

ASSESSMENT OF REMEDIATION OF Pb^{2+} , Cd^{2+} , Cu^{2+} , AND Zn^{2++} IN GROUNDWATER THROUGH SOLID SOLUTION FORMATION BY CARBONATE PRECIPITATION

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ABSTRACT

This study was conducted to assess the effectiveness of solid solution formation, experimentally, through carbonate precipitation for the *in situ* remediation of ground water contaminated with heavy metals. The study investigated the flow of ground water through an isotropic porous media. Remediation zones of different treatment solutions intercepted plumes of contamination containing Pb^{2+} , Cd^{2+} , Cu^{2+} , and Zn^{2++} produced by feeding of different treatment solutions. Among the precipitation zones, metal carbonate precipitation was the most effective treatment in terms of aqueous metal removal, whereas calcium carbonate (calcite) treatment was the most effective in terms of pH stability.

Keywords: Remediation, heavy metals, solid solution, and co-precipitation.

INTRODUCTION

Since the Industrial Revolution, the production of heavy metals such as lead, copper, zinc and others have increased exponentially. Between 1850 and 1990, production of these metals increased nearly 10-fold, with emissions rising in tandem (Jerome and Nriagu [17], Glover-Kerkvliet [18], Howari and Banat [19]). Heavy metals have been used in a variety of ways for at least 2 millennia. For example, lead has been used in plumbing, and lead arsenate has been used to control insects in apple orchards. The Romans added lead to wine to improve its taste, and mercury was used as a salve to alleviate teething pain in infants (Jerome and Nriagu [17]; and Glover-Kerkvliet [19]). Exposure to heavy metals has been linked with developmental retardation, various cancers, kidney damage, and even death in some instances of exposure to very high concentrations. Exposure to high levels of mercury, gold, and lead has also been associated with the development of autoimmunity, in which the immune system starts to attack its own cells, mistaking them for foreign invaders. Autoimmunity can lead to the development of diseases of the joints and kidneys, such as rheumatoid arthritis, or diseases of the circulatory or central nervous systems (e.g. Glover-Kerkvliet [18]).

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Despite abundant evidence of these deleterious health effects, exposure to heavy metals continues and may increase in the absence of concerted policy actions. Mercury is still extensively used in gold mining in many parts of Latin America. Arsenic, along with copper and chromium compounds, is a common ingredient in wood preservatives. Lead is still widely used as an additive in gasoline. Increased use of coal in the future will increase metal exposures because coal ash contains many toxic metals and can be breathed deeply into the lungs.

The existence and fate of heavy metals in soil is of concern not only because of their potential impact on microbial communities which comprise a "healthy soil", but also because of the potential for groundwater and surface water contamination and hence, toxicological impact on human health. A major problem associated with remediation of subsurface systems contaminated by heavy metals is the difficulty in delivering the metals to the surface for subsequent treatment. Typically, "pump and treat" remediation does not attain cleanup within predicted timetables due to a "tailing" effect once initial high heavy metal concentrations have been flushed out.

Often the fate of heavy metals is controlled by the physico-chemical processes which control the mobility of the metal. Immobilization is usually achieved by chemically altering the contaminants, making them stable with respect to dissolution in ground water (Nayer and Suthersan [10]; Kitano et al. [4], and Lorens [6]). This immobilization can be accomplished by the injection of different treatment solutions through wells into subsurface plumes of contamination to induce the precipitation and sequestration of metals during solid solution formation. If the precipitated phase is relatively stable in the subsurface environment, the contaminants can permanently stay immobilized and trapped (e.g. McIntire [8]; Davis, et al. 1987; Rimstidit [12]).

Also, the source and mobility of heavy metal in the subsurface environment is affected by an ion activity products which is calculated from measured total concentrations of dissolved trace metals in sediment-water systems often deviate from the solubility products (K_{SP}) of the respective pure solid phases. Trace metals, however, usually do not form pure minerals in nature, but rather are sorbed to other host minerals by substitution, forming solid solution — aqueous solution (SSAS) equilibria (Böttcher, [1]). Such solid solution systems often display non-ideal mixing behavior of the end-members, which, together with differences in aqueous speciation and activity coefficients of the participating trace metals, produces complex non-linear relationships between measurable bulk compositions of the co-existing aqueous solution and solid phases, usually expressed in terms of "distribution coefficients", K_d . Further complications result from the influence of precipitation kinetics on trace metal incorporation into natural mineral phases, which is especially pronounced for carbonates (e.g., Morse and Bender [9]; Rimstidit et al. [11]; Kolthoff [5]). Partitioning of a trace element (Tr) between a mineral of a major element (M) and aqueous solution is usually described by the distribution coefficient, D ; which relates the mole fraction in solid phase and molality in aqueous phase in a logarithmic form (McIntire [8]). Kolthoff [5] defined coprecipitation as the contamination of a precipitate by

substances that are normally soluble under the conditions of the precipitation. As a mineral grows from an aqueous solution, if equilibrium is maintained, trace components, if present in sufficiently small quantities, will partition between the two phases in a characteristic manner.

