DISSOLUTION OF LEAD PAINT IN AQUEOUS SOLUTIONS

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ABSTRACT: An analysis of the rate and extent of lead leaching from a lead-based paint was completed. At low-solution pH, dissolution was rapid and approached 80% of the total lead. Residual lead can be estimated based on the predicted solubility of lead carbonate and basic lead carbonate. Release of lead from the paint was slower than that from pure basic lead carbonate due to inhibition by the paint matrix. Although the dissolved concentration of lead in solution at neutral/high pH was low, the paint binder was apparently destroyed at these pH values, releasing colloidal lead pigment particles. The presence of ethylenediaminetetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) enhanced both the rate and degree of lead dissolution, while benzoic acid had a minimal effect.

INTRODUCTION

For many years, lead compounds were used in paints due to their color and opacity. Leaching of lead from paints can occur from the uncontrolled disposal of paint residuals, or with lead-based coatings currently protecting structures through contact with rainfall (possibly acidic) as a nonpoint source of lead to waterways. Much evidence showing that lead-paint-containing materials will fail the toxicity characteristic leaching procedure (TCLP) test for lead is available, thus classifying these materials as hazardous waste.

The purpose of this work is to evaluate the rate and extent of lead leaching from a paint matrix under various controlled conditions, and to compare measured lead levels with established models of lead solubility based on simple lead minerals. Two types of lead-containing paint were investigated, as was basic lead carbonate, the primary lead pigment used in residential paints. Three simple metal complexing agents with a range of stability constants were used to evaluate possible effects by natural organic matter complexation or the addition of a metal complexing agent to a lead-paint-containing waste material. Strong complexing agents are known to enhance the dissolution rate of metal oxides and carbonates (Furrer and Stumm 1983; 1986).

METHODS AND MATERIALS

Paint was obtained from two renovation projects (Symons and Chestertown) that were taking place on the University of Maryland campus. The paint is white, unknown age, obtained from the wood trim of brick buildings. Paint chips falling between ASTM sieve No. 4 (4.75 mm) and 30 (0.60 mm) were used in the testing. Both paints were tested for lead content in accordance with ASTM Designation D3335-85a.

For leaching investigations, samples containing 0.5 ± 0.0005 g of paint in 50 mL solution were prepared in plastic bottles. Initial experiments showed that the paint possessed an extremely high buffer capacity, thus necessitating the use of buffers to control pH. Acetate (Fisher), phosphate (Fisher, J. T. Baker), and borate (M.C.&B., J. T. Baker) at either 5×10^{-3} or 5×10^{-2} M were employed for pH values of 4.5, 6.8, and 8.8, respectively; pH 2.0 was also examined. Additional $NaNO_3$ (E.M. Sci.) was added to maintain total ionic strength at either 5×10^{-3} or 5×10^{-2} M. Water used in all experiments was deionized using a hydroservice reverse osmosis/ion exchange apparatus (Model LPRO-20). Basic lead carbonate (Pfaltz & Bauer) was examined at a loading such that the lead content was identical to 0.5 g of Symons paint.

In selected cases, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), or benzoic acid was added at concentrations ranging from 10^{-4} to 10^{-2} M. For comparison, the paint chips were also ground using a mortar and pestle to pass through an ASTM No. 30 sieve (0.60-mm opening).

Four samples were prepared for each pH value and were shaken for 24 h, after which one sample from each pH range was examined for dissolved lead content. The remaining bottles were shaken 1 h each day thereafter. Additional testing was done at three, seven, and 30 days. The pH of each sample was monitored on a daily-weekly basis throughout the sample run and adjusted with HNO_3 or NaOH as required. In most cases, the pH deviation was less than ± 0.2 units.

After the final pH was measured, each sample was divided into two fractions. The first fraction was filtered through a No. 40 Whatman qualitative filter (referred to as "filtered"). This process removed the large original paint chips, but may not capture colloidal particles. The second fraction was centrifuged to remove large particles and the supernatant was filtered through 0.2 or 0.45 μm Gelman filters, discarding the first few mL; lead in this filtrate is operationally defined as dissolved. After acidification with HNO_3, dissolved lead concentrations were determined in both fractions using atomic absorption spectrophotometry (Varian AA-5).

