

Article

Feasibility of Remediation Lead, Nickel, Zinc, Copper and Cadmium Contaminated Groundwater by Calcium Sulfide

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Abstract: Metals contamination in groundwater often occurs in various industrial processes. Studies have confirmed that polysulfide could reduce hexavalent chromium to trivalent chromium, achieving the effect of in-situ stabilization. For other metals contamination in groundwater, whether polysulfide also had a stabilizing ability to achieve in-situ remediation. This research focused on metals in addition to chromium that often contaminated in groundwater, including lead, nickel, zinc, copper, and cadmium to explore the feasibility of using calcium polysulfide (CaS_x) as an in-situ stabilization technology for these metals contamination groundwater. Results showed that CaS_x had a great removal efficiency for metals lead, nickel, zinc, copper, and cadmium. However, for nickel, zinc, copper and cadmium, when CaS_x was added excessively, complexes would be formed, causing the result of re-dissolve and this would also reduce the removal efficiency. Since it is difficult to accurately control the dosage of agents for in-situ groundwater remediation, the concentration of re-dissolved nickel, zinc, copper, and cadmium may not be able to meet the groundwater control standards. CaS_x had high lead removal efficiency, for a concentration of 100 mg/L, the dose of calcium polysulfide was more than the amount of 1/1,200 (volume ratio of CaS_x to groundwater), the removal rate was almost 100%, and it would not cause re-dissolution due to excessive CaS_x dosing. CaS_x can be used as an in-situ stabilization technique for lead contaminated groundwater.

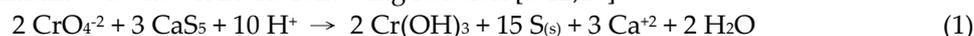
Keywords: metal; polysulfide; groundwater; stabilization; lead

1. Introduction

Due to the operation of high-concentration metal solutions, many industrial processes such as metal surface treatment, battery manufacturing, recycling, dyes manufacturing and so on, when tanks and pipelines were damaged, soil and groundwater contamination caused by metals often happens. Copper, zinc, chromium, and nickel contamination groundwater often occurred in metal electroplating and surface treatment processes; lead contamination occurs in battery manufacturing and recycling processes; chromium and cadmium contamination occurs in dyeing and colorant production processes. Since metals had the characteristic of being undegradable, the technology that could be applied to the remediation of metal contamination sites was quite limited. For sites with clear contamination scope and high contamination concentration, pumping and treating method had the advantages of easy operation and speeding up the efficiency [1]. However, for sites with a wide range of groundwater contamination and low contamination concentration, it was relatively economical and efficient to use in-situ stabilization. Chemical precipitation was the most commonly-applied method for in-situ stabilization [1].

Chemical precipitation methods included hydroxide precipitation and sulfide precipitation method [2]. The hydroxide precipitation method had the advantages of simplicity, low cost and easy pH control [3]. The sulfide precipitation method had the advantages of rapid reaction rate, lower solubility, good sedimentation, and it could operate in a wide pH range [2,4,5,6]. Sulfides included solid FeS and CaS; aqueous solutions of Na₂S, NaHS, (NH₄)₂S, or gaseous hydrogen sulfide (H₂S) were used in industrial wastewater treatment [5]. There was also the possibility of using the degeneration reaction of sodium thiosulphate (Na₂S₂O₃) as a source of sulphide for metal precipitation [5,6].

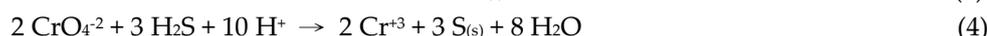
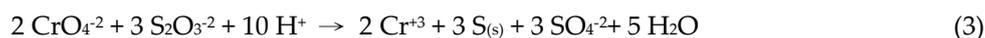
Polysulfide is a compound which contains polysulfide ions, generally expressed as MS_x, and the value of x is between 2-7 [7]. The most commonly-used polysulfide was calcium polysulfide (CaS_x) [8-12]. Sulfides contained in calcium polysulfide include: S₅²⁻, S₄²⁻, hydrosulfide (HS⁻), thiosulfate (S₂O₃²⁻), dithionate (S₂O₆²⁻), and H₂S [7,13,14]. When the pH value was less than 8.0, S₅²⁻, S₄²⁻ and H₂S were the main species [14]. Calcium polysulfide was a strong reducing agent for metals, and an alkali agent. The pH value of its aqueous solution was about 11-12 [7]. The literature confirmed that for soil and groundwater contaminated by hexavalent chromium, calcium polysulfide could reduce hexavalent chromium to trivalent chromium, forming Cr(OH)₃ precipitates, reducing the toxicity and mobility of chromium. Calcium polysulfide had the effect of reducing and stabilizing for hexavalent chromium contamination sites. The reaction of calcium polysulfide to hexavalent chromium was shown in the following reaction [8-12,15]:



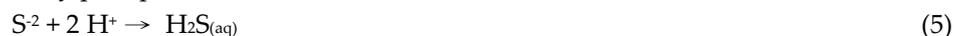
This reaction was reported to be theoretically reversible. However, under natural groundwater conditions the equilibrium condition was dominated by the right side of the reaction [8]. Chrysochoou and Ting (2011) [11] pointed out that the reduction of hexavalent chromium by calcium polysulfide was affected by aqueous pH and dissolved oxygen (DO). In the presence of oxygen, an oxidation reaction of polysulfide would take place and thiosulfate (S₂O₃²⁻) formed, the reaction was shown as follows [16]:



Research indicated that S₂O₃²⁻ and H₂S also had the ability to reduce hexavalent chromium to trivalent chromium [8,11,13,14]. The reaction was shown in the following reactions:



Soya et al. (2010) [4] removed heavy metals such as Cu, Zn and Ni in industrial wastewater with Na₂S, H₂S and CaS. Under acidic conditions, sulfides could react with heavy metal ions such as copper to form metal sulfides, which could achieve heavy metal removal by precipitation and the reaction was as follows:



Maletic et al. (2015) [17] added calcium polysulfide to soil contaminated by copper, lead, and nickel. The results showed that metals can be stabilized by calcium polysulfide. It could also reduce the concentration of metals in the soil solution, and reduce the bioavailable fraction of metals.

CaS_x, which is volatile and is also an unstable nature, especially in aqueous solution or exposing to air [7,11,18]. Long-chained polysulfides were stable in high pH, and tends to breakdown into shorter-chained species when the pH is lower than the pK_a value. At pH values less than 8.0, S₅²⁻, S₄²⁻, and H₂S becomes the dominant species [7,11,19]. The calcium polysulfide solution was only stable in the concentrated form because a precipitate of finely dispersed sulfur was formed in 10 days in a dilution solution (< 2g/L of sulfide ions) [18]. Calcium polysulfide also called lime sulfur, was used in the form of Liquid-Lime Sulfur (LLS), which was commonly used for insecticides in agricultural industries. This was prepared by the combination of CaO, elemental Sulphur with water heating at 100 °C by the reaction [7, 18]:



This study explored the feasibility of using calcium polysulfide to remediate groundwater contaminated by metals such as lead, nickel, zinc, copper and cadmium, while it was compared with hexavalent chromium. In order to maintain the stability and reactivity of calcium polysulfide, this study referred to the above-mentioned agricultural methods to synthesize calcium polysulfide in the laboratory before the test.

2. Experimental Methods

In this research, liquid lime sulfur mixture was synthesized referred to the method of used in agricultural [18], industrial-grade quicklime, sulphur powder and distilled water were mixed in a weight ratio of 1:2:10 and a little surfactant was added and heated up to 100°C for 1 hour to synthesize calcium polysulfide. Chromium, lead, nickel, zinc, copper, and cadmium aqueous samples with concentrations of 5 mg/L and 100 mg/L were prepared by diluting various metal standard solutions (metal in 5% HNO₃ · Merck) with groundwater for test. Groundwater was collected by pump from the campus (Chaoyang University of Technology) groundwater well. 500 mL aqueous samples were taken each time to test. For samples with a concentration of 5 mg/L, the test dosage of calcium polysulfide were at the amount of 20000~1000, in the volume ratio of groundwater sample to calcium polysulfide; for sample concentration of 100 mg/L, the test dosage of calcium polysulfide were about 2000~100 in the volume ratio of groundwater sample to calcium polysulfide. After the dosage of calcium polysulfide in different proportions, stir it evenly, and let it stand for 1 hour to measure its pH (HOTEC, HTC-201U), oxidation-reduction potential (HOTEC, HTC-200), dissolved oxygen (HOTEC, HTC-208U), and conductivity (HOTEC, HTC-202U) by using electrode. The upper solution was taken to analyze the residual metal concentration with an inductively coupled plasma atomic emission spectrometer (Corporation IRIS Intrepid II XSP, Thermo Electron). The average was calculated after three repeated tests were carried out for each concentration and dosage.

