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# 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 ($Ca(OH)_2$) 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.


*Keywords:* Calcium carbonate; Coagulation; Contaminated groundwater; Floc; Lime

## 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]. Concentrations 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 ($Ca(OH)_2$) 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 μg/l of As, 260 μg/l of Ni, and 2315 μg/l of Zn, a range of 2–10 times higher than the Korean groundwater tolerance limit (As: 50 μg/l). The pH of contaminated water was controlled at 8 using 1N of NaOH solution (similar to pH of real groundwater 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 μg/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.%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | CaO | MgO | $SiO_2$ | $Fe_2O_3$ | $SO_3$ | $Al_2O_3$ | $As_2O_3$ | $Na_2O$ | Total |
| 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 |