The specific surface area of the crushed Symons paint was found to be 128 m^2/g using the ethylene glycol monoethyl ether (EGME) absorption method (Carter et al. 1986). This value seems high and may result from some of the EGME partitioning into the paint binder. The gross specific surface area of the paint chips, determined by measuring exposed areas of 0.2–0.5 cm^2 chips, was $1.4 \pm 0.7 \times 10^{-3}$ m^2/g per exposed side.

An initial lead dissolution rate ($mol \cdot g^{-1} day^{-1}$) was estimated based on one-day or one- and three-day samples to examine effects in nonequilibrium systems. The solubility was evaluated based on the dissolved lead concentration at the end of 30 days.

RESULTS AND COMMENT

Results of the ASTM total lead analysis demonstrated that the Symons paint contained 13.85% lead by weight. Thus the total available lead loading is 1,385 mg/L (6.7×10^{-3} M). Based on energy dispersive x-ray spectroscopy (EDX) analyses, the average elemental makeup (by mass) of the Symons paint (elements larger than Na) is: 24% Pb, 23% Ti, 20% Al, 10% Si, 9% Ca, 8% Zn, 5% Cu, and 2% Fe. X-ray

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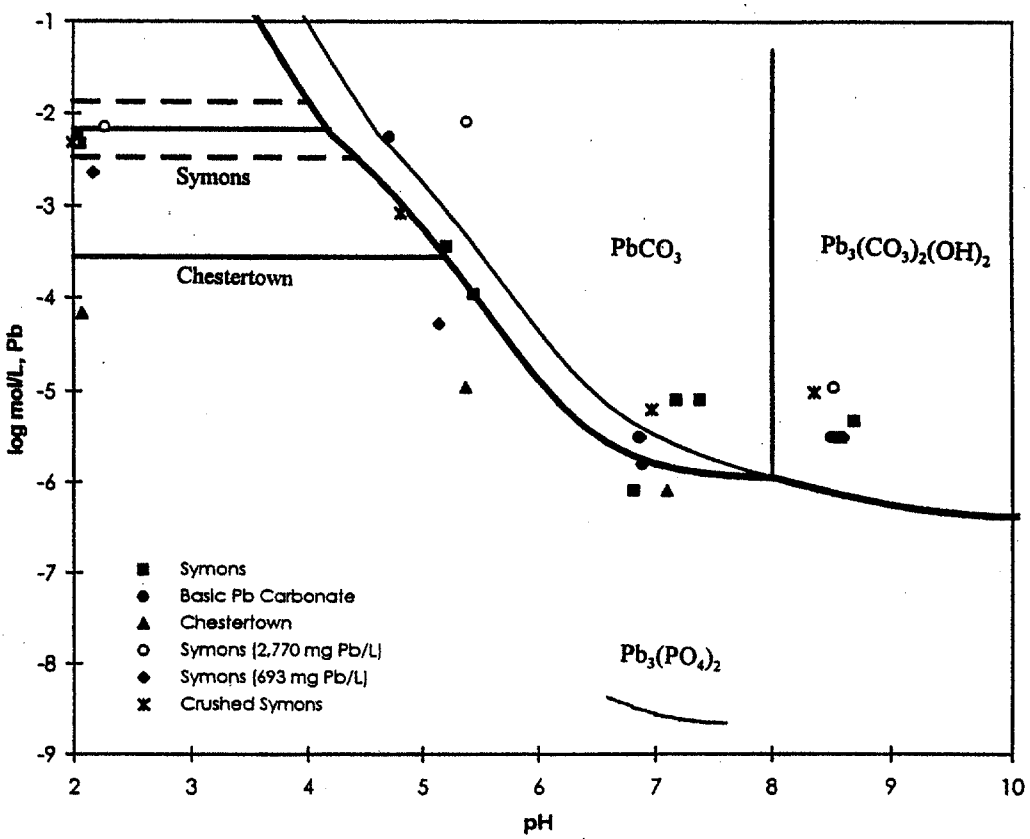

FIG. 1. Lead Solubility Diagram with Experimental Dissolved Lead Concentrations from 30-Day Leaching from Lead Paint; Curves Developed from Equilibriums of Table 1 (TIC = 10^{-3} M Except at Very Low pH Where Dissolution of Lead Paint is Considered, Ionic Strength = 5×10^{-2} M, T = 25°C); Horizontal Lines Indicate Total Available Lead in Respective Systems

diffraction of Symons paint showed a complex pattern with peaks characteristic of $Pb(OH)_2$, SiO_2, and $2PbCO_3 \cdot Pb(OH)_2$, as well as suggestion of rutile TiO_2. Sources of several peaks were not readily identified.

