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Effect of Physical Sequestration on Long-term Stability of Heavy Metal Sulfides Formed by Calcium Polysulfide: Based on Dissolved Oxygen and pH

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Calcium polysulfide (CPS) is utilized as a precipitant for the remediation of heavy metal contamination in groundwater; however, its long-term stability under varying subsurface environments, such as inconsistent dissolved oxygen and pH, requires thorough evaluation. Previous studies on cadmium (Cd) contaminated solution confirmed that cadmium sulfide (CdS) exhibits high stability under acidic and oxic conditions through aggregation with the complex of sulfur species, the precipitant formed by CPS injection. This study aims to monitor the re-dissolution and the stability of heavy metal sulfides in on-site contaminated solutions containing both cadmium and zinc (Zn) under varying pH and redox conditions.

In the contaminated solution, the concentrations of Cd^{2+} and Zn^{2+} were 216.9 mg/L and 5833.2 mg/L, respectively, with the initial pH of 3.47. CPS was injected according to the concentrations of each heavy metal, and oxic and anoxic experiments were conducted in ambient air and an anaerobic chamber, respectively. In Phase 1 (70 days), re-dissolution did not occur under both oxic and anoxic conditions. To evaluate the stability under acidic conditions, in Phase 2 (52 days), the pH was decreased to 3.0 using nitric acid (HNO_3). Despite acidic conditions, Cd was not re-dissolved in both oxic and anoxic environments. Moreover, in the case of oxic conditions, nearly all Cd (> 99.7%) was extracted in the fourth step of the Tessier sequential extraction (using 0.02 M HNO_3 and 30% hydrogen peroxide at pH 2). This indicates that Cd can stably exist in sulfide form even under oxidizing conditions. In contrast, 3% and 5% of Zn were re-dissolved in anoxic and oxic conditions, respectively. Besides, 95.9% of Zn was extracted in the fourth fraction. This is attributed to the initial heavy metal concentrations; while the relatively small amount of CdS was effectively sequestered by sulfur species complexes, zinc sulfide (ZnS) was not as thoroughly encapsulated, leading to the oxidation of partially exposed ZnS. These results demonstrate that CPS injection alone can remediate heavy metals and ensure the long-term stability of the metal sulfide precipitates.