3. Results and Discussion

3.1. The effect of calcium polysulfide application on the aqueous properties of various metal aqueous solutions

Figure 1 showed the changes of dissolved oxygen (DO) in solutions of chromium, lead, copper, zinc, nickel, and cadmium aqueous when different dosages of calcium polysulfide were added. Figure 1(a) showed the change of dissolved oxygen in low-concentration (5 mg/L) samples. The dosage of calcium polysulfide was shown as the ratio of groundwater to calcium polysulfide volume (GW/CaS_x). The experiment range was the (GW/CaS_x) ratio of volume from 20000 to 1000. The initial DO of various metal samples were about 6 mg/L. When the volume ratio of (GW/CaS_x) was about 20,000-8,000, the DO of sample decreased slowly. When the ratio of (GW/CaS_x) volume dropped to 8,000-1,000, the dissolved oxygen of the sample decreased rapidly. When the volume of the groundwater sample was 1,000 times more than the calcium polysulfide, the dissolved oxygen of various samples could be reduced to less than 1 mg/L. Figure 1(b) showed the changes of DO in high-concentration, 100 mg/L samples. The adding ratio of calcium polysulfide in high-concentration samples were in the range of 2,000 and 100. In terms of the volume ratio of groundwater sample to calcium polysulfide. When the adding ratio of calcium polysulfide (CaS_x/GW) was higher than 1/600, the DO of various samples could quickly dropped below 1 mg/L. When the adding ratio (CaS_x/GW) reached 1/100, the dissolved oxygen was quite close to 0.

Figure 2 showed the changes in the oxidation-reduction potential of various metal samples when different doses of calcium polysulfide were added. The initial ORP of the sample was approximately 200-400 mV. As the dosage of calcium polysulfide increased, the ORP of various metal samples showed a gradual decline. When the calcium polysulfide dosage (volume ratio of GW to CaS_x) was at the amount of 4,000, the ORP of the metal samples could show negative values except for nickel. When the dosage rate of calcium polysulfide reached 1,000, the ORP could reach below -300 mV. For high concentration of

100 mg/L metal samples, when the calcium polysulfide dosage rate reached 200 (volume ratio of GW/CaS_x), the ORP was almost reduced to below -400 mV. When the adding rate reached 100 (volume ratio of GW/CaS_x), the ORP could drop to nearly -470 mV.

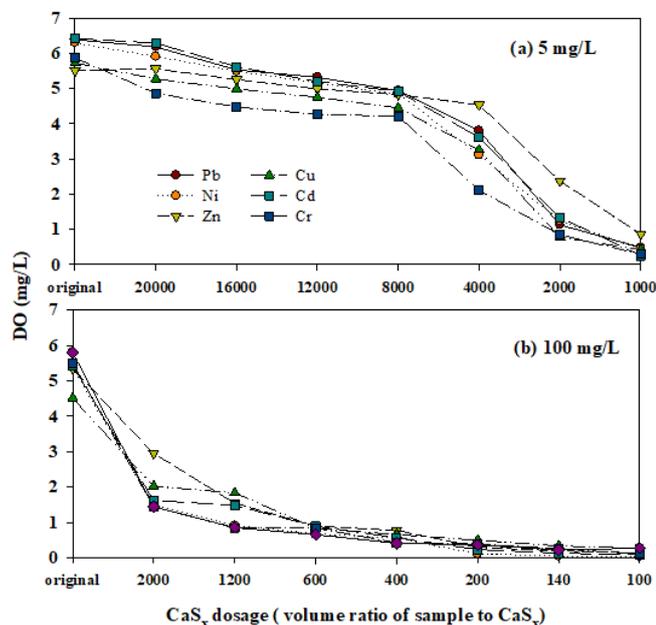


Figure 1. The changes of DO of various metals aqueous when different dosages of calcium polysulfide were added.

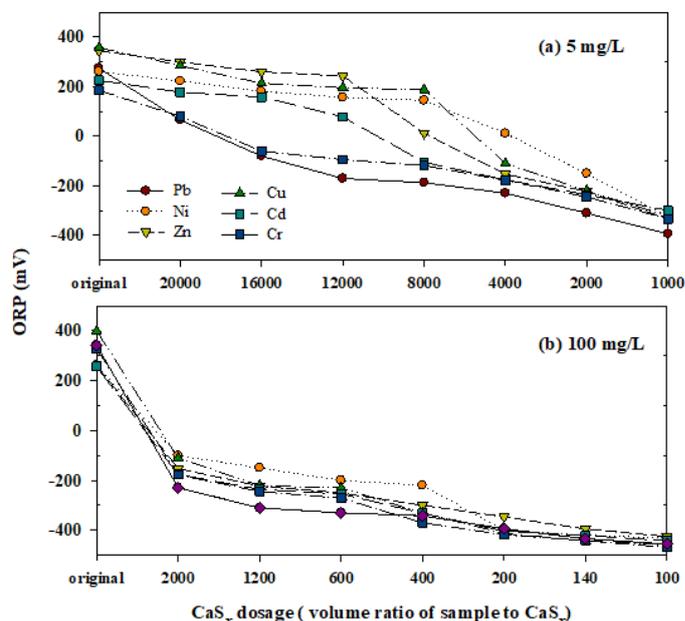


Figure 2. The changes in the ORP of various metal aqueous solutions when different dosages of calcium polysulfide were added.

