IN-PLACE PRECIPITATION IMMOBILIZATION OF LEAD
AT UNCONTROLLED HAZARDOUS WASTE SITES

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A significant percentage of the identified waste sites in the United States are considered high risk areas for potential release of dissolved heavy metals into nearby surface waters and groundwaters. While earlier remedial action efforts concentrated on waste containment or relocation, more emphasis is now being placed on in-place treatment technologies which permanently eliminate the hazards of these wastes. In-place precipitation is considered the most promising of these technologies for immobilizing dissolved heavy metals such as lead, cadmium and zinc (U.S. EPA, 1985a). This paper outlines a general methodology used to assess the effectiveness of in-place precipitation immobilization techniques for controlling lead release into nearby ground waters from uncontrolled waste sites. This methodology includes the use of site geochemistry, waste characterization, solubility controls, and selected laboratory batch and column leaching studies, to aid in the development of additive design strategies which will limit lead release to below target values. It is hoped that this methodology will serve as a guideline to those involved in developing or reviewing remedial action alternatives at sites where precipitation immobilization may be effective.

INTRODUCTION

Lead is the most ubiquitous inorganic hazardous contaminant identified at Superfund sites across the United States. Of the 951 proposed and final waste sites on the National Priority List, 309, or about 32 percent, contain concentrations of lead in the soil or waste

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significantly exceeding normal background levels (Superfund Data Base, May 26, 1987). There is a tremendous concern that these sites pose substantial human health risks because of the potential for release of high dissolved lead concentrations into nearby surface waters and groundwater.

There are currently two methods being used to assess the extent of remedial action required at sites with high lead concentrations in soils or wastes. The first is based solely on proposed soil lead concentration guidelines that take into account planned land use or potential exposure hazard to the population at risk. Davies and Wilson (1986) and the Ontario (Canada) Ministry of Environment (1986) have proposed an interim guideline of 1,000 µg/g lead in soil as a suggested regulatory limit for land designated for industrial redevelopment. Recently, the Minnesota Pollution Control Agency and Department of Health (1987) has recommended a state interim guideline of 1,000 µg/g lead in soil as a referral level for health screening of the local population.

The second approach used to assess the extent of remedial action is the evaluation of the leaching potential at a site as determined by performing the U.S. EPA Extraction Procedure (E.P. Toxicity) test on samples of the contaminated soil or waste. In this test, the soil or waste is contacted with a mild acetic acid leachant for 24 hours, after which time the leachant is analyzed for specific metals concentrations. Test results for lead exceeding 5.0 mg/l classify a sample as hazardous according to the regulations.

Although the soil lead concentration guideline or EP Toxicity test approach may serve as an indicator of potential health risks during initial screening of sites, they are severely limited in their ability to predict actual lead leaching levels based on site specific conditions. Both approaches do not take into account the in-situ geochemical and groundwater flow conditions that control lead transport, and ultimately affect the extent of remedial action that is required to limit future dissolved lead concentrations to below acceptable levels. Consequently, a more detailed assessment methodology is proposed for determining the potential release of dissolved lead and for developing in-place precipitation immobilization strategies to control future aqueous metal concentrations. The methodology described incorporates site specific geochemical and subsurface characterization using chemical equilibrium relationships more common to standard waste water treatment practices (Lanouette, 1977; Westen and Morrell, 1977; Wing and Rayford, 1977) or groundwater studies (Brown et al., 1986).

LEAD GEOCHEMISTRY AND SITE CHARACTERIZATION

Although lead is a major constituent of more than 200 known natural minerals, most are not commonly found (Lovering, 1976). Only three are present in large enough quantities to be mineable: galena (PbS), cerrusite (PbCO$_3$), and anglesite (PbSO$_4$). The geochemistry of lead, as well as other heavy metals in soil systems, is extremely complex and not yet fully understood. Depending on the specific conditions that are present, lead can appear in many forms in a groundwater system. Studies of the various physico-chemical forms of lead are hindered by the wide range of its possible forms (Figure 1) and the extreme difficulty in distinguishing them.

There are several geochemical conditions at a site that can either enhance or reduce the potential long-term mobility of lead in groundwater. It is apparent that lead in the soluble form is mobile, and thus free to move with the groundwater. Increased aqueous complexation of lead with inorganic or organic ligands means greater mobility and higher dissolved lead concentrations, while decreased complexation and increased precipitation or sorption results in lower aqueous lead concentrations.

Table 1 lists common inorganic aqueous lead complexes in groundwater containing carbonate, sulfate, nitrate, chloride, and fluoride. The relative distribution of inorganic complexes in a real system is dependent on the total aqueous concentration of each of the anions. Competition for available lead and other cations is a complex function of the assumed equilibrium relationships for all the possible reactants, and may be determined by using one of the many available multicomponent batch chemistry programs. In addition, the presence of organic complexing compounds such as the humic and fulvic acids, or sorptive hydrous ferric and manganese oxides surface coatings or clay minerals may significantly affect the availability of lead in the dissolved form, although actual evidence regarding the extent of these interactions is still very limited (Harrison and Laxen, 1981).