McIntire [8] has also shown that a homogeneous distribution is obtained from aqueous solutions either by continued recrystallization of the earlier formed crystals or by slow growth of the crystals from a non-agitated solution in which supersaturation is gradually relieved, whereas the logarithmic law is followed when there is a slow growth of crystals from a supersaturated solution in which the degree of supersaturation remains essentially constant. The homogeneous and logarithmic distributions may be considered limiting cases in a natural system. There will be some tendency to establish equilibrium between the interior of a crystal and the liquid so that the logarithmic distribution is not strictly adhered to, and at the same time true equilibrium will not be reached so that the homogeneous distribution is not completely followed either.

For systems in which K_d (or λ) is smaller than 1, a large amount of calcite must precipitate before there is a significant reduction in the trace element content of the solution. When K_d (or λ) is equal to 1, the trace element and major element are removed from solution at the same rate. Finally, when K_d (or λ) is larger than 1, precipitation of a small amount of calcite removes a large fraction of the trace element. All K_d values approach one as precipitation rate is increased, so under these conditions elements with $K_d < 1$ will be incorporated at high levels but they will be more easily released back into solution if later on recrystallization occurs at a slower rate. On the other hand, those elements with $K_d > 1$ will be more strongly sequestered if calcite recrystallizes after having been precipitated at a faster rate. The principle aims of is to show the effectiveness of solid solution formation through carbonate precipitation to clean plumes of metal contamination in calcite poor formations (McInter [8]; Davis et al. [2]; Rimsdit et al. [11], and others)

MATERIALS AND METHODS

A small aquarium filled with sand was used to model the two-dimensional groundwater flow in an unconfined aquifer. The aquarium was equipped with injection and sampling systems consist of polyethylene tubes. Four tubes were set in the sand to inject distilled water, pH-controlled solutions, Ca^{+2} solutions, and CO_3^{-2} solutions. Sampling point was placed down gradient from the injection points. New silica sand was used after each run. Table 1, gives the concentrations of the injected solutions, the operational flow, and the pH values during the experimental runs. The sand was leached before the experimental run with Nitric acid to leach any possible heavy metals and/ or standardize its content in each experimental run. The concentration of heavy metal before and after the interception by the remediation zones was determined according to EPA method 200.8, and the pH value using pH-meter (US EPA [18]). Prior to every run, the tank was flooded and flushed with distilled water. The

effectiveness of each remediation zone was determined by the comparing the differences of introduced pollutants over time after passing that zone. The mass of heavy metal after each run was estimated by multiplying the contraction of the metal (mg/cm^3) by the volume of the sampled water, then the mass per unit time of the several runs were compared for all the runs and the results were expressed in graphical format. Details on the formation of carbonate solid solution and for further explanation of experimental set up can be found in US EPA [18]; Davis et al. [2]; Rimsdit et al. [12]; Bottcher [1]; McBeath et al. [7]; Starbeck [13].

Table 1. Injections used

| Solution | Flow [mL/min] | pH | Concentrations [ppb] | | | | | | |
|-------------------------------|------------------|------|----------------------|------------------|------------------|------------------|------------------|------------------|-------------------------------|
| | | | Ca ²⁺ | Cu ²⁺ | Zn ²⁺ | Sr ²⁺ | Cd ²⁺ | Pb ²⁺ | CO ₃ ²⁻ |
| DI water | 89.6 | 6.3 | --- | --- | --- | --- | --- | --- | --- |
| Ca ²⁺ | 1.6 | 6.4 | 270,000 | --- | --- | --- | --- | --- | --- |
| CO ₃ ²⁻ | 1.7 | 10.6 | --- | --- | --- | --- | --- | --- | 850,000 |
| Me ²⁺ | 1.7 | 5 | --- | 156,000 | 300,000 | 36,000 | 30,000 | 18,000 | --- |

RESULTS AND DISCUSSION

A seepage velocity of 164 mm/hr and a residence time of about 4 hours were registered on average. The average pH from selected sampling points during the four experimental runs; all pH values start at about 6.4, which is about the value of the DI water inflow system. During the control run, the pH decreases to a minimum, which is registered at 7 hours when the metal plume has a uniform zone of influence between sampling points. Later on pH increases back to background levels as the pulse injection leaves the system. During the pH run, the metal plume influences pH until its injection ceases, after which the pH recovers to above-background levels to then follow a rather rapid drop to background levels. The excess CO₃²⁻ injected during the carbonate run keeps pH relatively constant during the time of its injection; however pH is observed to drop to background levels rather rapidly after this injection.

