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Sodium silicate impacts on lead release in a blended potable water distribution system

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ABSTRACT

The effects sodium silicate corrosion inhibitor doses (ranging from 3 to 12 mg/L-SiO_2) on lead release were investigated during a pilot study. Samples were taken from a system of copper loops within a pre-existing pilot drinking water distribution system. The source of lead for the loop system was 50/50 lead/tin coupons. Variations in water quality were implemented through blending differing proportions from 3 different source waters; groundwater, surface water, and desalinated water, and studied in four specific blending phases. The study analyzed both total and dissolved lead release while monitoring several other water quality parameters. A non-linear regression model was developed to describe total lead release in terms of dose and water quality. The model suggested that the dose, temperature, alkalinity, chlorides, and pH had an effect on lead release ($R^2 = 0.60$). The response of total lead to silicate suggested that increasing dose significantly decreased lead release. Solubility modeling suggested that hydrocerussite would theoretically exist as the predominant lead solid. The solubility model was compared to lead release data from samples that were given months to approach equilibrium.

Keywords: Sodium silicate; Silica; Corrosion inhibitor; Lead release; Lead and Copper rule

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1. Introduction

The water quality produced from reverse osmosis treatment is generally characterized by a lack of stability when compared to conventional treatment processes. As such, various post treatment strategies may be implemented to mitigate the corrosivity of finished water prior to its release into the distribution system. Of the various methods available for corrosion control, blending and the use of corrosion inhibitors were evaluated during a study that was conducted by the University of Central Florida in collaboration with Tampa Bay Water (TBW). A pilot distribution system that had been previously designed and operated during 2005 [1] was used to evaluate the effects of sodium silicate on controlling lead release. For approximately one year, weekly samples were collected from the pilot distribution system for different blended source waters treated with sodium silicate. This study is intended to expand the literature pertaining to sodium silicate and the effects on lead release. Successful attempts of reducing lead release with sodium silicate have been documented as early as the 1920's [2]. Despite its history of application, there have been few studies documenting quantitative relationships between sodium silicate and lead release. Of the few studies, there remains a general uncertainty regarding how sodium silicate mechanistically affects lead release. Early studies carried out by Lehrman and

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Shuldener assessed the possible mechanism of silica film formations in distribution systems [3]. However, the solid suspensions used during the study did not include lead compounds.

More recent studies have had mixed implications on the effectiveness and role of sodium silicate. Generally, sodium silicate addition has been documented within the literature as beneficial [4–8,10]. However, the association between sodium silicate dose and pH has made it difficult to distinguish between the effects. The beneficial effect of pH increase for lead control has been well documented [9]. Because of the increase in pH associated with sodium silicate addition, some researchers have suggested that the effect essentially equivalent to pH adjustment [11]. It should be noted that some studies have reported that sodium silicate showed little to no improvement in lead control [12,13].

A limited amount of research has been conducted during which a pH-adjusted control was established [6,12]. Pinto et al suggested that, initially, lead levels were reduced primarily because of the increase in pH [6]. However, later observations were described as a consequence of the slow formation of a surface film as suggested by previous studies [14]. MacQuarrie et al [12] found that lead levels were typically higher for the sodium silicate treatment when compared to the pH adjustment.

Although the mechanism describing sodium silicate addition and lead release has not been clearly identified, a general theory speculates that silica may form a protective film on already corroded metal layers through an adsorption mechanism [15,16]. This film supports a diffusion barrier that slows the rate at which the equilibrium of the system is attained with the bulk solution [17]. Schock (2005) sites that there exists no strong evidence that suggests this as the mechanism [4].

The results from the study are presented, while a regression model is provided to quantitatively describe the effects of dose and water quality parameter on lead release. A solubility model was also developed for the study to investigate the possibility of a lead-silicate controlling solid.

2. Experimental methods

2.1. Pilot distribution system

This project used existing facilities from a previous study that examined the effects of varying water quality on metal release [1]. Blended source water was pumped into 14 different pilot distribution systems (PDS) labeled lines 1 to 14. The inhibitor was fed downstream of the PDS. Lines 1 to 14 were hybrid lines that consisted of the pipe materials shown in Table 1. The PDSs were designed to operate at a 2-day hydraulic residence time.

Table 1
Description of pipe materials used in hybrid system (i.e. PDS).

Order of entry	Pipe material	Length (feet)	Nom. diameter (inch)
1st	PVC	20	6
2nd	Lined Cast Iron	20	6
3rd	Unlined Cast Iron	12	6
4th	Galvanized Steel	40	2

Table 2
Blend composition for each phase of operation.

Phase	Time Period	%GW	%SW	%RO	Observations
I	Feb–May 2006	62	27	11	14
II	May–Aug 2006	27	62	11	13
III	Aug–Nov 2006	62	27	11	13
IV	Nov 2006–Feb 2007	40	40	20	12

Upon approaching the effluent sampling port, a portion of effluent water from each PDS line was pumped into a system of copper loops. These copper loops were housed within a non-airconditioned shed. Each copper loop was 30 feet in length and 5/8 inch in diameter, and was thus able to hold approximately 1.8 L of water. One lead/tin coupon was placed between two standard brass fittings within the copper tubing where the coupons remained throughout the study. These lead/tin coupons were located approximately 1 ft from the effluent end of the copper loop system. The copper loops were flushed with approximately 2 gallons of water every morning.

2.2. Blending of source waters

Blends were prepared from various proportions of (1) conventionally treated groundwater (GW), (2) enhanced coagulation-sedimentation-filtration surface water (SW), and (3) desalinated water by reverse osmosis (RO). While the GW and RO were obtained from the project site, SW was obtained from the TBW regional surface water treatment plant.

The project duration was segmented into four phases of operation. The phases represented a difference in blend, and thus a difference in water quality, that was obtained from predetermined ratios of source water. The corresponding ratios of GW, SW, and RO for each phase as well as the weeks of operation (shown as number of observations) are shown in Table 2. Although the ratios for Phase I and Phase III are identical, water quality was somewhat dissimilar as a consequence of seasonal variations with source waters (namely SW).