The Chestertown paint was found to have a lead content of only 0.59%, indicating that it is a more recently produced material. The total available lead in the Chestertown samples was 59 mg/L (2.8×10^{-4} M).

Solubility Analyses and pH

Fig. 1 shows the solubility of lead as predicted through the modeling of Schock (1980, 1990), including hydroxide and carbonate species, with stability constants presented in Tables 1–3. A background total inorganic carbon (TIC) concentration of 10^{-3} M is assumed based on typical TIC levels in contact with the atmosphere (Marani et al. 1995); at lower pH, the TIC is increased to account for dissolution of basic lead carbonate from the paint. The predicted stable solids are lead carbonate below pH 8 and basic lead carbonate above pH 8. Marani et al. (1995) experimentally identified these two compounds as the dominant lead precipitates in simple suspensions, even though the speciation program MINTEQA2 frequently predicted $Pb(OH)_2$ as controlling lead solubility.

The 30-day dissolved lead concentrations for the two paints and the basic lead carbonate are listed in Table 4 and plotted on Fig. 1. In most cases lead dissolution plateaus by the 30th day, suggesting that an equilibrium is reached. A strong effect of pH on the leaching of the lead is clearly noted. At pH 2, nearly all available lead is dissolved for the three materials. The leachability, both in terms of initial rate and 30-day concentration, decreases in the pH order 2.0 > 4.5 > 8.8 > 6.8.

Assuming that the paint pigment is composed primarily of basic lead carbonate, it is expected to possess Pb-OH and Pb-CO_3H surface functional groups, as with other carbonates (Van Cappellen et al. 1993). The rapid dissolution rate at low pH can be attributed to proton-promoted dissolution, in which excess protons in solution induce protonation of the metal hydroxide/carbonate surface groups, favoring the release of the hydrated metal into solution (Furrer and Stumm 1983, 1986). Thus, exposure to low pH conditions of, for example, an acidic rain or an acid leach process, encourages more rapid lead release from the paint than at higher pH values.

It proved difficult to evaluate effects of the buffers on solubility due to drastic changes in pH. Effects of the acetate and borate are expected to be minor; however, that of the phosphate may not. To analyze possible interactions with phos-

TABLE 1. Equilibrium Constants Used for Lead Solubility Diagram Construction (Smith and Martell 1977; Schock 1980; Schock and Gardels 1983; Holm and Schock 1991)

Lead Complexation Reactions	
Reaction (1)	Log β (2)
$Pb^{2+} + OH^- \rightleftharpoons PbOH^+$	6.77
$Pb^{2+} + 2OH^- \rightleftharpoons Pb(OH)_2^0$	11.07
$Pb^{2+} + 3OH^- \rightleftharpoons Pb(OH)_3^-$	13.9
$2Pb^{2+} + OH^- \rightleftharpoons Pb_2OH^{3+}$	7.63
$3Pb^{2+} + 4OH^- \rightleftharpoons Pb_3(OH)_4^{2+}$	32.1
$4Pb^{2+} + 4OH^- \rightleftharpoons Pb_4(OH)_4^{4+}$	35.09
$6Pb^{2+} + 8OH^- \rightleftharpoons Pb_6(OH)_8^{4+}$	68.31
$Pb^{2+} + CO_3^{2-} \rightleftharpoons PbCO_3^0$	7.1
$Pb^{2+} + 2CO_3^{2-} \rightleftharpoons Pb(CO_3)_2^{2-}$	10.33
$Pb^{2+} + HPO_4^{2-} \rightleftharpoons PbHPO_4^0$	3.1
$Pb^{2+} + H_2PO_4^- \rightleftharpoons PbH_2PO_4^+$	1.5