Figure 3 showed the changes in pH value of various metal aqueous solutions when different dosages of calcium polysulfide were added. Figure 3(a) was the pH value for 5 mg/L. The initial pH of various metal water samples were about 5-6. When the dosage of calcium polysulfide (volume ratio of GW to CaS_x) was around 20,000-8,000, the pH of the chromium sample could gradually rise up to about 8.9; the pH value of the lead, nickel, zinc, and cadmium samples maintained about 6 without a significant increase. However, the pH value of the copper sample initially decreased with the increase of the calcium polysulfide dose. When the dose was at the amount of 1/8000 (volume ratio of CaS_x/GW), the pH value was only 4.99, which was the lowest. Then the pH value rebounded afterwards. When the application rate of calcium polysulfide was greater than 1/4000, the pH of all metal samples gradually increase as the dosage increased. Figure 3(b) showed the change of pH value of various metal aqueous samples with a concentration of 100 mg/L. The pH of the chromium sample gradually rose with the increase of calcium polysulfide addition rate. When the calcium polysulfide dosage ratio (volume ratio of CaS_x/GW) reached 1/600, the pH value could be nearly 11; the dosage ratio was above 1/200, and the pH value was maintained nearly 12. When the dosage ratio of calcium polysulfide was less than 1/600 (volume ratio of CaS_x/GW), the pH of copper, zinc, and cadmium samples all appear to decrease with the increase of calcium polysulfide addition rate. The case of copper sample was the most significant among these metals. When the dosage of calcium polysulfide reached 1/600, the pH value of the copper sample could drop to 3.58. When the dosage of calcium polysulfide reached 1/400 or more, the pH value rebounded and rose. Calcium polysulfide is an alkaline agent. When it was added to copper, cadmium, and zinc aqueous samples, the pH value decreased. This indicated that the reaction mechanism of calcium polysulfide to these metals was different from chromium. Referred to the reaction formula (1) of calcium polysulfide and chromium, the reaction would consume H⁺ and the pH value would increase. The reaction between calcium polysulfide and other metals was inferred as formula (6), forming metal sulfide MS, which released H⁺. Therefore, when the dosage of calcium polysulfide was low, all calcium polysulfide reacted with metal ions and released H⁺, leading to a drop in the pH value. When the dosage

of calcium polysulfide was greater than the dosage required for the reaction with metal ions, the remaining calcium polysulfide showed the characteristics of an alkali agent, causing the pH of the aqueous sample to rebound and rise.

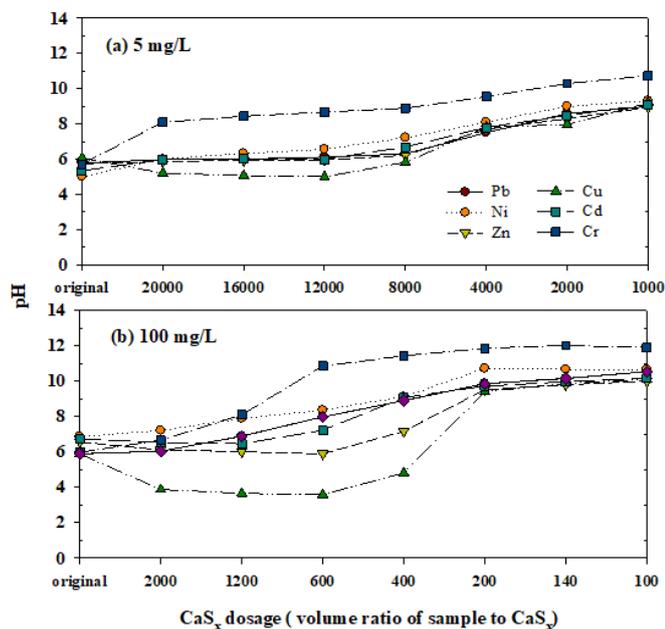


Figure 3. The changes in pH value of various metal aqueous solutions when different dosages of calcium polysulfide were added.