2.3. Silicate addition

PDS 10, 11, and 12 were treated with sodium silicate inhibitor (Si). The Si used was N-type® sodium silicate solution with a SiO_2/Na_2O weight ratio of 3:22 (PQ Corporation, Valley Forge, Pa.). The solution was diluted and stored in two separate chemical storage tanks that were prepared weekly. One stock tank was designated for PDS 10 (low dose), while the other was designated for PDS 11 and PDS 12 (medium and high dose, respectively). The solutions were diluted to approximately 110 mg/L-SiO_2 for the low dose, and to approximately 220 mg/L-SiO_2 using the low alkalinity RO source water. This protocol prevented the precipitation of calcium carbonate in the stock tank resulting from the alkaline properties of the Si solution. The flow of the inhibitor into the system represented approximately 6% of the total flow for the highest dosing condition. The accuracy for each dose was measured at least twice a week.

Originally doses were established at 10, 20, and 40 mg/L-SiO_2 for PDSs 10, 11, and 12, respectively. However, after the fourth week of operation during Phase I, the doses were lowered to 3, 6, and 12 mg/L-SiO_2 above the silica concentration associated with the blended source water. Lowering the doses was necessary to prevent the precipitation of calcium carbonate in PDS 11 and PDS 12, which had impeded operations early in Phase I.

Neither PDS 13 nor PDS 14 were treated with a corrosion inhibitor. PDS 13 was fed by blended source water with a pH that had been lowered to pH_s with the addition of HCl. The pH_s was typically 0.3 units less than the pH of the blended source waters. PDS 14 represented the blended source water prior to Si addition. Due to the pH relationship between PDS 13 and PDS 14, PDS 14 will be referred to as pH_s+0.3. The resultant pH for PDS 13 and PDS 14 is displayed in Table 5.

2.4. Sampling and data collection

Influent and effluent water quality data was collected weekly from PDSs 1–14 during the first phase of operation. Sampling was limited for some water quality monitoring to a bi-weekly schedule. For analyses conducted at both the field lab and at the UCF lab, the number of replicates assigned represented at least 10% of the samples. Blind duplicates and spikes were taken to represent at least 10% of the samples for selected water quality parameters. The analytical methods performed throughout the study are shown in Tables 3 and 4.

Lead release data was obtained from samples taken directly from the outlet port of the copper loops. During Phase I other water quality parameters were collected from the copper loops as well. Following Phase I, it was

Table 3
Selected water quality parameters and methods performed at university laboratory.

Parameter	Method reference	Method description	MDL
Aluminum	SM 3120B	ICP method	0.001 mg/L
Bicarbonate	SM 2320B	Titration method	5 mg/L
Calcium	SM 3120B	ICP method	0.1 mg/L
Chloride	SM 4110	Ion chromatography with chemical suppression	0.1 mg/L
Color	SM 2120A	Or Hach 8025 Cobalt–Platinate method (with spec)	1 CPU
Conductivity	SM 2510B	Laboratory method	1 µmho/cm
Copper	SM 3120B	ICP method	0.001 mg/L
Iron	SM 3120B	ICP method	0.001 mg/L
Lead	SM 3120B	ICP method	0.001 mg/L
Magnesium	SM 3120B	ICP method	0.1 mg/L
NPDOC	SM 5310C	Persulfate–UV oxidation method	0.1 mg C/L
ORP	SM 4500	Laboratory method	± 1 mV
pH	SM 4500-H^+ B	Electrometric method	± 0.01 pH units
Phosphorus	SM 3120B	ICP method	0.001 mg/L
Silica	SM 3120B	ICP method	0.001 mg/L
Sodium	SM 3120B	ICP method	0.1 mg/L
Solids (TDS)	SM 1030E	Estimation of TDS by major ion sum	1 mg/L
Sulfate	SM 4110	Ion chromatography with chemical suppression	0.1 mg/L
Turbidity	SM 2130B	Nephelometric method	0.01 NTU
UV-254	SM 5910	UV absorption at 254 nm	0.0001 cm^{-1}
Zinc	SM 3120B	ICP method	0.001 mg/L

Table 4
Selected water quality parameters and methods performed at field laboratory.

Parameter	Method reference	Method description	MDL
Alkalinity	SM 2320 B	Titration	5 ppm
Ammonia-N	SM 4500-NH3 C	Membrane Probe method	0.1 ppm
Chloride	SM 4500-Cl^- B	Argentometric titration	1 mg/L
Chlorine, free	SM 4500-Cl G or Hach 8021	DPD colorimetric	0.1 ppm
Chlorine, total	SM 4500-Cl-G or Hach 8167	DPD colorimetric	0.1 ppm
Color, apparent	SM 2120 B	Visual comparison (by spectrometer)	1 CPU
Conductivity	SM 2510 B	Conductivity bridge	1 µmho/cm
Hardness (total, calcium)	SM 2340 C	EDTA titration	5 mg/L
Nitrate	Hach 8192	Cadmium reduction	0.1 mg/L
Nitrite	Hach 8507	Diazotization	0.1 mg/L
Oxygen, Dissolved (DO)	SM 4500-O G	Membrane probe	0.1 mg/L
pH	SM 4500-H^+ B	Electrometric	± 0.01 pH units
Phosphate-P (Reactive)	SM 4500-P E. or Hach 8048	Ascorbic acid method	0.1 mg/L
Silica, SiO_2 (reactive)	SM 4500-SiO_2 or Hach 8185	Molybdosilicate method	0.1 mg/L as SiO_2
Temperature	SM 2550 B	Direct reading	0°C
Turbidity	SM 2130 B	Nephelometric	0.01 NTU
UV254	SM 5910 A	UV spectrometry	0.0001 cm^{-1}

determined that for water quality parameters of interest, such as pH, alkalinity, and inhibitor dose, the differences between the effluent PDS ports and the copper loop outlet ports were insignificant. Thus following Phase I only copper and lead were monitored from the copper loops. These samples were collected following a 6-hour stagnation time that began at approximately 7:00 a.m.

3. Results and Discussion

3.1. Water quality parameters

Water quality parameters that were considered for the regression analysis are shown in Table 5. The quantities shown, represent the range and average for water quality parameters measured in the pH_s, pH_s+0.3, and Si treated PDSs for each phase.

3.2. Dose maintenance

The box plots shown in Figure 1 illustrate the accuracy of the Si target doses during the project as depicted by the mean, 25th and 75th percentiles, and minimum and maximum measurements. The silica concentrations represent the contribution of the inhibitor alone. These concentrations were determined as the amount of silica measured above the background silica concentration of the pH_s+0.3 line. Figure 1 suggests that the targeted doses were significantly different from one another.