TABLE 2. Equilibrium Constants Used for Lead Solubility Diagram Construction (Smith and Martell 1977; Schock 1980; Schock and Gardels 1983; Holm and Schock 1991)

Weak Acid Equilibriums	
Reaction (1)	Log K (2)
$H_2CO_3^* \rightleftharpoons HCO_3^- + H^+$	−6.35
$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+$	−10.33
$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$	−7.2
$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$	−12.33

TABLE 3. Equilibrium Constants for Lead Solubility Diagram Construction (Smith and Martell 1977; Schock 1980; Schock and Gardels 1983; Holm and Schock 1991)

Lead Solids Equilibriums	
Reaction (1)	Log K_{so} (2)
$PbCO_3(s) \rightleftharpoons Pb^{2+} + CO_3^{2-}$	−13.11
$Pb_3(OH)_2(CO_3)_2(s) \rightleftharpoons 3Pb^{2+} + 2OH^- + 2CO_3^{2-}$	−45.9
$Pb_3(PO_4)_2(s) \rightleftharpoons 3Pb^{2+} + 2PO_4^{3-}$	−44.5
$Pb_5(OH)(PO_4)_3(s) + H^+ \rightleftharpoons 5Pb^{2+} + 3PO_4^{3-} + H_2O$	−62.79

phate, lead orthophosphate and hydroxypyromorphite solids, as well as soluble $PbHPO_4^0$ and $PbH_2PO_4^+$ (Tables 1–3), were included in solubility calculations for pH 6.5–7.6 (Schock 1990). Very low dissolved lead concentrations are predicted ($<10^{-8}$ M, Fig. 1). Nevertheless, at pH 6.8, the experimental lead concentrations are near the solubility curves of lead carbonate, even in the presence of a large phosphate concentration. It is likely that slow kinetics limit the conversion to lead phosphate (Schock 1989).

At pH 2.0, the initial dissolution rate for the crushed paint is greater than the uncrushed Symons (dissolved) due to the increase in paint surface area. Similarly, investigations of samples containing 0.25 and 1.0 g paint/50 mL (3.3×10^{-3} and 1.3×10^{-2} M total lead, respectively) demonstrate that the initial dissolution rate is proportional to the loading at all pH values (nearly equal on a per-gram basis). At the end of the 30 days, however, the concentrations are nearly identical as most of the available lead was dissolved and solubility becomes the controlling factor.

These data suggest that the leachability of the lead from lead paint was controlled by the solubility of the expected lead solids: lead carbonate and basic lead carbonate. Even though the paint-derived Pb(II) concentrations at pH 8.8 were somewhat inside the calculated solubility curves, Pb concentrations from the synthetic basic lead carbonate were also.

At pH 2.0 and 4.5 there was no difference between the qualitative filtered and dissolved lead levels (Table 4). However, filtered lead was considerably higher than the dissolved lead at pH 6.8 and 8.8, indicating the presence of colloidal-sized lead particles. This difference is attributed to small particles of pigment that pass through the qualitative filter, with subsequent dissolution upon acidification. The liberation of these colloidal particles may result from destruction of the organic binder of the paint, possibly hydrolysis of the fatty acid chains that comprise the binder, which would produce glycerol and a soap (Streitweiser and Heathcock 1981). Qualitatively, it was observed that the pH 6.8 and 8.8 suspensions exhibited a milky-white color and were topped with a layer of foam. As the binder matrix is destroyed, the small pigment particles are released from the original paint chips (which were 0.6–4.8 mm in size) and suspended in solution. However, the basic lead carbonate of the pigment is still stable at these pH values and consequently the dissolved lead concentration is low. Thus, under neutral-to-basic conditions, lead may be mobilized from the paint—not as dissolved lead, but as particulate lead mineral—and solubility analyses alone may not completely describe the mobility of lead resulting from contact of lead paints with water.

