CDM

Case Studies in the Integrated Use of Scale Analyses to Solve Lead Problems

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Presentation Outline

- Background
  - Pb control mechanisms
  - Limitations of “conventional” methods of analysis
- Techniques for characterization of pipe scales
- Case study details – three categories:
  - Predictive
  - Diagnostic/forensic
  - Tracking changes

Pb Control Mechanisms

- <u>All</u> methods involve immobilizing lead into relatively insoluble compounds (pipe deposits)
- Many different solid phases can form:
  - Carbonates – pH/alkalinity adjustment
  - Phosphates – orthophosphate
  - Silicates??
- Examples:
  - Basic Pb(II) carbonate = $Pb_3(CO_3)_2(OH)_2$
  - Pb(II) orthophosphate = $Pb_5(PO_4)_3OH$
  - Pb(IV) oxide = PbO_2

Pb Control Mechanisms *(continued)*

- Distribution system water quality parameters can vary and affect scale formation and composition:
  - Natural water quality fluctuations
  - Treatment impacts
    - Chemical feed disruptions
    - Improved organics removal
    - Changes in coagulant
    - Installation of oxidizing removal processes
    - Changes in disinfection chemistry

Limitations of Conventional Methods of Analysis

- Equilibrium solubility models are useful, but dependent upon
  - Accuracy of characterization of solids and complexes
  - Accuracy of the thermodynamic constants used
  - Model completeness (e.g., kinetics, interaction with organic/unknown complexes or tuberculation/corrosion products
  - Post-treatment deposition of various scales (such as compounds of Fe, Ca, Mn)

Limitations of Conventional Methods of Analysis (con't)

- Empirical coupon tests
  - Adequate control of variables
  - Representativeness of coupon materials
  - Cannot address treatment changes (pre-existing scales)
- Corrosion rate measurements
  - Limited usefulness for Pb (corrosion rates too low)
  - Poor correlation to observed Pb release

Pipe Scale Analysis

- Scales reflect actual distribution system conditions
  - Direct indication of the effectiveness of a current treatment protocol
  - Reality check on theoretical models

Pipe Scale Analysis (con't)

- Characteristics and behavior of the lead solids can be integrated with water quality and operational data to:
  - Understand mechanisms of corrosion inhibition and uniformity throughout the system
  - Understand speciation of metals and predict mobility/stability
  - Follow impacts of treatment changes
  - Avoid making a major treatment change mistake

Solids Characterization Methods

- Numerous and highly varied in cost and complexity
- Some are specific to crystalline compounds
- Some provide only quantitation of certain chemical elements
- Some give detailed information on chemical bonding and structure at the surface of the corrosion deposits

Some Analysis Methods and What They Can Tell You

Method	Type of Sample	Information
XRD X-ray diffraction	Ground, randomly-oriented powder	Identification of crystalline compounds
ICP-OES, ICP-MS Inductively Coupled Plasma	Digested or fused (then dissolved) powder	Quantitative elemental composition for most metals and some others, e.g., S, Si, P
SEM	Small piece of pipe or material	Very small scale sample particulate morphology
EDS, EDXA Energy-dispersive spectrometry	Small piece of pipe or material, or packed powder	Qualitative to semi-quantitative elemental analysis (>Al)
XANES (X-ray Absorption Near-Edge Spectroscopy)	Ground, randomly-oriented powder In-situ mounted sample	Identification and speciation of compounds of targeted metals
Elemental Analyzer (TIC, TC, S)	Ground powder, combusted or digested	Quantitation of specific elements such as C, S, N

Case Study Categories

1. Predictive (e.g., systems contemplating change in treatment)
2. Diagnostic/forensic (e.g., why something went wrong)
3. Track results/changes (e.g., understand and follow progress of treatment)

ALL case studies have lead service lines…

Case Studies
Category 1 – Predictive

Newport

- Surface water; multiple sources
- Conventional treatment – two plants
- High organics; high reactivity
- Free chlorine
- Corrosion Control Treatment (CCT) is carbonate passivation
  - pH ~ 8.3
  - 90th Percentile Pb < 15 ppb
- Contemplating NH_2Cl conversion for DBP control

Newport – LSL Specimens

Calvert Street Lead Pipe Prior to Harvesting of Scale

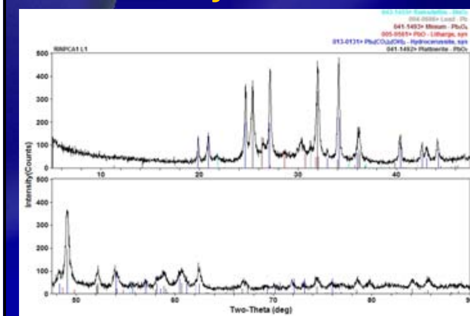
Images of Layers 1 & 2 of the 6 Calvert Street Lead Pipe

Scale bar divisions are in millimeters.