It should be noted that Figure 1 does not include data from the first 4 weeks of sample collection. As previously mentioned, the intended doses for silica were originally designated as 10, 20, and 40 mg/L, during which the average doses were 8.4, 21.6, and 43.1 mg/L. However, following the fourth week of operation, the accumulation of a precipitate was found to be impeding the flow for the PDS treated with the high dose. The average pH was 8.7 for the high dose, while the highest alkalinity and hardness occurred during Phase I. Such conditions favored the precipitation of calcium carbonate, and following analysis of an observed reduction in calcium through the system, its presence was confirmed.

3.3. Performance of Si treatment

Table 5 lists the range and average for the release of lead within the system during the study. Analysis for both total and dissolved lead was performed using the ICP method, SM 3120B [18]. The detection limit for the analysis was 1 ppb for Pb. Lead was recorded as 1 ppb rather than zero for measurements that were measured below the detection limit. This approach provided that there would be, at worse, a conservative bias when analyzing the impact of Si.

From the results shown in Table 5, it would appear that Si treatment was generally effective for reducing lead release. For Phases I, II, and III, all the levels of Si treatment performed better than the pH_s (PDS 13) and pH_s+0.3 (PDS 14). For Phase IV, however, an apparent anomaly presented itself within the data for the low dose (PDS 10). The average lead concentration for Phase IV was greater than the pH_S and pH_s+0.3. The maximum observation for the low dose was unusually high as well, perhaps suggesting that the average was skewed by an outlying observation. In order to thoroughly evaluate the differences between treatments, the distribution of the data was assessed using box plots shown in Figure 2.

Table 5
Average and range of lead release and influent water quality parameters

Phase	PDS	Dissolved lead (ppb-Pb)			Total lead (ppb-Pb)			Silica (mg/L-SiO_2)			Alkalinity (mg/L as $CaCO_3$)			pH			Chloride (mg/L)		
		Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max
I	Low dose	1	1	1	1	1	1	12.8	10.0	15.6	160	151	168	8.1	8.0	8.3	43	38	54
	Medium dose	1	1	1	1.4	1	5	16.5	15.8	17.6	160	154	168	8.2	8.0	8.4	45	37	56
	High dose	1	1	1	1	1	1	21.6	19.8	23.5	157	130	165	8.4	8.1	8.6	42	37	53
	pHs	3.9	1	8.2	8.3	1	16.3	10.2	9.8	11.0	143	119	159	7.8	7.5	8.1	69	53	98
	pHs+0.3	1.6	1	6.2	2.4	1	13.3	10.1	9.1	11.2	162	157	168	8.0	7.7	8.2	44	38	55
II	Low dose	1.6	1	4.5	4.1	1	11	7.8	6.3	9.5	105	99	108	8.0	7.8	8.2	63	47	79
	Medium dose	1	1	1	1.1	1	2	11.7	9.7	12.9	106	100	110	8.2	8.0	8.4	63	48	78
	High dose	1	1	1	1	1	1.3	17.2	13.9	19.6	106	100	110	8.4	8.0	8.6	62	50	75
	pHs	4.8	1	10.2	11.6	1	24	4.9	4.0	6.5	92	84	99	7.9	7.4	8.2	83	59	109
	pHs+0.3	3.7	1	10.9	8.4	1	23.1	5.2	4.0	6.6	106	98	114	7.9	7.7	8.1	65	49	79
III	Low dose	5.2	1	13.4	10.1	1	24.4	13.3	10.2	14.4	149	146	150	8.2	7.9	8.4	63	49	70
	Medium dose	1	1	1.3	1.4	1	2.5	17.0	14.9	18.7	150	147	153	8.3	8.0	8.5	64	50	70
	High dose	1	1	1	1.1	1	2.6	22.6	20.2	24.8	147	144	153	8.4	8.1	8.6	63	49	69
	pHs	16.6	2.8	34.8	32.1	4.7	64.2	10.2	8.4	10.9	149	139	158	7.7	7.6	7.8	88	74	123
	pHs+0.3	5.2	1	21.7	10.2	1	36.1	10.5	9.1	11.1	151	142	154	8.1	7.8	8.4	65	50	73
IV	Low dose	5	1	19.5	8.9	1	27.7	9.2	7.8	10.5	122	115	126	8.0	7.7	8.2	57	48	62
	Medium dose	1	1	1.2	1.2	1	1.6	13.1	12.4	13.8	123	116	126	8.2	7.8	8.4	56	46	62
	High dose	1.1	1	1.6	1.1	1	2.2	17.7	16.1	18.6	123	116	125	8.4	8.0	8.6	55	47	61
	pHs	2.7	1	6.8	4.3	1	9.4	6.3	5.5	7.0	119	108	131	7.6	7.5	7.8	68	49	87
	pHs+0.3	1.7	1	5.2	3.4	1	13.6	6.3	5.4	7.0	125	118	132	7.9	7.6	8.1	58	44	65

