공학석사 학위논문

Remediation of Cadmium and Zinc in Groundwater by Calcium Polysulfide
: Precipitation Mechanism, Oxidation Resistance

다황화칼슘을 이용한 지하수 내 카드뮴과 아연 저감
: 침전 기작, 산화 저항성에 관한 연구

2023 년 2 월

서울대학교 대학원

건설환경공학부

윤 성 희

Remediation of Cadmium and Zinc in Groundwater by Calcium Polysulfide : Precipitation Mechanism, Oxidation Resistance

다황화칼슘을 이용한 지하수 내 카드뮴과 아연 저감 : 침전 기작, 산화 저항성에 관한 연구

지도교수 남 경 필

이 논문을 공학석사 학위논문으로 제출함
2023 년 2 월

서울대학교 대학원
건설환경공학부
윤 성 희

윤성희의 석사 학위논문을 인준함
2023 년 2 월

위 원 장 김 재 영 (인)

부위원장 남 경 필 (인)

위 원 최 용 주 (인)

Abstract

Remediation of Cadmium and Zinc in Groundwater by Calcium Polysulfide : Precipitation Mechanism, Oxidation Resistance, Field Application

Sunghee YOON
Civil and Environmental Engineering
The Graduate School
Seoul National University

Heavy metals in sludge or leachate discharged from abandoned mines and smelters flow into the surrounding water system, causing serious water contamination. In particular, heavy metal contamination and acidification in groundwater are serious due to cadmium (Cd^{2+}), zinc (Zn^{2+}), and sulfate (SO_4^{2-}) generated during the smelting process. In this regard, there are some cases of removing Cd^{2+} and Zn^{2+} from groundwater using calcium polysulfide (CPS), one of the reducing agents for remediation of groundwater, however, the mechanism of the heavy metal removal of CPS is not clearly known. In addition, heavy metals precipitated in the form of sulfides could be oxidized and dissolved in aqueous phase by dissolved oxygen (DO). Therefore, this study aimed to quantify the polysulfide (S_x^{2-}), derive the precipitation mechanism of Cd^{2+} and Zn^{2+} by CPS, evaluate the effect of DO on precipitate formed from CPS injection, and finally apply the batch results to the contaminated groundwater.

As a result of this study, the concentration of S_x^{2-} in CPS 1% (w/v) was 82.2 mM, and 76.8 mM of Cd and 77.6 mM of Zn were removed per 1% of CPS injection. In addition, referring to the X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) analysis, elemental sulfur (S_8 or S_0), gypsum ($CaSO_4 \cdot 2H_2O$), CdS, and ZnS were present in the precipitate, and hydroxides such as $Cd(OH)_2$ and $Zn(OH)_2$ were not found. Moreover, there was little change in the pH in the aqueous solution before the heavy metal precipitation was completed, but after the heavy metal precipitation was completed, the pH showed a tendency to increase. Taken together, it was concluded that when CPS is injected into a heavy metal contamination source, CPS does not cause a change in pH if overdose is not injected and one S^{2-} molecule is released from S_x^{2-} and precipitates with heavy metals in the form of sulfide, and the rest is precipitated as S_8. In addition, by exposing the precipitate to the aerobic conditions, it was revealed that S_x^{2-} and bisulfide (HS^-) react with DO suppressing the oxidation of heavy metals. Based on these results, CPS injection into the field groundwater confirmed that Cd^{2+} and Zn^{2+} in the groundwater could be successfully removed and the precipitate exists stably without dissolution for up to 21 days.

Key words: Calcium polysulfide, Cadmium sulfide, Zinc sulfide, Elemental sulfur, Dissolved oxygen, Bisulfide
Student Number: 2021-27635

Contents

Contents of Table

Contents of Figures

1. Introduction

1.1 Background

Heavy metals are diffused and contaminated into surrounding water systems, soil and groundwater due to heavy metal sludge and leachate generated during mining, beneficiation, and smelting processes (Coynel, Alexandra, et al., 2007). Especially, high concentrations of cadmium (Cd^{2+}), zinc (Zn^{2+}), and sulfate (SO_4^{2-}) generated by the sulfuric acid process continuously flow into the surrounding groundwater (Li, Meng, et al., 2017), and the pH of the groundwater is also very acidic. Accordingly, the health of the residents around the smelter is threatened by the drinking of contaminated groundwater, therefore, heavy metals in groundwater near the smelter should be removed. There are two ways to remediate groundwater contaminated with heavy metals: *Ex situ* and *In situ*. Pump and treat, a representative *Ex situ* groundwater remediation method, is inefficient when the area of contamination is large and the degree of contamination varies (Mackay et al., 1989). In addition, public perception is not good in that it pumps contaminated groundwater to the surface. In the case of *In situ* remediation method, installing a permeable reactive barrier and using bioremediation is not suitable for removing high concentrations of heavy metals (Liu, Yuanyuan, et al., 2015, Azubuike et al., 2016) However, there are several cases of successful removal of severely contaminated groundwater by injecting chemicals into the contaminant plume and precipitating heavy metals (Hashim, M. A, et al., 2011).

There are three types of heavy metal precipitation forms: sulfide, carbonate, and hydroxide. Since hydroxides and carbonates have high solubility product (K_{sp}) values and are sensitive to changes in pH, there is a possibility of the dissolution of heavy metal precipitates (Chen, Quanyuan, et al., 2018). Therefore, precipitating heavy metals in the form of sulfide is suitable for heavy metal removal. Moreover, because it is advantageous to remove sulfate by using calcium (Ca^{2+}), chemicals in which Ca^{2+} and sulfide are combined were considered. In this context, Calcium polysulfide (CaS_x; CPS), which also acts as a reducing agent that could create reducing conditions in the groundwater (Wazne, Mahmoud, et al., 2007) was selected for target material.

1.2 Literature review

Chrysochoou, M et al., (2011) determine the influence of pH and oxygen conditions on the reaction kinetics of hexavalent chromium (Cr^{6+}) with CPS. From this research, CPS is likely to have a longer residence time and greater reducing capacity in the subsurface compared to sulfide at neutral and basic pH environments.

Graham, Margaret C., et al., (2006) aimed to reduce Cr^{6+} to trivalent chromium (Cr^{3+}) in past disposal of high-lime chromite ore processing residue from chemical works in the UK. Accordingly, a series of laboratory experiments were conducted and possibility of large-scale use of CPS to make Cr^{3+}, which is less toxic and mobile in groundwater was shown.

Wazne, Mahmoud, et al., (2007) conducted bench and pilot scale applicability to remediate Cr^{6+} in soil using CPS. Cr^{6+} 567 mg/kg, initial concentration before treatment, was decreased to about 0.05 mg/kg. In addition, from *Ex-situ* pugmill pilot program, Cr^{6+} concentration met regulatory standard over a period of 15 months.

Tu, Chen, et al., (2018) applied CPS to stabilize Cd-polluted wetland soil. The stability of Cd, soil enzyme activity, and microbial diversity were investigated according to the CPS concentration injected into the soil. the study derived that 1% of CPS is an efficient and safe dosage for Cd stabilization.

From the past studies, it can be inferred that most of the previous studies were limited to reducing Cr^{6+} to Cr^{3+} using CPS and the maximum efficiency (ME) ratio of CPS injection for heavy metal removal and precipitation mechanism is insufficient.

In addition, heavy metals precipitated in the form of sulfide could be easily dissolved into solution when continuously exposed to oxidizing conditions (Li, Haiyan, et al., 2013). Therefore, depending on seasonal precipitation variations, sulfides precipitated by CPS may be exposed to aerobic conditions. However, no studies have yet been conducted on the stability of heavy metal precipitates formed by CPS.

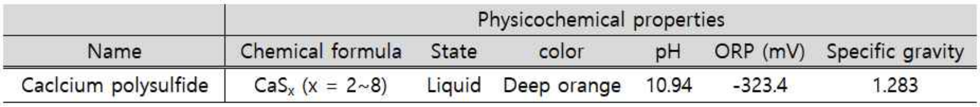
1.3 Research objectives

Since previous studies did not consider injection ratio or mechanisms for removing heavy metals, the objectives of this research aim to derive the precipitation mechanism of Cd^{2+} and Zn^{2+} by CPS. In addition, mobility of heavy metal sulfide by exposure to aerobic condition and dissolution to groundwater could be increased, therefore, evaluation of the possibility of dissolution when heavy metals removed by CPS are exposed to oxygen was performed, and finally apply the experimental results to actually contaminated groundwater near a smelter.

2. Materials and method

2.1 Quantification of polysulfide concentration in CPS

Industrial grade CPS (29% w/v) was purchased from Changsha Easchem co., Ltd, China. The physicochemical properties of CPS are summarized (Table 2.1).



	Physicochemical properties					
Name	Chemical formula	State	color	pH	ORP (mV)	Specific gravity
Caclcium polysulfide	CaS_x (x = 2~8)	Liquid	Deep orange	10.94	-323.4	1.283

Table. 2.1. Physicochemical properties of 29% (w/v) calcium polysulfide

When the pH of polysulfide (S_x^{2-}) is decreased to 8.20, it is divided into elemental sulfur (S^0 or S_8) precipitate and bisulfide (HS^-) ions (Equation 2.1) (Kamyshny, Alexey, et al., 2004).

$$S_x^{2-} + H^+ \rightarrow HS^- + \frac{1}{8}(x-1)S_8 \qquad \text{(Eq. 2.1)}$$

Since the pk_{a1} of hydrogen sulfide (H_2S) is 7.00 (Yongsiri et al., 2005), when the pH is 8.20, sulfide is mostly present in HS^- form. Through Equation 2.1, it is assumed that the concentration of S_x^{2-} and HS^- are almost the same. Therefore, after sufficiently injecting 99.999% purity nitrogen gas (N_2 gas) at least 1 hour to remove dissolved oxygen (DO) in 0.5 M borate buffer with pH 8.20, CPS solution was diluted with the buffer in anaerobic chamber (VS-5600A, VISION SCIENTIFIC, Daejeon, Korea) and HS^- peak was analyzed and quantified at 230 nm (Guenther et al., 2001) using a UV-Vis spectrophotometer (UV-Vis, Cary 3500 UV-Vis, Agilent, California, USA). Sodium sulfide (Na_2S, ACS reagent, Sigma-Aldrich) was selected to make a standard curve for HS^- quantification and 0.5 M borate buffer was used for dilution. The standard curve for absorbance was linearly well shown (Figure 2.1).

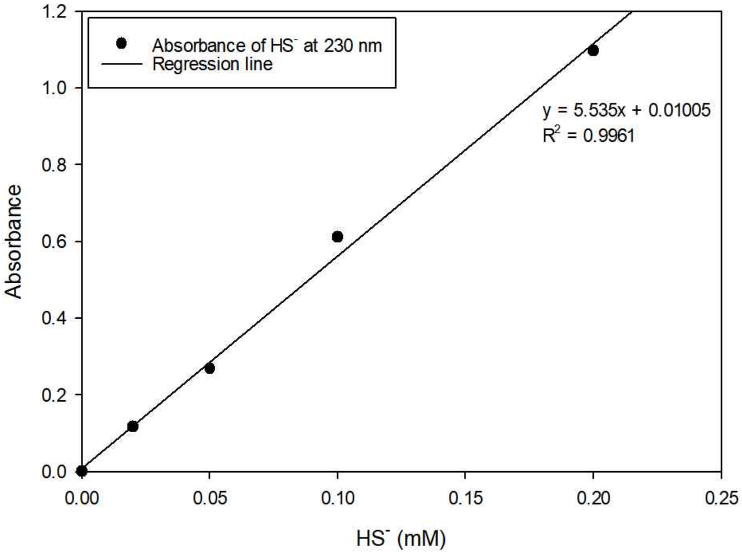
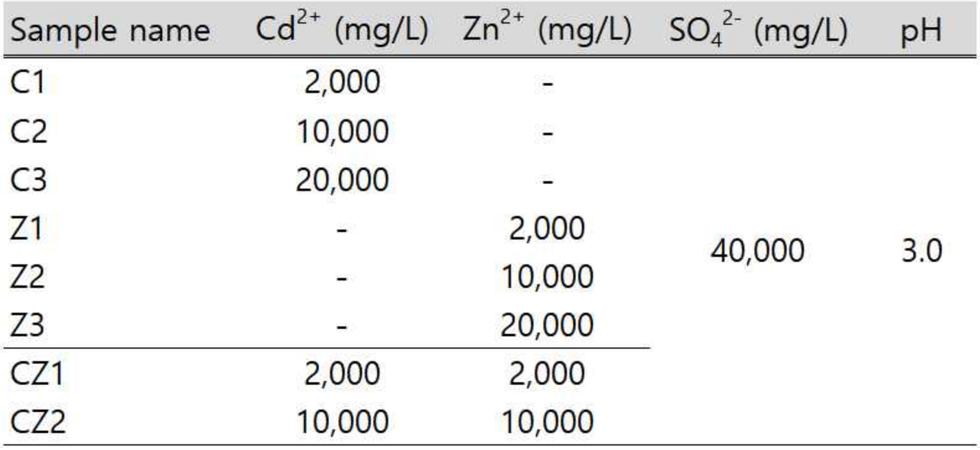


Figure. 2.1. The standard curve for HS^- at 230 nm in 0.5 M borate buffer with pH 8.20

The precipitate generated by lowering the pH of the solution was obtained and an X-ray diffractometer (XRD, D8 ADVANCE with DAVINCI, BRUKER, German) analysis (All XRD analysis conditions conducted in this study are as follows: 40 kv, 40 mA, and copper radiation $K_{\alpha 1}$ - 1.5418 Å) was performed. In addition, Ca^{2+} concentration in CPS was determined by Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES, iCAP 7400 Duo, Thermo Fisher Scientific, Waltham, Massachusetts, USA).