SOLUBILITY CONTROLS

The solubility of lead in most natural water systems is generally controlled by the most abundant anions in the system. This is primarily due to the outstanding characteristic of lead to form compounds of low solubility with native soil hydroxides, carbonates, sulfates, and phosphates. In many transient systems, the comparison of observed lead concentrations with theoretically calculated values based on solubility controls can normally not be expected to give more than a very approximate indication

of what is occurring in the real system. The influence of changing temperature, pH, ionic strength, etc. may be substantial and close adherence to an equilibrium based solubility model may not occur.

There is evidence, however, that in some systems, an equilibrium based solubility model may be an acceptable approach. Calculations described by Hem and Durum (1973) showed that many river waters in the United States have lead concentrations near the solubility limit imposed by their pH levels and content of dissolved CO_2 species. Lead solubility at several hazardous waste sites has also been shown to be limited by equilibrium geochemistry (Mundell, 1987).

To determine if a simplified equilibrium solubility approach can describe the relationship between observed aqueous lead concentrations, pH, and total anion concentration levels at a waste site, a site specific solubility diagram may be developed as shown in Figure 2. For one specific lead contaminated waste site (Atec Associates, Inc., 1987), ground water quality data obtained during the site characterization portion of the project showed a total carbonate concentration, C_t, of 3.6×10^{-3} M and a total sulfate concentration, S_t, of 1.8×10^{-3} M. To mathematically describe the system, lead was assumed to hydrolyze as $PbOH^+$, $Pb(OH)_2^0$, and $Pb(OH)_3^-$, and to form the insoluble precipitates litharge (lead oxide), $PbO(s)$, cerussite (lead carbonate), $PbCO_3(s)$, and anglesite (lead sulfate), $PbSO_4(s)$.

The solubility lines shown in Figure 2 for lead carbonate and lead sulfate are dependent on both the total carbonate and sulfate concentrations observed at the site as well as the pH. The figure illustrates that for the existing site conditions, lead sulfate controls the solubility of lead below a pH of about 5.5, shown as point A in the figure. From approximately pH 5.5 to 11.8, lead carbonate controls, and at pH values greater than 11.8, shown as point B, lead oxide governs the dissolved lead concentration. These results are based on the specific set of soluble lead complexes considered in a groundwater of zero ionic strength at a temperature of $25^{\circ}C$ in a closed system.

Comparison of these theoretical relationships with actual site pH and total aqueous lead concentration data should indicate whether other inorganic or organic ligands are forming lead complexes that cause significant deviations from the expected lead solubility. Figure 3 plots site specific values of pH and total aqueous lead determined for the previous waste site (Figure 2) from groundwater samples taken from monitoring wells. As indicated in the

figure, these values tend to cluster around the
theoretical lead carbonate solubility region, indicating
that lead carbonate is indeed controlling the total
aqueous lead concentration in the system. The
distribution around this line is indicative of the
variability of total carbonate, C_t, observed during the
time period the groundwater samples were obtained.

Although Figure 3 demonstrates that for some waste sites,
idealized theoretical solubility curves can be used to
describe the primary chemical reactions controlling the
release of dissolved lead, for other sites more complex
solubility diagrams incorporating additional lead
reactions must be developed to fully describe the
subsurface geochemical conditions. This may be especially
true when a site contains soils contaminated with several
heavy metals and/or organic compounds that may affect the
relative distributions of lead complexes through competing
reactions.

Minimizing Lead Solubility

Precipitation immobilization strategies should be designed
to control leaching of selected heavy metals by adjusting
the in-situ pH and/or increasing the total dissolved
concentration of major anions such as carbonate, sulfate,
or phosphate so that the particular metal(s) of concern
will be soluble at concentrations below those considered
toxic. Chemical additives that have shown the greatest
potential for achieving this objective are listed in Table
2.

From Figure 2, it is apparent that for the site conditions
shown, the theoretical minimum solubility of lead will be
approximately 0.0024 mg/l at about pH 8.5. Therefore, the
solubility of lead at the site could be minimized by
increasing the average groundwater pH from its present
representative value of 7.27 to a value of around 8.5.
Based on the simple solubility diagram developed, there is
no apparent benefit to increasing the pH beyond this value
since for the conditions stated, lead solubility would
increase beyond this point. However, for sites where
other solid phases may be controlling lead solubility at
higher pHs (eg. lead-phosphate precipitates) it may be
appropriate to further increase pH.

