Lead Silicate Solubility and the Control of Lead Contamination in Drinking Water

by

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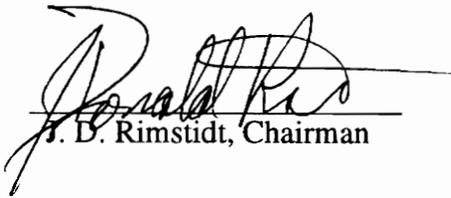
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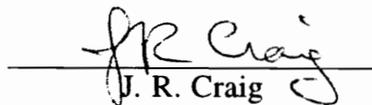
J. R. Craig

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LEAD SILICATE SOLUBILITY AND THE CONTROL
OF LEAD CONTAMINATIION IN DRINKING WATER

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(ABSTRACT)

The intake of lead into the human body has become an area of major concern because high levels of lead are harmful and can cause physiological damage, especially in children. It has been suggested that adding $NaSiO_3$ might control Pb^{2+} contamination of drinking water supplies (e.g., Thresh 1922). $PbSiO_3$ (am), the white, gelatinous precipitate formed by mixing Na_2SiO_3 solutions with Pb^{2+}-bearing solutions, dissolves at pH<7 by the reaction:

$$PbSiO_3 + H_2O + 2H^+ = Pb^{2+} + H_4SiO_4$$

Measurements of the solubility of $PbSiO_3$ show that the K_{eq} for this reaction is 7.41×10^5 and the ΔG_f° ($PbSiO_3$ (am)) is 1061.81 kJ mol^{-1}. This high value of K means that extreme amounts of a Na_2SiO_3 additive are required in a water supply system to reduce the Pb^{2+} concentration to the EPA MCL action level of 15 ppb. Furthermore, the high pH values that result from $NaSiO_3$ water treatments lead to the formation of lead hydroxycarbonate (hydrocerussite) because this carbonate phase is more stable in the pH range of natural waters (pH 5-8) than lead silicate.

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INTRODUCTION

Intake of lead into the human body has become an area of major concern because high levels of lead cause diminished mental and physical growth in children and elevated blood pressure in adults. Humans actually absorb most lead through the respiratory tract after inhaling Pb-oxides and particulate lead released from the burning of leaded gasoline (Moore and Ramamoorthy, 1984); other potential lead intake sources include contact with lead-containing paints and lead-bearing gasolines. However, it is now apparent that another primary way that lead enters the body is through the consumption of potable waters from private and public water supply systems. This lead comes from the corrosion of lead pipes, lead-bearing solders in copper pipes, and the dissolution of lead stearate coatings on plastic pipes. Lead contamination of drinking water is especially severe in areas that have soft water supplies (USEPA, 1991).

The potential health problems resulting from lead in drinking water systems have prompted the Environmental Protection Agency (EPA) to set the maximum contaminant level (MCL) of lead in potable water at 15 µg/kg (USEPA, 1991). With the implementation of the new drinking water standards, all large water systems (serving>50,000) will be required to conduct corrosion control studies and to recommend an optimal corrosion control treatment by 1995 (USEPA, 1991). These treatments could include using phosphate, silicate or lime compounds to correct the problem. The systems will have 2 years to implement the treatment and 1 year to conduct follow-up sampling. Water quality parameters are to be established for pH and alkalinity, and for calcium, orthophosphate, or silica depending on which corrosion control technique is used. Lead service lines must be replaced if the water lead levels exceed the EPA-mandated MCL.

Lead is a cumulative poison in the human body; consequently, consumption of water with even this low concentration may result in significant accumulation of lead in the

human body over long time periods. An adult that drinks 2 L of water at the MCL of lead (15 μg/kg) would ingest approximately 30 μg/day provided all of the lead were absorbed into body tissues from the water. Tsuchiya (1986) reported that absorption from drinking water probably ranges from 10 to 20 % (or 3 to 6 μg absorbed) for all lead ingested from water. However, the total lead intake from all sources of lead exposure (inhalation and ingestion) is probably still close to 30 μg/day.

Lead is excreted through the urinary tract with smaller amounts secreted in other body fluids such as sweat and breast milk, but there are two areas where the absorbed lead can be stored: the bones and the soft tissues including blood. The half-life of lead in bones ranges from 5 to 10 years, while soft tissues (such as the liver and fatty tissue) and blood retain the lead with a half-life of about 20 days (Freiberg, et al. 1986). Lead in the blood is mainly bound to the erythrocytes, but the mechanism for this bond is not fully understood (Tsuchiya, 1986). The total weight of lead in the body of an adult 70 kg man is estimated to be 100 - 400 mg and increases with age (NRCC, 1973). Lower lead levels are found in women primarily because they have lower hemoglobin values, i.e. fewer red blood cells which have an affinity for lead. Children are the most susceptible to damage from elevated levels of lead and appear to accumulate it at elevated rates. This is possibly due to the fact that the lead is locked into bones that are still forming (Tsuchiya, 1986). Thus, lead stays in their bodies for a longer period of time and appears to affect their mental and physical growth. Needleman (1983) has demonstrated that children with high levels of lead in their blood have lower than expected IQ's even though the children may not exhibit other physical signs of lead poisoning.

