area was sampled and its As, Ni, and Zn concentrations was 497, 40, and 22 $\mu\text{g/l}$, respectively. It was mainly contaminated with As and continuous column experiments were duplicated by using the contaminated groundwater. One column was filled with granulated lime to a height of 10 cm and a second column was packed with both lime and

Table 1
Results of XRF principle component analysis for coagulants used in this research and colloidal flocs in the reaction tank

	Chemical composition of coagulants and flocs by XRF analysis (units: wt.%)								Total
	CaO	MgO	SiO ₂	Fe ₂ O ₃	SO ₃	Al ₂ O ₃	As ₂ O ₃	Na ₂ O	
Lime	63.6	30.8	4.0	0.1	0.0	0.9	0.0	0.1	99.5
Calcium carbonate	96.6	0.0	0.7	0.0	2.1	0.2	0.0	0.6	100.2
Top layer flocs	39.6	10.2	29.1	11.7	1.5	8.4	0.7	0.4	101.6
In pore flocs	95.0	1.9	1.6	0.5	0.4	0.4	0.1	0.0	99.9

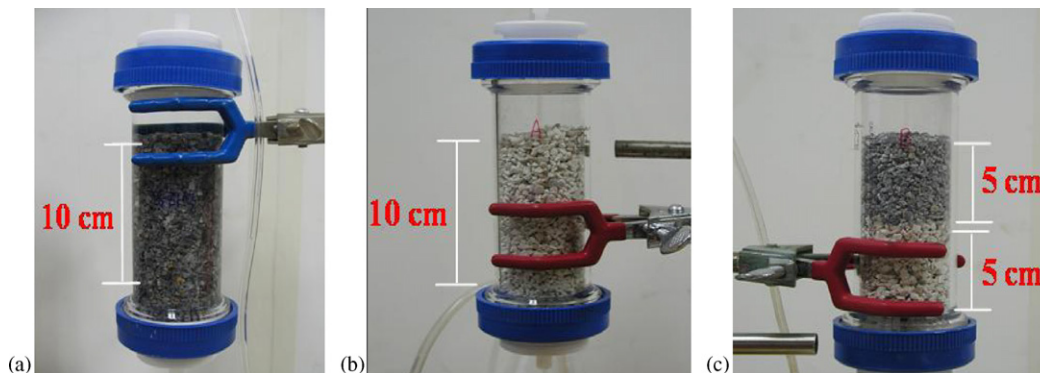


Fig. 1. Column packed with granulated coagulants. (a) Calcium carbonate; (b) lime; (c) lime and calcium carbonate.

calcium carbonate at a 1:1 volume ratio. A total of 13 l of groundwater was flushed in each column experiment. Flushing and analyzing conditions were the same as employed in the prior column experiment.

2.3. Pilot scale tank experiment using mixed lime and calcium carbonate

A pilot scale tank experiment was performed using real contaminated groundwater on the basis of the column experiment results. The tank was made of acrylic cylinder (34 cm in length and 24 cm in diameter: 18 l in capacity) and the bottom of the tank had a valve gear for injecting contaminated groundwater. The tank was packed with 2 l of granulated lime (2074.8 g) at the bottom of the column. Two liters of granulated calcium carbonate (2568.6 g) were added to the top of the lime layer (Fig. 2(a)). For the experiment, groundwater at Dalcheon mine area was extracted and its As, Ni, Cd, and Zn concentrations was 945, 30, 4, and 80 $\mu\text{g/l}$, respectively. Contaminated groundwater was

injected from the bottom of the tank at a constant velocity of 3 l/h and treated water was drained from the top of the tank. Ten milliliters of treated water was sampled at a constant time interval and analyzed on ICP-MS (PerkinElmer, Elan 6100) for heavy metal concentration. The mass removal efficiency of heavy metals for the chemical treatment process in the tank was calculated for specified time periods. Because the pH of the treated water was maintained at pH 10–12, drained water gathered into the pH-control tank (24 cm in length and 24 cm in diameter), and finally discharged from the top of the pH-control tank after adjusting the pH in a range of 7–8 by using 37% HCl solution (Fig. 2(b)).