Lead solubility may also be reduced by artificially
increasing the concentrations of the controlling major
anions in the groundwater. This may be done by mixing
additives into the lead containing soil/waste which create
a constant source of these anions to the subsurface
groundwater via infiltration through the waste. Minimum
lead solubility as a function of total carbonate and total

sulfate for the chemical reactions considered previously are presented in Figure 4. Based on these relationships, a site must have a total carbonate value of at least 4.32×10^{-4} M or a total sulfate concentration greater than 1.64×10^{-1} M to limit lead solubility to below the proposed EPA primary drinking water standard of 0.02 mg/l. Sites with actual values less than these will theoretically release dissolved lead at levels toxic to human health unless measures are taken to increase anion concentration through in-place treatment strategies. Sites with significant natural alkalinity or sulfate levels may require little or no in-place additions to assure control of lead release. These considerations strongly emphasize the need for a site-specific approach to determine the extent of remedial action required rather than using the results of soil lead concentrations or EP toxicity tests.

LABORATORY BATCH STUDIES

To provide support for the conclusions reached by the site-specific theoretical solubility assessment, laboratory batch and column leaching studies on treated and untreated site lead-contaminated soils or wastes may be performed. These tests may be run under varying conditions to gain a better understanding of the character of the wastes, and to determine the effect that different test parameters have on the results.

During the initial site characterization phase, total soil lead or EP toxicity testing of selected samples from the waste site can be performed to determine the general relative leaching potential. Using these test results as guidelines, composite samples representing the worst site conditions should be prepared and used for more detailed treatability studies. This should provide confidence that any in-place treatment strategy developed will result in long-term protection for the worst case condition.

Laboratory batch leaching tests are performed to characterize the leaching behavior under a variety of geochemical conditions. To examine the behavior of lead leaching as a function of pH, batch tests on untreated waste may be performed. Figure 5 presents the results of tests run on a composite sample of untreated foundry sand containing 2400 mg/kg of total lead. In these tests, 50g of sample were placed in a 250 ml beaker and 100 ml of distilled water added. The pH was adjusted using either 1N acetic acid (to decrease pH) or 1N NaOH (to increase pH). Samples were rotated and the pH maintained at the desired values. At the end of 24 hours, samples were filtered and analyzed for total aqueous lead concentrations. The results show that for these test

conditions, lead solubility after 24 hours is a minimum in the pH range of about 8 to 10. Note that the general leaching behavior in Figure 5 is somewhat consistent with the shape of the solubility curve developed in Figure 2, indicating that carbonate and sulfate components are most likely present in the foundry sand.

It should be emphasized that the absolute value of the lead concentrations obtained from batch tests are strongly dependent on the testing conditions used (Patterson et al, 1975; Bishop et al, 1985). Such variables such as soil/solution ratio and test duration can dramatically influence the results depending on the type of soil or waste. The soil/solution ratio is generally a measure of how dilute a specific system is, and it affects lead solubility by controlling the total concentration of all chemical constituents in the system (e.g. total carbonate and total sulfate). The length of time that the test is allowed to run prior to sample filtration and testing may significantly affect measured concentrations if chemical reactions are kinetically controlled. This factor is not significant if the reaction rate is fast compared to the test duration and chemical equilibrium has been established. Incomplete reactions result in measured concentrations being supersaturated or undersaturated in comparison to values expected using theoretical equilibrium assumptions.

Therefore, although batch results may provide general indications of relative solubility under specific testing conditions and can illustrate characteristics of the reaction mechanisms present, their use for predicting in-situ lead concentrations appears to be limited. This is primarily due to the inability of the batch tests to simulate actual in-place geochemical and groundwater flow conditions.

COLUMN LEACHING STUDIES

To best simulate expected in-situ lead leaching conditions, column leaching studies should be performed on treated and untreated waste samples. These leaching conditions are better able to represent the in-place soil/solution ratio and simulate the dynamic nature of lead transport. In addition, the expected chemical composition of the site infiltration may be included.

As an example, a column containing an untreated sample of lead-containing foundry sand was permeated under constant head flow conditions by a simulated acidic rainwater of pH=4.6. The pH and chemical composition of this simulated rainwater was based upon data developed by the National Atmospheric Deposition Program (NADP) and was considered

representative of acidic precipitation falling on the waste site studied. The foundry sand contained a small percentage by weight of carbonate material that had been mixed with the sand prior to its use as a casting material. Under leaching conditions, the untreated column sample was observed to neutralize the acidic input to a pH in the range of 8.0 to 8.5 beyond 2000 pore volumes. Measurements made of column effluent pH, total carbonate, and dissolved lead showed that the lead concentrations were very close to values predicted from theoretical equilibrium conditions.

A simplified discrete interface penetration model proposed by Mundell and Jennings (1987) was used to simulate the rate at which the acid neutralizing capacity (ANC) of this foundry sand was consumed, so that long-term predictions of lead release could be made. In general, the acidic front was assumed to advance through the column at the velocity (Mundell and Jennings, 1987):

$$dx/dt = (nNv)/\{\rho_s(ANC)\}$$

where n is the porosity, N is the normality of the acid, v is the interstitial velocity, ρs is the bulk soil density, and ANC is the acid neutralizing capacity measured by a dynamic acid titration of the soil in a batch system, in milliequivalents of H^+ per mass of soil (meg/100 g) exchanged or transformed into aqueous complexes.

