Updated: 29 April 2020

Print version

CEE 680: Water Chemistry

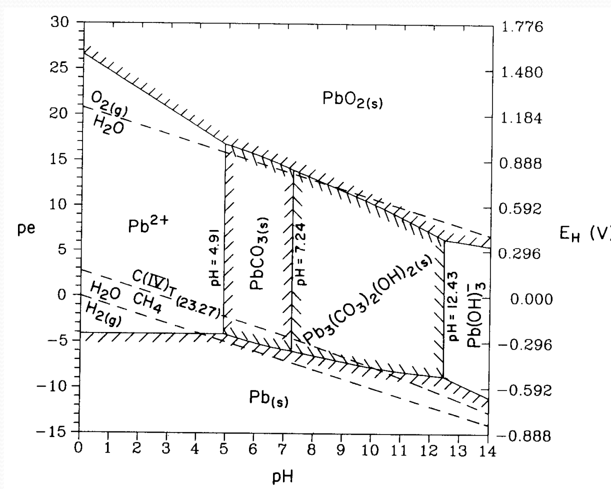
Lecture #51

Redox Chemistry: Lead II

(Stumm & Morgan, Chapt.8)

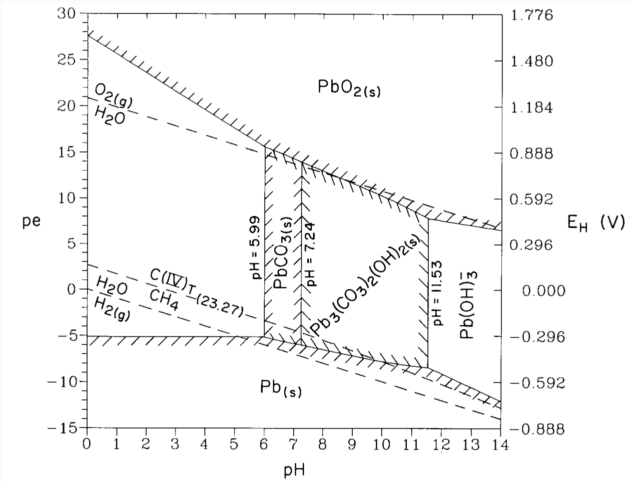
Benjamin; Chapter 9

- $Pb_T=10^{-4}$
- $C_T=10^{-2}$



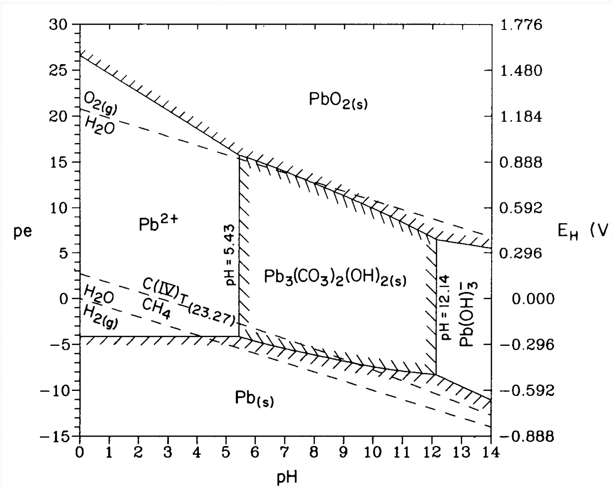
From: Aquatic Chemistry Concepts, by Pankow, 1991

- $Pb_T=10^{-6}$
- $C_T=10^{-2}$



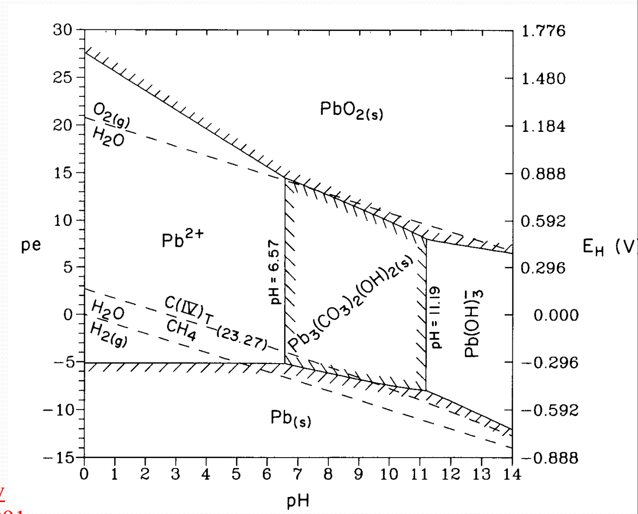
From: Aquatic Chemistry Concepts, by Pankow, 1991