Phase	PDS	Sulfate (mg/L as SO_4)			Calcium (mg/L as Ca)			Sodium (mg/L)			Total chlorine (mg/L as Cl_2)			UV$_{254}$ (cm^{-1})			DO (mg/L as O_2)			Temperature (°C)		
		Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max
I	Low dose	59	52	67	73	71	76	6.9	5.3	8.7	4.2	2.6	5.1	0.08	0.06	0.09	8.5	7.7	9.5	23.1	14.6	27.5
	Medium dose	59	52	65	72	70	75	7.3	5.4	9.2	4.3	2.6	6.1	0.07	0.05	0.08	8.4	7.6	9.5	22.9	14.5	27.4
	High dose	57	52	63	69	63	72	7.2	5.6	9.0	4.2	2.0	5.4	0.07	0.06	0.08	8.5	7.7	9.4	23.1	14.7	27.3
	pHs	61	54	66	75	72	81	8.5	5.5	12.2	4.1	3.0	5.6	0.07	0.06	0.08	8.6	7.9	9.6	23.2	16.4	27.3
	pHs+0.3	61	54	67	75	72	82	6.9	5.2	8.8	4.3	2.8	5.3	0.08	0.06	0.08	8.5	7.6	9.4	23.2	16.1	27.4
II	Low dose	101	93	110	70	66	75	34.9	8.8	45.7	5.8	4.2	7.0	0.07	0.06	0.08	7.7	7.3	8.3	26.3	23.2	28.0
	Medium dose	100	91	111	71	68	75	36.3	8.8	46.6	5.7	4.3	6.9	0.07	0.06	0.08	7.6	7.3	8.3	26.6	23.3	29.5
	High dose	98	92	108	70	65	76	36.4	8.8	46.4	5.7	4.5	6.5	0.07	0.06	0.08	7.7	7.3	8.3	26.1	21.9	29.6
	pHs	100	94	105	72	66	76	45.0	8.9	64.4	5.6	3.8	6.3	0.08	0.06	0.09	7.5	7.4	7.9	26.4	22.1	29.7
	pHs+0.3	102	97	115	72	66	79	36.4	8.4	44.2	5.9	4.5	6.8	0.08	0.06	0.09	7.6	7.2	8.4	26.5	23.6	29.0
III	Low dose	65	55	73	77	74	81	38.0	30.6	42.0	5.4	3.7	6.5	0.08	0.07	0.10	7.7	6.8	8.1	25.9	22.9	28.2
	Medium dose	65	54	73	75	73	77	38.5	30.7	43.4	5.3	3.6	6.3	0.08	0.07	0.10	7.5	6.7	8.0	26.1	22.9	28.1
	High dose	64	54	72	71	69	72	38.4	31.4	44.4	5.4	3.8	6.4	0.08	0.07	0.10	7.6	6.8	8.0	26.1	22.9	28.5
	pHs	66	58	74	75	72	79	51.0	34.8	72.7	4.8	3.2	6.7	0.08	0.06	0.09	7.9	6.7	9.2	25.3	19.9	28.3
	pHs+0.3	67	56	76	78	70	84	41.2	27.7	92.3	5.4	3.8	6.6	0.08	0.05	0.10	7.7	6.6	9.3	25.6	20.7	28.1
IV	Low dose	73	68	76	55	48	61	31.1	24.8	35.4	4.8	3.9	6.0	0.07	0.06	0.07	8.9	8.3	9.5	21.1	16.4	24.3
	Medium dose	73	68	77	54	48	61	31.0	23.1	35.9	4.8	3.4	6.0	0.07	0.06	0.07	8.9	8.2	9.5	21.0	16.3	24.2
	High dose	73	72	74	53	47	60	31.1	24.8	35.2	4.9	3.7	6.0	0.07	0.06	0.07	8.8	8.1	9.2	21.1	16.4	24.2
	pHs	76	70	78	57	47	68	33.2	19.4	40.9	4.2	3.7	4.9	0.06	0.04	0.08	8.9	8.2	9.6	21.0	15.6	24.0
	pHs+0.3	76	72	79	58	50	67	31.9	23.6	35.7	4.8	3.7	6.3	0.07	0.05	0.08	8.9	8.3	9.2	21.3	16.0	24.0

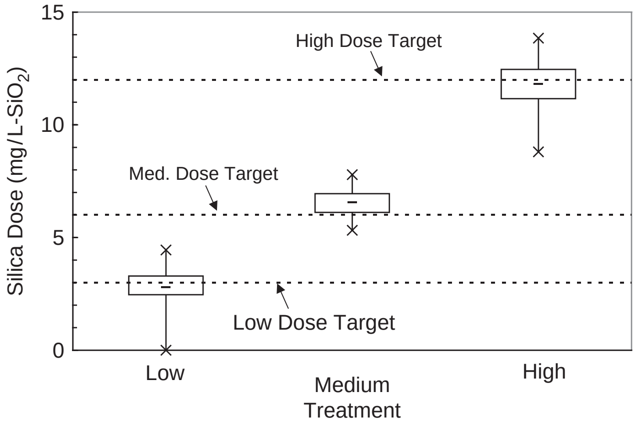

Fig. 1. Si addition for all phases.

The box plots shown in Figure 2 depict the mean, minimum and maximum observations, and the 25th and 75th percentiles of each treatment when applicable. Since lead release is regulated as a percentile rather than a mean average, Figure 2 may be used to assess the performance relative to the action level (shown as Lead Action Level) as well as the pH_s and pH_s+0.3 lines. Note that the USEPA Lead and Copper Rule (LCR) states that the 90th percentile of a sample should not exceed 0.015 mg/L, 15 ppb, as Pb [19] .

Both Phase I and Phase II clearly suggest that the Si-treated system operated well within the limits stated by the LCR. Phase I appears to have been the most effective of the phases; however, this may be a result of the early stages of treatment for Phase I. The initial doses of 10, 20, and 40 mg/L as SiO_2 were applied for weeks 1 through 5. In an effort to minimize bias that may have been introduced by the precipitation of calcium carbonate during those initial weeks, the data associated with that event was not included in Figure 2. The lead release for the initial weeks of the study can be seen in Figure 3. The time-series plot demonstrates the trend in lead release following the first five weeks of Phase I as well. Following the fifth week, it appears that lead release was relatively stable for the remainder of Phase I.

For Phase III and Phase IV, the trend between lead release and Si dose remained similar to that of prior phases. However, contrary to the trend, the low dose appears to be worse than pH_s and pH_s+0.3. A paired *t*-test between the low dose and pH adjusted for Phase III indicated that there was no significant statistical evidence to suggest that the collection of observations