As indicated by the equation, the greater the ANC of the soil or waste, the slower the acidic front will advance. Likewise, the higher the normality of the acidic infiltration, the more rapidly the buffering capacity will be consumed. Although this simple model does not include all of the complex chemical interactions that are possible, it does indicate that waste containing natural or artificially added buffering materials will substantially resist typical worst case acidic infiltration. For the foundry sand described above with an ANC range of 18.2 to 33.7 meg/100g, it was estimated that it would take between 13,500 and 27,100 pore volumes for the acidic front to penetrate a distance of 1 inch through the untreated sands. This estimate assumed the loss of approximately one-half of the measured ANC due to the transport of dissolved buffering carbonate complexes out of the sample at a pH of 8.0 to 8.5. Based on expected site infiltration quantities, this represents substantial long-term buffering of acidic infiltration to a pH range that is conducive to minimizing lead solubility.

The use of column leaching tests to better simulate actual in-situ leaching conditions together with an appropriate

model for predicting acidic penetration velocity provides a quantitative basis to assess the impact of varying in-place additive strategies on long-term lead release.

CONCLUSIONS

A general methodology used to assess the effectiveness of in-place precipitation immobilization of lead at uncontrolled hazardous waste sites has been presented. The motivation for this methodology is clear. The impacts of in-place precipitation immobilization on long-term metal release must be assessed within a more quantitative framework to provide a basis for regulating the extent of remedial action required. Over the next several years, billions of dollars will be spent in efforts to clean up waste sites across the United States. Methods are needed which can assess the type and extent of a remedial action required to control contaminant release to below acceptable levels. Because of the uncertainty that currently exists in this assessment using existing methods such as soil lead guidelines or EP Toxicity test results, remedial actions may be undertaken which are either unnecessarily conservative and costly or technically ineffective. An accurate, site specific assessment of appropriate alternatives for remedial action is an important element in providing technically effective, permanent solutions at minimum costs.

REFERENCES

Atec Associates, Inc., Volume I Expedited Response Action, Uncontrolled Foundry Waste Site, February 1987.

Bishop, Paul L., Brown, Todd M., and Shively, William E., "Alkalinity Releases and the Leaching of Heavy Metals from Stabilized/Solidified Wastes," Proc. 5th Int. Conf. on Chemistry for Protection of the Environment, Leuven, Belgium, 1985.

Brown, David S., Carlton, Roger E., and Mulkey, Lee A., "Development of Land Disposal Decisions for Metals Using MINTEQ Sensitivity Analyses," EPA/600/3-86/030 Office of Research and Development, Environmental Research Laboratory, Cincinnati, OH.

Davies, B.E. and Wixson, B.G., "Lead in Soil - How Clean is Clean?" In: Trace Substances in Environmental Health XX, University of Missouri-Columbia, Hemphill, D.P., ed., 1986 (In press)

Harrison, R.M. and Laxen, D.P.H., Lead Pollution Causes and Control, Chapman and Hall Ltd., 1981, 168 pp.

Hem, J.D. and Durum, W.H., "Solubility and Occurrence of Lead in Surface Water," Am. Water Works Assoc. Jour., Vol. 65, No. 8, 1973, pp 562-568.

Lanouette, K.H., "Heavy Metal Removal", Chem. Eng., Oct. 1977, pp. 73-80.

Lead in the Canadian Environmental: Science and Regulation. 1986. Final Report, the Commission on Lead in the Environment, The Royal Society of Canada, Toronto, Ontario, Canada. 374 pp.

Lovering, T.G. Ed., Lead in the Environment, U.S. Geol. Surv. Prof. Paper No. 957, U.S. Government Printing Office, Washington, D.C., 1976, 90pp.

Mundell, John A., Final Report In-Place Precipitation Immobilization Assessment, Uncontrolled Foundry Waste Site, prepared for Atec Associates, Inc., March 1987.

Mundell, John A. and Jennings, Aaron A., "Penetration Model for Dynamic Permeability Analysis," Journal of Environmental Engineering, ASCE, Vol. 113, August 1987 (in press)

Patterson, James W., Scala, John J., and Allen, Herbert E., "Heavy Metal Treatment by Carbonate Precipitation," Proc. of the 30th Industrial Waste Conference, Purdue University, May 6-8, 1975, pp. 132-150.

Santillan - Medrano, J. and Jurinak, J.J., "The Chemistry of Lead and Cadmium in Soil Solid Phase Formation," Soil Sci. Soc. Am. J., Vol 39, 1975, pp. 851-856.

Sims, R.C., Sims, J.L., Sorensen, D.K., McLean, J., Mahmood, R., and Dupont, R.R., Review of In-Place Treatment Techniques for Contaminated Surface Soils: Vol. 1 Technical Evaluation, EPA-540/2-84-003a. Office of Research & Development, Cincinnati, OH, 1984a.

Sims, R.C., Sims, J.L., Sorensen, D.L., McLean, J., Mahmood, R., and Dupont, R.R., Review of In-Place Treatment Techniques for Contaminated Surface Soils: Vol. 2 Background Information for In-Situ Treatment, EPA-540/2-84-003b. Office of Research and Development, Cincinnati, OH, 1984b.