Effect of Organic Complexing Agents

For both EDTA and NTA, as the concentration of chelate added to the suspensions is increased from 0 to 10^{-2} M, initial dissolution rates at pH 4.5–8.8 are increased approximately two orders of magnitude (Table 4). However, little effect on rate is noted at pH 2. A shift in the maximum initial dissolution rate from low to high pH as the concentration of chelate is increased is observed. At 10^{-2} M chelate, much of the lead is dissolved for all pH values after 30 days.

Additions of 10^{-2}, 10^{-3}, and 10^{-4} M EDTA at pH 8.8 produced increases in dissolved lead over that without EDTA of 52, 40, and 39%, respectively, of the added EDTA concentration. Similar values were found at pH 4.5 and 6.8. Slightly lower values of 35, 16, and 10% of the added NTA concentrations were noted for this chelate at pH 8.8.

TABLE 4. Initial Lead Dissolution Rates and 30-Day Lead Concentrations (Unless Otherwise Noted, Total Lead Is 6.7×10^{-3} M)

Condition (1)	Initial Rate (mol Pb/g Paint-Day)				30-Day Pb Concentration (M)			
	pH 2.0 (2)	pH 4.5 (3)	pH 6.8 (4)	pH 8.8 (5)	pH 2.0 (6)	pH 4.5 (7)	pH 6.8 (8)	pH 8.8 (9)
Symons paint								
Dissolved	1.2×10^{-4}	6.2×10^{-6}	1.7×10^{-7}	2.0×10^{-6}	4.7×10^{-3}	1.1×10^{-4}	8.2×10^{-7}	4.8×10^{-6}
Filtered	1.2×10^{-4}	6.5×10^{-6}	2.4×10^{-6}	3.3×10^{-6}	4.8×10^{-3}	1.1×10^{-4}	1.9×10^{-5}	1.9×10^{-5}
EDTA								
10^{-4} M	1.0×10^{-4}	1.0×10^{-5}	1.9×10^{-6}	4.8×10^{-6}	1.9×10^{-3}	2.0×10^{-4}	1.1×10^{-5}	4.4×10^{-5}
10^{-3} M	5.8×10^{-5}	3.2×10^{-5}	4.1×10^{-5}	3.2×10^{-5}	2.7×10^{-4}	4.8×10^{-4}	2.8×10^{-4}	4.0×10^{-4}
10^{-2} M	1.4×10^{-4}	7.5×10^{-5}	3.1×10^{-4}	3.4×10^{-4}	4.7×10^{-3}	4.2×10^{-3}	5.0×10^{-3}	5.2×10^{-3}
NTA								
10^{-4} M	1.2×10^{-4}	6.0×10^{-6}	6.4×10^{-7}	2.7×10^{-6}	4.4×10^{-3}	4.4×10^{-4}	4.8×10^{-6}	1.5×10^{-5}
10^{-3} M	1.1×10^{-4}	3.2×10^{-5}	1.6×10^{-5}	2.4×10^{-5}	4.8×10^{-3}	3.2×10^{-4}	8.0×10^{-5}	1.6×10^{-4}
10^{-2} M	1.9×10^{-4}	8.9×10^{-5}	3.7×10^{-4}	4.1×10^{-4}	5.5×10^{-3}	4.0×10^{-3}	4.8×10^{-3}	3.5×10^{-3}
Benzoic acid: 10^{-2} M	9.3×10^{-5}	9.9×10^{-6}	2.3×10^{-7}	2.3×10^{-7}	4.3×10^{-3}	5.2×10^{-4}	3.2×10^{-6}	8.1×10^{-6}
Crushed paint	2.5×10^{-4}	1.4×10^{-5}	3.2×10^{-6}	8.1×10^{-7}	4.8×10^{-3}	8.5×10^{-4}	6.4×10^{-6}	9.7×10^{-6}
Total Pb = 3.3×10^{-3} M	1.2×10^{-4}	1.0×10^{-5}	3.2×10^{-7}	3.2×10^{-7}	2.3×10^{-3}	5.2×10^{-5}	3.2×10^{-6}	3.2×10^{-6}
Total Pb = 1.3×10^{-2} M	4.9×10^{-5}	2.2×10^{-6}	8×10^{-8}	1.6×10^{-7}	7.2×10^{-3}	8.2×10^{-5}	3.2×10^{-6}	1.1×10^{-5}
Chestertown paint	5.2×10^{-6}	1.6×10^{-6}	8×10^{-8}	1.6×10^{-7}	6.8×10^{-5}	1.1×10^{-5}	8.1×10^{-7}	3.2×10^{-6}
Basic Pb carbonate	3.7×10^{-3}	1.9×10^{-6}	1.9×10^{-6}	2.9×10^{-6}	5.9×10^{-3}	5.6×10^{-3}	1.6×10^{-6}	3.2×10^{-6}