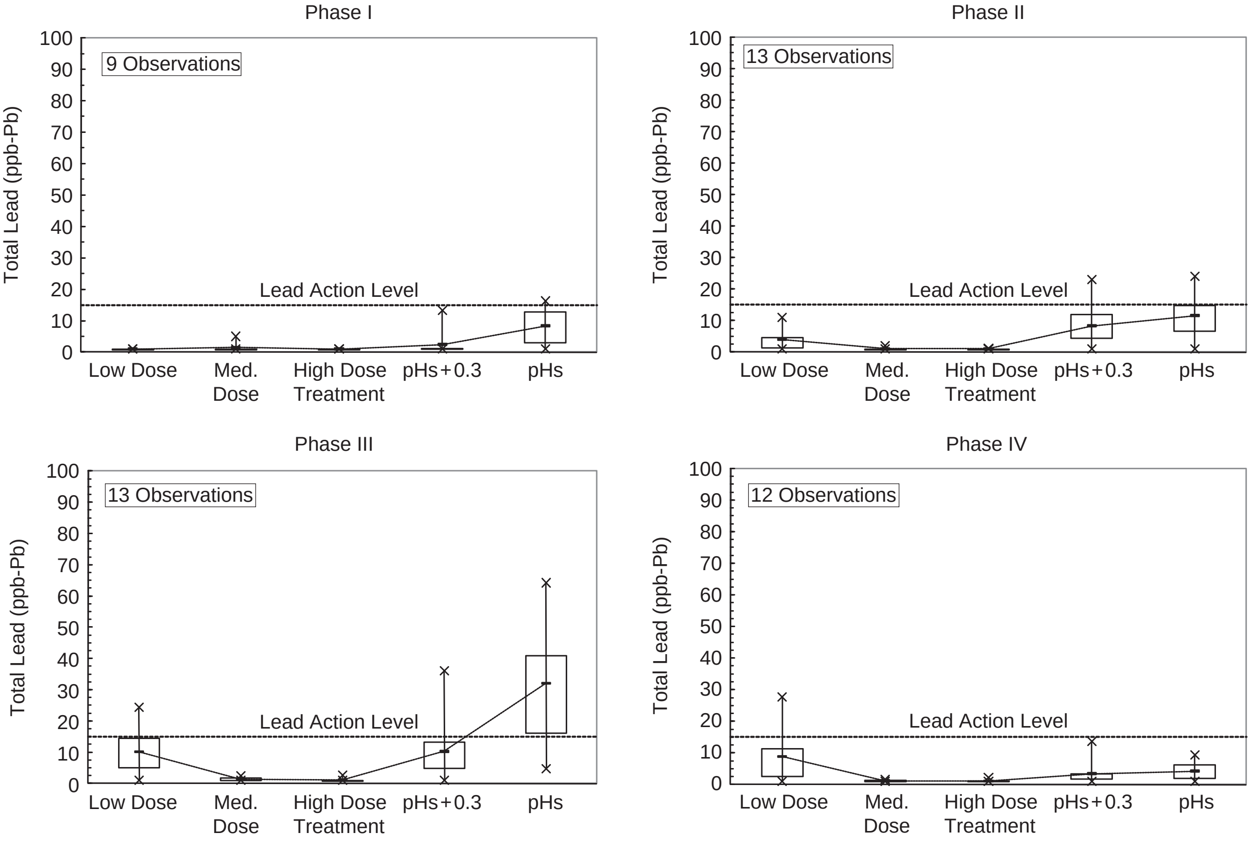

Fig. 2. Total lead release for Si treated and control PDSs.

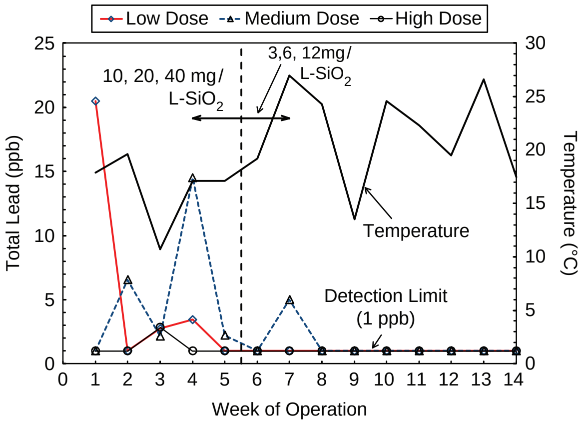

Fig. 3. Time-series plot of lead release for Si treated PDSs during Phase I.

differed. However, the same method applied to Phase IV suggested, with relatively high confidence, that the low dose was greater than the pH adjusted treatment (p-value of 0.01).

One possible explanation for this observed anomaly was the stabilization of a complex associated with a silicate-based ligand. However, literature provides no evidence supporting the presence of such a species. Further investigation was conducted to determine if there was some response to a change in operations. There was no indication of a significant difference in variance between phases for the silica concentration. Similar analysis of the effluent pH also suggested no significant difference.

An interesting difference between Phase IV and the other phases was found while conducting a qualitative assessment of data independence. Although it appeared that control was not violated through variance disparities, the effluent pH data hinted on a consistent rising trend as the weeks progressed for Phase IV. There was no evidence that Phases I, II, and III were significantly dependent of the duration of the study. This was verified through linear regression techniques to determine the statistical significant of each respective slope. For Phase IV, the pH_s+0.3 line data suggested that the effluent pH may have been dependent on project duration (p-value < 0.001 and $R^2 = 0.85$).

3.4. Dissolved fraction of lead

Statistical comparisons between phases determined that there was insufficient evidence to suggest a difference in the percentage of dissolved lead between phases. Percentages were obtained only from observations in which both the total and dissolved lead concentrations were defined (i.e. greater than the detection limit). The measurements suggested that dissolved lead represents approximately half of the total concentration. It was not possible to verify this claim for the medium and high Si dose (PDS 11 and PDS 12). There were no observations in which both the dissolved and total lead concentrations were above detection limit for PDS 12. While only five observations satisfied the criteria for PDS 11, likely allowing only extreme, and thereby possibly misrepresentative, observations to provide an estimate of the dissolved fraction. The average percentage for PDS 11 was approximately 75%.

3.5. Solubility modeling

Corrosion of lead often results in the formation of a passivating scale that may govern the release of soluble lead species into the bulk. Prior surface characterization analysis of the lead coupons within the pilot system had identified PbO, $Pb(OH)_2$, $PbCO_3$, and $Pb_3(CO_3)_2(OH)_2$ scales [20]. These solids were thereby considered in the development of an equilibrium model. The soluble species considered during the development of this model were Pb^{2+}, $Pb(OH)^+$, $Pb(OH)_2^0$, $Pb(OH)_3^-$, $Pb(OH)_4^{2-}$, $PbHCO_3^+$, $PbCO_3^0$, and $Pb(CO_3)_2^{2-}$. Although the selection of complexes was not limited to the choices previously stated, incorporation of any other complexes cited by the literature proved to be insignificant (e.g. $PbSO_4^0$).

Figure 4 represents a pe–pH diagram varied across a range of alkalinities. It should be noted that the alkalinity shown in the figure is intended to establish a C_T specifically at a pH of 8.0, thus the alkalinity and pH axes are independent. The diagram was developed while assuming a constant total soluble species concentration (Pb_T) of 10^{-6} M. This concentration corresponds to a concentration of 207 ppb as Pb. Although this may seem relatively high when compared to the data previously presented, this concentration is more appropriate for a system that has reached equilibrium with the entire bulk as has been described by Pinto and coworkers [6]. Since the source of lead within the copper loops accounted for a small fraction of the total copper loop surface area, the process was diffusion limited. Thus, the solubility modeling within this section is limited to an equilibrated system and is not intended to describe kinetic properties.