2.2 Production of artificially contaminated solution & CPS injection batch

To simulate groundwater contaminated with heavy metals, cadmium(II) sulfate ($CdSO_4$, ACS reagent, ≥99.0%, Sigma-Aldrich) or zinc(II) sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$, ACS reagent, 99%, Sigma-Aldrich) was dissolved in deionized (DI) water, and then the concentration of sulfate and pH were adjusted by using sodium sulfate anhydrous (Na_2SO_4, 99%=(EP), DAEJUNG), sulfuric acid (H_2SO_4, ACS reagent, 95.0~98.0%, Sigma-Aldrich), and sodium hydroxide (NaOH, 98%, DAEJUNG). The initial batch conditions before CPS injection are described in Table 2.2.



Sample name	Cd^{2+} (mg/L)	Zn^{2+} (mg/L)	SO_4^{2-} (mg/L)	pH
C1	2,000	-	40,000	3.0
C2	10,000	-		
C3	20,000	-		
Z1	-	2,000		
Z2	-	10,000		
Z3	-	20,000		
CZ1	2,000	2,000		
CZ2	10,000	10,000		

Table. 2.2. Initial batch conditions before CPS injection

DO was removed by sufficiently purging N_2 gas in the artificially contaminated solution to minimize oxygen exposure, and CPS injection was performed in an anaerobic chamber. CPS was injected into the solution from which DO was removed, and the initial heavy metal concentration was finally diluted twice after CPS injection. The solution injected with CPS was reacted for more than 24 hours, the supernatant was filtered using syringe filters (Pall ValuPrepTM 0.45-μm wwPTFE membrane syringe filter was used for all filtering processes), and the pH of the solution was measured. The concentration of heavy metal in the solution was quantified using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, 7800 ICP-MS, Agilent, California, USA) and ICP-OES. For C2, Z2, and CZ2 injected with CPS, the sample was centrifuged (10,000g, 10 minutes, 25℃) to collect the precipitate and XRD, Scanning Electron Microscope (SEM, JSM-7800F Prime, JEOL Ltd, Japan), and Energy Dispersive X-ray Spectrometry (EDS) analysis was performed with carbon-coated samples (SEM mode: accelerating voltage 5.0 ~ 15.0 kV, working distance 9.3 ~ 10.3 mm).

2.3 Effect of iron(II) in heavy metal precipitation by CPS

Iron(II) (Fe^{2+}) 200 ~ 2,000 mg/L was added into the C1 (CF1), Z1 (ZF1), and CZ1 (CZF1) samples, and CPS was injected in the same manner as in Chapter 2.2. The initial CPS injection amount was determined to remove heavy metals by about 50% (0.29% for CF1, 0.50% for ZF1, and 0.79% for CZF1) and observed how the removal (%) of heavy metals changes according to the iron concentration. After 24 hours of CPS injection, the pH of the filtered supernatant was measured, and the Cd^{2+}, Zn^{2+}, and Fe^{2+} concentrations were analyzed using ICP-OES.

2.4 Evaluation of effect of dissolved oxygen

2.4.1 Oxidation experiment of precipitates formed by CPS with DO

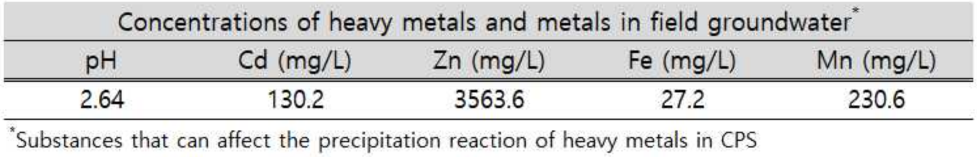
CPS was injected into the C2 and Z2 samples at a ME injection ratio, reacted in an anaerobic chamber for 24 hours, exposed to the atmosphere, and stirred at a speed of 450 rpm with a magnetic stirrer to maximize oxygen contact of heavy metal precipitates. After filtering the supernatant, pH, heavy metal concentration, and DO concentration of were measured for each time period (~49 days). The concentration of heavy metals in the supernatant was quantified using ICP-OES.

2.4.2 Cadmium sulfide oxidation by DO

Cadmium sulfide (CdS, ACS reagent, Sigma-Aldrich) powder was used to evaluate the possibility of oxidation by DO. The experiment was conducted by dividing it into two types: first when only CdS exists (WOS) and second when CdS and S_8 produced from CPS were mixed (WCS). The initial pH was adjusted to 3.0 using hydrochloric acid to prevent precipitate formation. In order to maximize oxygen contact with CdS, the mixture was stirred at 450 rpm. After exposure to the atmosphere, the supernatant was collected and filtered for each time period to measure pH and heavy metal concentration. XRD analysis for S_8 and SEM-EDS analysis for the precipitate in WCS were conducted.

2.5 Field applicability batch test

Immediately after collecting the field groundwater contaminated with heavy metals, it was filtered, placed in a Teflon bag, sealed with parafilm, and stored in the anaerobic chamber. The heavy metal and the metal concentration in groundwater that can serve as a scavenger for the CPS and heavy metal precipitation reaction due to the relatively small K_{sp} value (Waggoner et al., 1958) were measured using ICP-OES (Table 2.3) and the effect of removing heavy metals by CPS and pH change were analyzed. The CPS injection amount was calculated using the Cd^{2+} and Zn^{2+} concentration in groundwater and the injection ratio obtained in Chapter 2.2.



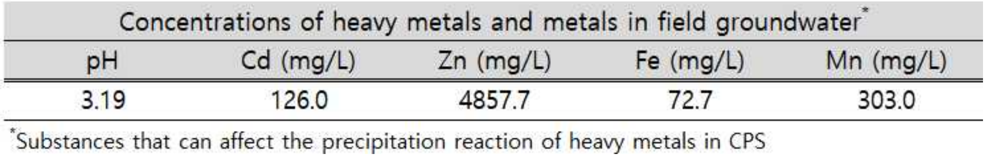
Concentrations of heavy metals and metals in field groundwater*

pH	Cd (mg/L)	Zn (mg/L)	Fe (mg/L)	Mn (mg/L)
2.64	130.2	3563.6	27.2	230.6

*Substances that can affect the precipitation reaction of heavy metals in CPS

Table. 2.3. The heavy metal and the metal concentration in field groundwater for CPS injection batch test

After CPS was injected, for samples with Cd^{2+} and Zn^{2+} removal completed, the effect of DO was monitored by exposing the sample to aerobic condition and analyzing heavy metals concentration, pH, and DO. At this time, the concentration of heavy metals and metals was measured again due to the difference in the collection period (Table 2.4), accordingly, the CPS injection amount was also recalculated according to Chapter 2.2.



Concentrations of heavy metals and metals in field groundwater*				
pH	Cd (mg/L)	Zn (mg/L)	Fe (mg/L)	Mn (mg/L)
3.19	126.0	4857.7	72.7	303.0

*Substances that can affect the precipitation reaction of heavy metals in CPS

Table. 2.4. The heavy metal and the metal concentration in field groundwater for oxidation experiment

3. Results

3.1 Concentration of polysulfide in CPS

UV-Vis analysis of CPS aqueous solution diluted with borate buffer and lowered pH to 8.20, showed a peak around 230 nm (Figure 3.1), and quantitative results showed that HS^- concentration in 29% CPS was 2.384 M. In addition, by XRD analysis, elemental sulfur was observed in the precipitates formed when CPS pH was lowered (Figure 3.2).

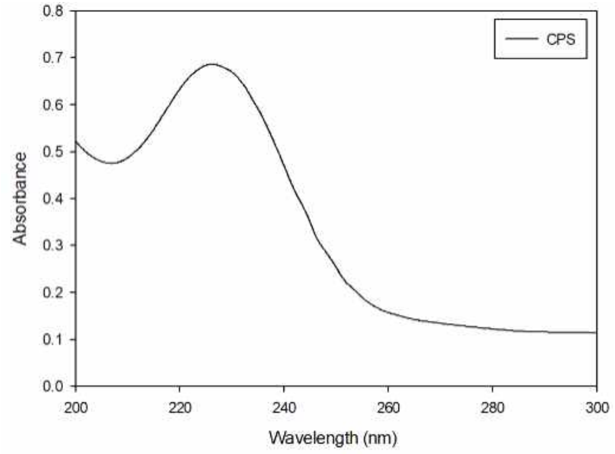


Figure. 3.1. UV-Vis spectroscopy of CPS showing peak wavelength at around 230 nm

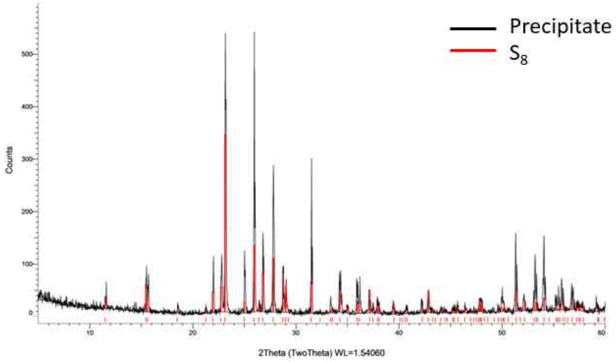


Figure. 3.2. XRD pattern for precipitate form from CPS (black) and S_8 reference peak (red)

As a result of quantifying the Ca^{2+} concentration in CPS using ICP-OES, the Ca^{2+} concentration in 29% CPS was 2.315 M. Through Figure 3.1 and ICP-OES analysis results, it was confirmed that the concentration of Ca^{2+} and S_x^{2-} in 29% CPS was almost the same as 2.3 M. Since most groundwater contaminated with heavy metals are acid conditions and elemental sulfur is a hydrophobic and stable solid at room temperature, it was concluded that since there is only one sulfide molecule that can precipitate heavy metals per one S_x^{2-} unless there is a material that can reduce S_x^{2-} to sulfide, so the sulfide concentration in 29% CPS participates in the heavy metal precipitation reaction is 2.384 M.

3.2 Deriving heavy metal precipitation mechanism by CPS

3.2.1 Single heavy metal contaminated solution (1) Cd^{2+}

In the case of Cd^{2+}, when CPS/Cd^{2+} (w/w) = 1.45 or higher, Cd^{2+} in aqueous solution was removed by more than 99.5%, therefore the ME injection ratio for Cd^{2+} removal is CPS/Cd^{2+} = 1.45 (Figure 3.3). When CPS/Cd^{2+} = 1.16 or less, the pH of the aqueous solution is near 3.0, and the pH was increased at ME injection ratio. When the initial concentration of Cd^{2+} is 1,000 mg/L, it is inferred that the reason why the pH does not increase rapidly at CPS/Cd^{2+} = 1.45 is that the amount of sulfide remaining through heavy metal precipitation reactions is small.

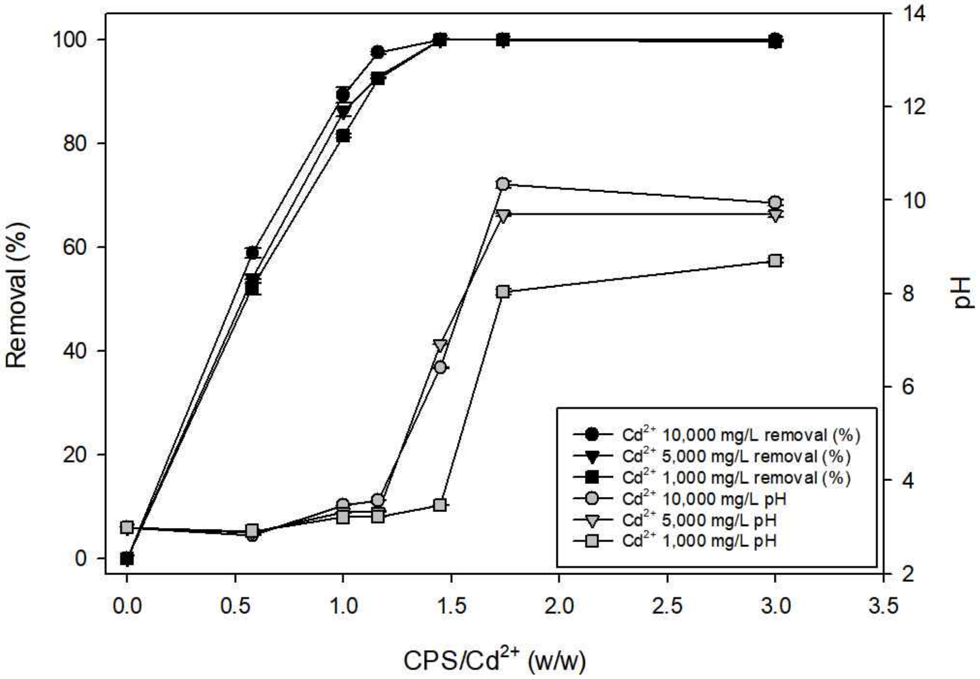


Figure. 3.3. Removal (%) and pH change graph according to CPS injection ratio (Cd)

The relationship of the number of moles of removed Cd to the number of moles of injected polysulfide was shown for CPS/Cd^{2+} = 0.58 ~ 1.16, before the Cd^{2+} removal was completed by more than 99.5% (Figure 3.4). As a result, it was confirmed that Cd^{2+} was removed at a molar ratio of 1:1 to the injected polysulfide, which reinforces the assumption that one sulfide is provided per polysulfide to remove heavy metals in chapter 3.1.