- $Pb_T=10^{-4}$
- $C_T=10^{-3}$



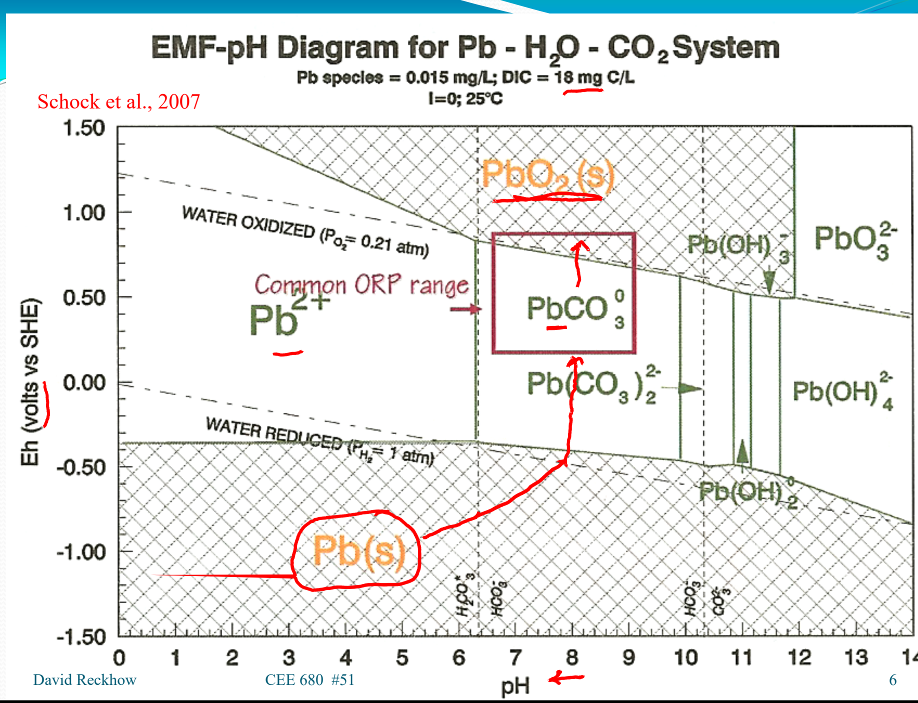
From: Aquatic Chemistry Concepts, by Pankow, 1991