Lead piping is still common in Europe and in older, urbanized areas of the U.S., such as New England. Because it is essentially impossible to remove all the lead piping and solder in public and private drinking water supplies in a reasonable time and at a reasonable cost, removal of lead by precipitation as a low solubility solid seems the best

method to limit lead solubility and corrosion rate. The corrosion of lead produces PbO which has a very high solubility at low pH (Fig. 1). In the pH range of most potable waters (5.5 to 7.5) the dissolution of PbO releases Pb^{2+} ions into solution by the reaction:

$$PbO + 2H^+ = Pb^{2+} + H_2O \tag{1}$$

In order to reduce the solubility of lead, Na_2CO_3, Na_3PO_4, and/or Na_2SiO_3 have been added to water supplies to precipitate lead-carbonates, -phosphates, -hydroxides, and -silicates. Sodium silicate additives have been suggested by many researchers as a technique to prevent the corrosion of iron and copper piping (e.g. Dart and Foley, 1970; Lane et al., 1977; Shuldener and Lehrman, 1957; Alexander, 1937; Eliassen et al., 1959; Fujita, et al., 1989; Shuldener and Sussman, 1960), but Thresh (1922) was one of the first to propose sodium silicate additives as a means to control corrosion in lead piping. One effect of the addition of Na_2SiO_3 is to raise the pH of the solutions thus lowering the solubility of PbO (Fig. 1). The Na_2SiO_3 is injected into the flow system at set time intervals at the water treatment facility. With this method, the silica ions are adsorbed onto the pipe surface where they bind with the lead ions to form a corrosion resistant film. This reaction creates a lead silicate by the following equation:

$$Na_2SiO_3 + Pb^{2+} = PbSiO_3 \text{ (am)} + 2Na^+ \tag{2}$$
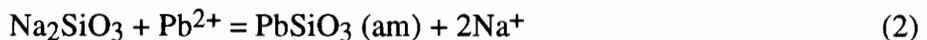
This film is a gelatinous white material that adheres to the pipe walls. The level of silica in the water must be maintained, however, because the films are not permanent and will be scoured and dissolved away (Weldes and Lange, 1969). The effectiveness of this process is a function of pH and the silica concentration; experience shows that above pH 9 the lead silicate is much more efficient in creating a passivation film than at pH 8 (Eliassen and Skrinde, 1960). Eliassen, et al. (1959) concluded that sodium hydroxide additions that produced similar pH levels it did not reduce corrosion as well as the sodium silicate treatment. The usefulness of the Na_2SiO_3 process has been documented for stainless steel, iron, copper and zinc piping, but its effectiveness on lead piping has not been thoroughly
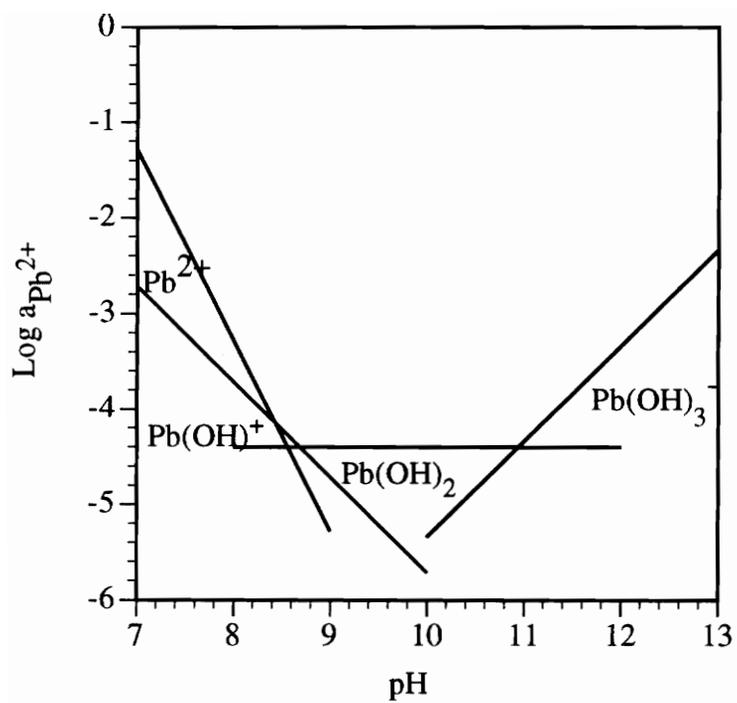
Fig. 1. PbO solubility as a function of pH

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documented (Lane, *et al.*, 1977; Fujita, *et al.*, 1989).

The effect of sodium silicate additives on water pipe corrosion has been documented in many instances (e.g. Eliassen, *et al.*, 1959; Dart and Foley, 1970; Lane *et al.*, 1977; Shuldener and Lehrman, 1957; Alexander, 1937; Eliassen *et al.*, 1959; Fujita, *et al.*, 1989; Shuldener and Sussman, 1960) and most of these studies concluded that the silicates do have an effect on metal solubility beyond the effect of the increased pH that accompanies the addition of the silicates. However, these studies did not address the solubility of any silicate phases that might have formed. The purpose of the present study was to determine the solubility of the lead silicate phase that forms in lead water piping where sodium silicate has been added. The reaction that governs the solubility of $PbSiO_3$ (am) is:

$$PbSiO_3 \text{ (am)} + 2H_2O + 2H^+ = Pb^{2+} + H_4SiO_4 \tag{3}$$
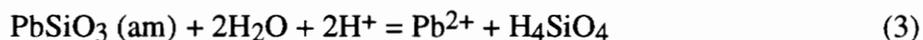
By comparing the solubility of this phase with phases such as phosphates and carbonates that form during the use of other control technologies, more informed judgements can be made about the most effective method to reduce the amount of lead that is dissolved into drinking water from the transport pipes.