U.S.E.P.A. Handbook Remedial Action at Waste Disposal Sites (Revised). EPA/625/6-85-006, Office of Research and development, Hazardous waste Engineering Research Laboratory, Cincinnati, OH, 1985a.

U.S.E.P.A., Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants in Surface and Ground Water - Part I, EPA/600/6-85/002a, Environmental Research Laboratory, Athens, GA, 1985b.

U.S.E.P.A. Superfund Program Office. "Final & Proposed NPC Sites With Lead," May 26, 1987.

Weston, R.F. and Morrell, R.A., "Treatment of Water and Wastewater for Removal of Heavy Metals," In: Viruses and Trace Contaminants in Water and Waste Water, ed. J.A. Borchardt et al., Ann Arbor Science, Ann Arbor, MI, 1977, pp. 167-182.

Wing, R.E. and Rayford, W.E., "Heavy Metal Removal Processes for Plating Rinse Waters," Proc, of the 32nd Industrial Waste Conference, Purdue University, Ann Arbor Science, Ann Arbor, Michigan, May 1977, pp. 838-852

Wixson, Bobby G., Ghazifard, Akbar, and Davies, Brian E., "Industrial Wastes and Soil Lead Concentrations as a Basis for Remedial or Other Action," Proc. of the 42nd Industrial Waste Conference, Purdue University, May 13, 1987.

1985 Minnesota Lead Bill. Minnesota State Legislature 1985 Laws, 1st Special Session, Chapter 14, Article 19, Section 8-11, 1985.

Table 1. Dissolved Species of Lead

Free Ion	Inorganic Complexes
Pb^{2+}	$PbCO_3^0(aq)$
	$Pb(CO_3)_2^{2-}$
	$PbHCO_3^+$
Hydrolyzed Complexes	$PbSO_4^0(aq)$
$PbOH^+$	$PbNO_3^+$
$Pb(OH)_2^0(aq)$	$Pb(NO_3)_2^0$
$Pb(OH)_3^-$	$PbCl^+$
$Pb_2(OH)^{3+}$	$PbCl_2^0(aq)$
$Pb_3(OH)_4^{2+}$	$PbCl_3^-$
$Pb_4(OH)_4^{4+}$	$PbCl_4^{2-}$
$Pb_6(OH)_8^{4+}$	PbF^+
	$PbF_2^0(aq)$
	PbF_3^-
	PbF_4^{2-}

Table 2. Chemicals used for heavy metal precipitation (Sims et al, 1984; Lanoutte, 1977; U.S.E.P.A., 1985a)

Quicklime, CaO
Hydrated Lime, $Ca(OH)_2$
Caustic Soda, 50% NaOH
Limestone, $CaCO_3$
Soda Ash, Na_2CO_3
Sodium Sulfate
Sodium Sulfide
Iron Sulfide
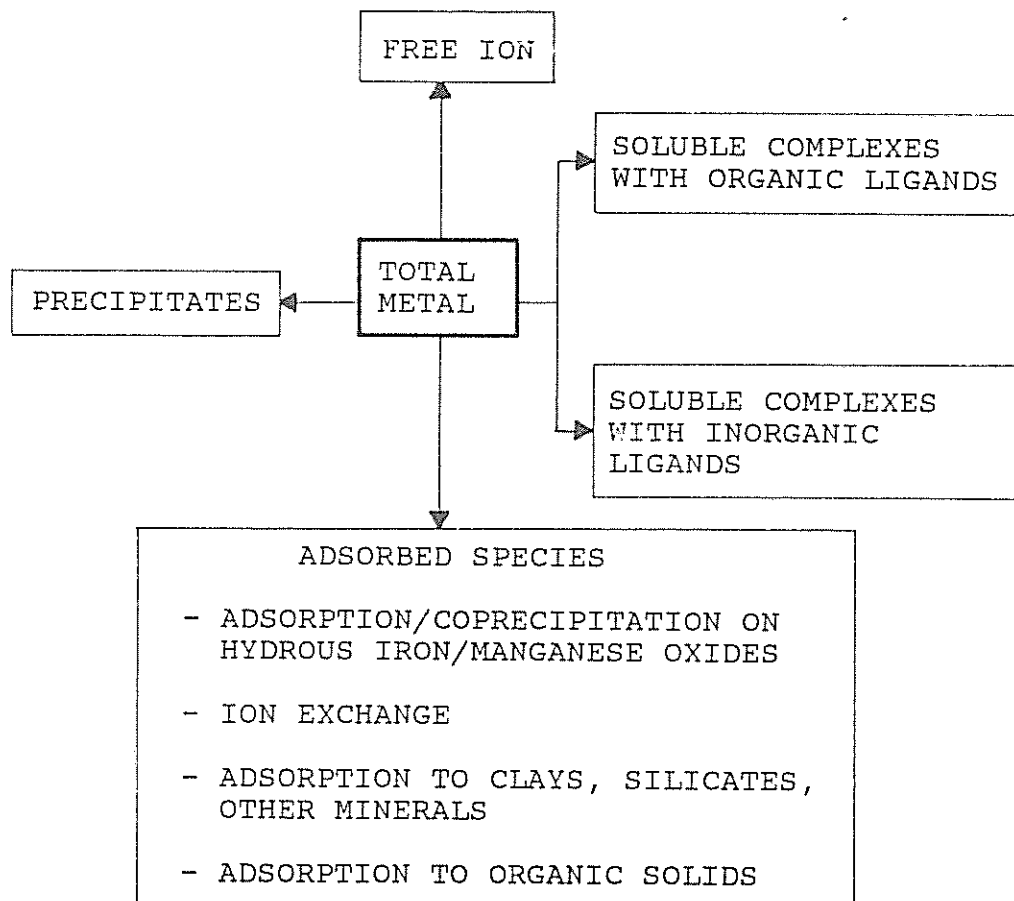Trisodium Phosphate
Treble Superphosphate, $Ca(H_2PO_4)_2$