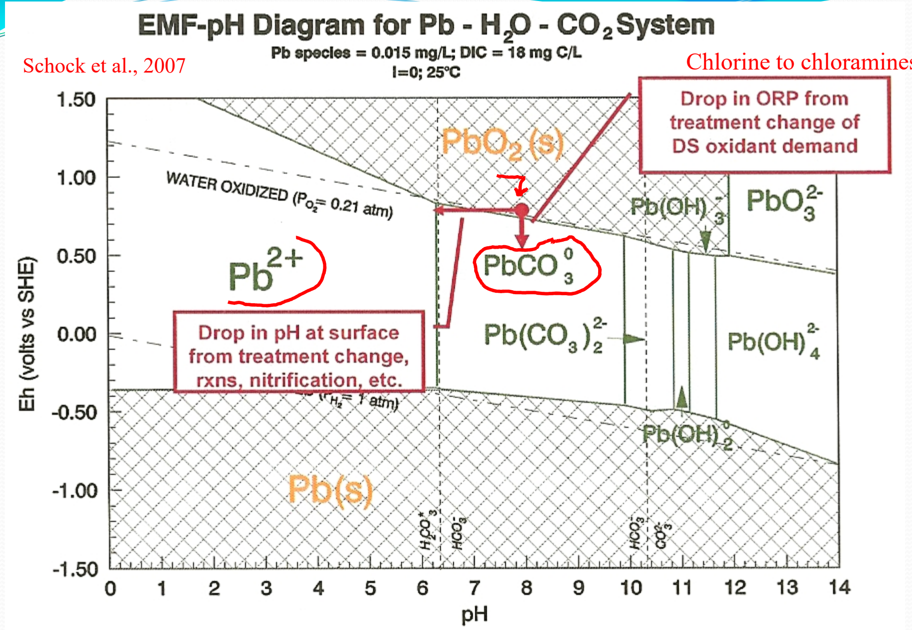
- $Pb_T = 10^{-6}$
- $C_T = 10^{-3}$



From: Aquatic Chemistry Concepts, by Pankow, 1991

Schock et al., 2007





Effect of chloramines: experimental data

- Rajasekharan et al., 2007
  - ES&T 41:4252
- 15 ppb Pb_T
- CO_{3T} = 1.5 mM

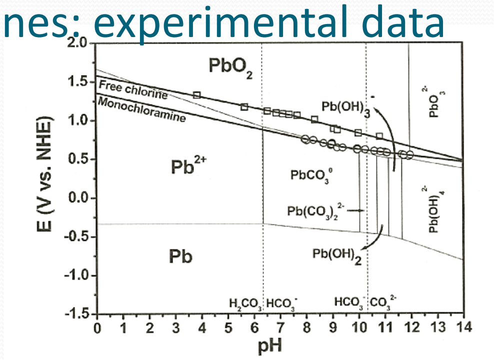
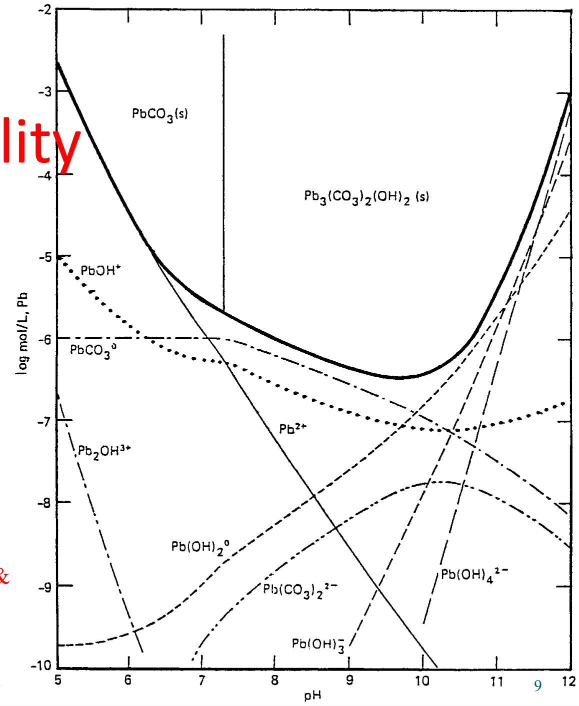


FIGURE 7. Pourbaix diagram for Pb—H_2O—CO_2 system with the concentration of dissolved Pb species equal to 7.25 × 10^{-8} M (15 ppb) and the concentration of dissolved inorganic carbon equal to 1.5 × 10^{-3} M (18 ppm) at 25 °C. Measured equilibrium potentials are shown as open squares for free chlorine, and as open circles for NH_2Cl. A linear fit to the measured equilibrium potentials for free chlorine gives two linear regions. Below pH 7.5 (corresponding to the pK_a = 7.5 of HOCl) the slope is 70 mV/pH, and above pH 7.5 the slope is 90 mV/pH.

Pb(II) solubility

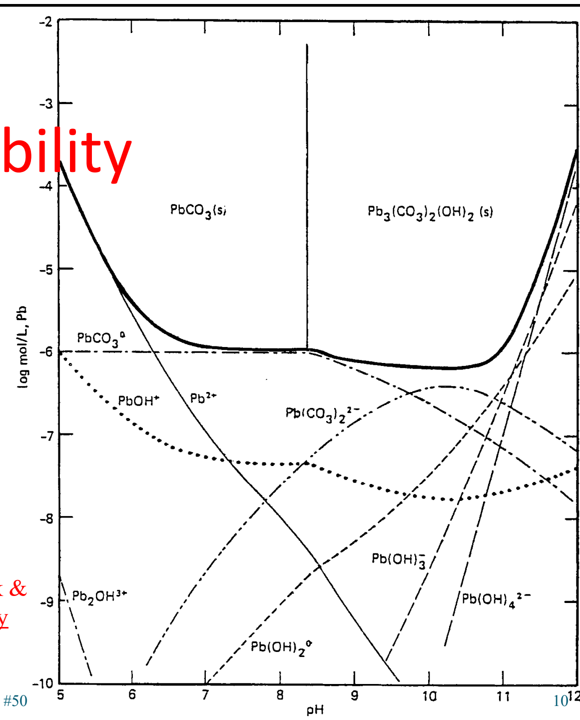
- 3 mg/L DIC



From: Internal Corrosion and Depositional Control, by Schock & Lytle, Chapt. 20 in Water Quality and Treatment (6th ed), 2011