The shaded cube shown in Figure 4 represents the region of the diagram that would be typical of the conditions experienced in this study. The pH spans from 7.5 to 8.5, while the pe spans from 9.0 to 12.5 (determined from the 5th and 95th percentiles of the ORP measurements during the study). Hydrocerussite is the predominant form of scale as suggested by the pe–pH diagram. Note that the development of the diagram

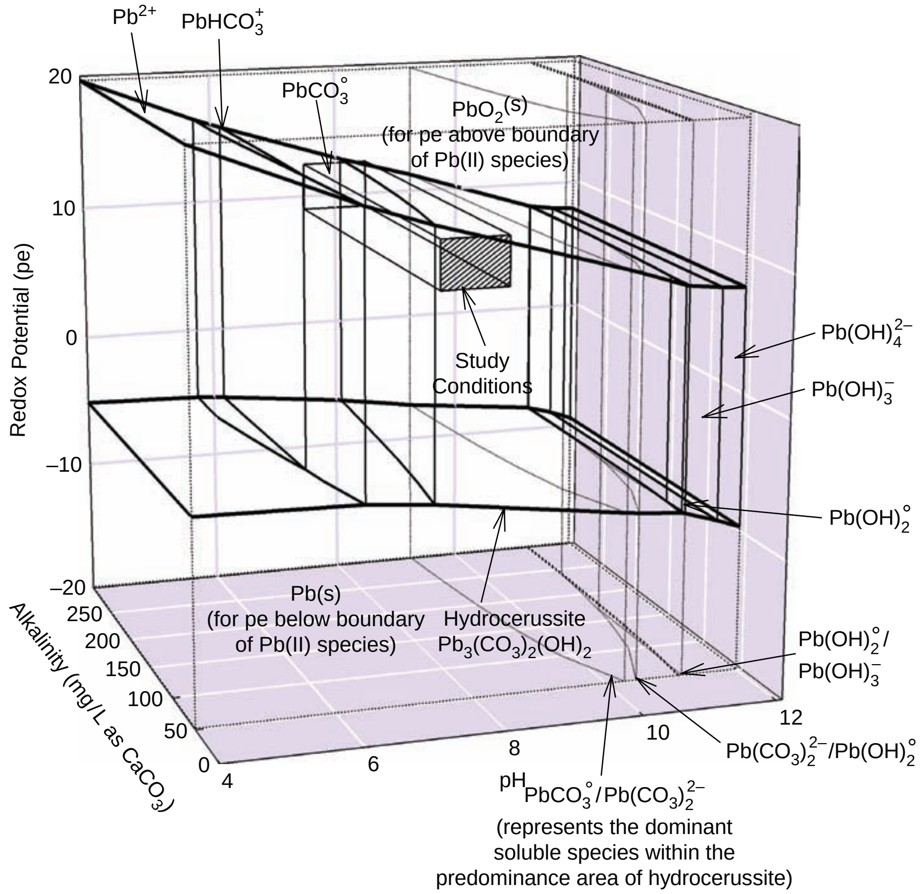

Fig. 4. pe–pH equilibrium diagram for lead species, $Pb_T = 10^{-6}$ M.

considered the Pb(II) silicate solids referenced during research affiliated with USEPA [9]. The reactions of these solids are written as follows:

$$PbSiO_3\,(s) + H_2O + 2H^+ = Pb^{2+} + Si\,(OH)_4 \qquad (1)$$

$$Pb_2SiO_4\,(s) + 4H^+ = 2Pb^{2+} + Si\,(OH)_4 \qquad (2)$$

As implied from Figure 4, there was no thermodynamic evidence to suggest that these solids persisted during the study. This analysis was further extended beyond project conditions spanning a pH of 4–12, and still found no indication of $PbSiO_3$(s) or Pb_2SiO_4(s). Possibilities with respect to scale formation include the following: (1) the equilibrium constants used for $PbSiO_3$(s) and $PbSiO_4$(s) are inaccurate for the conditions applied, (2) a Pb(II) silicate exists, however, there is no data pertaining to it found within the literature, and (3) the effect of silicate is inconsistent with Pb(II) silicate scale formation. The literature provides inconsistent conclusions that fail to resolve the limitations of thermodynamically predicting a Pb(II) silicate solid. Shock and Wagner (1985) could not identify any solids on a pipe treated with silicate, however, hydrocerussite was found on the control loop for that same experiment [10]. Silicate has been found to have little to no effect on the release of lead for a constant pH, implying the effect may be attributed to the pH increase [12,13]. Unfortunately, no surface analyses were conducted during these studies to confirm these findings.

Lead release as governed by hydrocerussite was plotted as a log C-pH diagram with varying C_T (alkalinity used as a surrogate) and compared to the data from the study. The model was adjusted to approximate the conditions rendered by the diffusion properties of lead release in the system. The following expression was used to describe the lead concentration at distance x from the lead coupon in the copper loops.

$$C_x = C_S\left(1 - erf\left(\frac{x}{\sqrt{4D_{eff}t}}\right)\right) \qquad (3)$$

where C_x is the concentration at distance x and during time t, and C_S is Pb_T at equilibrium. Since the lead coupon