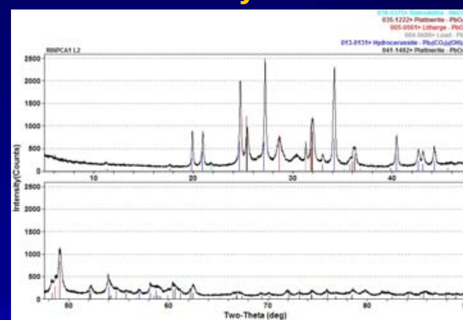
XRD Trace for Layers 1 and 2 of the Calvert Street Lead Pipe

Prominent Pb(II) mineral = $Pb_3(CO_3)_2(OH)_2$

Layer 1



Layer 2



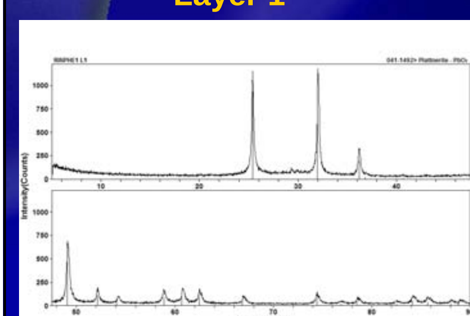
19 Heath Street Lead Pipe Prior to Harvesting of Scale

Image of Layers 1 (Brown) and 2 (Red) in the 19 Heath Street Lead Pipe

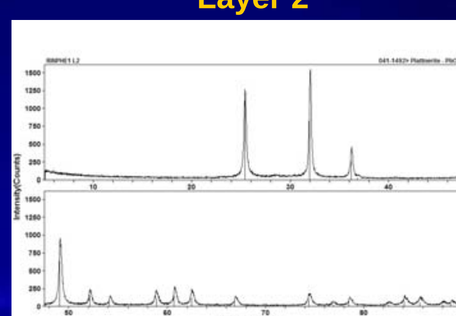
XRD Trace for Two Layers of 19 Heath Street Lead Pipe

Prominent Pb(IV) mineral = PbO_2

Layer 1



Layer 2



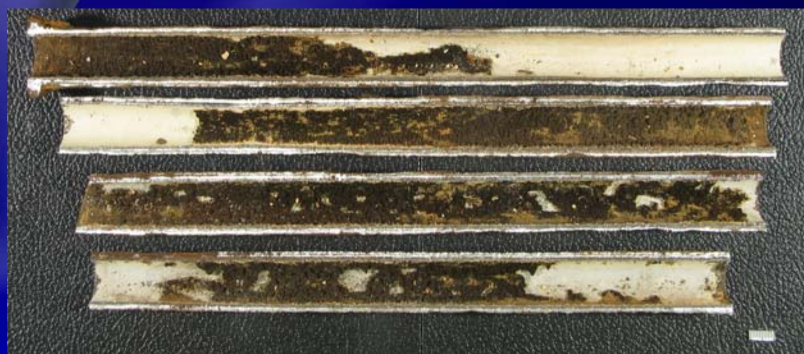
Significance of Findings

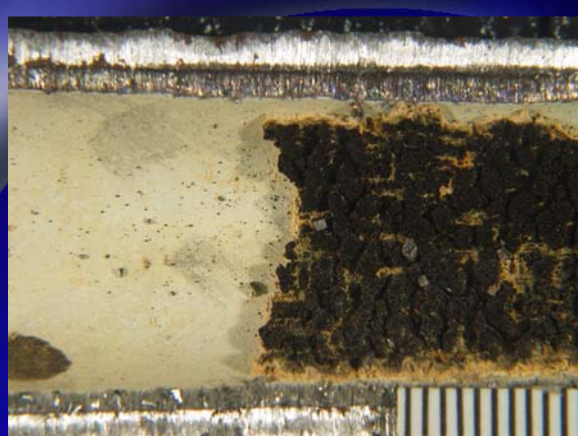
- Issue: contemplating NH_2Cl conversion for DBP control
- Conclusions:
  - Analyses confirmed predominance of Pb(IV) mineral in scales
  - Explains 90^{th} Percentile Pb level below EPA Action Level despite lower-than-optimal pH for carbonate passivation
  - Some scales are mixtures of Pb(II) and Pb(IV) indicating that conversion to NH_2Cl will not be straightforward
  - Results being used to design a pipe loop testing program to evaluate alternatives

Reading

- Ground water
- Conventional treatment – Fe, Mn, TOC removal
- Free chlorine
- CCT is carbonate passivation
  - pH ~ 9.5
  - 90^{th} Percentile Pb << 15 ppb
- Contemplating using 100% MWRA surface water (NH_2Cl residual disinfectant; pH ~9.5)