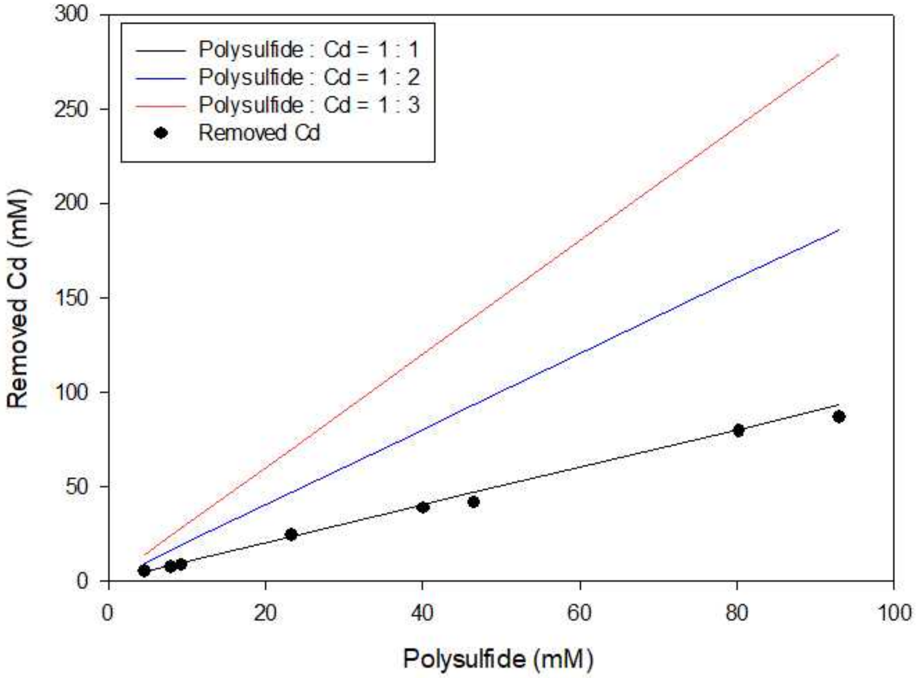


Figure. 3.4. Polysulfide (mM) vs Removed Cd (mM)

XRD analysis was performed with the precipitate before (CPS/Cd^{2+} = 1.16) and at the ME injection ratio (CPS/Cd^{2+} = 1.45) (Figure 3.5). In the case of CPS/Cd^{2+} = 1.16, CdS, S_8, and gypsum ($CaSO_4 \cdot 2H_2O$) were found in the precipitates. Although more than 90% of Cd^{2+} in the aqueous solution has been removed, Cd was present in the form of sulfide, not hydroxide. gypsum was formed by a reaction between Ca^{2+} in CPS and SO_4^{2-} in the solution, and it is thought that S_8 was precipitated in CPS as the pH decreased. At the ME injection ratio, the same kinds of precipitates as at CPS/Cd^{2+} = 1.16 were detected. In addition, cadmium hydroxide ($CdOH_2$) was not found even though the pH of the aqueous solution increased to 9 or more.

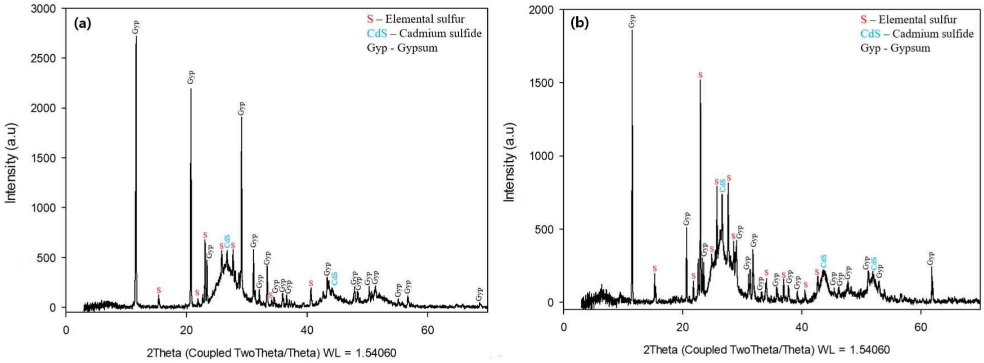


Figure. 3.5. XRD pattern of precipitate according to CPS injection (a) CPS/Cd^{2+} = 1.16 (b) CPS/Cd^{2+} = 1.45

According to Figure 3.6, in the case of the inside of the green circle (bar shape), Ca, S, and O are clearly present but Cd was not present, so it is expected to be gypsum. Inside the red circle area, Cd and S were present, but Ca and O were less detected, so expected to be CdS. However, S_8 found on XRD data was not identified.

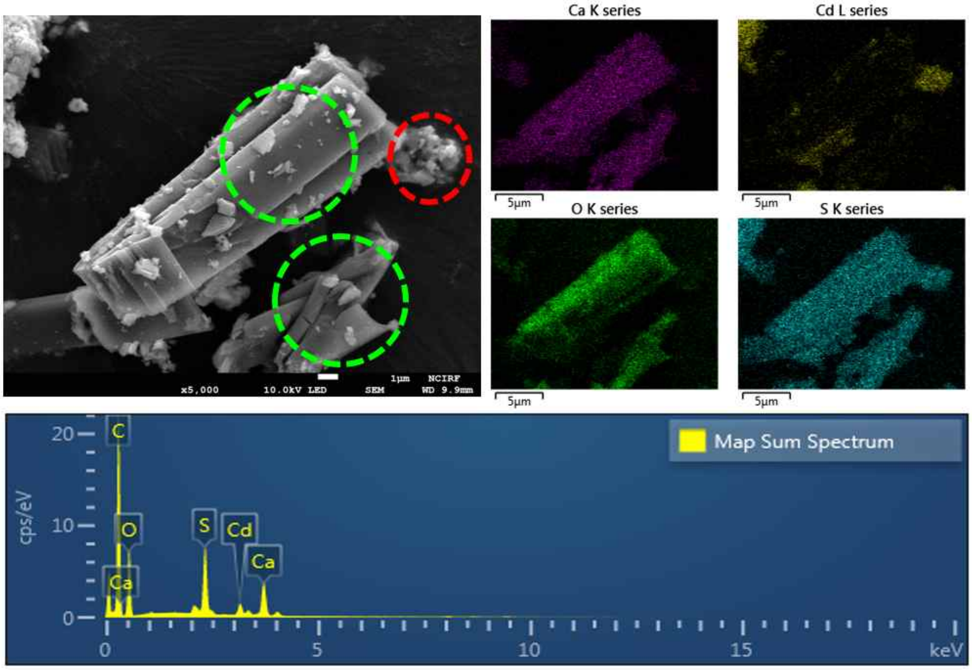


Figure. 3.6. SEM image, EDS mapping, and map sum spectrum of CPS/Cd^{2+} = 1.16 (gypsum & CdS)

Based on SEM-EDS data for CPS/Cd^{2+} = 1.45 (Figure 3.7), in the case of the inside of the green circle, only S was clearly present, which is expected to be S_8. In the red circle, Cd and S were present, but Ca and O were less detected, so expected to be CdS. The bar-shaped orange circle region is expected to be gypsum (Figure 3.8), referring to CPS/Cd^{2+} = 1.16 SEM data (Figure 3.6)

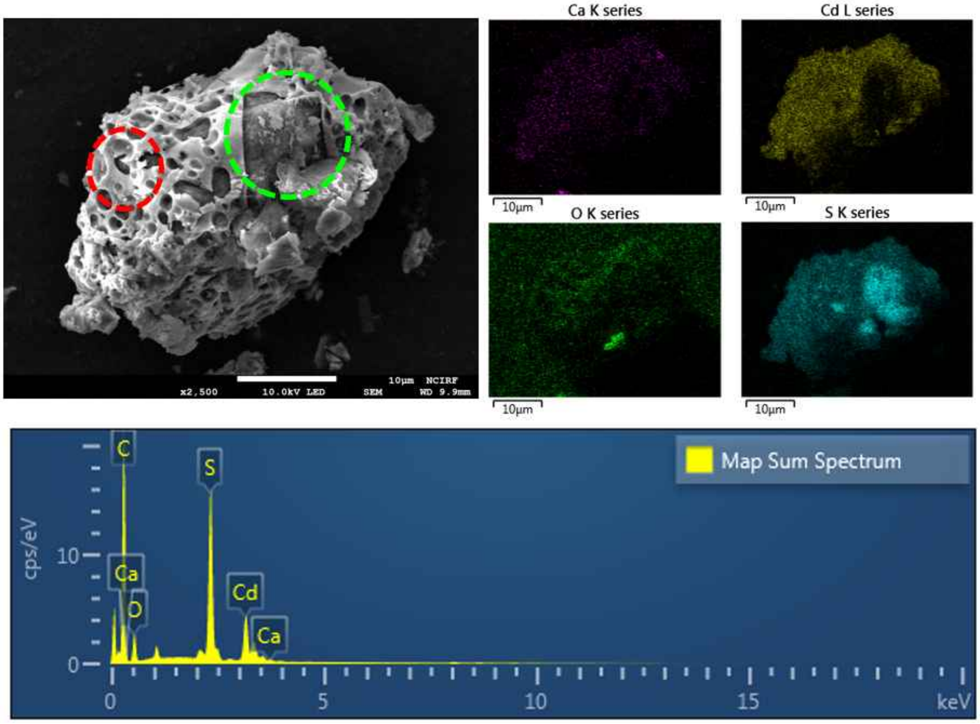


Figure. 3.7. SEM image, EDS mapping, and map sum spectrum of CPS/Cd^{2+} = 1.45 (CdS & S_8)

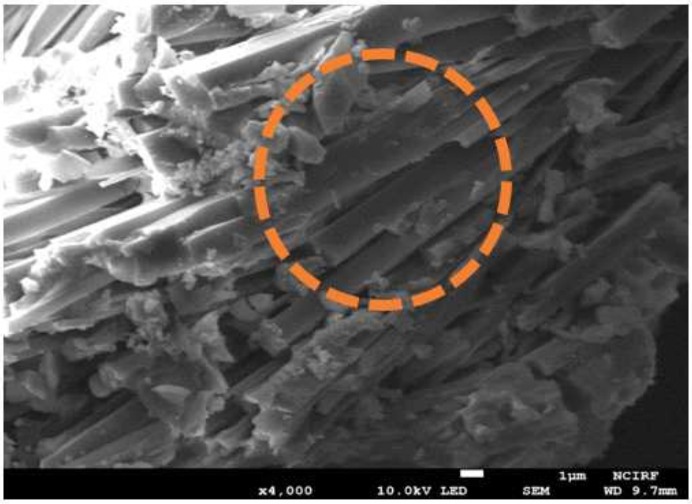


Figure. 3.8. SEM image of CPS/Cd^{2+} = 1.45 (gypsum)

3.2.1 Single heavy metal contaminated solution (2) Zn^{2+}

For Zn^{2+} contaminated solution, when CPS/Zn^{2+} (w/w) = 2.50 or higher, Zn^{2+} in aqueous solution was removed by more than 99.5%, therefore the ME injection ratio for Zn^{2+} removal is CPS/Zn^{2+} = 2.50 (Figure 3.9). When CPS/Zn^{2+} = 2.00 or less, the pH of the aqueous solution is near 3.0 and it was increased at ME injection ratio. When the initial concentration of Zn^{2+} is 1,000 mg/L, the reason seems to be that the amount of sulfide remaining after precipitating heavy metals as in Cd^{2+} 1,000 mg/L is small.

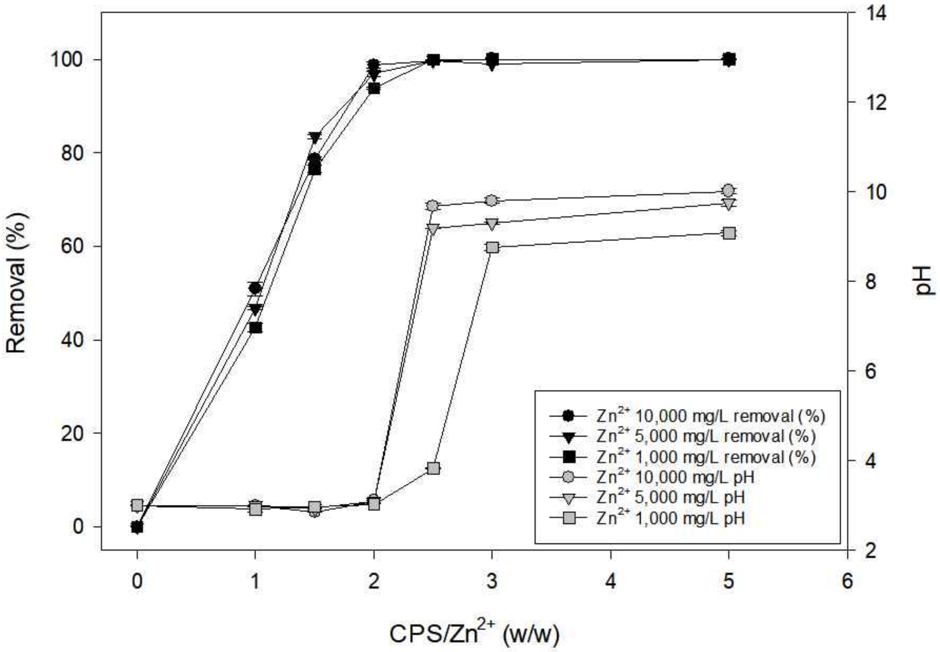


Figure. 3.9. Removal (%) and pH change graph according to CPS injection ratio (Zn)

The relationship of the number of moles of removed Zn to the number of moles of injected polysulfide was shown for CPS/Zn^{2+} = 1.00 ~ 2.00, before the Zn^{2+} removal was completed by more than 99.5% (Figure 3.10). As a result, it was confirmed that Zn^{2+} was removed at a molar ratio of 1:1 to the injected polysulfide, which CPS injection batch for Zn^{2+} single contaminated solution also has the same tendency as the assumptions in 3.1 and the results in 3.2.1.