3. Results and discussion

3.1. Continuous column experiment with artificially contaminated water

In the column experiment using granulated lime, As and Ni removal efficiencies for artificially contaminated water were

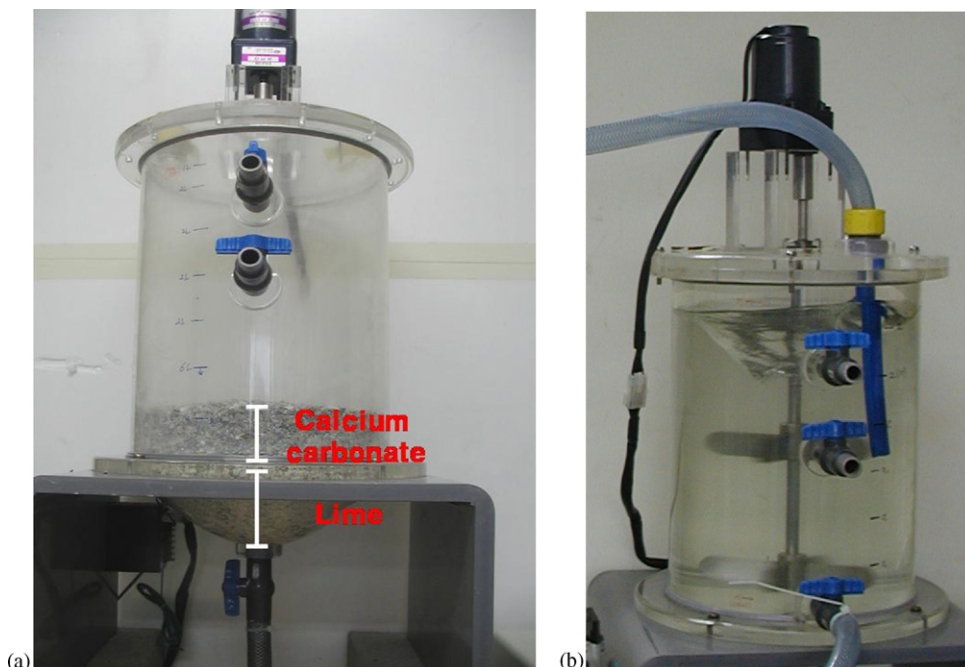


Fig. 2. Pilot scale tank experiment. (a) Reaction tank packed with mixed lime and calcium carbonate and (b) pH-control tank.

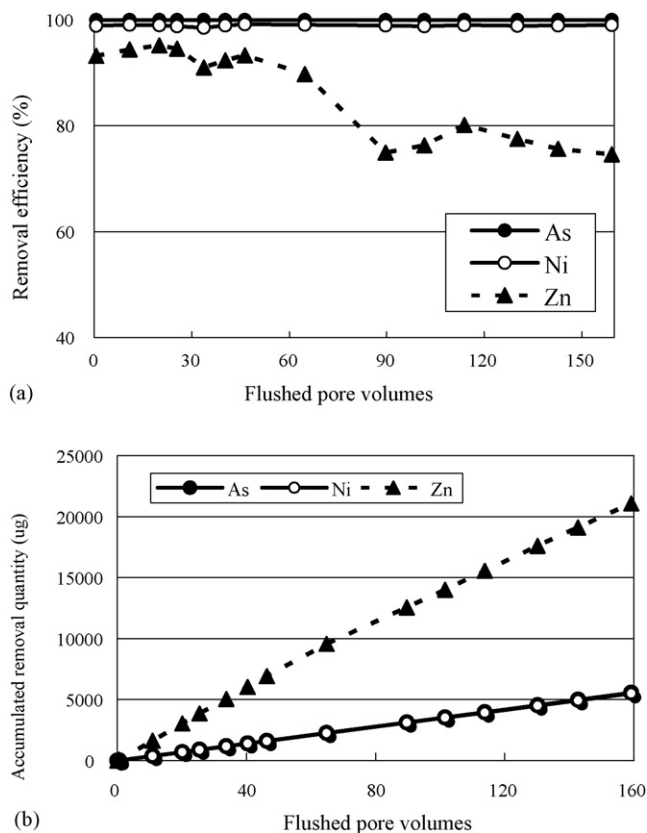


Fig. 3. Results of continuous column experiments using lime only for artificially contaminated water. (a) Removal efficiencies by using lime and (b) accumulated removal mass by using lime.