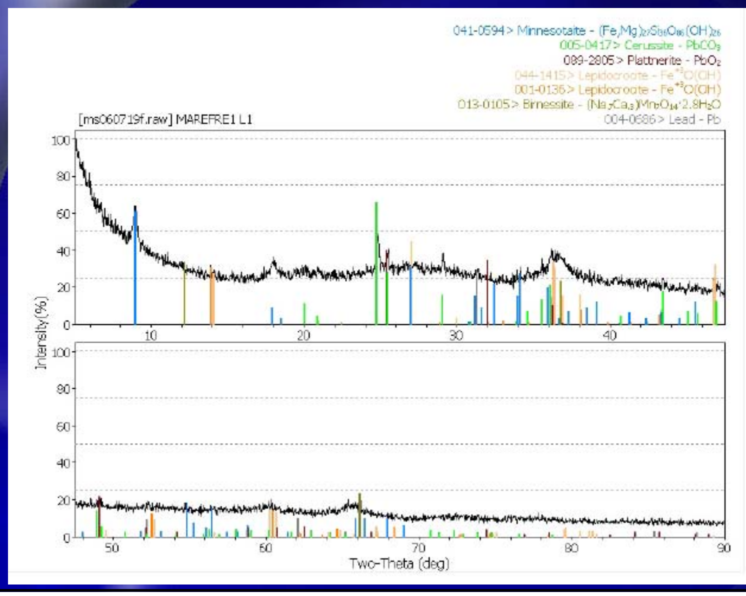
Reading LSL Sample





Lead Minerals	Mineral Formula	Layer 1	Layer 2	Layer 3
Cerussite	$PbCO_3$	+	+	++++
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	ND	ND	++
Litharge	PbO	ND	ND	+

Non-Distinctive Peaks



Significance of Findings

- **Issue: utility contemplating using 100% MWRA surface water (NH_2Cl residual disinfectant; pH ~9.5)**
- **Conclusions:**
  - **Predominantly Pb(II) minerals in the scale**
  - **Absence of Pb(IV) solids suggests system redox potential (ORP) not high enough to form PbO_2**
  - **Consequently, chloramination not likely to destabilize mineral forms of Pb(II) on the pipes**
  - **Thick outer layer of nearly-amorphous material (Mn) could be acting as diffusion barrier preventing maximum effectiveness of the pH/DIC adjustment treatment**

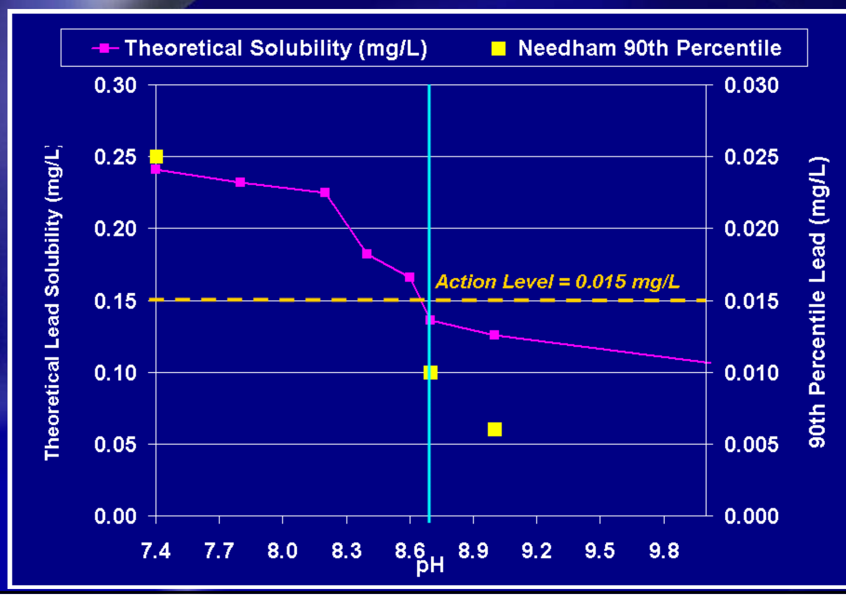
Needham

- Ground water
- Adsorptive media treatment – Mn removal
- Free chlorine
- CCT is carbonate passivation
  - pH ~ 9.0
  - 90^{th} Percentile Pb < 15 ppb
- Contemplated decreasing pH to alleviate seasonal $CaCO_3$ scaling

Calcium Carbonate – Theoretical Saturation Index and Precipitation Potential

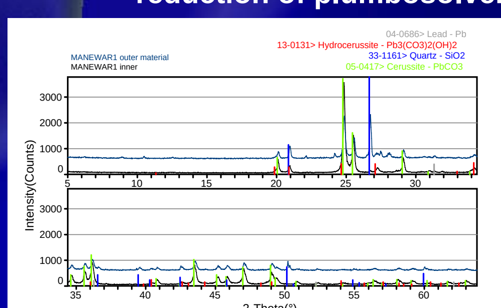
Parameter/Index	Source Water pH	Finished Water pH			
	6.8	9.0	8.7	8.2	8.0
LSI	- 1.71	1.33	1.22	0.30	- 0.18
CCPP (mg/L)	- 40	35	26	2.1	- 1.21
Precipitation?		Yes	Yes	Maybe	No