During the next run the excess carbonate is depleted by reaction with the Calcium source in addition to the contaminants plume, this depletion is indicated by the decrease in pH at 7.9 and 11 hours, after which the pH recovers to later on start gradually decreasing. Towards the end of the experiment a final pH of 8.4 is registered after DI water have passed through the system. The CO₃²⁻ treatment appears to be the best one with the lowest amount of mass passing through the sampling screen. Solid solution is the second best whereas the pH treatment is the worst of the treatments tested. The major contribution to the cumulative mass flux occurred between the 7.5 and 11 hour increments. Increments in cumulative mass flux after this time are not noticeable as indicated by the horizontal lines in most of the elements tested. This may be due to the ejection back to solution of these metals. The percentage of mass precipitated for each one of the treatments studied in relation to the control run for

each one of the elements tested is given in Figure 1, according to the following equation:

$$\% \text{ Precipitated} = 100 \times \left(1 - \frac{\text{Cumulative Mass Flux of Treatment}_{t=44\text{hr}}}{\text{Cumulative Mass of Control run}_{t=44\text{hr}}} \right) \quad (1)$$

The elements have been ordered in the graph from left to right in order of increasing solubility product. The CO_3^{2-} treatment shows the largest removal from solution followed by the solid solution treatment whereas the pH treatment shows the lowest removal of the three treatments tested. The field application of this technology will require a preliminary viability assessment including a set of chemical analyses of the groundwater to determine the background ion activity product to establish whether or not the groundwater will be in equilibrium with calcite after the treatment is completed (Davis et al. [2]; Rimsdit et al. [12]; Bottcher [1]; McBeath, et al. [7]; Starbeck [13]; US EPA [16]).

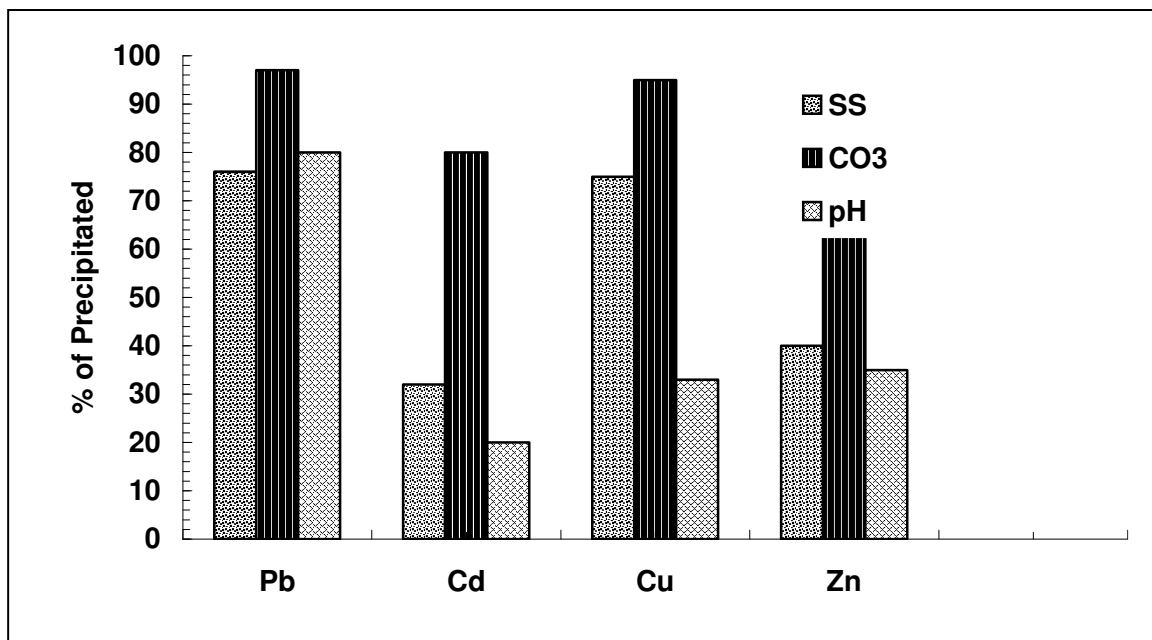


Figure 1. Percentage of mass precipitated by the intercepted zones (solid-solution controlled [ss], carbonate controlled [CO₃]; pH controlled [pH])

CONCLUSION

Remediation techniques relying on the physico-chemical process especially those utilize an in situ solution-to-solid phase reaction/ co precipitation can be an effective and secure for making rapid cleaning of heavy metals. However, good understanding of the geochemical behavior of heavy metals and site specification (volume, flow direction, chemical and physical properties, etc.) should be known before start drafting engineering design for field test of this technology.

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