maintained at more than 99% for treatment of 11 l (about 160 pore volumes of lime packed column layer) (Fig. 3(a)). More than 90% of Zn was removed with 5 l of water treatment, whereas the Zn removal efficiency decreased to 75% as the treated water amount increased to 10 l. The removal rate of As in the column with granulated lime was about $548 \mu\text{l}^{-1} \text{h}^{-1}$, and that of Ni and Zn was 543 and $2250 \mu\text{l}^{-1} \text{h}^{-1}$, respectively. When 11 l of contaminated water (about 56 times the lime volume and 160 pore volumes of lime packed column) were treated, the accumulated removal quantity of heavy metal linearly increased, and a straight slope for the removal capacity was maintained, suggesting that the high removal capacity of lime was maintained for treatment of 11 l (Fig. 3(b)). Consequently, 161 g (196 ml) of granulated lime could successfully treat more than 11 l of contaminated water having $500 \mu\text{g/l}$ of As concentration.

For the continuous column experiment with granulated calcium carbonate, removal efficiencies of Ni and Zn were more than 97% for treatment of 15 l of contaminated water (about 220 pore volumes of calcium carbonate packed column) (Fig. 4(a)). However, in the case of As, the removal efficiency was lower than 50% for treatment of 15 l of water, suggesting that the use of calcium carbonate alone is not adequate to treat As contaminated water. The maximum removal rate of As in the column experiment was $159.42 \mu\text{l}^{-1} \text{h}^{-1}$ while that for Ni and Zn was 335.86 and $3779.56 \mu\text{l}^{-1} \text{h}^{-1}$, respectively. The removal capa-

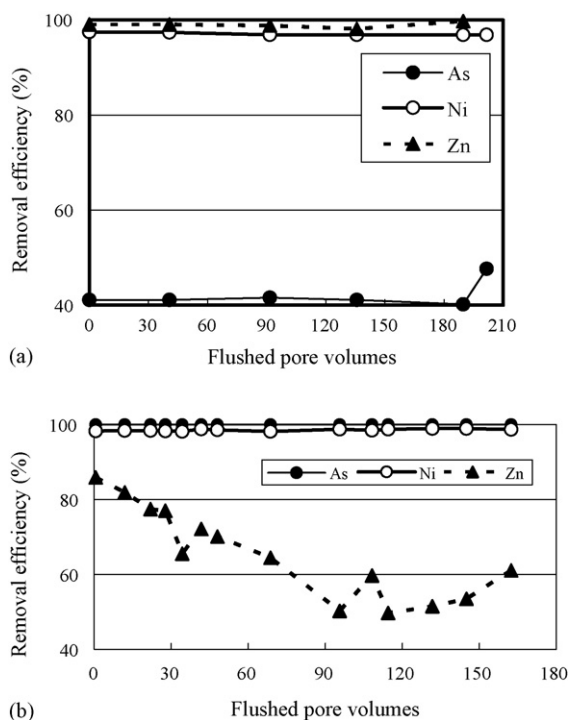


Fig. 4. Results of continuous column experiments using calcium carbonate only and the mixed lime and calcium carbonate for artificially contaminated water. (a) Removal efficiencies by using calcium carbonate and (b) removal efficiencies by using the mixed lime and calcium carbonate.

bility of Zn, Ni, and As in the column with calcium carbonate maintained linearly even beyond 15 l of contaminated water treatment.