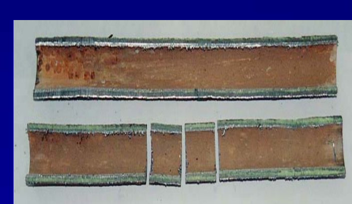
Pb (II) Solubility versus pH



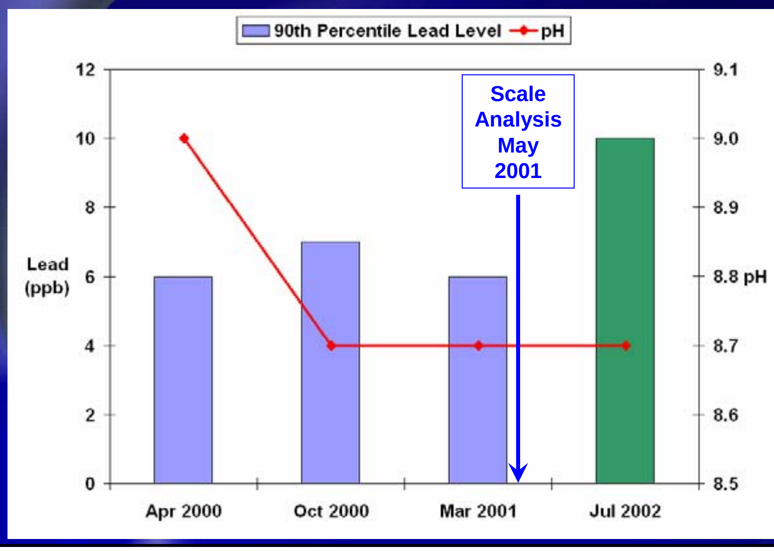
XRD Trace Showed $PbCO_3$ Dominant

- Prevalence of cerussite ($PbCO_3$)
  - Stable Pb(II) phase at pH 8–8.5
  - Much more soluble than hydrocerussite at higher pH (≥9.0)
  - Indication that pH not high enough for <u>optimal</u> reduction of plumbosolvency

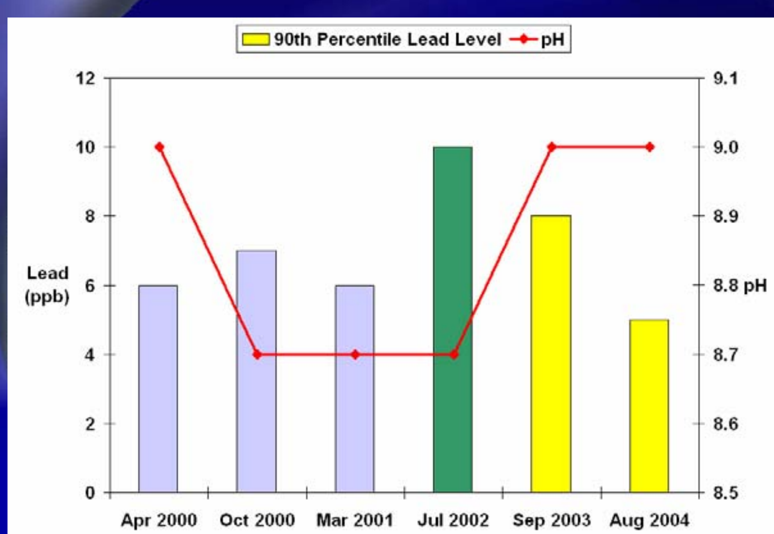




90th Percentile Lead Levels



Full-Scale Results: 90th Percentile Pb



Significance of Findings

- Issue: utility contemplated decreasing pH to alleviate seasonal $CaCO_3$ scaling
- Conclusions:
  - Theoretical solubility calculations indicated lower pH limit for lead was 8.7
  - At pH 8.7, $PbCO_3$ was the dominant scale mineral; indication that pH not high enough for optimal reduction of plumbosolvency
  - Scale analysis combined with solubility modeling provided good prediction of treatment impacts on metal release
  - Supported decision to return to pH 9.0 and seek alternate means (blended phosphate) to control $CaCO_3$ precipitation

Case Studies
Category 2 – Diagnostic/Forensic

New Britain

- Surface water
- Conventional treatment
- Free chlorine
- CCT is carbonate passivation
  - pH ~ 8.2
  - Historical 90th Percentile Pb < 15 ppb
- No changes – unanticipated increase in 90th percentile Pb levels