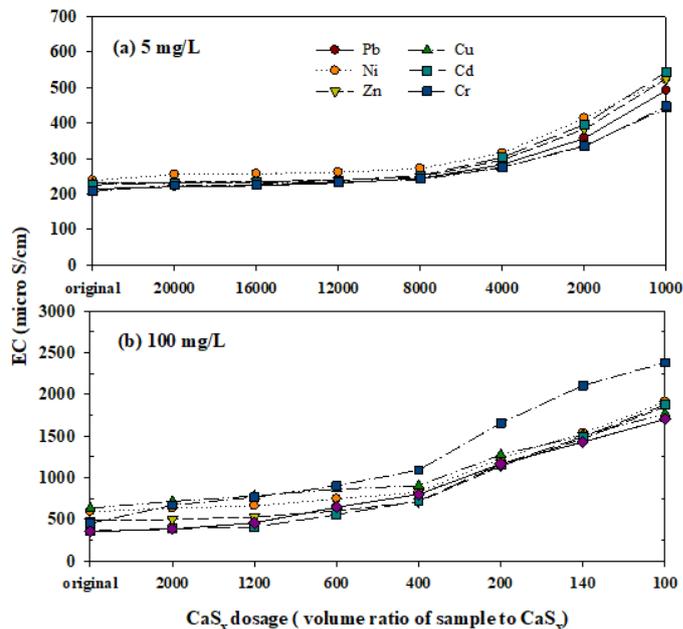


Figure 4. The variation in EC of various metal aqueous solutions when different dosages of calcium polysulfide were added.

The most frequently concerned issue of groundwater remediation with in-situ chemical technology was whether the application of chemical agents will cause an unrecoverable impact on groundwater properties or not. Conductivity was one of the indicators that was often paid attention to among them. Figure 4 was the variation in conductivity of various metal aqueous samples with concentrations of 5 mg/L and 100 mg/L when different doses of calcium polysulfide were added. Results showed that there were little differences in conductivity no matter what metals they were. Only the chromium sample of high concentration had a slightly higher conductivity increase than the other metals. The conductivity of various metal samples with a concentration of 5 mg/L was about 200-250 $\mu\text{S}/\text{cm}$. When the calcium polysulfide dosage was at the amount of 1/8,000 (volume ratio of CaS_x/GW), the conductivity of various metal samples were 240-270 $\mu\text{S}/\text{cm}$; When the dose was at the amount of 1/2,000, the conductivity was 335-415 $\mu\text{S}/\text{cm}$. When the dose reached 1/1,000, the conductivity was 440-545 $\mu\text{S}/\text{cm}$. That is, this still met the irrigation water conductivity standard, which was 750 $\mu\text{S}/\text{cm}$. It was an acceptable range. For various metal samples with a concentration of 100 mg/L, the initial conductivity was about 350-630 $\mu\text{S}/\text{cm}$. When the calcium polysulfide dose was at the amount of 1/600 (volume ratio of CaS_x/GW), the conductivity rose to about 550-900 $\mu\text{S}/\text{cm}$; when the dose was at the amount of 1/200, the conductivity of chromium samples were about 1,650 $\mu\text{S}/\text{cm}$, and the other metal samples were about 1,150-1,250 $\mu\text{S}/\text{cm}$; when the dose reached 1/100, the conductivity of chromium samples were at the amount of 2,380 $\mu\text{S}/\text{cm}$, and the other metal samples were about 1,700-1,900 $\mu\text{S}/\text{cm}$. Calcium polysulfide has a characteristic which is high water solubility. The conductivity of groundwater rose up to about 2,000 $\mu\text{S}/\text{cm}$, and it was expected that the groundwater could return to the background groundwater quality within a few months.

3.2. The removal efficiency of metals lead, nickel, zinc, copper, cadmium and chromium in groundwater by calcium polysulfide