For the column experiment using mixed lime and calcium carbonate at a 1:1 (v/v) ratio, the removal efficiencies of As and Ni were more than 99%, which were similar to those of the column experiments using only granulated lime (Fig. 4(b)). For Zn, the removal efficiency ranged from 82 to 50% for 12 l of contaminated water flushing (about 170 pore volumes of the packed column). Concentrations of heavy metals in treated water were lower than Korean groundwater tolerance limits. For treatment of 12 l of contaminated water, the accumulated removal amount of heavy metals linearly increased, suggesting that the mixed column with lime and calcium carbonate can successfully remediate more than 12 l of contaminated water having $500 \mu\text{g/l}$ of As concentration.

3.2. Continuous column experiment with contaminated groundwater

Results of continuous column experiments to remediate contaminated groundwater at Dalcheon mine are shown in Fig. 5. With only granulated lime treatment, more than 95% of Zn and more than 93% of Cd were removed for 13 l of groundwater flushing (about 190 pore volumes of lime packed column). Despite the high As concentration of the groundwater, the As removal efficiency was maintained above 99% (Fig. 5(a)). For the column with mixed lime and calcium carbonate at a 1:1 volume ratio, As removal efficiency was also maintained at more

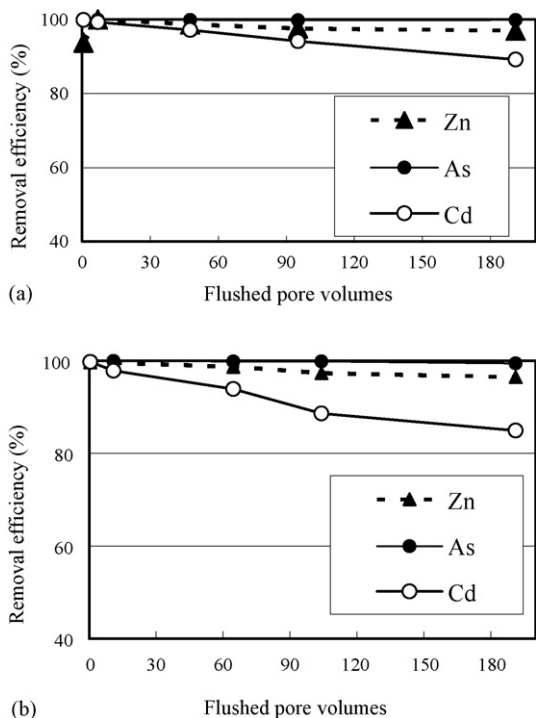


Fig. 5. Results of continuous column experiments using lime only and the mixed lime and calcium carbonate for the real contaminated groundwater. (a) Removal efficiencies by using lime in the column experiment and (b) removal efficiencies by using the mixed lime and calcium carbonate in the column experiment.

than 99% (Fig. 5(b)). For Zn and Cd, removal efficiencies were greater than 93 and 85% for 131 of groundwater flushing. If the removal efficiency of lime treatment only for heavy metals was similar to that of the mixed lime and calcium carbonate column, application of the mixed treatment would be better to clean contaminated groundwater because of low SS (suspended solids) production, low pH condition of treated water, and economic considerations. The accumulated removal quantity of all heavy metals used in the experiment also linearly increased even at treatment of 131 of water. Results of the column experiments indicate that mixed lime and calcium carbonate has considerable potential in terms of removing As as well as Zn and Cd from contaminated groundwater. Results of column experiments indicate that a huge amount of contaminated groundwater (more than 85 times the coagulant volume and 190 pore volumes of the column) could be successfully remediated by lime or mixed lime and calcium carbonate.

In contrast to the case of artificially contaminated water, coagulant flocs and precipitates were generated on the top layer of the coagulant in the column with increased treated water volume. These precipitations occurred by “sweep floc precipitation” on the top of the coagulant layer or in pores among coagulants, resulting from colloids and clay particles included in real groundwater, unlike the artificially contaminated water [17,20]. Concentrations of heavy metals and floating colloids in treated groundwater decreased because of these sweep floc precipitations, which is considered to be one of the main mechanisms for heavy metal removal. The additional layer packed with coarse sand media in the column will maximize the removal effi-

ciencies of suspended solids and colloids including heavy metals in the column tests.