METHODS

Synthesis

Amorphous lead silicate with a stoichiometry approximate to $PbSiO_3$ (am) was synthesized by mixing equal volumes of a 0.1 molal lead nitrate ($PbNO_3$) solution adjusted to pH 4 with 4 or 5 drops of concentrated HNO_3 acid and a 0.1 molal sodium silicate (Na_2SiO_3) solution in a 500 mL flask. In this synthesis, the Na_2SiO_3 solution was added with vigorous mixing into the acidified $Pb(NO_3)_2$ solution so the precipitate was always in contact with an acid solution. This procedure avoided the formation lead hydroxycarbonate (hydrocerussite, $Pb_3CO_3(OH)_2$) which readily forms at pH>7.0. After the precipitate settled, the supernatant was decanted, and the precipitate was recovered by vacuum filtration. It was dried for less 6 hours because the amorphous lead silicate reacts fairly rapidly with CO_2 from the atmosphere to form hydrocerussite.

Characterization

The precipitate formed by mixing the Na_2SiO_3 solution into the $Pb(NO_3)_2$ solution was a gelatinous, hydrous material that is milky white in color. It was examined using X-ray diffraction (XRD) prior to dissolution to confirm that it was amorphous. The resulting scan revealed no cystalline compounds but did show a broad peak between 15 and 60° 2θ which is typical of amorphous silicates (Fig. 2). Also, some of the unreacted precipitate was dried in a vacuum oven for approximately 4 hours at pressures of $<10^{-0.7}$ torr. Scanning electron imaging was performed using a Cam Scan Scanning Electron Microscope (SEM) with an Hnu Energy Dispersive System to determine the exact distribution and structure of the substances. Microphotographs of the material were obtained from the SEM, and bulk chemical analyses of the remaining precipitate were performed by determining bulk Pb:Si ratios on a Cameca SX-50 Electron Microprobe. The

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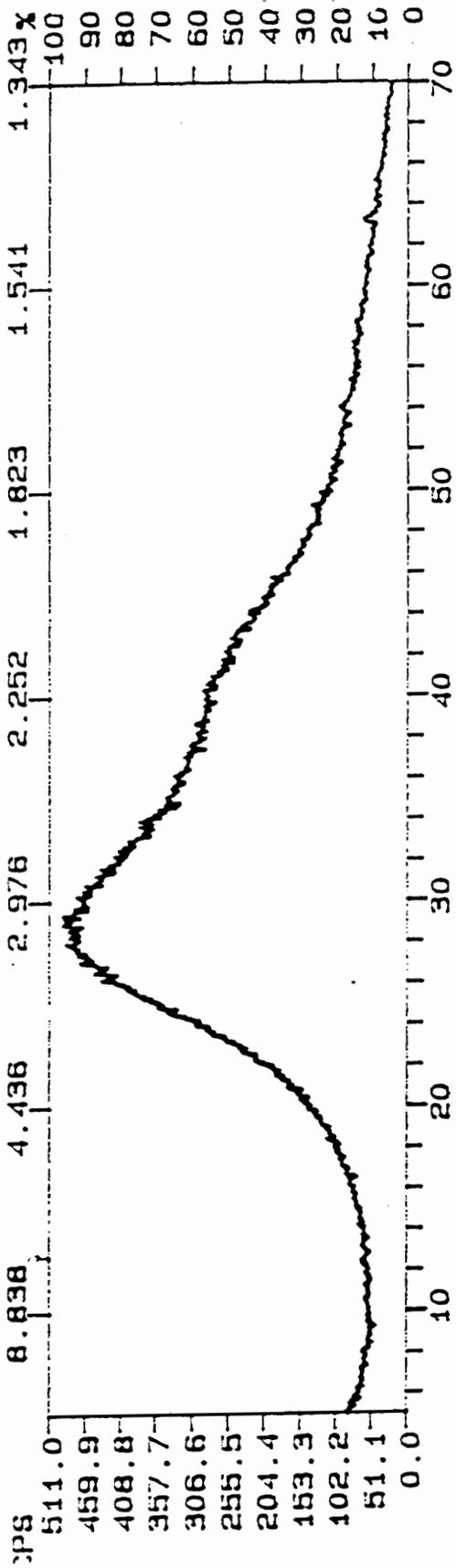
Fig. 2. X-ray diffraction pattern of the amorphous lead silicate phase.

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SEM images revealed highly irregular particles ranging from 2 to 30 microns in diameter (Fig. 3). The sample was then analyzed under the electron microprobe and the Pb:Si ratio determined by the electron microprobe was 1:1 (see analyses in Appendix III.). This material was immediately used in the solubility experiments.

Dissolution Procedure

Nine solubility experiments were performed under different ionic strength and pH conditions in order to simulate the variation in natural water systems. Factorial combinations of three concentrations of HNO_3 solutions (0.001 m, 0.0001 m, and 0.00001 m) and three concentrations of KNO_3 solutions (0.001 m. 0.01 m, and 0.1 m) were prepared to cover a range of ionic strengths and pH (see Table 1). Approximately 0.5 g of the lead silicate was placed in contact with each solution and allowed to reach equilibrium as determined by a constant pH. The dissolution reaction (Eqn 3) consumes hydrogen ions so when the solution pH becomes constant the system has attained equilibrium. These nine mixtures reacted for approximately 8 days during which time the pH stabilized.