Figure 5 showed the removal efficiency of various metal solutions with a concentration of 5 mg/L under different dosages of calcium polysulfide. The initial concentration of lead in the aqueous sample was about 5.0 mg/L. The calcium polysulfide dosage was at the range of 1/20,000 -1/8,000 (volume ratio of CaS_x to GW), the removal efficiency of lead was not significant. When the calcium polysulfide dosage was about 1/4,000, the lead concentration was 3.68 mg/L, and the removal rate was about 26.5%. When the dosage of calcium polysulfide increased to 1/2,000, the concentration of lead was below the detection limit (0.0005 mg/L), and it was almost completely removed. The initial concentration of nickel in the groundwater sample was about 4.8 mg/L, and when the volume ratio of the groundwater sample to calcium polysulfide was at the range of 20,000-8,000, the residual nickel concentration decreased significantly with the increase of calcium polysulfide addition rate. When the CaS_x dosage was at the amount of 1/8,000 (volume ratio of CaS_x to GW), the residual concentration of nickel was 1.38 mg/L, and the removal rate was about 71.4%. Besides, when the CaS_x dosage was at the amount of 1/4,000 (volume ratio of CaS_x/GW), the residual concentration of nickel was lower than the detection limit (0.0009). The removal rate reached 100%, indicating that calcium polysulfide has good removal efficiency for nickel. However, when the dose of calcium polysulfide increased again, causing the volume ratio of calcium polysulfide to groundwater reach 1/1,000. This made the concentration of nickel rose again, reaching a concentration of 3.7 mg/L. The removal efficiency of calcium polysulfide on zinc, copper and cadmium was similar to that of nickel. As for zinc, when the dosage of calcium polysulfide was around 1/20,000 and 1/8,000 (volume ratio of CaS_x/GW), the removal efficiency of zinc increased rapidly with the increase of calcium polysulfide adding rate. When the dosage of calcium polysulfide was 1/8,000, the residual zinc concentration was 0.057 mg/L, and the removal rate was about 98.8%. However, when the dose of calcium polysulfide continuously increased, more than 90% of the zinc concentration returned to the aqueous solution. The removal efficiency of copper with a concentration of 5 mg/L by calcium polysulfide was generally not good. The highest removal efficiency occurs when the dosage was at the amount of 1/8,000 (volume ratio of CaS_x/GW). The residual concentration of copper was about 2.8 mg/L. We could find that the removal efficiency was only about 45.3%. For cadmium, when the dosage of calcium polysulfide was relatively low, the removal efficiency of cadmium was great. When the dosage of calcium polysulfide was at the amount of 1/20,000 (volume ratio of CaS_x/GW), the removal rate of cadmium was 66.7%. Meanwhile, when the dosages was at the amount of 1/12,000, the removal rate could rise up to 91.1%. However, when the dosage of calcium polysulfide reached 1/8,000, the concentration of cadmium was almost completely dissolved out again. The removal efficiency of chromium increased regularly with the increase of the calcium polysulfide dosage. When the calcium polysulfide dosage reached the amount of 1/12,000 (volume ratio of CaS_x/GW), the chromium removal rate could reach more than 50%. When the dosage reached the amount of 1/4,000, the chromium removal rate was nearly 100%. The removal of chromium was different from nickel, zinc, copper, and cadmium. The adding of excessive calcium polysulfide did not cause the chromium concentration in aqueous to rebound.