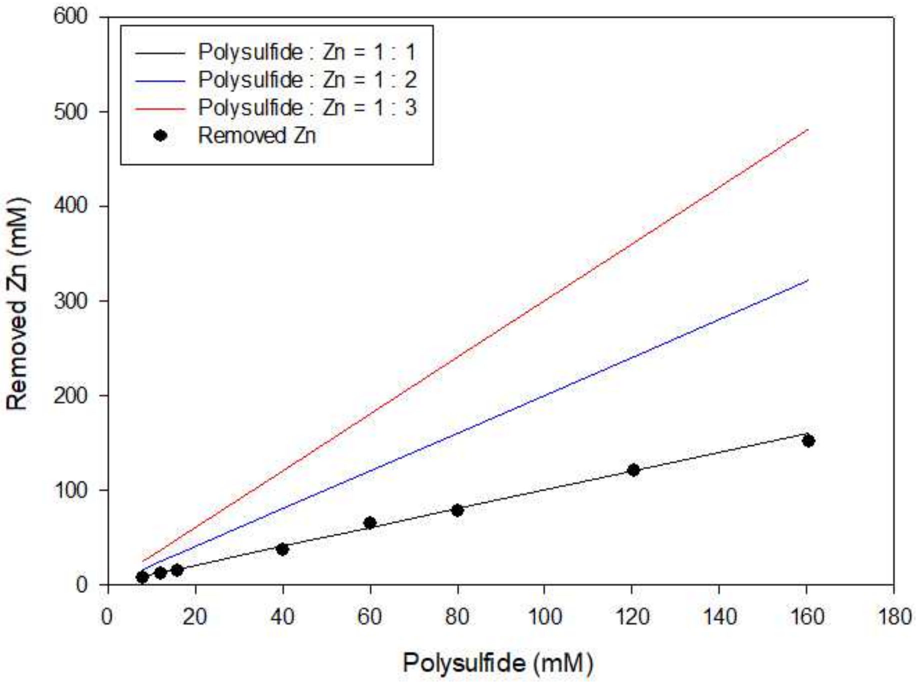


Figure. 3.10. Polysulfide (mM) vs Removed Zn (mM)

For the solution artificially contaminated with Zn^{2+}, XRD analysis was performed with the precipitates before the ME injection ratio (CPS/Zn^{2+} = 2.00) and at the ME injection ratio (CPS/Zn^{2+} = 2.50) (Figure 3.11). Before the ME injection ratio, zinc sulfide (ZnS), S_8, and gypsum were found. ZnS seems to be formed by the reaction of polysulfide and Zn^{2+}, S_8 by pH decrease of CPS, and gypsum by Ca^{2+} in CPS and SO_4^{2-} in an aqueous solution. Although nearly 95% of Zn^{2+} was removed from the aqueous solution, similar to the Cd batch result, the Zn precipitate existed in the form of sulfide rather than hydroxide. In the case of ME injection ratio, the same kinds of precipitates as at CPS/Zn^{2+} = 2.00 were detected. Moreover, although the pH was around 9.0. Zn precipitated in the form of hydroxide did not exist.

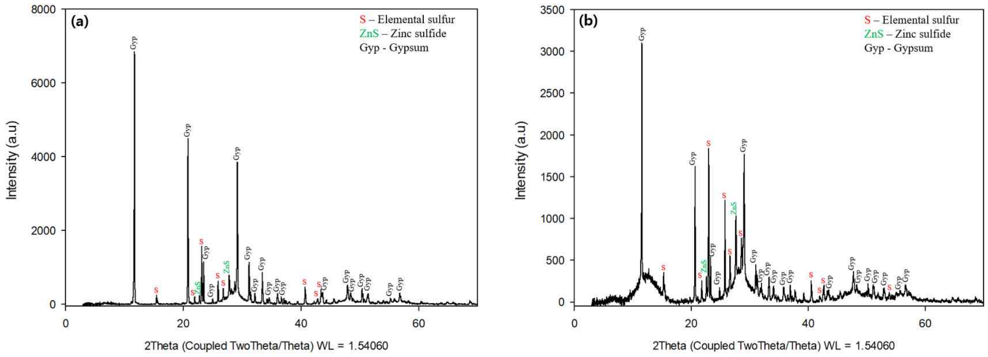


Figure. 3.11. XRD pattern of precipitate according to CPS injection (a) CPS/Zn^{2+} = 2.00 (b) CPS/Zn^{2+} = 2.50

Based on the SEM-EDS results for CPS/Zn^{2+} = 2.00 (Figure 3.12), inside the green circle area, Ca, S, and O were clearly present but Zn was not present, which is expected to be gypsum. In the case of the red circle (Figure 3.13), Zn and S were present, but Ca was less detected, thus expected to be ZnS. However, S_8 found on XRD data was not observed.

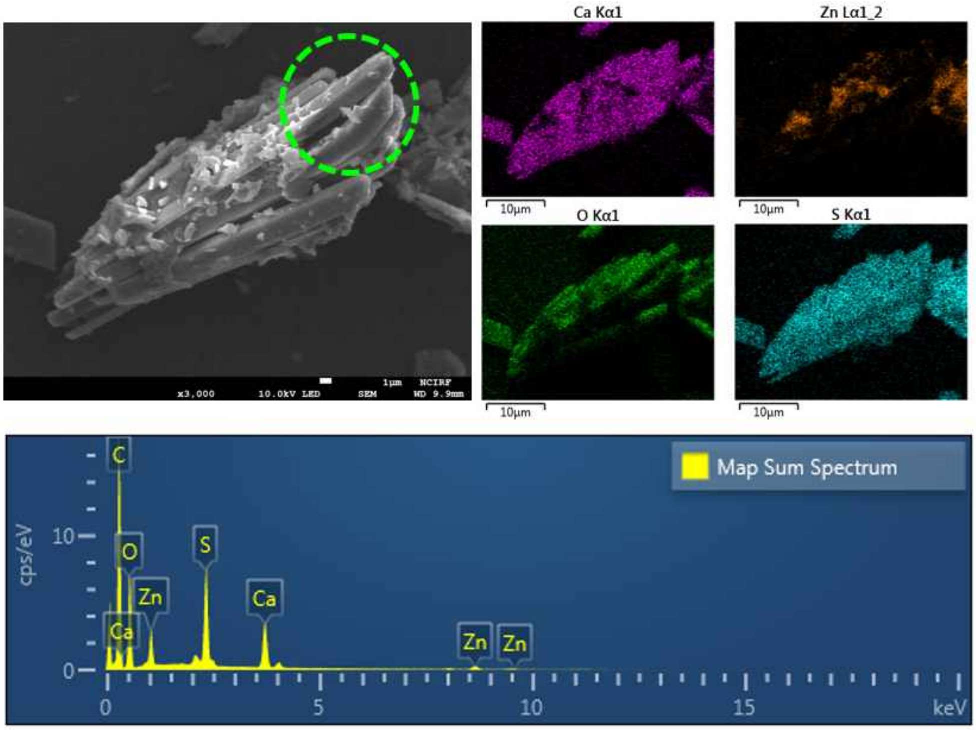


Figure. 3.12. SEM image, EDS mapping, and map sum spectrum of CPS/Zn^{2+} = 2.00 (gypsum)

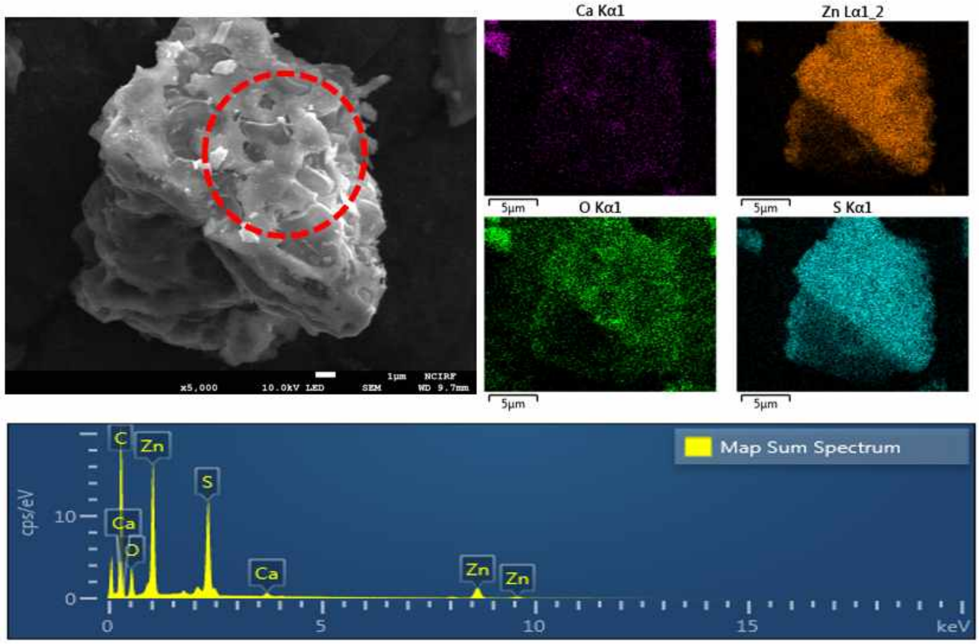


Figure. 3.13. SEM image, EDS mapping, and map sum spectrum of CPS/Zn^{2+} = 2.00 (ZnS)

According to Figure 3.14, for CPS/Zn^{2+} = 2.50, inside of the green circle (bar shape), Ca, S, and O were clearly present but Zn was not present, thus it is expected to be gypsum. In the case of the red circle, Zn and S were present, but Ca was less detected, thus expected to be ZnS. In the case of the inside of the blue circle (Figure 3.15), only S was detected, which means S_8.

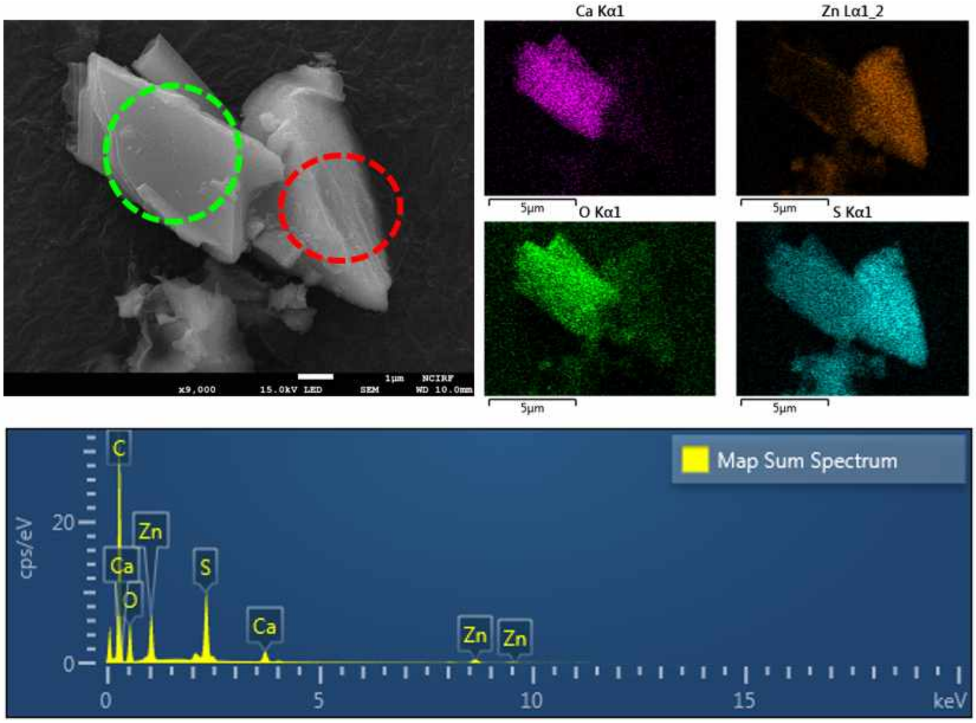


Figure. 3.14. SEM image, EDS mapping, and map sum spectrum of CPS/Zn^{2+} = 2.50 (gypsum & ZnS)