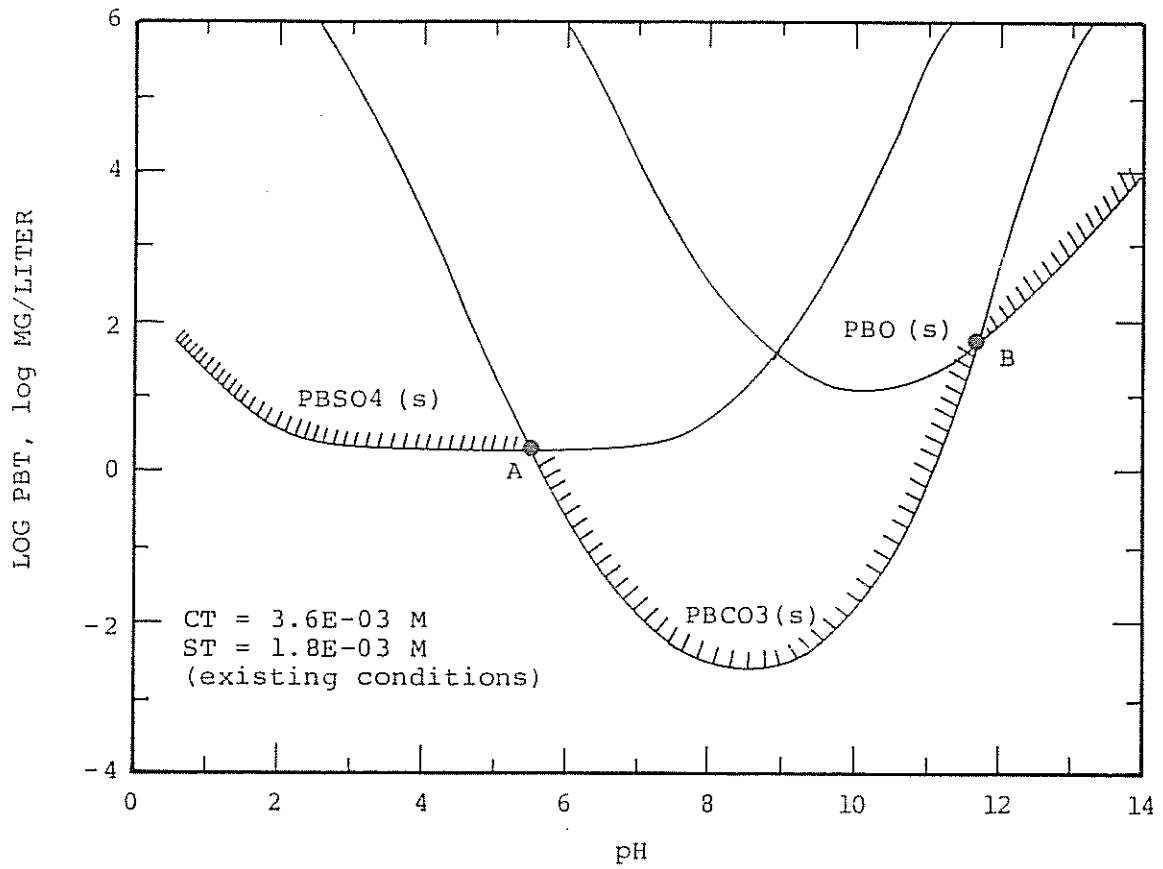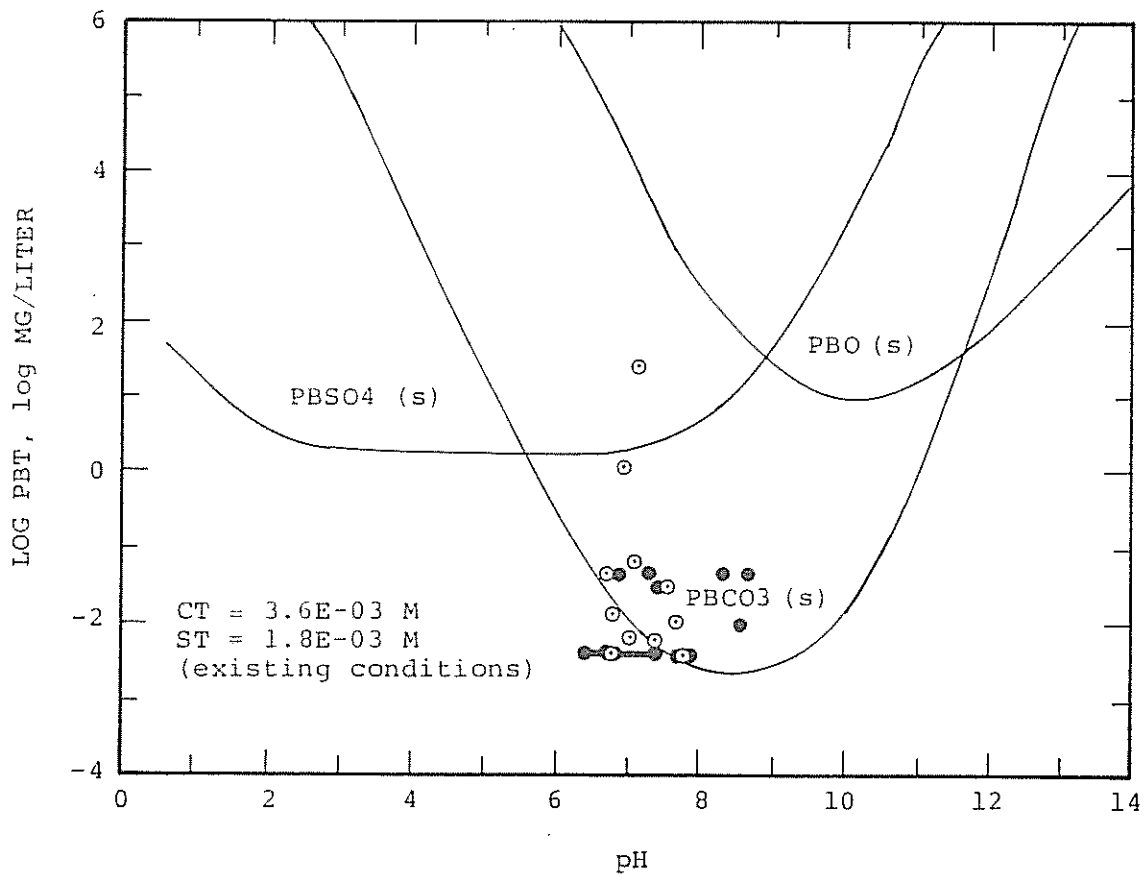Figure 1. Forms of Lead in Natural Water (after U.S. EPA,1985)