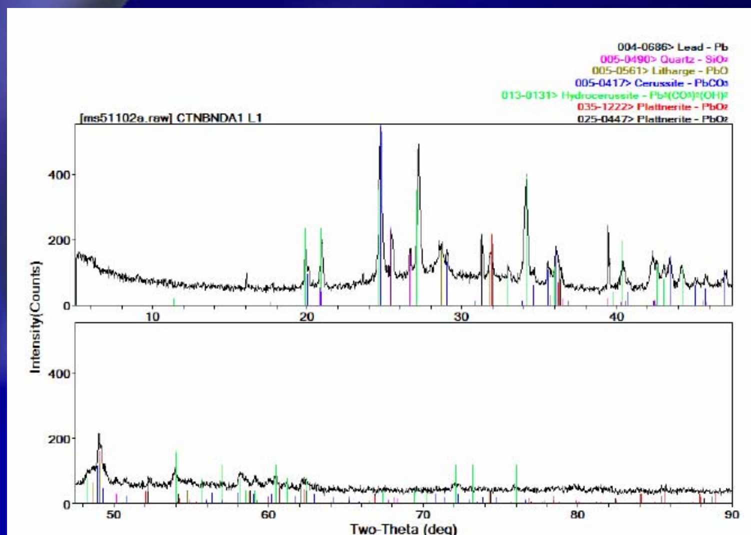
New Britain – Carbonate Passivation

2005 LCR Monitoring Results

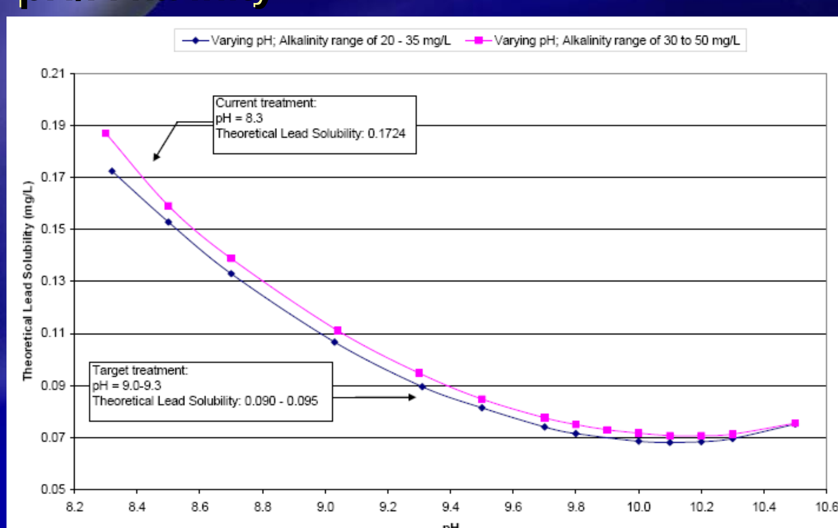
Range of Lead Results (ug/L)	Lead (% of Samples) 2005
≤ 5	60%
> 5 and ≤ 10	10%
> 10 and ≤ 15	4%
> 15 and ≤ 20	4%
> 20 and ≤ 25	4%
> 25 and ≤ 30	0%
> 30 and ≤ 50	6%
> 50 and ≤ 100	6%
> 100 and ≤ 500	2%
> 500	2%
Average (mg/L)	0.0264
50th Percentile (mg/L)	0.0031
75th Percentile (mg/L)	0.0126
90th Percentile (mg/L)	**0.0429**
Number of Samples (n)	48

Based on Monthly Averages	pH	Alkalinity (mg/L as $CaCO_3$)	Hardness (mg/L as $CaCO_3$)	Iron (mg/L)	Manganese (mg/L)	Free Chlorine (mg/L)	Total Chlorine (mg/L)
Average	8.1	20	35	0	0.02	0.61	0.76
Maximum	8.5	24	44	0.1	0.04	0.86	0.95
Minimum	7.8	14	20	0	0.02	0.40	0.50

