Stabilization and solidification of lead-contaminated soils

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STABILIZATION and solidification of hazardous waste forms has become an acceptable remediation technique owing to its simplicity and cost effectiveness. Until recently, the stabilization problems have been treated as civil engineering problems. Physical parameters such as unconfined compressive strength (UCS), permeability, and diffusion were the determining factors for a successful stabilization/solidification (S/S) technology. In essence, the fundamental concepts of chemistry, which ultimately control the S/S process, were totally ignored.[1] The selection of an S/S binder was done mostly on a trial-and-error basis rather than on the basis of solution/precipitation chemistry.

The purpose of an S/S process is to make any hazardous material unavailable to the environment. This can be achieved by converting the waste (for example, lead) into its most insoluble form, and then placing it in a cementitious matrix.

A few binders were developed for lead on the basis of the solubility product constant, solubility curves, and other related aspects. The fundamental concepts governing the S/S process and the performance of the binders based on a variety of leach tests are presented in this paper.

Experimental

Several binders were prepared by thoroughly mixing varying amounts of Portland cement, kiln dust, flyash, and slag powder. All of these binders had at least three components in their formulas. The waste used in this investigation was a soil contaminated with 78,000 ppm of lead. The binder and the waste were mixed thoroughly in 15:85, 25:75, and 35:65 ratios. Water was added until the binder and the waste formed a smooth paste. The pastes were then cast into cylindrical molds and left out for curing. When the binders were made, their pH during treatment conditions (an aqueous slurry) was measured. Binders with pH values far outside of the range 8.5–11.5 were excluded. After the binder and the waste were mixed, several binder-waste mixtures showed pH values outside of the above-mentioned pH range. For those mixtures, small amounts of buffering agents were added to retain the pH in the desired range.

The treated wastes were cured for 28 days, then they were subjected to the toxicity extraction procedure (EP TOX), multiple extraction procedure (MEP), and the American Nuclear Society leach test (ANS 16.1).

Results and discussion

The MEP data (including EP TOX and ANS 16.1 data) are presented in *Tables 1* and *2*. These data reveal that the leach values approach drinking water standards. This phenomenon can be explained in terms of solution chemistry.

The first step in any inorganic S/S process is to convert the metal ion into its most insoluble form. The second step would be to incorporate the insoluble precipitate in a cementitious matrix. Lead hydroxide, $Pb(OH)_2$, is one of the most insoluble compounds of lead. Further, $Pb(OH)_2$ would be a natural reaction product of lead when placed in a cementitious matrix, which is always alkaline.

A precipitate of $Pb(OH)_2$ can be studied in equilibrium with the surrounding groundwater. The equilibrium constant can be derived as follows:

$$\underset{\text{solid}}{Pb(OH)_2} \rightleftharpoons Pb^{2+} + 2OH^- \quad (1)$$

$$K = \frac{[Pb^{2+}][OH^-]^2}{\underset{\text{solid}}{[Pb(OH)_2]}} \quad (2)$$

where $[Pb^{2+}]$, $[OH^-]$, and $[Pb(OH)_2]$ are the respective concentrations of each species expressed as mol/L. In a chemical equilibrium the concentration of a solid is considered as unity.

The equation can be rewritten as:

$$K_{sp} = [Pb^{2+}][OH^-]^2 \quad (3)$$

where K_{sp} stands for the new solubility product constant, that is, it is the product of the concentrations of ions (where the number of moles are raised as powers) present in a solution that is in equilibrium with the precipitate.

The K_{sp} for $Pb(OH)_2$ has been determined experimentally as:

$$K_{sp} = 1.2 \times 10^{-15} \quad (4)$$

at constant temperature.

Any cementitious binder normally yields a pH of approximately 11–12 when water is added for curing.