The equilibrated solution was recovered and filtered using a 0.1μm syringe filter. XRD patterns were obtained from the precipitate remaining after each experiment. The detection limit for hydrocerussite is approximately 5 weight percent. If the XRD patterns revealed crystalline material (hydrocerussite), the solubility products calculated from those data were excluded from the study.

Analyses and calculations

The silica concentration in each solution was determined using the colorimetric molybdate blue method (from Grovett, 1961, see Appendix I). The uncertainty on these measurements is approximately ±3%. The lead concentration was determined by direct
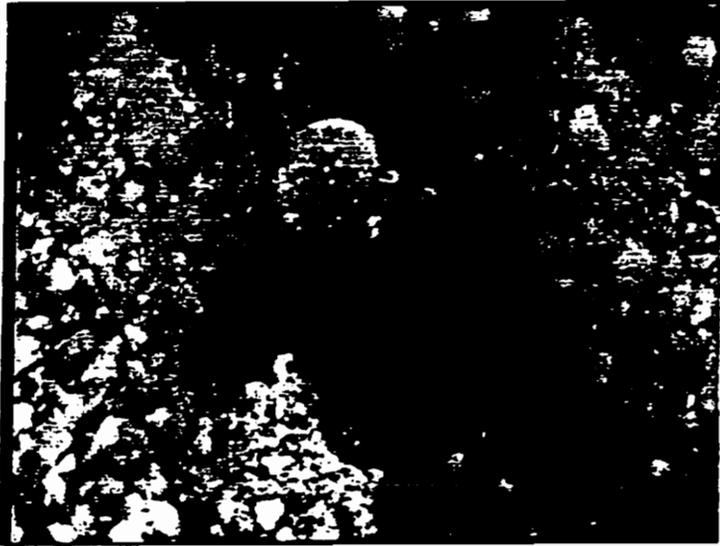
Figure 3. SEM photomicrograph of experimental material

Table 1. Acid concentrations and ionic strength calculations for the experimental solutions

SOLUTION (m_{HNO_3} / m_{KNO_3})	I
0.001 m/ 0.001 m	0.002
0.001 m/ 0.01 m	0.011
0.001 m/ 0.1 m	0.101
0.0001 m/ 0.001 m	0.001
0.0001 m/ 0.01 m	0.010
0.0001 m/ 0.1 m	0.100
0.00001 m/ 0.001 m	0.001
0.00001 m/ 0.01 m	0.010
0.00001 m/ 0.1 m	0.100

aspiration atomic absorption spectrophotometry (see Appendix II). The uncertainty associated with this instrument is $\pm 1\%$. The final ionic strength of the solutions depends on the concentrations of contributing ions which in this case are K^+, NO_3^-, and, to a small extent, Pb^{2+}. The concentrations of H^+ and OH^- are assumed to be approximately zero. Ionic strength was calculated by the following equation:

$$I = \frac{1}{2} \Sigma \left((m)(Z^2) \right) \tag{4}$$

where m is the concentration of the contributing ions and Z is the charge of each ion.

The concentrations of lead, silica and the final pH of the solutions were used to determine the equilibrium constant for the lead silicate dissolution reaction (Eqn 3) by the following equation:

$$K = \frac{\gamma_{Pb^{2+}} m_{Pb^{2+}} \gamma_{H_4SiO_4} m_{H_4SiO_4}}{\gamma_{H^+}^2 m_{H^+}^2} \tag{5}$$

where the activity coefficient for H_4SiO_4 was assumed to equal 1 and the denominator of the equation can be simplified to (10^{-2pH}). The activity coefficient of lead ($\gamma_{Pb^{2+}}$) for each of the nine experiments was calculated using the Debye-Hückel equation:

$$\log \gamma_{Pb^{2+}} = \frac{Az^2\sqrt{I}}{1 + Ba_0\sqrt{I}} \tag{6}$$

where $A = 0.5098$; $z = 2$; $B = 0.3284$; and $a_0 = 5$. A table of the chemical reactions used in this study are given in Table 2. The calculated values of m_{H4SiO4}, m_{Pb2+}, γ_{Pb}^{2+}, and K are listed in Table 3.

Table 2. Reactions considered in this research and their log K values.

Equation:	Log K
$PbSiO_3$ (am) + $\cancel{A}H_2O$ + $2H^+$ = Pb^{2+} + H_4SiO_4	5.87[*]
PbO (s) + $2H^+$ = Pb^{2+} + H_2O	12.72[**]
Pb^{2+} + H_2O = $Pb(OH)^+$ + H^+	-7.71[**]
Pb^{2+} + $2H_2O$ = $Pb(OH)_2$ + $2H^+$	-17.1[**]
Pb^{2+} + $3H_2O$ = $Pb(OH)_3^-$ + $3H^+$	-28.1[**]
H_4SiO_4 = $H_3SiO_4^-$ + H^+	-21.2[***]
H_4SiO_4 = SiO_2 (am) + $2H_2O$	2.97[#]

* this study, ** Baes and Mesmer (1976), *** Naumov, et al. (1974),
# Robie, et al. (1989)

RESULTS

Five of the nine experiments yielded acceptable results that were used to calculate the solubility constants (K) listed in Table 3. The ionic strengths ranged from 0.002 to 0.101. Data from the four experiments not rejected either because there was total dissolution of the solid or because hydrocerussite peaks were observed in the XRD pattern (See Appendix IV). The log K calculated from the experiments ranged from 5.25 to 6.22 and the average was 5.87 with a standard error equal to 0.183.