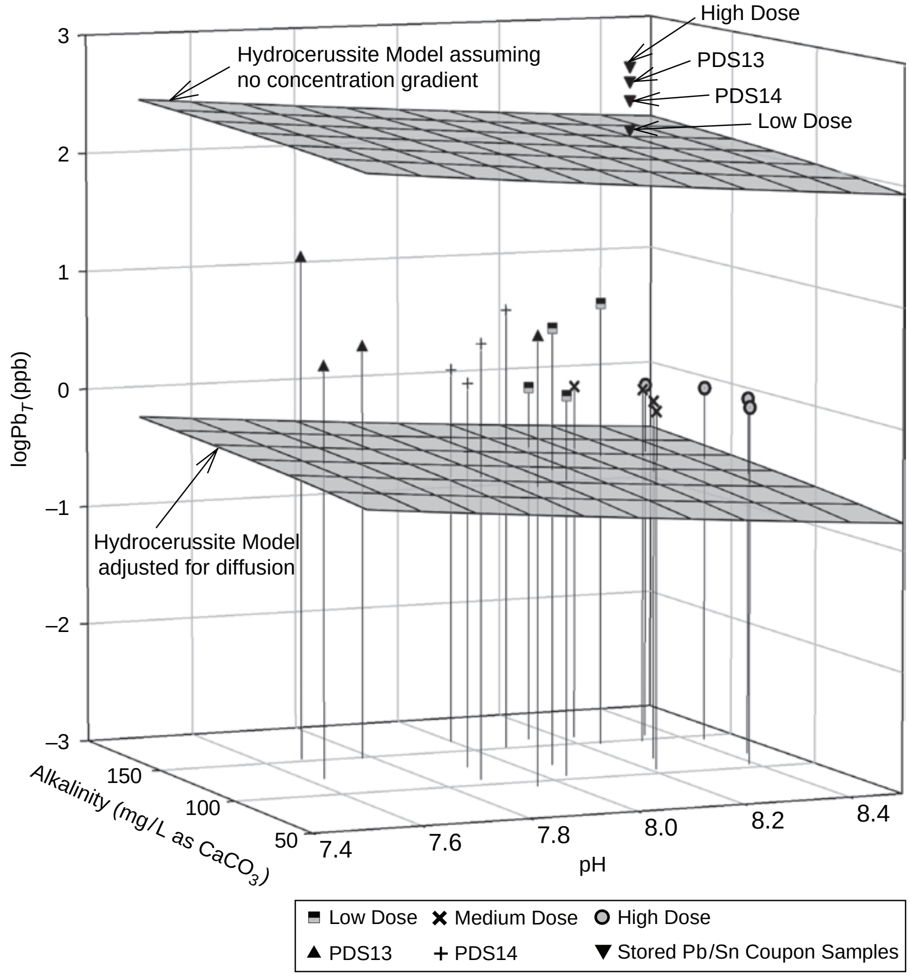

Fig. 5. Hydrocerussite model comparison to actual conditions.

is placed approximately 1 foot (0.3 m) from the sample port, and a typical 1 L sample represents approximately 5 m of drawn sample, the lead collected within a sample represents lead that has diffused both toward the sample port and entry point of the copper tubing. Given a 1 L sample, the concentration of that sample was estimated using the previous relationship as follows.

$$\begin{aligned} dM &= C_x dV = AC_x dx \\ &= AC_S\left(1 - erf\left(x'\right)\right)dx \text{ or } AC_S\, f\left(x'\right)dx \end{aligned} \tag{4}$$

The total mass is thus,

$$\begin{aligned} M &= AC_S\left\{\int_0^{0.3\,m} f\left(x'\right) + \int_0^{4.7\,m} f\left(x'\right)\right\} \\ \Rightarrow C_{sample} &= \frac{M}{AL} = \frac{C_S}{L}\left\{\int_0^{0.3\,m} f\left(x'\right) + \int_0^{4.7\,m} f\left(x'\right)\right\} \end{aligned} \tag{5}$$

where M represents the mass of lead, V represents the volume of the sample, and A represents the area of the copper pipe. Equation 3 is substituted into C_x, and x' defines $\frac{x}{\sqrt{4D_{eff}t}}$. The variable L, represents the length from which the sample is drawn (5 m). Since $\int_0^{0.3m} f(x')$ and $\int_0^{4.7m} f(x')$ are essentially identical after 6 hours,

$$C_{sample} = \frac{2\int_0^{0.3m} f(x')}{L} C_S \tag{6}$$

A numerical approximation of this relationship suggests that with a 1 L sample, and after a stagnation time of 6 hours, $C_{sample} = 0.002C_S$. This relationship was used to adjust the predicted equilibrium concentrations from the hydrocerussite model to the expected concentrations under the conditions previously discussed. The resulting lead release models are shown in Figure 5. The model represents the summation of the lead species assumed during the description of the pe–pH diagram. Data from the study are shown in Figure 5 as well. Two sets of data are compared against the lead release models. One set of data, shown as the up-side down triangles, represents dissolved lead measurements from lead coupon samples following a storage period of approximately one year. The other set of data represents the average dissolved lead data collected from the pilot distribution system for each phase. Data recorded below detection limit was designated as 1 ppb.

The data points labeled as stored Pb/Sn coupon samples represent measurements taken after Phase III. These lead coupons were stored in air-tight plastic containers that were filled with water drawn from the PDS of each respective lead coupon treatment. Given the long stagnation time and small volume of the container (100 mL), it was clear that these measurements would more accurately reflect the equilibrium concentration. Only the pH and dissolved lead was able to be measured because of the small amount of sample available. These measurements suggested that the pH difference between the samples was no longer significant after one year of storage. The pH was approximately 8.3 for all samples. In order to display the lead release from the stored coupons on Figure 5, the alkalinity was assumed to be the average alkalinity of Phase III for each treatment with a pH of 8.3.

The hydrocerussite model shown as Figure 5 predicted much higher lead release than was observed during the study. Since this model represents a system in equilibrium, these results were expected from a system that had not reached equilibrium. Adjustment of the same model dramatically underestimated lead release in the system. Since the hydrocerussite model appears to describe the pH_s and pH_s+0.3 lines just as well as the data representing the Si treatment, there still remains the possibility that hydrocerussite may maintain its role as the controlling solid phase following Si treatment.

Perhaps the most intriguing observation from Figure 5 is the relationship for data of the equilibrated samples (i.e. stored Pb/Sn coupon samples). The insignificant difference in pH between the samples implies that the effect of silicate can be isolated. Prior to these measurements, all other analyses were forced to tolerate the confounding relationship between Si dose and pH. As can be seen from the stored coupons, lead release responded differently from the typical trends observed during the study. For instance, the high dose appears to provide no benefit to controlling lead, whereas the low dose was the most effective treatment. Notice also that the difference in lead release between the treatments was not as significant as that observed during the study. Observations from the study suggest that lead release was consistently decreased by approximately an order of magnitude for the high dose. The analysis suggests that hydrocerussite may be controlling lead release for the conditions evaluated in this pilot study. It should be noted that the accuracy of solubility models depend on (1) the reliability of the equilibrium constants for the conditions of the study, (2) an adequate representation of the aqueous species that are actually present, and (3) the form and solubility properties of the controlling solid phase.