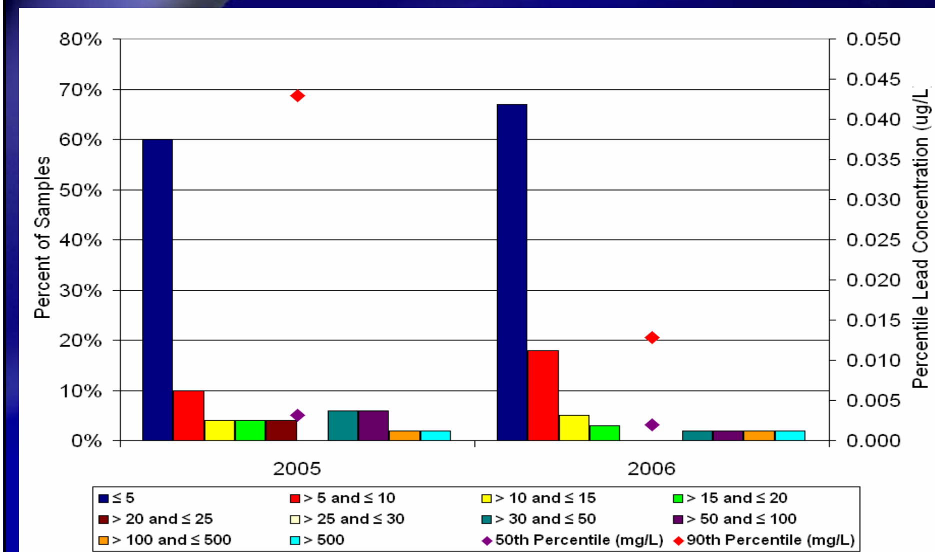
XRD Trace for Layer 1



Theoretical Pb (II) Solubility vs. pH/Alkalinity



Pb Frequency Distribution *(2005 vs. 2006)*



Significance of Findings

- **Issue: no changes were made – the utility experienced an unanticipated increase in 90th percentile Pb levels**
- **Conclusions:**
  - **$PbCO_3$ dominant scale mineral, which is much more soluble than hydrocerussite is at higher pH (≥9.0)**
  - **Indication that pH not high enough for <u>optimal</u> reduction of plumbosolvency**
  - **Scale analyses consistent with Pb(II) solubility modeling**
  - **Recommendation to increase pH, resulting in decrease in Pb levels in follow-up monitoring**

Cambridge

- Surface water
- Conventional treatment
- Chloramine
- CCT is carbonate passivation
  - pH ~ 9.0
  - Historical 90th Percentile Pb << 15 ppb
- No changes – unanticipated, sudden mechanical equipment failure

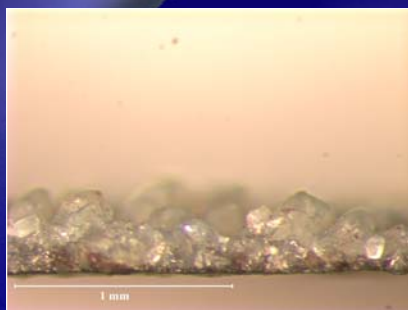
Cambridge High Lift Pumps

Investigations and Follow-Up Actions

- Physical examination of pump and motor components, electrical systems
- Underwater observations
- *Analysis of scale composition*
- *Impact on Pb control mechanism*
- Water quality
- Plant operating practices