Figure 2.   Solubility of Lead versus pH for Estimated
Site Conditions, Uncontrolled Foundry Waste
Site.

● below detection limit

Figure 3. In-situ Lead Concentrations versus Theoretical
Solubility for Uncontrolled Foundry Waste Site.
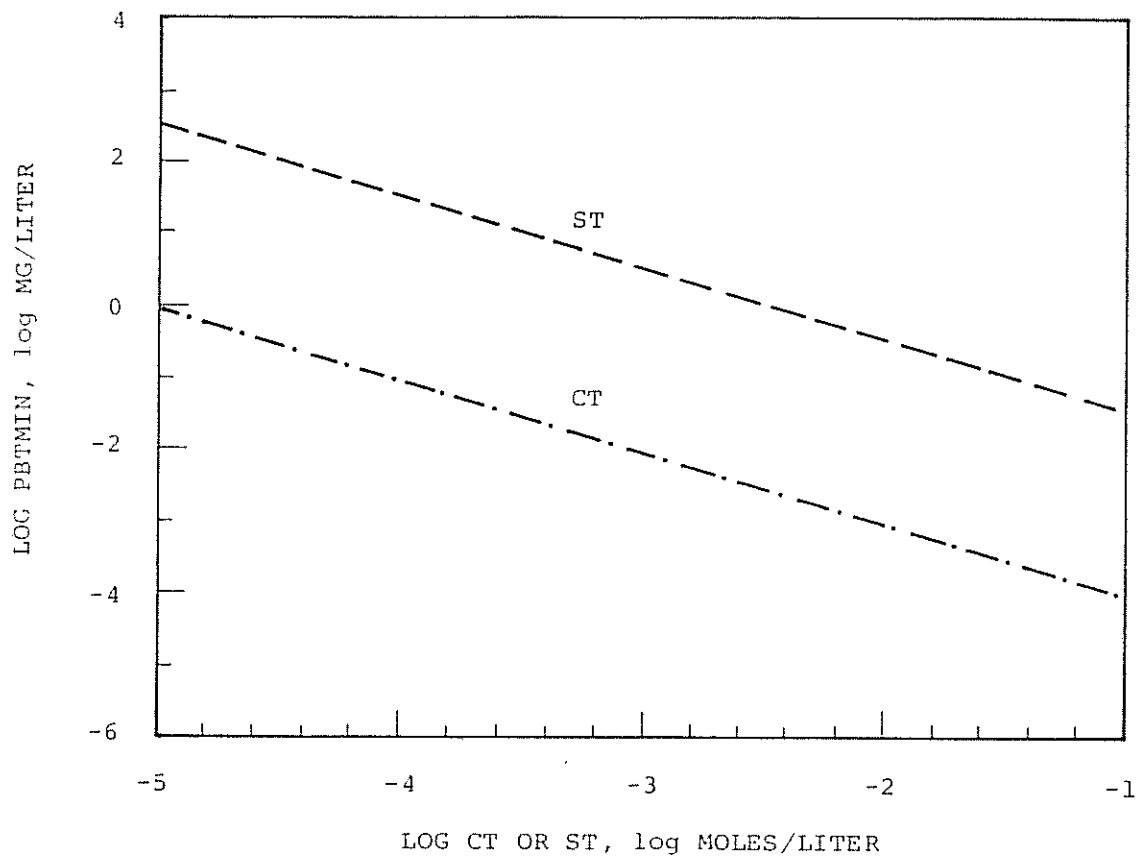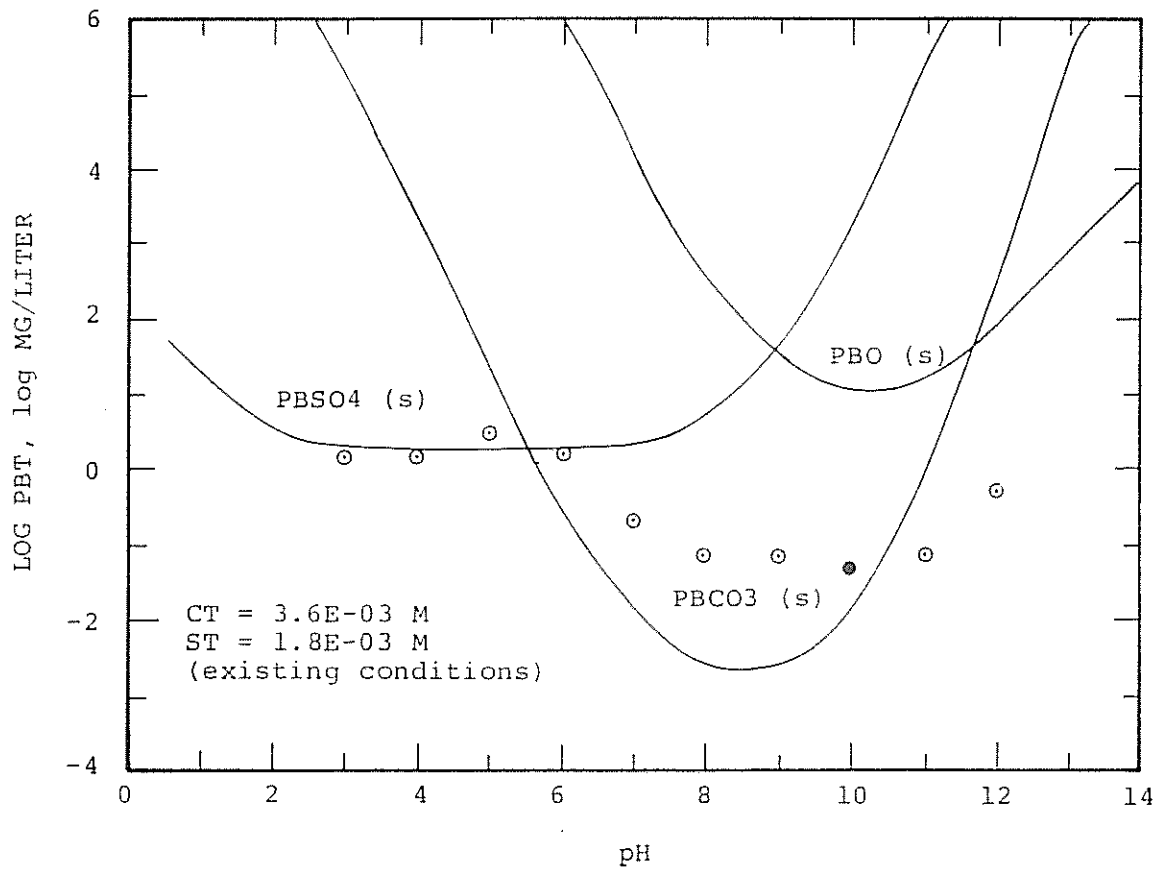
Figure 4.   Minimum Solubility as Function of $[C_t]$ and $[S_t]$

● below detection limit

Figure 5.   Variable pH Leaching Tests on Untreated Foundry
             Sand versus Theoretical Solubility for Composite
             Foundry Sand Sample Containing 2400 mg/kg of
             Total Lead.