Pb(II) solubility

- 30 mg/L DIC



From: Internal Corrosion and Depositional Control, by Schock & Lytle, Chapt. 20 in Water Quality and Treatment (6th ed), 2011

Pb(II) solubility; hydropyromorphite

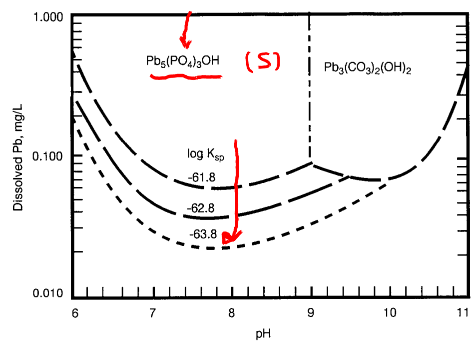
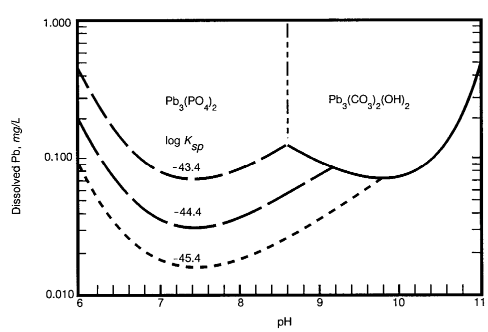


Figure 4-16 Predicted Pb(II) solubility with DIC = 6 mg C/L (0.0005*M*) and PO_4 = 0.5 mg/L, assuming the formation of only $Pb_5(PO_4)_3OH$ (hydropyromorphite) as the orthophosphate phase, with slightly different assumed solubility constant values, temperature = 25°C, I = 0.005 mol/L

From: <u>Internal Corrosion of Water Distribution System</u>, (2nd ed) by Snoeyink, Wagner et al., 1996

Pb(II) solubility; lead orthophosphate

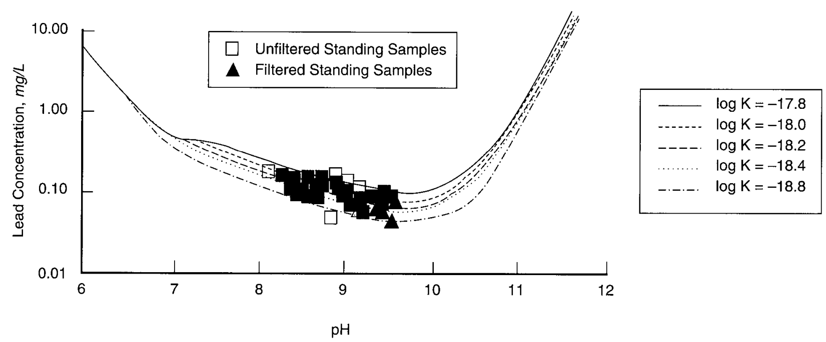


From: <u>Internal Corrosion of Water Distribution System</u>, (2nd ed) by Snoeyink, Wagner et al., 1996

Figure 4-17 Predicted Pb(II) solubility with DIC = 6 mg C/L (0.0005*M*) and PO_4 = 0.5 mg/L, assuming the formation of only $Pb_3(PO_4)_2$ (tertiary lead orthophosphate) as the orthophosphate phase, with slightly different assumed solubility constant values, temperature = 25°C, I = 0.005 mol/L

Pb Solubility

From: Internal Corrosion and Depositional Control, by Schock Chapt. 17 in Water Quality and Treatment (5th ed), 1999



NOTE: Reference lines represent theoretical solubility curves for DIC = 3.6 mg C/L, I = 0.0075 mol/L at two different assumed K_{sp} values.