3.3. Pilot scale tank experiment using mixed lime and calcium carbonate

For the pilot scale tank experiment, 200 l of contaminated groundwater were taken at Dalcheon mine and As concentration was 945 $\mu\text{g/l}$, almost 19 times higher than the Korean groundwater tolerance limit (50 $\mu\text{g/l}$ for living water supply). For the treatment of contaminated groundwater, As removal efficiency of the reaction tank was maintained at over 96% for 200 l of groundwater treatment and the maximum As concentration of treated water was 38.3 $\mu\text{g/l}$ (arithmetic mean: 8.2 $\mu\text{g/l}$), which was lower than Korean groundwater limit (50 $\mu\text{g/l}$) (Fig. 6(a)). The arsenic removal rate of the reaction tank ranged from 500 to 1000 $\mu\text{l}^{-1} \text{h}^{-1}$, and the accumulated removal capacity of As linearly increased for the whole experiment. The removal efficiencies of Ni, Cd and Zn of the reaction tank were also more than 90% for 200 l of groundwater treatment (Fig. 6(b)). From the results of the experiment, it is determined that 200 l of groundwater (50 times the volume of coagulant used and 150 pore volumes of the packed medium) could be effectively treated by mixed lime and calcium carbonate.

Sweep precipitation of coagulants with heavy metal ions also occurred in the reaction tank during the experiment in a manner similar to that of the continuous column experiments (Fig. 7). Colloidal flocs precipitated on the top of the coagulant layer

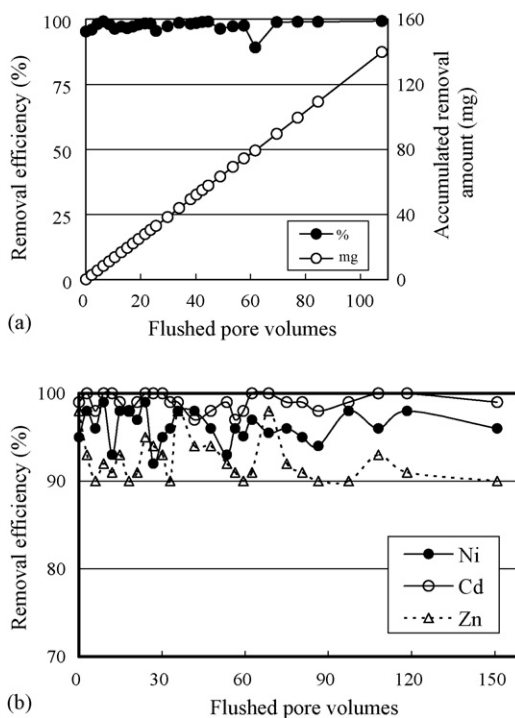


Fig. 6. Results of the pilot scale experiment for the real contaminated groundwater. (a) As removal efficiencies by using the mixed and calcium carbonate in the pilot scale experiment and (b) Ni, Cd, and Zn removal efficiencies by using the mixed lime and calcium carbonate in the pilot scale experiment.

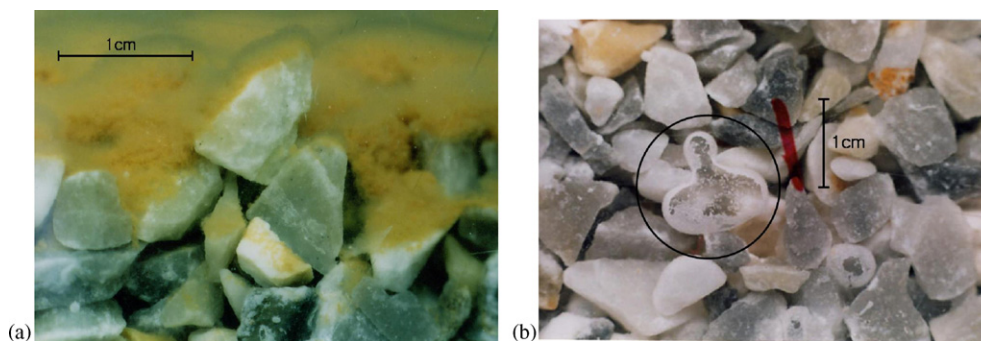


Fig. 7. Formation of sweep precipitants in the reaction tank during water treatment. (a) Precipitation on the top of coagulation layer and (b) precipitation in pore spaces among coagulants.