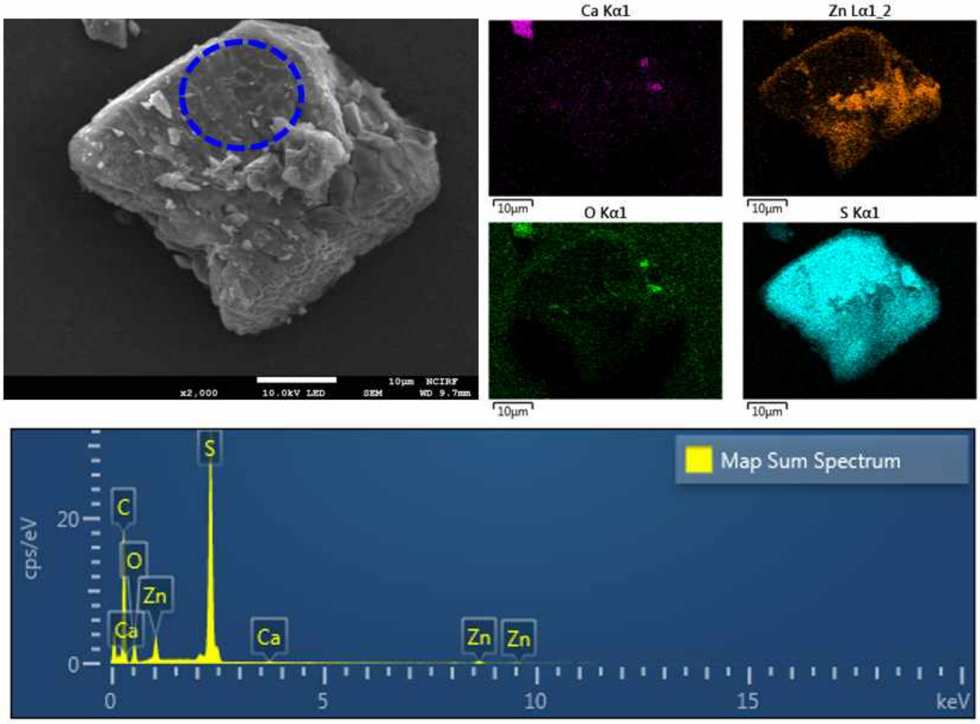


Figure. 3.15. SEM image, EDS mapping, and map sum spectrum of CPS/Zn^{2+} = 2.50 (S$_8$)

3.2.2 Complex heavy metal contaminated solution

The concentration of each heavy metal and pH of the supernatant according to the injection amount of CPS were measured for the aqueous solutions that were artificially contaminated with Cd^{2+} and Zn^{2+} (Figure 3.16). When the inital concentration of Cd^{2+} and Zn^{2+} was 1,000 mg/L, ME injection amount was 0.40%, which was almost identical to 0.395% calculated based on the ME injection ratio for each heavy metal derived through an experiment conducted on a single contaminated solution (Table 3.1). Moreover, before ME injection amount, although the initial concentration of Cd^{2+} and Zn^{2+} was the same, precipitation of Cd^{2+} occurred predominantly over Zn^{2+}. When the initial concentration of Cd^{2+} and Zn^{2+} was 5,000 mg/L, ME injection amount was 2.00%, which was increased in proportion to the initial heavy metal concentration (Figure 3.16 (b)). Overall, it shows a similar trend to Figure 3.16 (a).

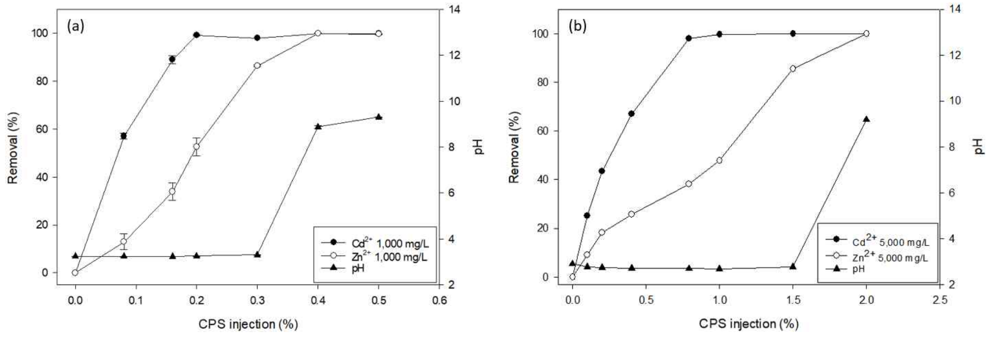


Figure. 3.16. Removal (%) and pH change graph according to CPS injection ratio (CdZn) (a) Cd, Zn 1,000 mg/L (b) Cd, Zn 5,000 mg/L

(a)	ME ratio	CPS injection (%)
		Initial conc. of Cd^{2+} and Zn^{2+} 1,000 mg/L
CPS/Cd^{2+}	1.45	0.145
CPS/Zn^{2+}	2.50	0.250
Total		**0.395**

(b)	ME ratio	CPS injection (%)
		Initial conc. of Cd^{2+} and Zn^{2+} 5,000 mg/L
CPS/Cd^{2+}	1.45	0.725
CPS/Zn^{2+}	2.50	1.250
Total		**1.975**

Table. 3.1. Theoretical ME values calculated from CPS ME injection for a single heavy metal (a) Cd, Zn 1,000 mg/L (b) Cd, Zn 5,000 mg/L

XRD analysis was performed with the precipitates produced by CPS injection to CZ2 before the ME injection amount (CPS 1.50%) and at the ME injection amount (CPS 2.00%) (Figure 3.17). Before the ME injection amount, CdS, ZnS, S_8, and gypsum were found. Cd and Zn exist in the form of sulfide rather than hydroxide. In the case of ME injection ratio, the same kinds of precipitates as at ME CPS injection amount were detected. Moreover, although the pH was around 9.0. heavy metals precipitated in the form of hydroxide did not exist.

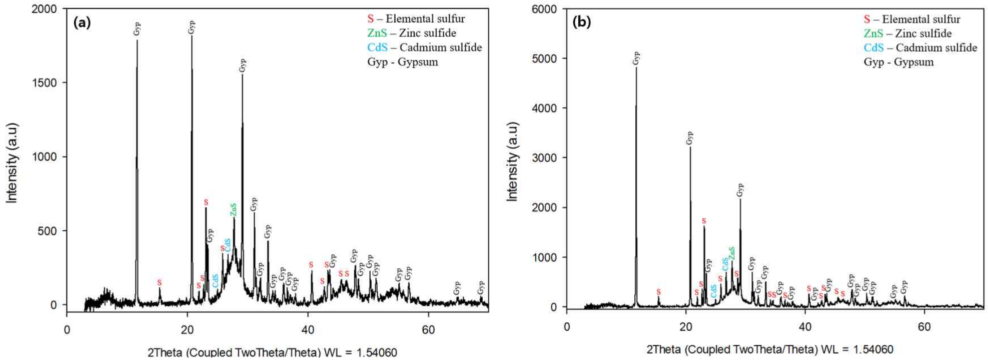


Figure. 3.17. XRD pattern of precipitate according to CPS injection (a) CPS 1.50% (b) CPS 2.00%

For the precipitate formed from CZ2 that injection concentration of CPS was 1.50%, SEM-EDS analysis was conducted (Figure 3.18). Inside the green circle (bar shape), Ca, S, and O were clearly present but Cd and Zn were not present, so it is expected to be gypsum. Inside the red circle, Cd, Zn, and S were present, but Ca and O were less detected, so expected to be CdS and ZnS. Elemental sulfur was hard to apparently detect in EDS mapping.

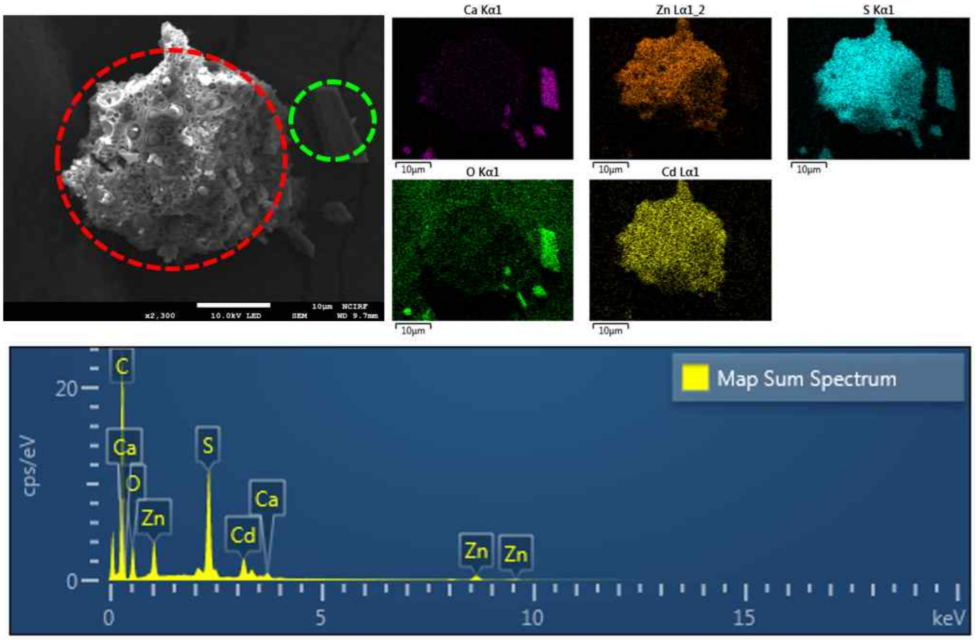


Figure. 3.18. SEM image, EDS mapping, and map sum spectrum of CPS 1.50% (gypsum & CdS & ZnS)

Based on the SEM-EDS data from precipitate formed by injecting 2.00% of CPS to CZ2 (Figure 3.19), in the case of the inside of the green circle (bar shape), Ca, S, and O were clearly present but Cd and Zn were not present, so it is expected to be gypsum. In the red circle, Cd, Zn, and S were present, but Ca and O were less detected, so expected to be CdS and ZnS. Inside the blue circle, S was relatively well observed alone, which means S_8 (Figure 3.20).

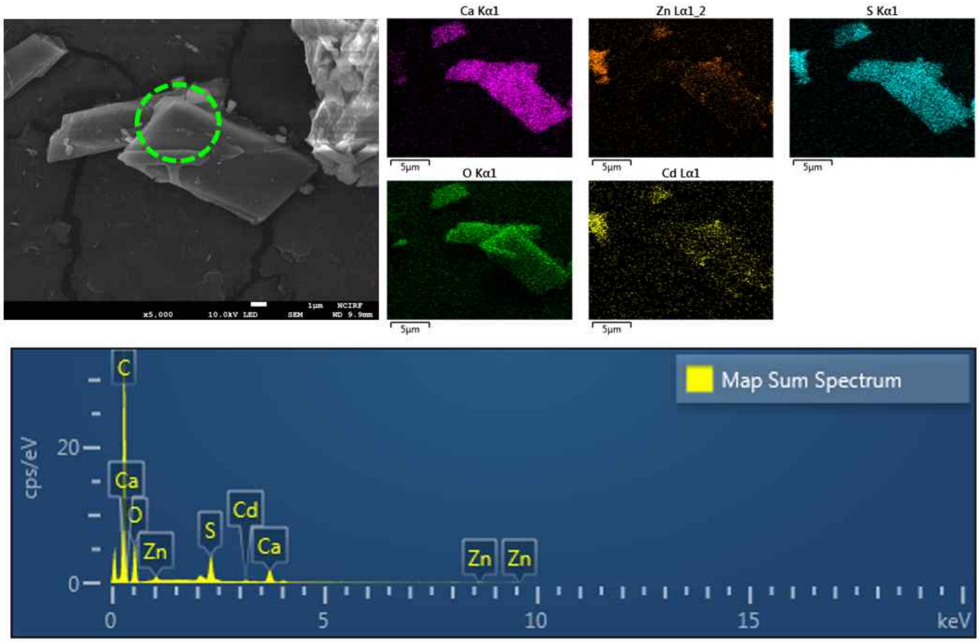


Figure. 3.19. SEM image, EDS mapping, and map sum spectrum of CPS 2.00% (gypsum)

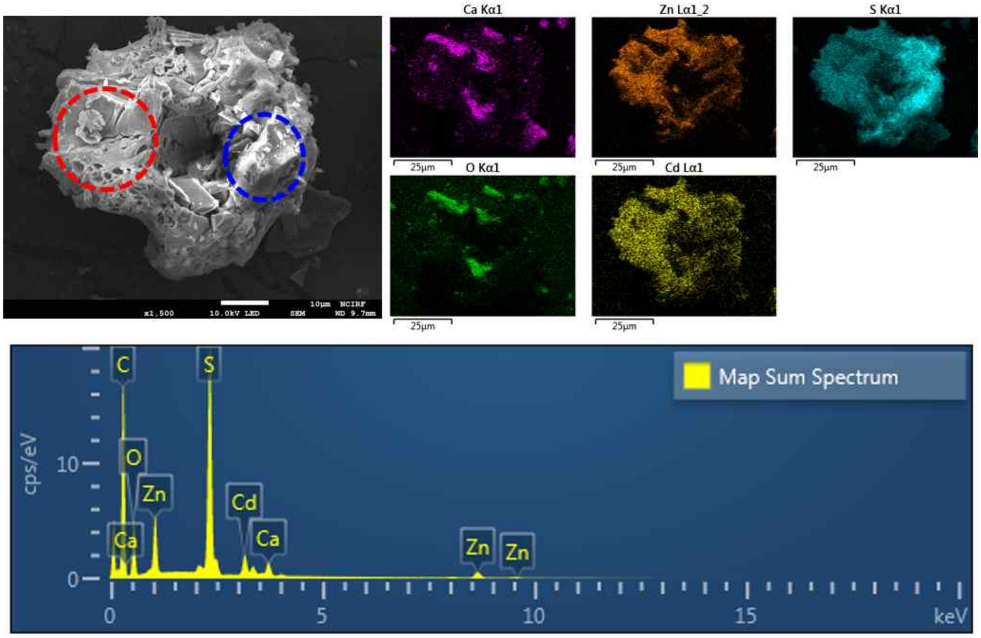


Figure. 3.20. SEM image, EDS mapping, and map sum spectrum of CPS 2.00% (CdS & ZnS & S_8)

3.3 Effect of Fe^{2+} in heavy metal precipitation by CPS

According to Figure 3.21 (a) and (b), regardless of the Fe^{2+} injection amount, the change in the heavy metal removal (%) by CPS and pH were small for CF1 and ZF1. However, based on Figure 3.21 (c) and (d), removal from the supernatant by CPS tend to be completed in order of small K_{sp} value in that Cd^{2+} was removed by more than 90%, Zn^{2+} was decreased by about 30%, and Fe^{2+} concentration was consistent or very slightly lowered while there is little difference between total heavy metal removal amount and injected polysulfide. Meanwhile, pH was almost the same for CZF1 in Figure 3.21 (c).