The free energy of formation of $PbSiO_3$ (am), $\Delta G_f^\circ(PbSiO_3, am)$, was calculated from:

$$\Delta G_f^\circ(PbSiO_3 \text{ am}) = \Delta G_f^\circ (Pb^{2+}) + \Delta G_f^\circ(H_4SiO_4) - (-2.303RT \log K) \qquad (7)$$

where $R = 8.314$ J mol^{-1} and $T = 298.15$ °K. The ΔG_f° values used in this calculation are given in Table 3 and other relevant thermodynamic data are given in Table 4. The calculated ΔG_f° ($PbSiO_3$ am) ranged from -1059.77 kJ mol^{-1} to -1065.34 kJ mol^{-1} with an average of -1061.81 kJ mol^{-1}. This value is bracketed by two values from the literature: Wagman, *et al.*. (1982) reported a value of -1062.10 kJ mol^{-1} for crystalline $PbSiO_3$ (alamosite) and Babushkin, *et al.* (1985) reported a value of -1059.8 kJ mol^{-1} for $PbO \cdot SiO2$ glass. (Table 5).

TABLE 3. Results of $PbSiO_3$ (am) solubility experiments

SOLUTION (HNO₃ / KNO₃)	I	m_{Pb}^{2+}	m_{H4SiO4}	pH	γ_{Pb}^{2+}	K	Log K	ΔG_f $PbSiO_3$ (am)
0.001 / 0.001 m	0.002	1.60×10^{-4}	1.02×10^{-3}	6.24	X	X	X	X
0.001 / 0.01 m	0.011	1.56×10^{-4}	5.97×10^{-4}	6.44	0.654	4.618×10^{5}	5.664	-1062.96
0.001 / 0.1 m	0.101	1.32×10^{-4}	9.91×10^{-4}	6.25	X	X	X	X
0.0001 / 0.001 m	0.001	1.38×10^{-4}	6.86×10^{-4}	6.56	0.849	1.059×10^{6}	6.025	-1060.91
0.0001 / 0.01 m	0.010	1.37×10^{-4}	8.81×10^{-4}	6.66	0.664	1.674×10^{6}	6.224	-1059.77
0.0001 / 0.1 m	0.100	1.37×10^{-4}	7.52×10^{-4}	6.32	0.376	1.770×10^{5}	5.248	-1065.34
0.00001 / 0.001 m	0.001	1.55×10^{-4}	4.33×10^{-4}	6.61	X	X	X	X
0.00001 / 0.01 m	0.010	1.62×10^{-4}	1.19×10^{-3}	6.52	X	X	X	X
0.00001 / 0.1 m	0.100	1.49×10^{-4}	1.21×10^{-3}	6.67	0.376	1.483×10^{6}	6.171	-1060.07
Valid Experimental Average		1.26×10^{-4}	8.25×10^{-4}	6.53	0.584	1.290×10^{6}	5.866 ± 0.183	-1061.81

(X) indicates that the experiment was not used to determine the free energy of formation for $PbSiO_3$ (am) due to the formation of $Pb_2CO_3(OH)_2$ or the total dissolution of the sample as determined by XRD patterns.

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Table 4. Thermodynamic data for lead species considered in this study.

SPECIES	$\Delta H_f°$, kJ mol^{-1}	$S°$, J mol^{-1} K^{-1}	$\Delta G_f°$, kJ mol^{-1}
Pb^{2+} (1)	-1.70	10.50	-24.43
PbO (yellow) (1)	-217.32	68.70	-187.89
PbO (red) (1)	-218.99	66.50	-188.93
H_2O (l) (1)	-285.83	69.91	-237.13
OH$^-$ (1)	-229.99	-10.75	-157.24
$Pb(OH)^+$ (1)			-226.30
$Pb(OH)_2^°$ (1)			-400.80
$Pb(OH)_3^-$ (1)			-575.60
SiO_2 (am) (1)	-903.49	46.9	-850.70
$H_3SiO_4^-$ (2)			-1253.95
H_4SiO_4 (aq) (4)	-1460.	180.	-1308.
$PbO·SiO_2$ (am) (3)			-1059.80
$PbO·SiO_2$ (xtln) (3)			-1066.54
$PbSiO_3$ (am) (1)	-1137.60		
$PbSiO_3$ (alamosite) (1)	-1145.70	109.60	-1062.10
$PbSiO_3$ (am) (this study)			-1061.81

(1) Wagman, et al. (1982), (2) Naumov, et al. (1974), (3) Babushkin, et al. (1985), (4) Robie, et al. (1979).

DISCUSSION

The equilibrium constant for the $PbSiO_3$ (am) dissolution reaction is 7.76×10^5 and the ΔG_f° is -1061.81 kJ mol^{-1}. In theory the solubility of $PbSiO_3$ used in this study should be higher than that of crystalline $PbSiO_3$ (alamosite). The calculation of log K for crystalline $PbSiO_3$ from the free energy data of Wagman, *et al.* (1982) gives a value of 6.61×10^5 based on value of -1062.10 for the ΔG_f°(alamosite). Babushkin, *et al.* (1985) reported a value of ΔG_f° for $PbO \cdot SiO_2$ (glass) of -1059.8 kJ mol^{-1} and a value of -1066.54 kJ mol^{-1} for the ΔG_f° of crystalline $PbSiO_3$. As can be seen in Table 5, the K value determined in this study is virtually identical to the material cited as crystalline $PbSiO_3$ in Wagman, *et al.* (1982) and is only 0.5 orders of magnitude below the K value of $PbO \cdot SiO_2$ (glass) reported by Babushkin, *et al.* (1985). The $PbSiO_3$ (am) created here has a more positive ΔG_f° than the crystalline phases.