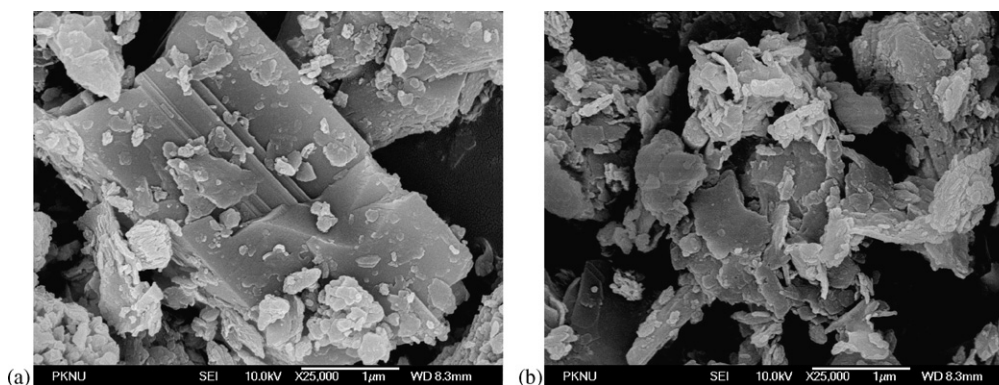


Fig. 8. SEM images of precipitants created in the reaction tank during water treatment (magnified by 25,000 \times). (a) Planar shaped clay mineral and (b) calcium carbonate.

and in pores among the coagulants in the tank (Figs. 7(a) and (b)). To identify their components, precipitants were dried and analyzed on XRF (SHIMADZU, Japan, XRF-1700). Table 1 shows the major components of flocs created on the top of the coagulants and in pores. They were mainly clay minerals, iron–aluminum oxides (or hydroxides), and Ca-salts such as lime or calcium carbonate [12,16]. Arsenic oxides constituted 0.7% of the precipitants produced, suggesting that most arsenic in the dissolved phase was transferred to a solid state, which was separated from the treated water (Table 1). Precipitants recrystallized among the coagulants (Fig. 7(b)) were mainly Ca-salts such as calcium carbonate. Results of the SEM (Hitachi, S-2400) analysis suggest that colloidal flocs and precipitants in the tank are mainly composed of calcium carbonate and clay mineral (Fig. 8). Formation of these solid precipitants plays an important role in lowering the concentration of heavy metals in treated groundwater, because dissolved heavy metals are gushed out from the groundwater and fixed to the solid phase.

4. Conclusion

A chemical treatment process using granulated lime and calcium carbonate was applied for heavy metal contaminated groundwater in continuous column and pilot scale reaction tank experiments. From the results of the continuous column experi-

ments with artificially contaminated water, removal efficiencies of As, Zn, and Ni using only granulated lime or mixed lime and calcium carbonate were higher than 95%. For the column experiment with only granulated calcium carbonate, removal efficiencies of Ni and Zn were similar to those of the column with granulated lime only. However, As removal efficiency was lower than 50% for 131 of water treatment (190 pore volumes of lime packed column). Using real, contaminated groundwater, removal efficiencies of heavy metals for lime only and mixed lime and calcium carbonate treatment were very high, similar to those of the column experiment using artificially contaminated water.

For the pilot scale experiment, As and Cd removal efficiencies were greater than 96% for treatment of 200 l of groundwater, which was more than 50 times the volume of coagulant used in the reaction tank (150 pore volumes of packed medium in the reaction tank). The removal efficiencies of Ni and Zn were also more than 90%. The removal capacity of mixed lime and calcium carbonate for heavy metals was very high, suggesting that chemical treatment using mixed lime and calcium carbonate has considerable potential to remove heavy metals from contaminated groundwater. From the results of XRF and SEM analyses for flocs and precipitates generated in the column and the tank, it was found that heavy metals are successfully separated from the groundwater by a sweep precipitation process of lime and calcium carbonate.

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