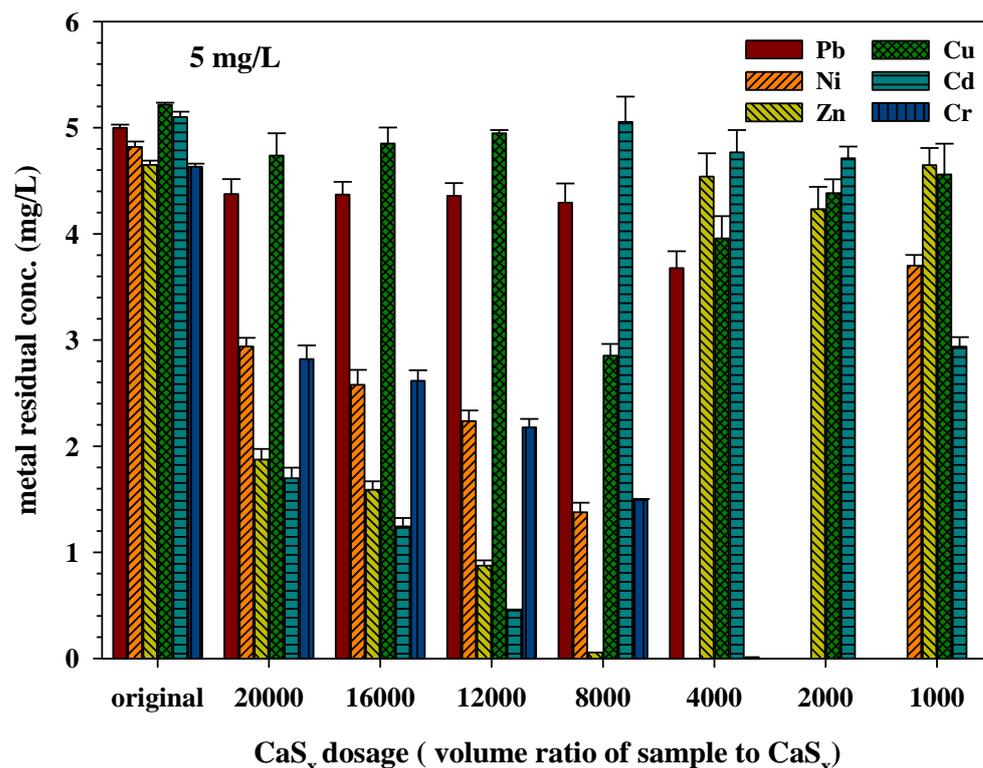


Figure 5. The removal efficiency of calcium polysulfide on various metals at low concentrations (5 mg/L).

Figure 6 showed the removal efficiency of calcium polysulfide on various metals at high concentrations (100 mg/L). As for lead, when the dose of calcium polysulfide was at the amount of 1/2,000 (volume ratio of CaS_x to GW), the removal rate could reach 87.5%. When the dose was more than the amount of 1/1,200, the residual concentration of lead was less than 0.01 mg/L, which meant the removal rate was almost 100%. As the dose of calcium polysulfide continuously increased, the lead concentration in the aqueous did not rebound. The removal efficiency of chromium increased steadily with the increase of calcium polysulfide dosage. When the dose of calcium polysulfide was at the amount of 1/400 (volume ratio of CaS_x to GW), the chromium removal rate was about 60%; When the dose was 1/200, the chromium removal rate was about 87%; When the dose was at the amount of 1/140, the chromium removal rate was nearly 98%, and when the dose reached 1/100, the chromium removal rate could reach 100%.

When the dosage of calcium polysulfide was less than 1/400 (volume ratio of CaS_x to GW), the removal efficiency of nickel, zinc, copper, and cadmium was higher than that of chromium. When the dose of calcium polysulfide was at the amount of 1/400 (volume ratio of CaS_x/GW), the residual concentration of nickel in the aqueous was about 6.5 mg/L, and the removal rate was about 93.3%. However, as the dose of calcium polysulfide increased continuously, the residual concentration of nickel rose slightly, reaching a maximum concentration of 9.1 mg/L. Although the nickel concentration had rebounded, the removal rate could still reach more than 90%. Zinc also had a minimum residual concentration of 0.03 mg/L when the dosage of calcium polysulfide was at the amount of 1/400 (volume ratio of CaS_x/GW), and the removal rate was almost 100%. However, the zinc concentration continued to increase with the increase of the calcium polysulfide dose. When the calcium polysulfide dose was at the amount of 1/200, the zinc concentration was 4.35 mg/L; when the dose was at the amount of 1/100, the zinc concentration was 21.87 mg/L, and the re-dissolution rate reached 21.9%. The situation of copper and zinc were similar. When calcium polysulfide was applied at a dosage of 1/400 (volume ratio of CaS_x/GW), the residual copper concentration in the solution was 0.223 mg/L, which was the lowest. That is, the removal rate was nearly 100%. However, the copper concentration

rebounded quickly. When the calcium polysulfide dosage was increased to 1/200, about 95% of the copper was re-dissolved into the aqueous. The removal efficiency of calcium polysulfide to cadmium was higher than that of nickel, zinc and copper. When the dosage of calcium polysulfide was at the amount of 1/600 (volume ratio of CaS_x/GW), the removal rate of cadmium was nearly 100%. Similarly, with the increase of the calcium polysulfide dosage, the concentration of cadmium in the aqueous also appeared to be re-dissolved, and the rebounded concentration was about 1.65 -5.025 mg/L.

