Feasibility of in-situ immobilization of heavy metals in groundwater using calcium polysulfide

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Flow-through field soil column experiment examined the insitu immobilization of high-concentration heavy metals (Cd2+, Zn²⁺) in groundwater using calcium polysulfide (CaS_x, CPS) for field application. When CPS introduced into the column, CPS solution descended rapidly, formed a stable CPS layer similar to dense nonaqueous phase liquid, and reacted with heavy metals in groundwater since the density ($d = 1.27 \text{ g/cm}^3$) of CPS solution was greater than that of water. Both Cd^{2+} and Zn^{2+} in filed groundwater were rapidly reacted with injected CPS solution and effectively immobilized by more than 99%. In addition, comparison of the reduced amounts of heavy metals (Cd²⁺, Zn²⁺, etc.) by the CPS solution using both cumulative mass approach and mass balance method suggested that majority of heavy metals in complexly-contaminated field groundwater generated insoluble metal sulfide precipitations inside the column. Injected CPS was partially dissolved at the CPS-water interface and a partially-miscible CPS layer continuously moved and reacted with heavy metals in the direction of groundwater flow and gravity. As is also evident by both XRF and SEM/EDS results, metal sulfide precipitates were clearly observed through the reaction between the CPS solution and heavy metals. In addition, microbial communities in the soil of column were analyzed using next-generation sequencing after column experiment. After CPS injection, the microbial diversity of soil was reduced, and sulfurrelated bacteria were dominant in the column-depth where most of heavy metal were immobilized, indicating that microbial communities in soil also play important roles in of heavy-metal immobilization by CPS usage. Finally, an injection protocol optimized for various factors such as injection concentration, injection amount, and injection method of CPS solution for sitespecific subsurface systems should be established to prevent clogging, re-mobilization and relocation of heavy metals.

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