focus of this presentation

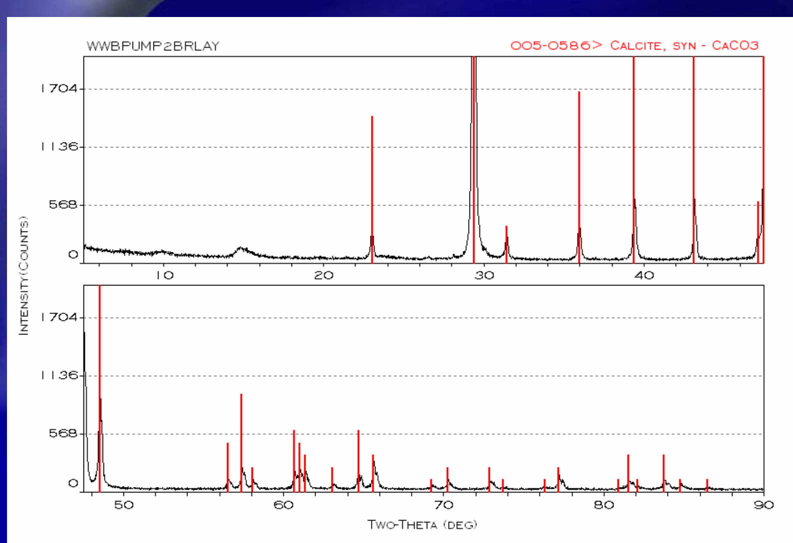
Analysis of Scale Composition



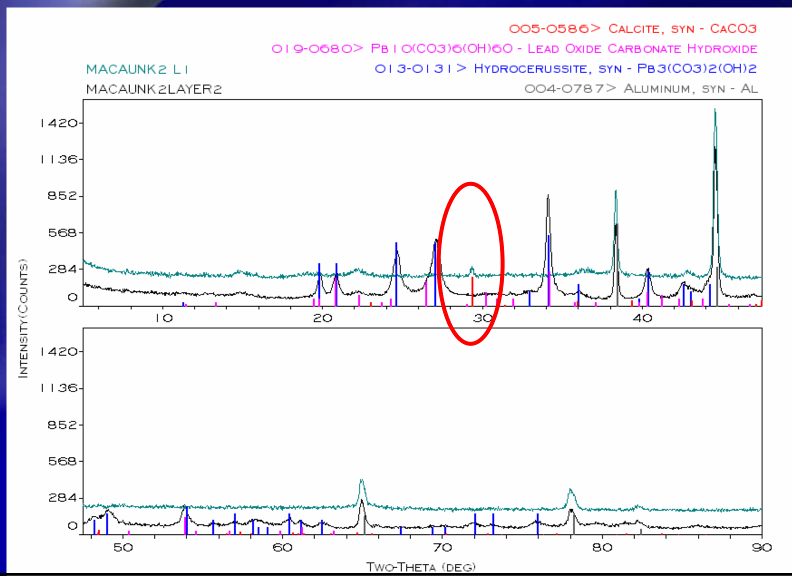
Pump Housing
Edge of Scale

Pump Housing
Top Side of
Scale

XRD Pattern for Pump Impeller Scale



No Impact on Lead Control Mechanism



Significance of Findings

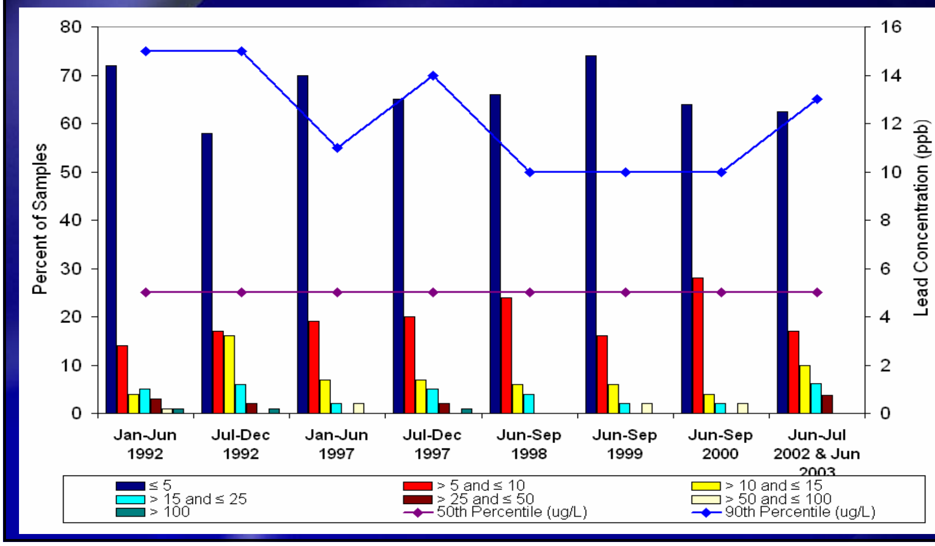
- Issue: no changes made – the utility experienced an unanticipated, sudden mechanical equipment failure
- Conclusions:
  - Impeller and pump housing scales predominantly $CaCO_3$ (calcite)
  - Scales on domestic lead service line samples mainly hydrocerussite [$Pb_3(CO_3)_2(OH)_2$], expected dominant Pb(II) mineral at pH 9.0; only trace amounts of calcite
  - Calcite precipitation at the treatment plant not interfering with predominant carbonate passivation Pb control mechanism

Case Studies
Category 3 – Tracking Changes

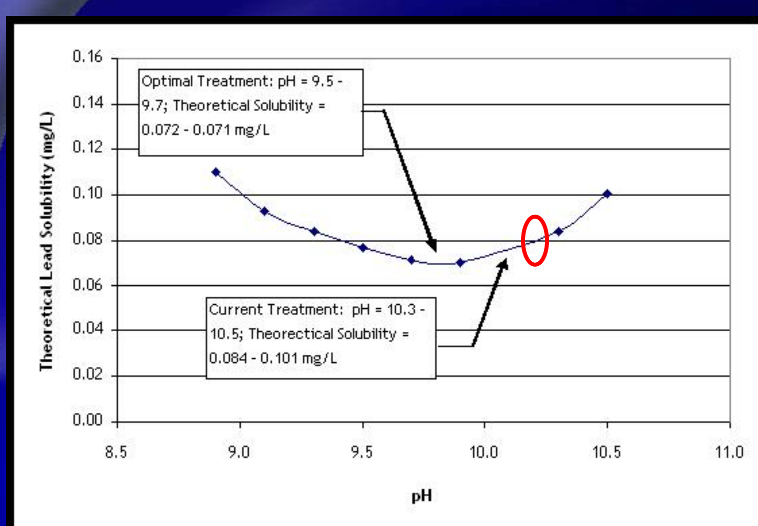
Providence

- Surface water
- Conventional treatment
- Free chlorine
- CCT is carbonate passivation
  - pH ~ 10.3
  - Historical 90th Percentile Pb slightly < 15 ppb
- CCT changed to further optimize Pb control