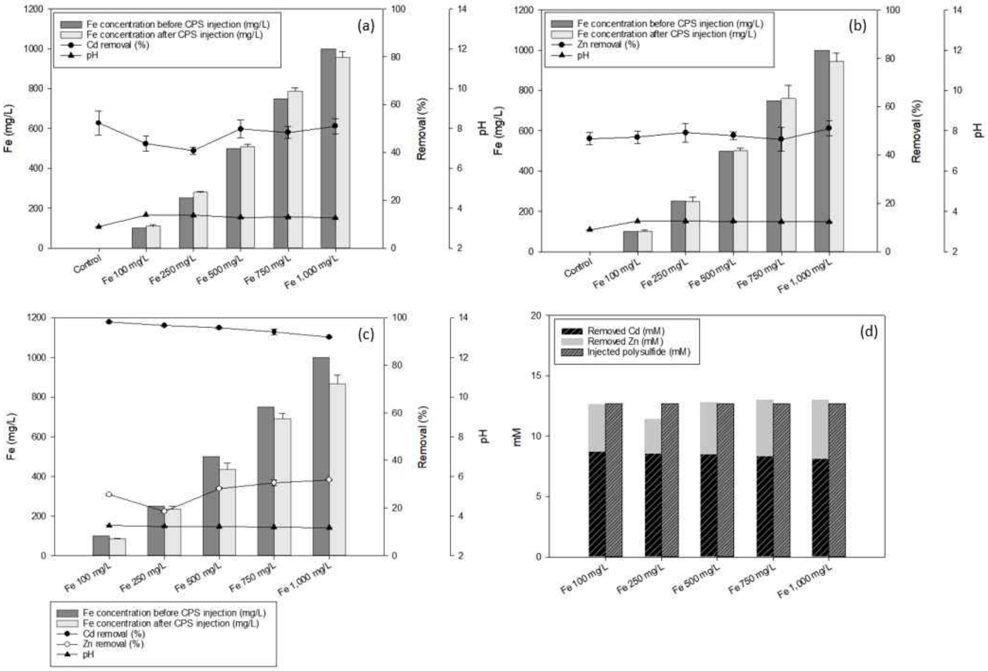


Figure. 3.21. Removal (%) and pH change graph according to Fe^{2+} concentration (a) Cd (b) Zn (c) Cd, Zn (d) removed heavy metal (mM)

3.4 Evaluation of effect of dissolved oxygen

3.4.1 Evaluation of oxidation of precipitates formed by CPS with DO

During 49 days, the concentration of Cd^{2+} in the aqueous solution was not detected (under 0.2 mg/L) (Figure 3.22 (a)). In the case of DO, the equilibrium was reached at 8 mg/L after 6 to 12 hours (Figure 3.22 (b)). The initial pH (9.18) tended to slightly increase and maintain but the pH started to decrease as DO increased and equilibrated around 4.0 after 14 days.

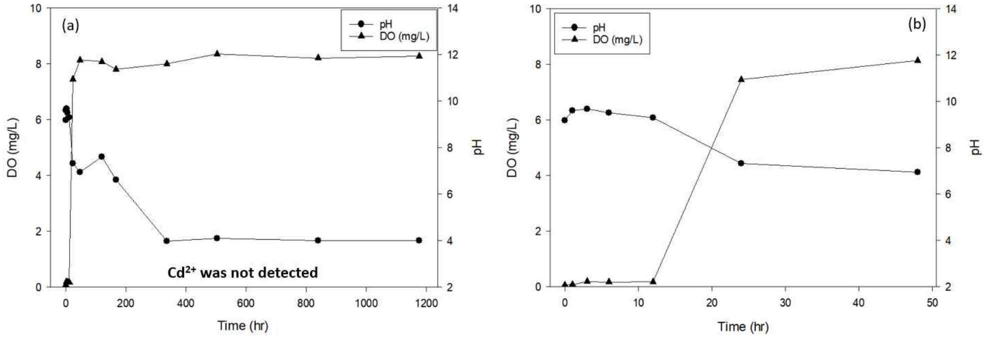


Figure. 3.22. pH, and DO change of CPS/Cd^{2+} = 1.45 sample after CPS injection and exposed to atmosphere (a) 0 ~ 49 days (b) 0 ~ 2 days

Based on Figure 3.23 (a), during 49 days, the concentration of Zn^{2+} in the aqueous solution was not detected (under 0.2 mg/L). In the case of DO, the equilibrium was reached at 8 mg/L after 12 to 24 hours (Figure 3.22 (b)). The initial pH (9.13 ~ 9.18) tended to slightly increase and maintain but the pH started to decrease apparently as DO increase and equilibrate around 7.8 after 14 days.

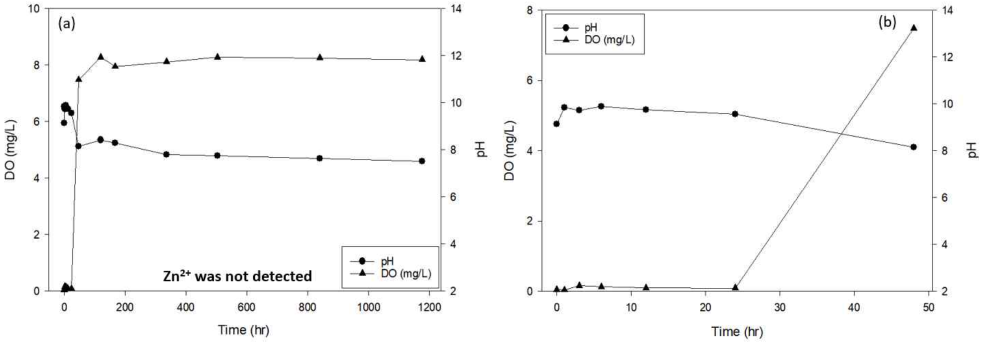


Figure. 3.23. pH, and DO change of CPS/Zn^{2+} = 2.50 sample after CPS injection and exposed to atmosphere (a) 0 ~ 49 days (b) 0 ~ 2 days

Kamyshny, Alexey, et al. (2004) elucidated polysulfide and sulfide species at pH 8 ~ 12. At pH 9.0 or higher, the concentration of HS^- is similar to or smaller than that of S_x^{2-} (Figure 3.24). The initial pH before exposure to the atmosphere in Figure 3.22 (b) and 3.23 (b) are around 9.1 and since CPS was injected more than the theoretical amount to react with all heavy metals, S_x^{2-} remains in the solution. Therefore, it's important to consider the oxidation of both HS^- and S_x^{2-}. First, when S_x^{2-} reacts with DO, thiosulfate ($S_2O_3^{2-}$) and S^0 are produced (Equation 3.1).

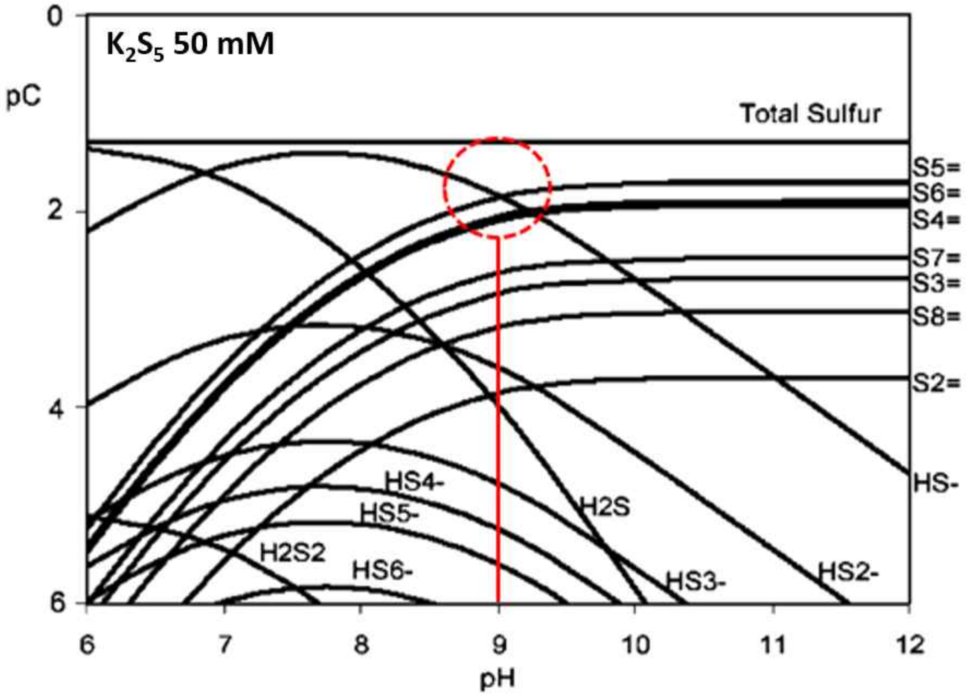
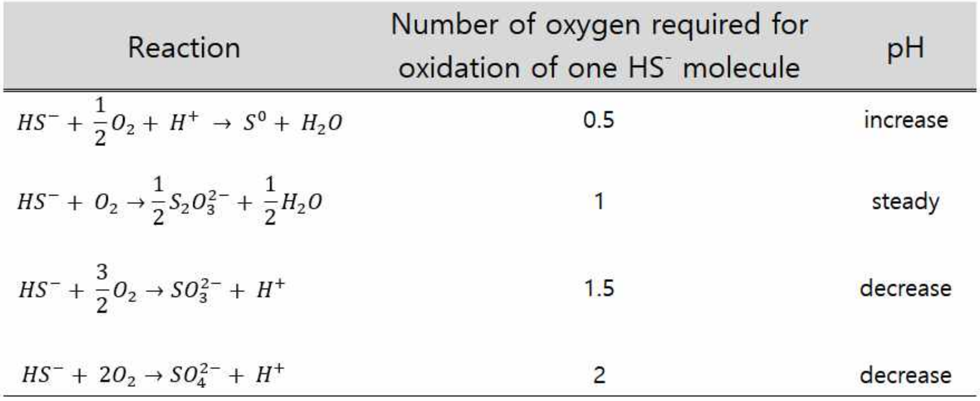


Figure. 3.24. Concentration of different sulfide and polysulfide species in 50 mM K_2S_5 as a function of pH

$$S_x^{2-} + \frac{3}{2}O_2 \rightarrow S_2O_3^{2-} + (x-2)S^0 \qquad \text{(Eq. 3.1)}$$

In the case of HS^-, the oxidation by DO has four possible reactions as follows (Table 3.2). Each chemical reaction is determined by the ratio of oxygen to sulfur.



Reaction	Number of oxygen required for oxidation of one HS⁻ molecule	pH
$HS^- + \frac{1}{2}O_2 + H^+ \rightarrow S^0 + H_2O$	0.5	increase
$HS^- + O_2 \rightarrow \frac{1}{2}S_2O_3^{2-} + \frac{1}{2}H_2O$	1	steady
$HS^- + \frac{3}{2}O_2 \rightarrow SO_3^{2-} + H^+$	1.5	decrease
$HS^- + 2O_2 \rightarrow SO_4^{2-} + H^+$	2	decrease

Table. 3.2. Possible oxidation reactions of HS^- by dissolved oxygen

According to Kleinjan, et al. (2005), oxidation of S_x^{2-} by DO is 3 to 5 times faster than that of HS^-. Therefore, during the early stage of the exposure, DO reacts more predominantly with the remaining S_x^{2-} than HS^- generating $S_2O_3^{2-}$. Consequently, the concentration of DO that HS^- can react with is decreased, and S^0 or $S_2O_3^{2-}$ with low oxygen demand is produced during the reaction. Accordingly, pH is slightly increased or maintained and DO is kept low because of S_x^{2-}, which is highly reactive with DO. As S_x^{2-} is oxidized and decreased, DO increases because of the relatively low reaction rate of HS^-, and the reaction between the remaining HS^- and oxygen increases. As the DO concentration increases, the amount of oxygen that can react with HS^- increases, and sulfite (SO_3^{2-}) or SO_4^{2-} is produced accordingly, resulting in lowering pH. In short, in the early stages of atmospheric exposure, S_x^{2-} and HS^- react predominantly with DO to prevent oxidation of heavy metals, so the dissolution of heavy metals does not appear to have occurred.

3.4.2 Evaluation of oxidation of CdS without elemental sulfur by DO

Cd generally exists as Cd^{2+} below pH 6.0 (Ford, Robert G et al., 2007) but according to Figure 3.22 (a), although the solution pH was 4.0, Cd^{2+} concentration was below 2 mg/L, which means only less than 0.1% of Cd was dissolved compared to the initial Cd^{2+} (5,000 mg/L). Therefore, additional experiment was conducted related to the oxidation of CdS. For WOS, Cd^{2+} was continuously dissolved over time and the concentration and pH were increased to 550 mg/L and to around 5.5 respectively after a week of stirring (Figure 3.25). The results are well suited to the fact that sulfides are easily oxidized when they are exposed to aerobic condition.