The effect of sodium silicate additives on water pipe corrosion has been documented in many instances (e.g. Eliassen, *et al.*, 1959; Dart and Foley, 1970; Lane *et al.*, 1977; Shuldener and Lehrman, 1957; Alexander, 1937; Eliassen *et al.*, 1959; Fujita, *et al.*, 1989; Shuldener and Sussman, 1960). Most of these studies concluded that the silicates do have an effect on metal solubility beyond the effect of the increased pH that accompanies the addition of the silicates. However, these studies did not address the solubility of any silicate phases that might have formed. Shuldener and Sussman (1960) indicate that silicate treatments for water systems are beneficial in reducing corrosion, but stress that design and operating conditions, such as the alkalinity (HCO_3^- content) of the water, can greatly influence the effectiveness of the silicate treatment. Some of these studies have shown the presence of a white gelatinous material similar to the substance created here when Na-silicates have been used to treat potable water in lead piping (Thresh, 1922; Lane, *et al.* 1977); presumably, this material is $PbSiO_3$ (am).

The USEPA drinking water limit MCL of 15 ppb of lead is equivalent to 7.25×10^{-8}

Table 5. Comparison of the $\Delta G_f°(PbSiO_3)$ and $\log K_{eq}$ for the dissolution in water for various forms of $PbSiO_3$.

Phase	ΔG_f (kJ mol^{-1})	$\log K_{eq}$	Source
$PbSiO_3$ (glass)	-1059.80	6.22	Babushkin *et al.* (1985)
$PbSiO_3$ (am)	-1061.81	5.87	this study
$PbSiO_3$ (alamosite)	-1062.10	5.82	Wagman *et al.* (1982)
$PbSiO_3$ (alamosite)	-1066.54	5.04	Babushkin *et al.* (1985)

moles of Pb per kilogram of water (EPA, 1991). Based on Eqn 3, a plot of $\log a_{H_4SiO_4}$ versus $\log (a_{Pb2+}/(a_{H+})^2)$ can be drawn to show the stability fields of the lead species of interest here. As is shown in Fig. 4, in pH 7 water at the MCL of lead, amorphous silica is the stable solid phase. The pH must be increased to at least pH 8 before $PbSiO_3$ (am) becomes stable with this lead concentration. While this shows that lead silicate does become stable, it is rare for water systems to have such high pH values.

Fig. 5 shows that the amount of silica needed as H_4SiO_4 or, equivalently as Na_2SiO_3, to be added to the water supplies to form $PbSiO_3$ (am) depends on pH. It ranges from 1000 moles of silica per kilogram of water at pH 5 down to 0.001 moles per kilogram of water at pH 8. However, Fig. 4 and Fig. 5 also show that below pH~8, the treated water reaches saturation with respect to amorphous silica before forming $PbSiO_3$ (am). Because the pH of drinking waters seldom exceed 7, it is unlikely that adding Na_2SiO_3 to the water supply to form $PbSiO_3$ (am) will be a useful way to reduce the lead content.

Furthermore, there is another reason to question the value of Na_2SiO_3 as an additive. When Na_2SiO_3 is added to water the SiO_3^{2-} hydrolyzes according the reaction:

$$SiO_3^{2-} + H_2O + 2H^+ = H_4SiO_4$$
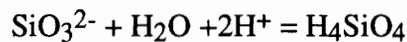
This reaction consumes two moles of H^+ per mole of Na_2SiO_3 added raising the pH and converting HCO_3^- to CO_3^{2-} which causes hydrocerussite ($Pb_2CO_3(OH)_2$), to form. Schock (1990) showed that hydrocerussite commonly occurs in water systems. Because hydrocerussite is so insoluble and because water supplies are exposed to atmospheric carbon dioxide, hydrocerussite will form instead of $PbSiO_3$ (am) at the pH ranges of most potable waters. An earlier study by Thresh (1922) showed that carbon dioxide in solution in excess of 15 ppm resulted in the formation of a very insoluble carbonate phase. The presence of hydrocerussite in my samples supports these findings that hydrocerrusite readily forms around pH 6.5. Hydrocerussite was the only XRD pattern that appeared; no
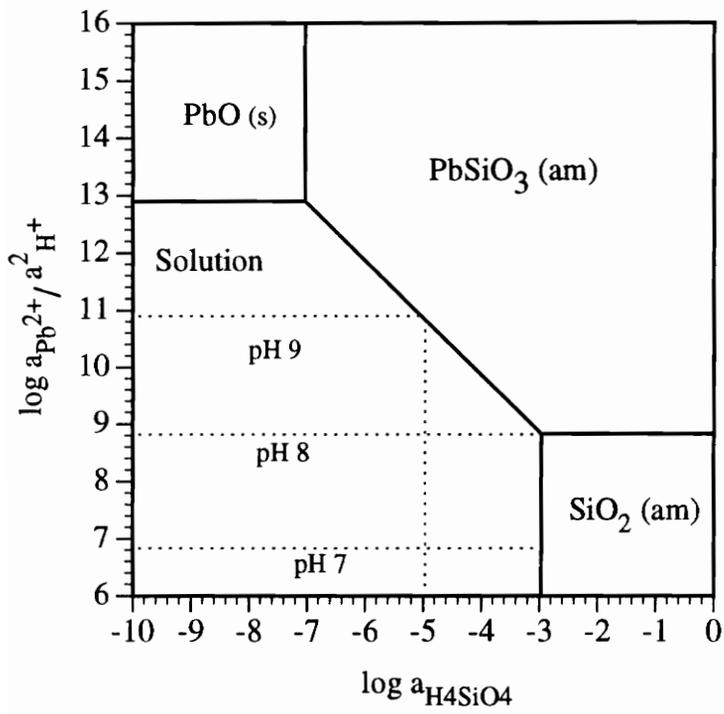
Fig. 4. PbSiO$_3$ (am) activity-activity diagram
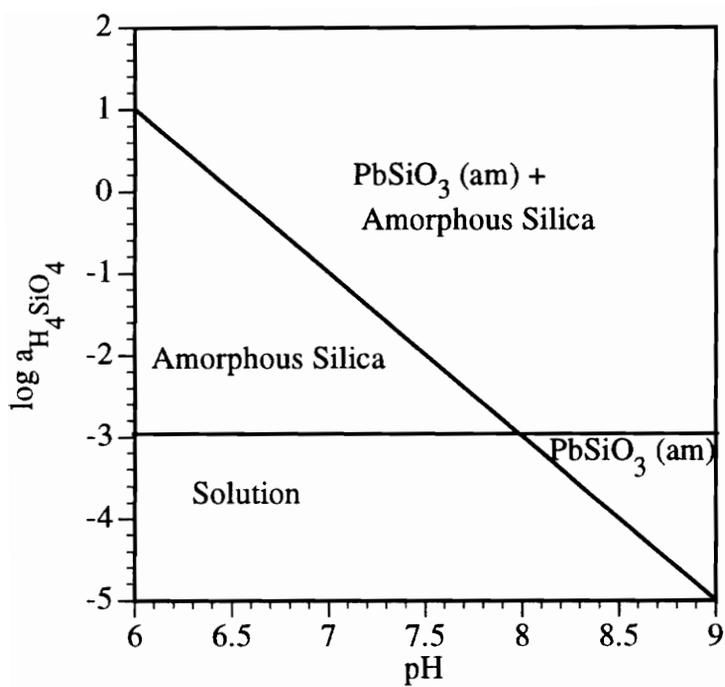
Fig. 5. Activity of H4SiO4 vs.pH for PbSiO$_3$ showing pH range where silica treatment would be effective without precipitation of amorphous silica.

alamosite ($PbSiO_3$, xl) peaks appeared. The solid that is expected to form with a carbonate passivation film in lead piping is cerussite ($PbCO_3$) as predicted by most models (Schock and Wagner, 1985; Schock, 1980; Gregory and Jackson, 1984, Mann and Deutscher, 1980), but there is no evidence for its formation in water piping. Instead, hydrocerussite $Pb_2CO_3(OH)_2$ forms. Also the corresponding solids in zinc and copper piping, copper and zinc hydroxycarbonates have been observed (Schock, 1990). Hydrocerussite controls lead solubility when cerussite is not present and this apparently is what usually occurs.

Because CO_2 is present in commercial and private water lines where Na_2SiO_3 might be added to control pipe corrosion and lead solubility, this technology appears to be an expensive and inefficient way to increase the pH to precipitate hydrocerussite. Schock's (1990) study shows that carbonate phases control lead solubility in most water systems having pH values between 5 and 8. The addition of Na_2CO_3 or lime is just as effective as a lead reduction technology as adding Na_2SiO_3, but these compounds are less expensive.

CONCLUSIONS

The white gelatinous material created by mixing Pb^{2+}-bearing and Na_2SiO_3 solutions is $PbSiO_3$ (am). This material forms when sodium silicate is added to potable waters passing through lead piping to remove the lead from solution. The equilibrium constant for the $PbSiO_3$ (am) dissolution reaction (Eqn 3) is 7.41×10^5 which is very similar to the K for crystalline $PbSiO_3$ (alamosite) and $PbSiO_3$ (glass) calculated from tabulated free energy values in Wagman, et al. (1982) and Babushkin (1985) (Table 2). The relatively high solubility of $PbSiO_3$ found in this study confirms previous studies by Shock (1988) and Schock (1980) that suggested that the addition of sodium silicates is not an effective means of controlling the lead content of drinking waters. In order to maintain lead concentrations at the MCL of 15 ppb, the silica concentrations ranging from 1000 moles of silica per kilogram of water at pH 5 down to 0.001 moles of silica per kilogram of water at pH 8 must be maintained in the water system. Fig. 5 shows that for pH<8 so much Na_2SiO_3 must be added to the water to try to precipitate $PbSiO_3$ that the solution will reach saturation with respect to amorphous silica before $PbSiO_3$ (am) forms.