Note: EGME specific surface area of Symons paint = 128 m^2/g. Gross specific surface area of Symons paint = $1.4 \pm 0.7 \times 10^{-3}$ m^2/g (1 side).

The significant rate and extent of dissolution at the three higher pH values in the presence of EDTA and NTA can be attributed to the strong metal-chelating ability of these compounds. These ligands bind with the surficial metals of the lead pigment, creating an adsorbed surface complex, allowing a more rapid metal release into solution (ligand-promoted dissolution). The dissolution rate is proportional to the active surface complex, which in turn is a function of the dissolved ligand concentration (Stumm and Furrer 1987). At pH 2 the dissolution is mostly proton-promoted, the EDTA/NTA has little effect since complexation is less, and the lead release is independent of chelate concentration.

The difference between filtered and dissolved lead concentrations with EDTA and NTA decreased with increasing concentration of chelate at pH 6.8; at 10^{-2} M, the differences were negligible. Even if the paint binder is destroyed, the colloidal pigment particles are readily dissolved in the presence of the strong chelating agents.

The addition of 10^{-2} M benzoic acid has little effect on both the rate and extent of lead leaching from the paint matrix since it is a weak, monodentate ligand; slight enhancements are demonstrated at pH 4.5 and 6.8. This same outcome with benzoic acid was observed in the dissolution of mineral oxides (Furrer and Stumm 1986).

EDTA/NTA and benzoic acid represent extremes of strong and weak lead-complexing ability, and likely associated effects on lead leaching. Although these compounds may not fully represent the complexing characteristics of natural organic matter, the effects noted demonstrate that complexation is important to the lead leaching process.

Other Paint/Basic Lead Carbonate

As compared to the Symons, the lower-lead Chestertown paint exhibits a much slower initial dissolution rate at all pH values (Table 4). On a relative basis, (dissolved lead/total lead) more lead is leached from the Symons paint at pH 2. At pH 4.5, 6.8, and 8.8, total dissolved lead levels are similar, with a higher fraction of the total lead leached from the Chestertown paint.

The dissolution of basic lead carbonate at pH 2 is much more rapid than the paints. Greater than 90% of the lead from this compound is rapidly solubilized and a constant dissolved Pb(II) concentration is reached after day 1. The high dissolution rate results from the surface site accessibility of the basic lead carbonate; it is not constrained by the binder or other inorganic compounds as is the lead pigment in the paint.

SUMMARY

It is demonstrated that lead was readily leached from a lead paint matrix under a variety of conditions—in many cases high dissolved lead concentrations resulted. The highest degree of leaching occurred under low pH (~2) conditions, or in the presence of 10^{-2} M EDTA or NTA. Dissolution in all of these cases was greater than 80% of the total lead in the paint. Even at neutral pH (6.7), measurable lead was dissolved and strong chelating agents drastically enhanced the rate and extent of Pb(II) leaching. In instances where strong metal complexing agents are naturally present, codisposed with paint wastes, or anthropogenically added, dissolution enhancements are expected.

In the neutral-high pH range, the paint binder was apparently destroyed, releasing colloid-sized lead particles into the solution. Even though the lead is not dissolved, these smaller particles are likely more mobile than the larger paint chips. Ultimate concentrations of soluble lead from a lead paint are controlled by the solubility of lead carbonate and basic lead carbonate. However, the rate of the lead release is inhibited due to interferences from various constituents in the paint pigment matrix.

Lead release can occur at any point during the lifetime of the paint: when it is still on the structure, during removal, or after it is disposed of. Estimates of lead leaching rates can be made from stockpiles of removed paints (based on the total mass of paint present) or from paint that is still present on a structure (based on exposed surface area).

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