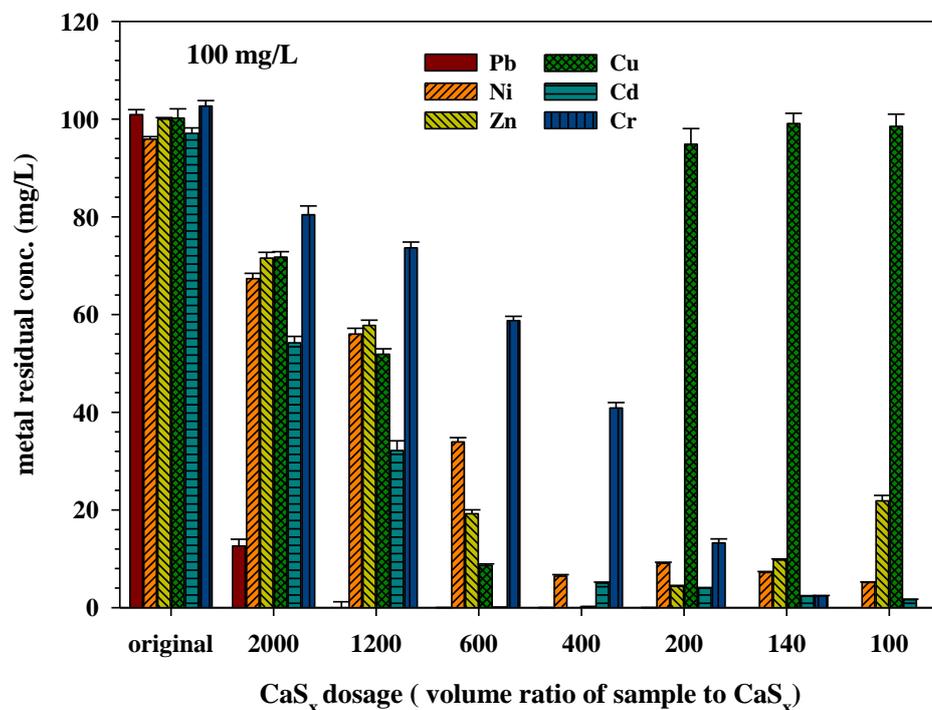


Figure 6. The removal efficiency of calcium polysulfide on various metals at high concentrations (100 mg/L).

Calcium polysulfide had a high removal efficiency for nickel, zinc, copper, and cadmium within an appropriate dosage range, and its removal rate was higher than that of chromium. However, when the dosage exceeded the appropriate range, the four metals, which were nickel, zinc, copper, and cadmium would be re-dissolved in aqueous. Lewis et al. [5, 20] pointed out that the metal sulfide (MS) formed by the reaction of calcium polysulfide and metal may complex with HS^- derived from calcium polysulfide in solution, which formed complexes like $\text{MS}(\text{HS})_n$. Copper was taken as an example, the complexes that could be formed include $\text{CuS}(\text{HS})_2$, $\text{CuS}(\text{HS})_3$, $\text{CuS}(\text{S}_5)_2$, $\text{Cu}(\text{S}_4)(\text{S}_5)_3$ and $\text{CuS}(\text{S}_5)_2$, etc.

Here are the control standard for the four metals in groundwater in Taiwan. It is 1.0 mg/L for nickel; 0.05 mg/L for cadmium; 10 mg/L for copper, 50 mg/L for zinc; 0.5 mg/L for chromium and 0.1 mg/L for lead. Although calcium polysulfide had a great removal efficiency for nickel, zinc, copper, and cadmium when an appropriate dosage range was applied, for soil and groundwater remediation, due to the heterogeneous characteristics of geological, it was very difficult to accurately deliver the appropriate dosage to the remediation location. It was usually necessary to add excessive amounts of chemicals to ensure that the required dosage was evenly reached. Therefore, in the application of calcium polysulfide in the in-situ remediation of groundwater contaminated by nickel, zinc, copper, and cadmium, the re-dissolution concentration may exceed the groundwater control standards and fail to meet the groundwater remediation goals. After long-term monitoring of the precipitate formed by the reaction of calcium polysulfide with chromium and lead, the re-dissolution concentration was very low, much lower than the allowable

concentration of groundwater. In this study, the precipitates were collected and analyzed by XRD. The chromium precipitate was mainly composed of chromium hydroxide and the lead precipitate was mainly lead sulfide. It was inferred that the chemical reaction formulas of the two metals were reaction formula (1) and reaction formula (6) respectively.

4. Conclusions

Calcium polysulfide had a good stability and removal efficiency for lead-contaminated groundwater. For a concentration of 100 mg/L, the dose of calcium polysulfide was at the amount of 1/1,200 (volume ratio of CaS_x to groundwater), the removal rate of lead was almost 100%. The results showed that the stability of lead deposits was high, and the potential for re-dissolution was low. It could be used as an in-situ stabilization technology for lead-contaminated groundwater. Calcium polysulfide had a very good removal efficiency for nickel, zinc, copper, and cadmium in an appropriate dosage range. However, the range of appropriate doses was not wide. As for the in-situ remediation of groundwater, it was quite difficult to accurately control the dosage of calcium polysulfide within this appropriate range. When the dosage of calcium polysulfide was insufficient or excessive, the residual concentration of heavy metals may not meet the groundwater control standards. Since calcium polysulfide had a good removal efficiency for nickel, zinc, copper, and cadmium at an appropriate dose. This study recommended that calcium polysulfide could be combined with pump and treat method applied on groundwater remediation.

6. Acknowledgements

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