Source: Adapted from Shock and Gardels (1983).

Figure 4-4 Data for standing time >7 hours in USEPA lead pipe loop experiments

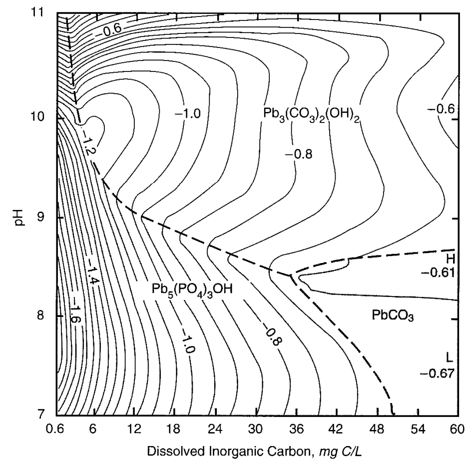
- Equilibria used in EPA's Leadsol program
  - Schock, Wagner and Oliphant, 1996

Equilibria	Log K
$Pb^{+2} + H_2O = PbOH^+ + H^+$	-7.22
$Pb^{+2} + 2H_2O = Pb(OH)_2^o + 2H^+$	-16.91
$Pb^{+2} + 3H_2O = Pb(OH)_3^- + 3H^+$	-28.08
$Pb^{+2} + H^+ + PO_4^{-3} = PbHPO_4^o$	+15.41
$Pb_5(PO_4)_3OH_{(s)} = 5Pb^{+2} + 3PO_4^{-3} + H_2O$	-62.83

From: Internal Corrosion of Water Distribution System, (2nd ed) by Snoeyink, Wagner et al., 1996

Pb(II): pH vs DIC

- 0.5 mg-P/L



From: Internal Corrosion of Water Distribution System, (2nd ed) by Snoeyink, Wagner et al., 1996

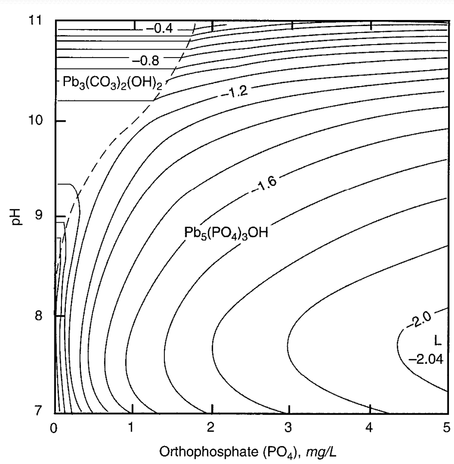
NOTE: Concentration units are log (mg Pb/L). Local high and low points are indicated.

Figure 4-18 Contour diagram of Pb(II) solubility in a system having 0.5 mg PO4/L orthophosphate, with varying levels of pH and DIC, at 25°C and I = 0.005 mol/L

David R

Pb(II): pH vs PO_{4T} ;low CO_{3T}

- 6 mg/L DIC



From: Internal Corrosion of Water Distribution System, (2nd ed) by Snoeyink, Wagner et al., 1996

AL = 15 μg/L = $10^{-1.8}$ mg/L

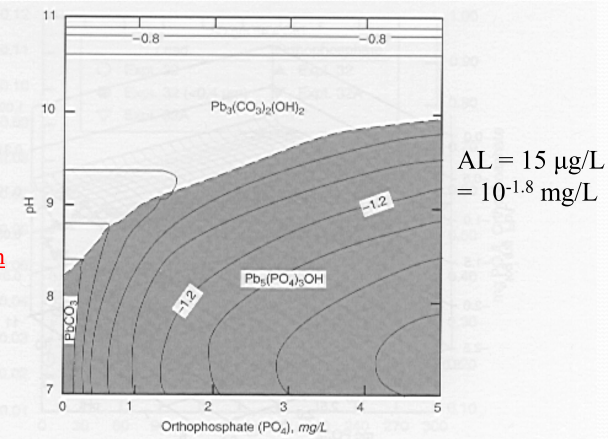
NOTE: Concentration units are log (mg Pb/L). The solid phase boundary lines are approximate.