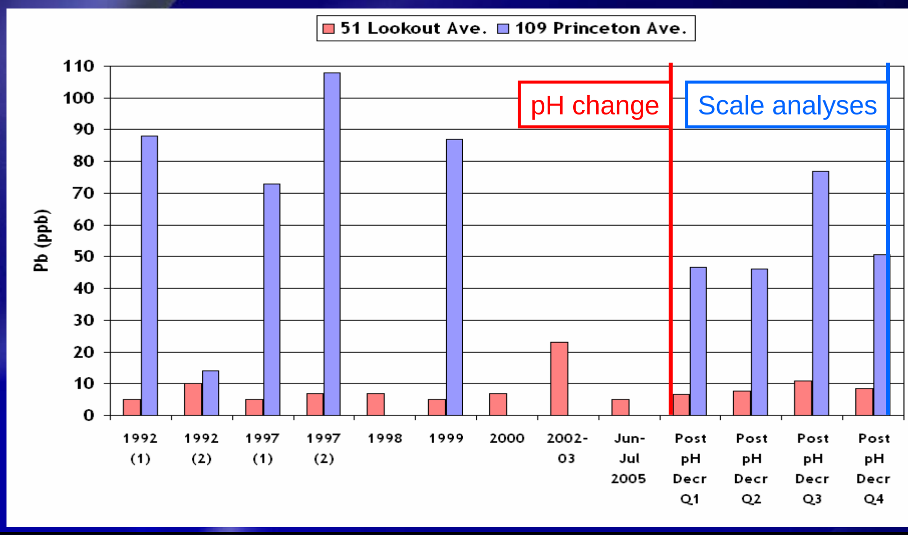
Pb History



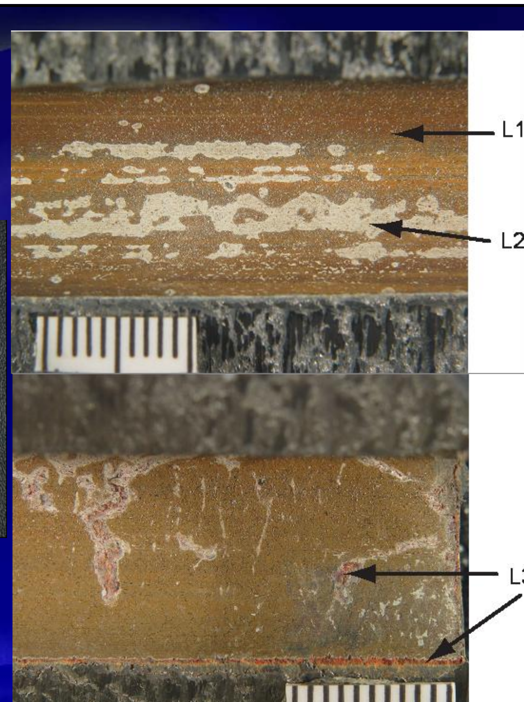
Theoretical Pb(II) Solubility Predictions



90^{th} Percentile Monitoring History – Selected Quarterly LSL Sampling Locations



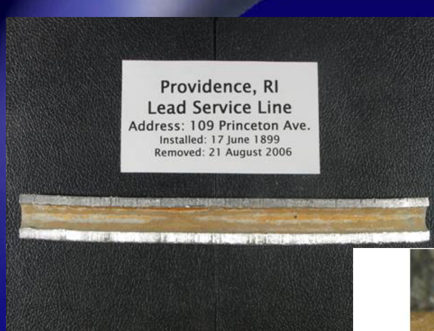
51 Lookout LSL Sample



51 Lookout

Lead Minerals	Mineral Formula	Layer 1	Layer 2	Layer 3
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	++	++	+
Litharge	PbO	+	+	+++
Lead Oxide Carbonate Hydroxide	$Pb_{10}(CO_3)_6(OH)_6O$ **"Plumbonacrite"**	+++	+++	+
Elemental Lead	Pb	D	D	D

109 Princeton LSL Sample



109 Princeton

Lead Minerals	**Mineral Formula**	**Layer 1**	**Layer 2**
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	+++	+++
Litharge	PbO	ND	+
Lead Oxide Carbonate Hydroxide	$Pb_{10}(CO_3)_6(OH)_6O$ "Plumbonacrite"	++	++
Elemental Lead	Pb	D	D

Significance of Findings

- Issue: Corrosion Control Treatment (CCT) changed to further optimize Pb control
- Conclusions:
  - Two roughly equal scale mineral populations – plumbonacrite and hydrocerussite
  - Suggests that pH change (decrease) may cause destabilize plumbonacrite before it can recrystallize into more stable hydrocerussite
  - Conventional Pb(II) solubility models do not predict plumbonacrite to form under the historical (pH 10.3) treatment conditions

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Significance of Findings

- Conclusions (cont'd):
  - More research needed on the significance and solubility of plumbonacrite in high pH systems using carbonate passivation to properly advise water systems
  - Establishes baseline to follow evolution of protective scales in response to CCT changes and monitoring results

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