In addition, the $PbSiO_3$ (am) synthesized in these experiments was quickly contaminated by hydrocerussite because the increased pH caused by the addition of the silicate converts HCO_3^- to CO_3^{2-}. Because hydrocerussite is much less soluble than the $PbSiO_3$ (am), hydrocerussite usually controls the lead concentration in water systems containing lead piping (Schock, 1990). A water system that uses less expensive treatments such as lime (CaO) or sodium carbonate (Na_2CO_3) to raise the pH will precipitate the Pb^{2+} as hydrocerussite just as effectively as ones that use Na_2SiO_3.

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SPECTROPHOTOMETRIC SILICA ASSAY

(After Grovett, 1961)

The silica concentration was determined by obtaining a small sample (~1 mL) of the supernatant from the experiments and using it in a colorimetric method that utilizes ammonium molybdate and a strong reducing agent that results in a blue color. With the spectrophotometer set at a wavelength of 815mµ and a 1 cm pathlength for the cell, the absorbance of the solution was determined. Standard absorbance versus concentration curves were prepared using 5 ppm, 10 ppm, 20 ppm and 25 ppm solutions diluted with distilled, de-ionized water from Fisher Scientific 1000 ppm Silica Standard solution. The average precision of the molybdate blue method is ± 1%.

Instrument: A Bausch & Lomb Spectronic 21-D spectrophotometer with 10 mm cuvettes was used for the spectrophotometric measurements.

Preparation of reagent solutions: Distilled, de-ionized water was used for all dilutions.

Ammonium Molybdate (0.3 M MoO_4^{2-}): Dissolve 52.97 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 900 mL of H_2O and adjust to pH 7-8 with NaOH pellets. (~60 pellets = 14 g. Add slowly after 13 g.) Then fill to 1 L volume. Store in a polyethylene container. Put this solution into a fixed volume 10 mL automatic pipette dispenser as needed for assay.

Sulfuric Acid (1 N): While stirring, add 28 mL of concentrated H_2SO_4 to ~800 mL of H_2O and then dilute to 1 L. Transfer this solution to a fixed volume 10 mL automatic pipette

dispenser as needed for assay.

<u>Reducing Agent</u>: Dissolve 0.5 g of 1-amino-2-napthol-4-sulfonic acid and 1 g of anhydrous sodium sulfite (Na_2SO_3) in 50 mL of distilled, de-ionized H_2O with gentle warming. Combine this solution with a solution of 30 g of $NaHSO_3$ in 150 mL of distilled, de-ionized H_2O. Filter the mixture into an opaque (light-tight) bottle and store at room temperature. Transfer this solution to a 2 mL fixed volume pipette dispenser as needed for assay. Always store in darkness.

Procedure: (for concentrations of 20 µg to 300 µg SiO_2 in sample; $\lambda = 815$ µ)

1. Add sample to a 50 mL Class A volumetric flask.

2. The 1 mL sample is acidified with 10 mL of 1 N H_2SO_4 (giving a pH~2)

3. Add 10 mL of the Ammonium Molybdate reagent.

4. Bring volume to 40 mL with de-ionized water and wait 5 minutes.

5. Then add 2.0 mL of the Reducing Agent. Bring the volume up to 50 mL with de-ionized water and wait for 5 minutes.

6. Read the absorbance from the spectrophotometer.

APPENDIX II

ATOMIC ABSORPTION SPECTROPHOTOMETRIC ANALYSIS FOR LEAD

These analyses were completed using a Buck Scientific Model 200A Atomic Absorption Spectrophotometer Flame System using a mixture of acetylene and air. This procedure provides a coefficient of variation of 0.5-2.0%. Optimal analytical results are obtained when the samples used have an absorbance ranging from 0.1 to 0.5 units. The sensitivity range is about 0.5 μg/mL for 1% absorption.

A standard containing 20 μg/mL Pb has an absorbance of approximately 0.18 units or 34% absorption. This value represents the highest value within the working range for Pb, i.e. the range of values where the plot of concentration vs. absorption is linear, using this process. Each of my samples were diluted 1 : 2 so that linearity was preserved. Betwen 5 and 10 mL of solution were decanted from the dissolution samples and saved for use with this procedure.

Standard solutions were prepared using a commercial Pb concentrated (1000 μg/mL) solution such that the values of the standards bracketed the expected concentration values of Pb in the solute. This involved standards of 5, 10, 15, 20, and 25 ppm Pb. Standards were stored and used for up to one month, then discarded, and new solutions were prepared. The set of standards was aspirated to calibrate the machine. Then the samples were run, with blanks of distilled deionized water being run in between individual samples to insure accuracy of the readings.

As with the moly-blue method for silica, standard absorbance versus concentration curves were calculated and were used to determine the Pb concentration in the dissolution samples.

Appendix III

Chemical Analyses of the Experimental Material

Analyses of lead and silica atomic percentages on the Electron Microprobe.

Analysis	Pb atomic %	Si atomic %	Pb : Si
1	20.08	19.06	1.05
2	18.55	19.85	0.934
3	19.28	19.76	0.976
4	18.41	19.97	0.922
5	19.84	19.13	1.04
6	18.68	19.94	0.937
7	18.94	19.72	0.960
Average	19.11	19.63	0.974

Vita

Cameron Lee Weaver was born on October 2, 1969 in Pinehurst, North Carolina. The author graduated from Pinecrest High School in June 1987 and entered Western Carolina University in September 1987 to obtain a Bachelor of Science Degree in Geology. After graduating in December 1991, the author entered VPI&SU in August 1992 to pursue of a Master of Science Degree in Geology. He completed this thesis in September 1994.