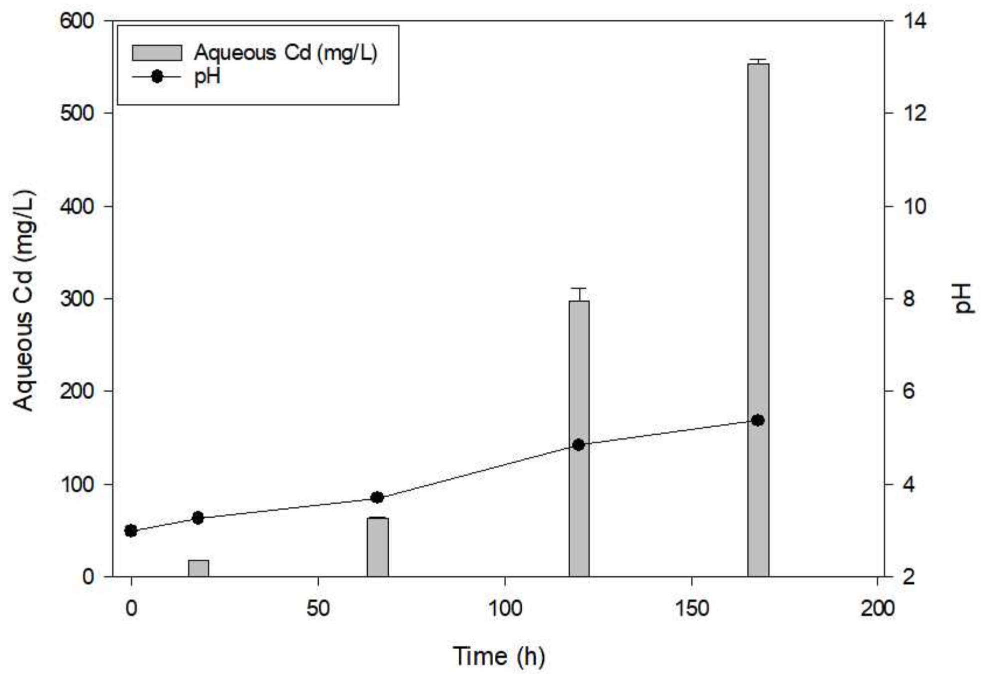


Figure. 3.25. Cd^{2+} concentration and pH change in CdS solid-water mixture as a function of time

In the case of WCS (Figure 3.26), in which CdS exist with elemental sulfur formed by lowering CPS pH, the concentration of Cd^{2+} was less than 2 mg/L even after 20 days of stirring. The solution pH tended to increase and slightly decrease after 18 days.

This is in contrast to the dissolution of Cd^{2+} concentration above 500 mg/L within a week after stirring under the same conditions without elemental sulfur (Figure 3.25). As a result of SEM-EDS analysis (Figure 3.27 (a) and (b)), refer to the orange circle where Cd, S, and O were found and the red circle in which S mainly exists, it seems that Cd^{2+} is adsorbed on the elemental sulfur surface.

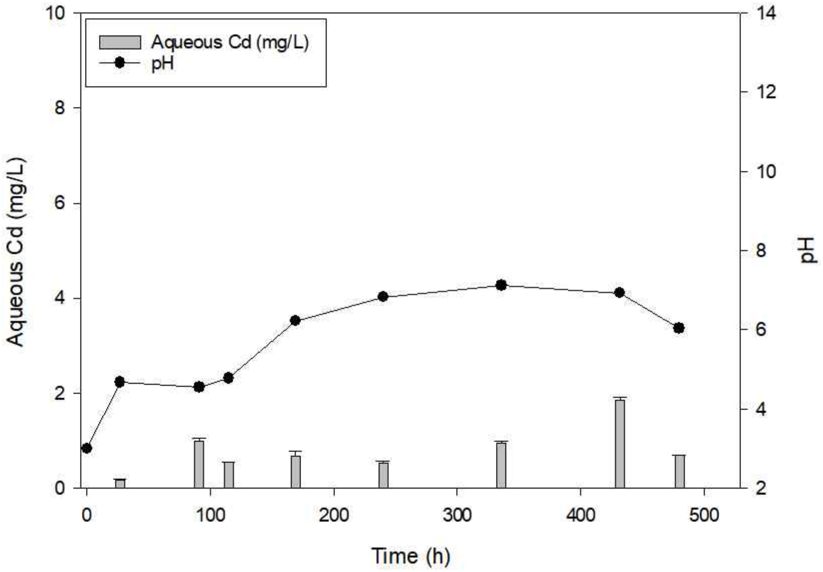


Figure. 3.26. Cd^{2+} concentration and pH change in CdS S_8-water mixture as a function of time

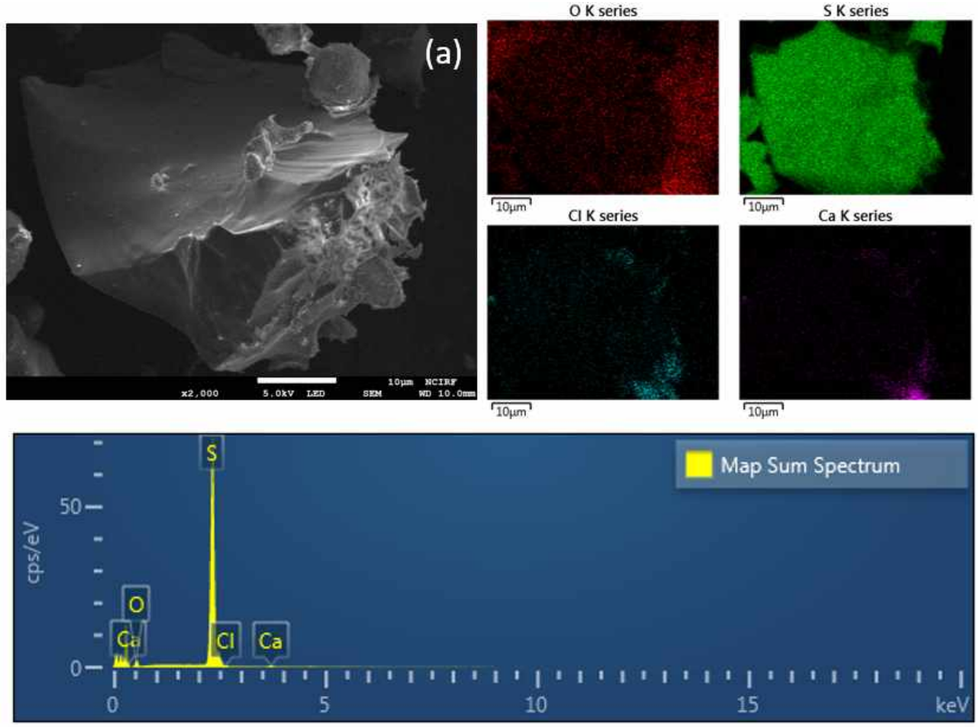


Figure. 3.27 (a). SEM image, EDS mapping, and map sum spectrum of elemental sulfur from CPS

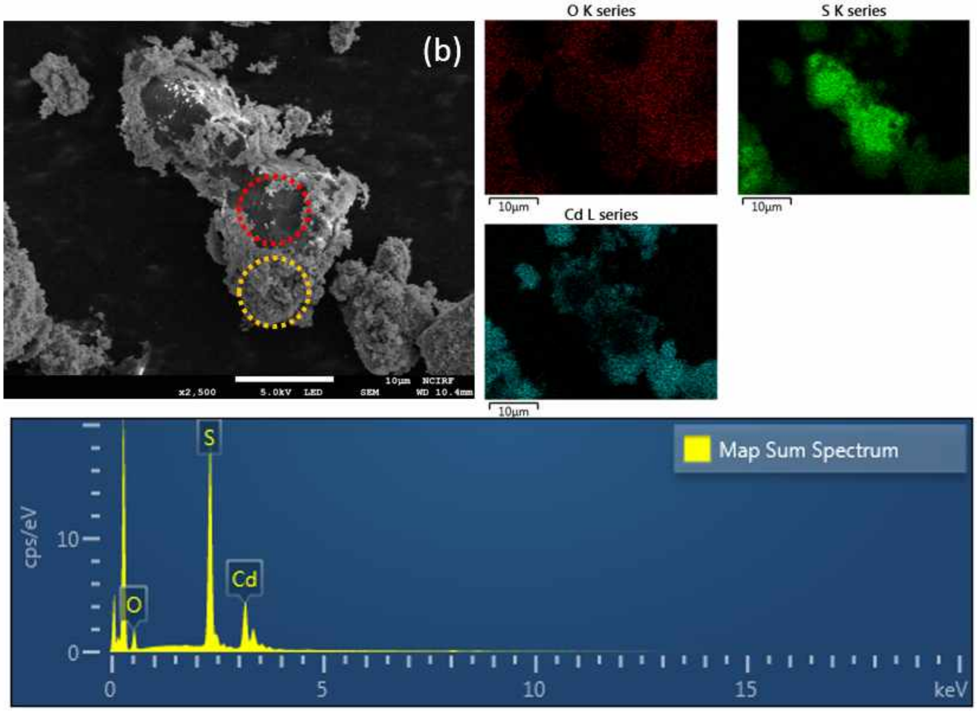


Figure. 3.27 (b). SEM image, EDS mapping, and map sum spectrum of elemental sulfur from CPS

3.5 Field applicability test for CPS

The removal of heavy metal (%) was completed in the order of small K_{sp} values, and there was little change in pH when Cd^{2+} or Zn^{2+} was removed, but when the concentration of Fe^{2+} and Mn^{2+} was decreased, the pH tended to increase (Figure 3.28). According to the color change of precipitate and pH-Eh diagram of Fe and Mn (Moslemi Hossein et al., 2017 and Langmuir, Donald et al., 2004), decrease of Fe and Mn concentration is due to precipitation in sulfide form. The ME injection amount through calculation was 0.91%, but even if only 0.60% was injected, Cd^{2+} and Zn^{2+} in the supernatant were almost removed.

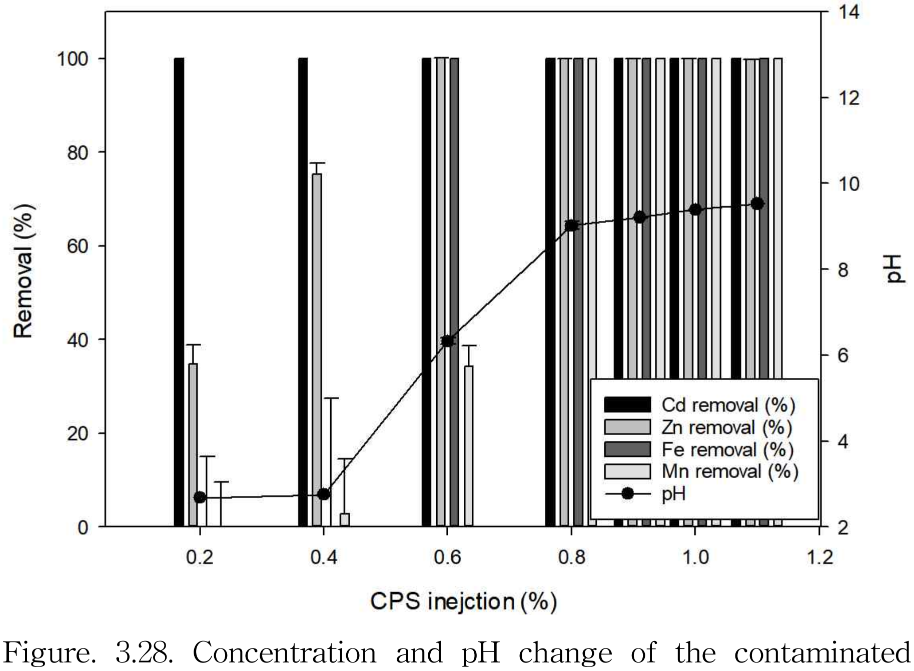


Figure. 3.28. Concentration and pH change of the contaminated groundwater with heavy metals and metals as a function of CPS injection (%)

In terms of the oxidation experiment of precipitate formed from field groundwater by CPS injection (Figure 3.29), after 21 days of exposure to the atmosphere, both Cd^{2+} and Zn^{2+} concentrations in the aqueous solution were 0.2 mg/L or less. DO equilibrium was achieved at 8 mg/L or more after 3 days, and the pH increased to 9 or more from the initial value of 8.5 immediately after CPS injection, and then decreased continuously to equilibrium around 8. These results show a similar trend to chapter 3.4.1.