The p^{OH} of a cementitious binder can then be calculated from the relationship:

$$p^H + p^{OH} = 14 \quad (5)$$

$$p^H = 12 \quad (6)$$

$$p^{OH} = 14 - 12 = 2 \quad (7)$$

$$\therefore [OH] = 0.01 \text{ mol/L}$$

Substituting this value in Eq (4) yields

$$[Pb^{2+}][OH^-]^2 = 1.2 \times 10^{-15} \quad (8)$$

$$[Pb^{2+}][0.01]^2 = 1.2 \times 10^{-15} \quad (9)$$

$$[Pb^{2+}] = \frac{1.2 \times 10^{-15}}{[0.01]^2} \quad (10)$$

$$= 1.2 \times 10^{-11} \text{mol/L}$$

Multiplying this value by the atomic weight of lead will give the amount of lead that would leach out under equilibrium conditions.

$$= 1.2 \times 10^{-11} \times 207.2 \text{ g/L}$$

$$= 2.48 \times 10^{-9} \text{ g/L} \quad (11)$$

$$\sim 2.5 \text{ ppb}$$

However, an examination of the solubility curve of lead hydroxide (*Figure 1*) reveals that when the pH becomes excessive, the cationic lead can go into solution as anionic plumbate.[2]

$$Pb(OH)_2 + 2OH^- \rightleftharpoons PbO_2^{2-} + H_2O \quad (12)$$

It is imperative that the pH of the binder matrix should not be allowed to go beyond 12.

Although the waste form can be a complex one, the solubility product laws do account for their immobilization.

Conclusions

Binders were developed for the successful stabilization/solidification of lead based on the principles of solution chemistry. This type of approach eliminates the trial-and-error-type binder development and can save considerable amounts of time and resources. In spite of the complex nature of the waste forms, the data from these studies reveal that the first principles of chemistry still control the S/S phenomenon. The same principles can be extended to the successful S/S of other metals.[3] Other chemical phenomena, such as redox reactions, complexation, and coprecipitation can also be used for an effective S/S process.

References

1. Soundararajan R. Theory and practice of inorganic/organic stabilization/solidification process. Third International KfK-TNO Conference on Contaminated Soil. Karlsruhe, Germany. December 1990.
2. Cotton F, Wilkinson G. Advanced Inorganic Chemistry. New York: Wiley, 1980.
3. Arthur P, Smith O. Semimicro Qualitative Analysis. New York: McGraw-Hill, 195.

Table 1

Acid rain series lead concentration (ppb)*

Binder no.	1	2	3	4	5	6	7
1	13.8	26.4	13.7	15.3	12.1	9.7	2.8
2	27.4	61.5	58.6	3.7	1.2	57.9	4.0
3	39.5	30.3	31.8	32.2	28.4	28.5	7.7
4	39.0	40.1	22.66	26.0	24.6	58.6	6.2
5	208.1	168.3	123.7	49.1	30.3	29.4	14.6
6	89.5	75.2	580.3	131.1	338.4	83.0	16.0
7	244.2	266.5	282.3	349.6	248.8	7.2	6.5

*Concentration of lead in original soil was approximately 78,000 ppm.

Table 2

American Nuclear Society leach test (ANS 16.1)

Binder no.	Concentration of Pb (mg/kg or ppb)
1	<5.0
2	<5.0
3	<5.0
4	<5.0
5	<5.0
6	<5.0
7	<5.0

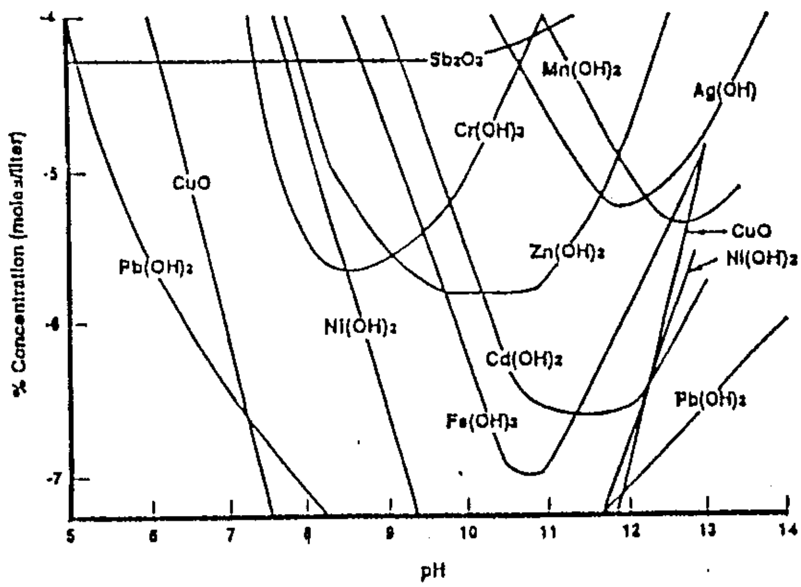

Figure 1 *Solubilities of some metal hydroxides and oxides.*

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