3.6. Empirical modeling of lead release

The release of total lead may be described by Equation 7. A series of stepwise methods were used to identify variables that were significant to at least $\alpha = 0.05$. All of the water quality parameters shown in Table 5 were investigated on a stepwise basis. A power model was used so that the temperature could be modeled as an exponent of some constant. Note the *Dose* term from Equation 7 includes the addition of the number 1. This provides a numerical convenience for the power model when dealing with *Dose* values of zero. The use of the Si dose, rather than the combined concentration of background silica and the Si inhibitor, was founded on evidence pertaining to an analysis of copper release during Si treatment [21]. The analysis suggested that the effect of the Si inhibitor was much more significant than that of the background silica. This was necessary for incorporating the pH_s and pH_s+0.3 data into the regressional analysis. The overall ANOVA for the model was significant, as were the estimated constants (p-values < 0.008). The R^2 value was 0.60 for the empirical model.

$$\text{Total Pb} = 1.15^{(T-25)} \left\{ \left(\text{Dose}_{SIO_2}+1\right)^{-0.45} \left(\text{pH}\right)^{-6.72} \left(\text{Alk}\right)^{1.90} \left(\text{Cl}\right)^{1.63} \right\} \tag{7}$$

where
Total Pb = total lead, ppb
Dose SiO_2 = silica concentration above background, mg/L-SiO_2
pH = $-\log[H^+]$
Alk = alkalinity, mg/L as $CaCO_3$
Cl = chloride, mg/L
T = temperature, °C

Equation 7 agrees with the observed relationship between Si dose and total lead release. This relationship is implied by the negative exponent for the dose variable. The magnitude of this exponent does not account for the full effect of Si dose on lead release. Instead it is the combined effect of Si dose and pH that best defines the effects of Si treatment within the system. Since the pH of the lines treated with Si was significantly dependent (i.e. confounded) on Si dose, the isolated effect of Si dose remains unclear. Reversing this idea, the isolated effect of pH associated with the Si lines is unclear as well. However, from the concepts of regressional analysis, the individual effect of pH that is shown in Eqn. 7 has a more valid estimate. This was because the pH_s and pH_s+0.3 lines were maintained to have a different pH. Thus the difference in lead release observed between PDS 13 and PDS 14 may be essentially regarded as a pH effect.

Equation 7 also identifies chloride, alkalinity, and temperature as the other significant water quality parameters affecting lead release, all of which the model implies are not beneficial within the water quality range of this study. It should be apparent from the actual data shown in Figure 2 that the variation in lead release between phases was more salient for the pH_s and pH_s+0.3 lines rather than for Si treated lines. Thus, the model should not be expected to accurately reflect the magnitude of water quality effects for Si. The model may be more appropriately understood as a compromise between data sets for the Si treated lines and the pH_s and pH_s+0.3 lines.

Phase I and Phase III of the study were intended to have the same blend composition. The only water quality parameter that was expected to differ between Phase I and Phase III was temperature. Thus the increase in lead release observed during operation of Phase III should represent the isolated effect of temperature. However, there was a difference in chloride between Phase I and Phase III due to seasonal variations of the surface water. During Phase III, chlorides were greater than during Phase I. If it had been lesser, then the effect of temperature would have been more clear. Instead, because both temperature and chlorides impart an undesirable effect, the increase in lead release during Phase III represents a combination of effects that may not be analyzed separately.

It should be noted that the significance of chloride may be a result of the consistent chloride difference between the pH_s and pH_s+0.3 lines. As previously explained, the pH of the blend for the pH_s line was lowered through addition of hydrochloric acid. As a consequence, the chloride concentration for the pH_s line was significantly higher than the pH_s+0.3 line.

The role of alkalinity may be associated with complex formation and scale formation if the controlling solid phase is lead carbonate-based. Regardless of the solid phase, Pb^{2+} governed by the solid has the potential to strongly coordinate with HCO_3^- and CO_3^{2-}. Equilibrium modeling for Figure 5 suggests, within the depicted range, that Pb(II) carbonate-based complexes account for greater than 90% of Pb_T. Thus, the dominant effect of C_T would likely be an increase in lead release, regardless of the solid phase present.

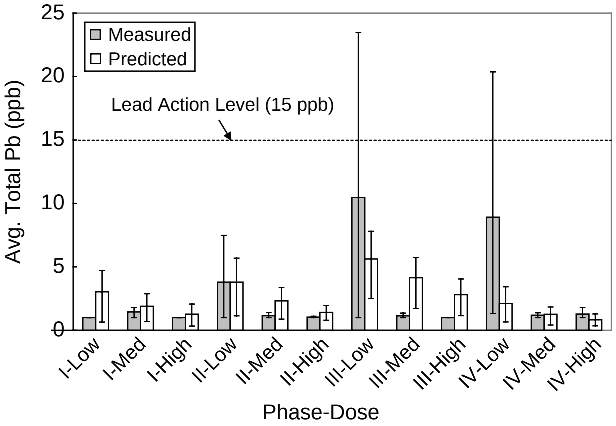

Fig. 6. Total lead release summary for Si treated samples by phase.

The overall performance of Eqn. 7 can be seen from the assessment of Figure 6. Figure 6 represents a comparison of average prediction and average measurements of lead release from the study. The upper limit whiskers represent the estimated 90th percentile from the predicted and measured lead release data, while the lower limit whiskers represent the minimum lead release value from the predicted and measured data. The model predicts the mitigating trends seen as the dose is increased as indicated by the negative exponent on the dose term. The trend is apparent from Figure 6.

The model fails to account for the violations observed for the low dose during Phase III and Phase IV. However, this data seemed anomalous, especially given the fact that the low dose performed worse than the blend despite consistently having a higher pH. For the medium and high doses the predicted data seems to have been overestimated due to the water quality effects established in the model. Since data was generally collected biweekly for the Si lines, while pH_s and pH_s+0.3 lines were collected weekly, there was a bias within the data set that favored the water quality terms corresponding to the lines not treated with Si.

4. Conclusions

Total lead release data collected during this study indicated that lead release can be effectively controlled with proper dosing of sodium silicate. Specific findings included:

- Data from this study generally suggested that reduction of lead release continued as the Si dose increased and was generally more effective than no treatment.

- PDSs that were treated with 6 and 12 mg/L-SiO_2 operated below the regulatory action level for the four phases of the pilot study.
- The pe–pH diagram suggested that the Pb(II) silicates, Pb_2SiO_3 and $PbSiO_4$, were not thermodynamically favorable. Instead, it suggested that hydrocerussite was favorable.
- Based on the solubility model, lead release could be governed by hydrocerussite in a system treated with Si.
- Empirical modeling of the data set suggested that temperature, alkalinity, chlorides, and pH had an effect on the release of lead during the study, along with the dose of Si. Note that the empirical model should be regarded simply as a tool for predicting lead release within a system of water quality similar to the study. Implications of the empirical model are not necessarily directly causal, and should not be used to propose a mechanism.

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