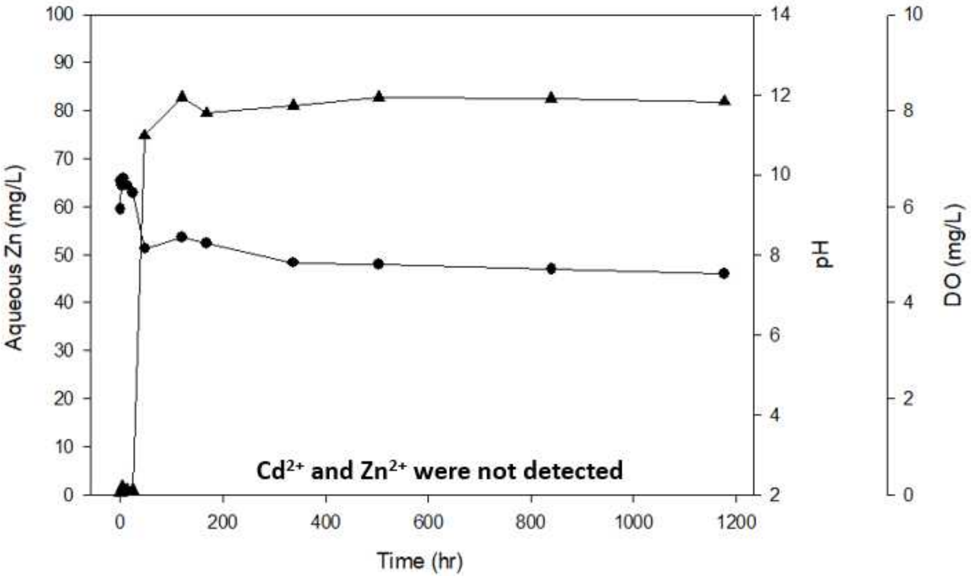


Figure. 3.29. pH, and DO change of contaminated groundwater after CPS injection and exposed to atmosphere (~21 days)

4. Conclusions

4.1 Precipitation mechanism of Cd^{2+} and Zn^{2+} by CPS

Groundwater contaminated with heavy metals are mostly acidic condition, which means pH is lower than 7.0. Therefore, reaction mechanism of heavy metal removal by CPS can be concluded in two stages: heavy metal (Cd^{2+}, Zn^{2+}) precipitation by CPS, and pH increase by residual polysulfide.

(a) Heavy metal (Cd^{2+}, Zn^{2+}) precipitation by CPS

Hydrogen sulfide provided in (a) reacts with heavy metal ions in groundwater to precipitate in sulfide form and release hydrogen ions (Equation 4.1 and Equation 4.2).

$$S_x^{2-} + Cd^{2+} \rightarrow CdS + \frac{1}{8}(x-1)S_8 \qquad \text{(Eq. 4.1)}$$

$$S_x^{2-} + Zn^{2+} \rightarrow ZnS + \frac{1}{8}(x-1)S_8 \qquad \text{(Eq. 4.2)}$$

When Cd^{2+} and Zn^{2+} are present together, precipitation of Cd^{2+} with a small solubility product (K_{sp}) occurs predominantly over Zn^{2+}. There is no change in the concentration of net hydrogen ions, so the pH change is not obvious. In addition, scavenging effect of metal ions such as Fe^{2+} and Mn^{2+} in natural groundwater by combining with polysulfide is thought to be small.

(b) pH increase by residual polysulfide

Since all the heavy metals have been removed, residual polysulfide and hydrogen ions react and increase pH (Equation 4.3 and Equation 2.1). In addition, as the pH of the supernatant is increased over 9, rather than forming bisulfide, polysulfide becomes the dominant species.

$$S_x^{2-} + 2H^+ \rightarrow H_2S + \frac{1}{8}(x-1)S_8 \qquad (\mathrm{pH} < 7.0) \qquad (\mathrm{Eq.\ 4.3})$$

$$S_x^{2-} + H^+ \rightarrow HS^- + \frac{1}{8}(x-1)S_8 \qquad (7.0 < \mathrm{pH} < 9.0) \quad (\mathrm{Eq.\ 2.1})$$

4.2 Oxidation resistance of heavy metal precipitate from CPS

Polysulfide and bisulfide react with DO suppressing the oxidation of heavy metals. For example, thiosulfate is produced by the reaction between polysulfide and dissolved oxygen, and bisulfide produces various oxidation reaction products according to the ratio of dissolved oxygen. After polysulfide and bisulfide are depleted, substances that can actively scavenge DO and be oxidized are unlikely to exist. In addition, from the oxidation experiment of CdS with elemental sulfur, the concentration of Cd^{2+} was also very low and stable for 20 days expecting that interaction between CdS and elemental sulfur inhibits dissolution of Cd.

4.3 Field applicability test for CPS

Heavy metals in the contaminated groundwater were well removed by CPS, and the lower the K_{sp} value, the earlier the removal. The tendency of DO and pH change and the concentration of heavy metals are thought to be due to oxidation of polysulfide and bisulfide and adsorption on sulfur, as shown in chapter 3.4.1. After oxidation of polysulfide and bisulfide, it is thought that heavy metals were not dissolved during stirring in the aerobic condition because heavy metal sulfides were adsorbed on the sulfur surface since pH and DO reached equilibrium.

5. Discussions

According to the XRD data for precipitate of C2, Z2, and CZ2, in which CPS was injected, the peak of S_8 was clearly well observed. In contrast, as a result of the SEM image for the same precipitate, it was difficult to find particles that existed alone in S8. It is thought that S_8 was not visible due to the SEM characteristics of observing the particle surface by providing a site where other particles can adsorb together. In addition, in terms of SEM image of CZ2 with CPS injection, Cd and Zn position were overlapped. Several research suggests that Cd can replace Zn through substitution, consequently, $Cd_xZn_{(1-x)}$ can be formed. Therefore, It is necessary to determine what form Cd and Zn exist on the surface by XPS analysis for precipitates injected with CPS in artificially contaminated solution of Cd and Zn.

The possibility that heavy metal was not dissolved even though materials that can react with oxygen to prevent oxidation of heavy metals are depleted was suggested by inferring adsorption of heavy metal sulfide on the surface of sulfur. Related to this, measuring the point zero charge of heavy metal sulfide and S_8 seems to be important.

CPS amount for heavy metal removal in the field was less than the value using the maximum efficiency injection ratio determined. Further research is needed related to dissolved organic materials.

Reference

Coynel, Alexandra, et al. "Groundwater contributions to metal transport in a small river affected by mining and smelting waste." Water research 41.15 (2007): 3420-3428.

Li, Meng, et al. "The leaching kinetics of cadmium from hazardous Cu-Cd zinc plant residues." Waste Management 65 (2017): 128-138.

Mackay, Douglas M., and John A. Cherry. "Groundwater contamination: Pump-and-treat remediation." Environmental Science & Technology 23.6 (1989): 630-636.

Liu, Yuanyuan, et al. "Cr (VI)-contaminated groundwater remediation with simulated permeable reactive barrier (PRB) filled with natural pyrite as reactive material: environmental factors and effectiveness." Journal of hazardous materials 298 (2015): 83-90.

Azubuike, Christopher Chibueze, Chioma Blaise Chikere, and Gideon Chijioke Okpokwasili. "Bioremediation techniques–classification based on site of application: principles, advantages, limitations and prospects." World Journal of Microbiology and Biotechnology 32.11 (2016): 1-18.

Hashim, M. A, et al. "Remediation technologies for heavy metal contaminated groundwater." Journal of environmental management 92.10 (2011): 2355-2388.

Khalid, Rashid A., Robert P. Gambrell, and William H. Patrick Jr. Chemical availability of cadmium in Mississippi River sediment. Vol. 10. No. 4. American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America, 1981.

Chen, Quanyuan, et al. "Comparison of heavy metal removals from aqueous solutions by chemical precipitation and characteristics of precipitates." Journal of water process engineering 26 (2018): 289-300.

Wazne, Mahmoud, et al. "Assessment of calcium polysulfide for the remediation of hexavalent chromium in chromite ore processing residue (COPR)." Journal of hazardous materials 143.3 (2007): 620-628.

Chrysochoou, M., and A. Ting. "A kinetic study of Cr (VI) reduction by calcium polysulfide." Science of the Total Environment 409.19 (2011): 4072-4077.

Graham, Margaret C., et al. "Calcium polysulfide remediation of hexavalent chromium contamination from chromite ore processing residue." Science of the Total Environment 364.1-3 (2006): 32-44.

Tu, Chen, et al. "Stabilizing effects on a Cd polluted coastal wetland soil using calcium polysulphide." Geoderma 332 (2018): 190-197.

Li, Haiyan, et al. "Effect of pH, temperature, dissolved oxygen, and flow rate of overlying water on heavy metals release from storm sewer sediments." Journal of Chemistry 2013 (2013).

Kamyshny, Alexey, et al. "Equilibrium distribution of polysulfide ions in aqueous solutions at 25 C: a new approach for the study of polysulfides' equilibria." Environmental science & technology 38.24 (2004): 6633-6644.

Yongsiri, Chaturong, Jes Vollertsen, and Thorkild Hvitved-Jacobsen. "Influence of wastewater constituents on hydrogen sulfide emission in sewer networks." Journal of environmental engineering 131.12 (2005): 1676-1683.

Guenther, Elizabeth A., Kenneth S. Johnson, and Kenneth H. Coale. "Direct ultraviolet spectrophotometric determination of total sulfide and iodide in natural waters." Analytical Chemistry 73.14 (2001): 3481-3487.

Waggoner, William H. "Textbook errors: Guest column. The solubility product constants of the metallic sulfides." Journal of Chemical Education 35.7 (1958): 339.

Kleinjan, Wilfred E., Arie de Keizer, and Albert JH Janssen. "Kinetics of the chemical oxidation of polysulfide anions in aqueous solution." Water Research 39.17 (2005): 4093-4100.

Ford, Robert G., Richard T. Wilkin, and Robert William Puls. Monitored natural attenuation of inorganic contaminants in ground water. Vol. 2. Naiontal Risk Management Research Laboratory, US

Environmental Protection Agency, 2007.

Moslemi, Hossein, and Mahdi Gharabaghi. "A review on electrochemical behavior of pyrite in the froth flotation process." Journal of Industrial and Engineering Chemistry 47 (2017): 1-18.

Langmuir, Donald. Issue paper on the environmental chemistry of metals. US Environmental Protection Agency, 2004.

초록

다황화칼슘을 이용한 지하수 내 카드뮴과 아연 저감 : 침전 기작, 산화 저항성에 관한 연구

서울대학교 대학원
건설환경공학부
윤성희

폐광산이나 폐제련소에서 유출된 유출수나 슬러지 내부에 존재하는 중금속들은 주변 수계로 유입되어 심각한 수질 오염을 야기할 수 있다. 특히, 중금속으로 인해 지하수가 오염되거나 산성화되는 문제가 심각한데 이는 제련 과정에서 발생하는 카드뮴 (Cd^{2+}), 아연 (Zn^{2+}), 황산염 (SO_4^{2-})으로 인해 야기된다. 이러한 문제를 해결하기 위해, 지하수를 정화하기 위한 환원제 중 하나로 쓰이는 다황화칼슘 (Calcium polysulfide; CPS)를 이용하여 지하수 내 Cd^{2+}와 Zn^{2+}를 제거한 몇몇 사례가 있지만 CPS에 의해 중금속이 제거되는 구체적인 기작에 대해선 명확하게 밝혀진 바가 없다. 또한 중금속이 황화물 형태로 침전할 경우, 용존 산소 (Dissolved oxygen; DO)에 의해 산화되어 수용액 상태로 용출될 수 있는 가능성이 있다. 따라서, 본 연구에서는 다황화물 (polysulfide; S_x^{2-})의 농도를 정량하고 CPS에 의한 Cd^{2+}와 Zn^{2+}의 침전 기작을 도출한 다음 CPS 주입으로 생성된 침전물의 산화와 관련된 DO의 영향에 관해서 평가하여, 실제 중금속으로 오염된 지하수에 회분식 실험 결과들을 적용해 보고자 한다.

본 연구 결과, CPS 1%에는 82.2 mM의 S_x^{2-}가 존재하고 이를

중금속 오염수에 주입할 경우 76.8 mM의 Cd^{2+}, 77.6 mM의 Zn^{2+}가 제거됨을 확인하였다. 또한 X선 회절 분석법 (X-ray diffraction; XRD)과 주사전자현미경 (Scanning Electron Microscope; SEM)을 이용하여 CPS에 의해 elemental sulfur (S_8 또는 S^0), gypsum ($CaSO_4 \cdot 2H_2O$), CdS, ZnS가 침전되고 수산화물 형태인 $Cd(OH)_2$나 $Zn(OH)_2$는 발견되지 않음을 밝혔다. 이에 더하여, CPS를 주입하더라도 중금속의 침전이 완료되기 전에는 pH에 큰 변화가 없다가 중금속의 침전이 완료된 후에는 pH가 증가하는 경향성을 보인다는 것을 실험을 통해 알 수 있었다. 이러한 결과들을 종합하면, S_x^{2-}에서 하나의 2가 황 (sulfide)만 방출되어 중금속 침전에 관여하고 나머지는 S_8 또는 S^0로 존재하고 CPS가 중금속으로 오염된 지하수 오염원에 주입될 경우 CPS가 과량 주입되지 않는 이상 지하수 내에는 pH 변화가 크지 않을 것이라고 결론내릴 수 있었다. 또한, 침전물들을 지속적으로 대기중에 노출시켜 산화 환경을 조성한 실험을 통해, S_x^{2-}와 bisulfide (HS^-)가 DO와 반응하여 중금속의 산화를 억제한다고 추론할 수 있었다. 이러한 결과들을 토대로, CPS를 실제 중금속으로 오염된 지하수에 주입해보았고 지하수 내 Cd^{2+}와 Zn^{2+}를 성공적으로 제거할 수 있었다. 또한 이렇게 제거된 침전물들은 산소가 지속적으로 공급되는 상황임에도 3주까지 용출되지 않고 안정적으로 존재하였다.

주요어: 다황화칼슘, Cadmium sulfide, Zinc sulfide, Elemental sulfur, 용존산소, Bisulfide
학번: 2021-27635