Figure 4-19 Contour diagram for the impact of varying concentrations of orthophosphate and hydrogen ion, with DIC = 6 mg C/L, temperature = 25°C, and I = 0.005 mol/L

Davi

Pb(II): pH vs PO_{4T} ;high CO_{3T}

- 24 mg/L DIC



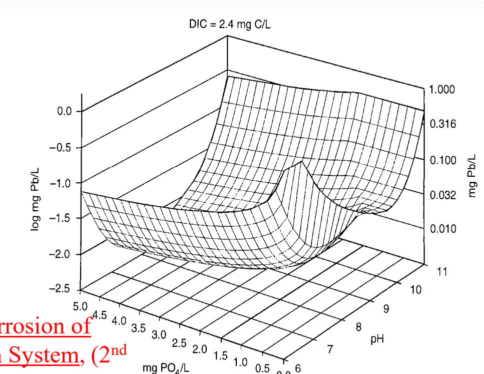
AL = 15 µg/L = $10^{-1.8}$ mg/L

From: Internal Corrosion of Water Distribution System, (2nd ed) by Snoeyink, Wagner et al., 1996

NOTE: Concentration units are log (mg Pb/L). The solid phase boundary lines are approximate.

Figure 4-20 Contour diagram for the impact of varying concentrations of orthophosphate and hydrogen ion, with DIC = 24 mg C/L, (0.002M), temperature = 25°C, and I = 0.005 mol/L

Pb(II); pH/PO_4 contour plot



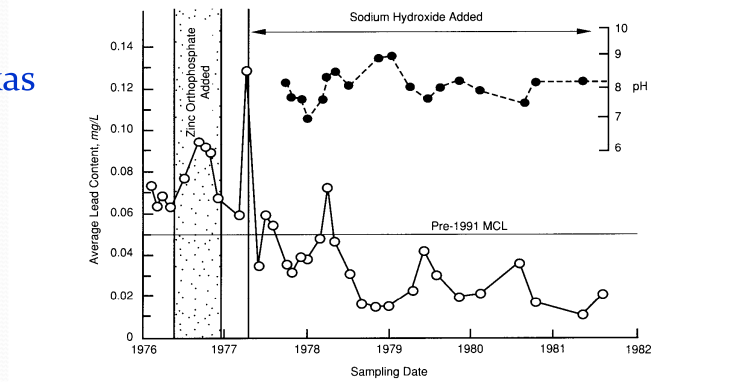
AL = 15 µg/L = $10^{-1.8}$ mg/L

From: Internal Corrosion of Water Distribution System, (2nd ed) by Snoeyink, Wagner et al., 1996

Figure 4-21 Three-dimensional surface plot of lead concentration versus orthophosphate dose for 2.4 mg C/L DIC (DIC = 2 × $10^{-4}M$, I = 0.01 mol/L, temperature = 25°C)

Pb mitigation in Boston

- Karalekas study



Source: Karalekas et al. (1983).
Figure 4-2 Mean levels of lead in samples taken from Boston, Massachusetts, and Somerville, Massachusetts, 1976-1981

From: Internal Corrosion and Depositional Control, by Schock Chapt. 17 in Water Quality and Treatment (5th ed), 1999

Pb Mitigation

- Impacts on other corrosion byproducts

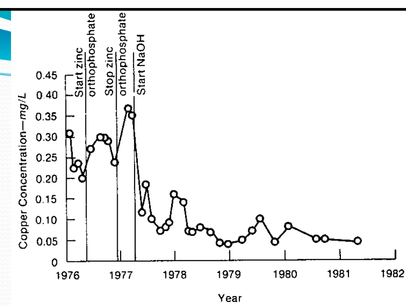


Figure 3. Mean levels of copper in samples taken from Boston and Somerville, Mass., 1976–1981

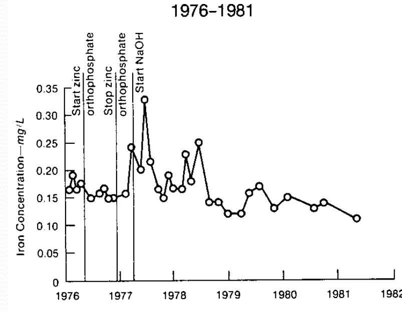


Figure 4. Mean levels of iron in samples taken from Boston and Somerville, Mass., 1976–1981

From: Karalekas et al., 1983 [J.AWWA 75:2:92]

Iron Scale

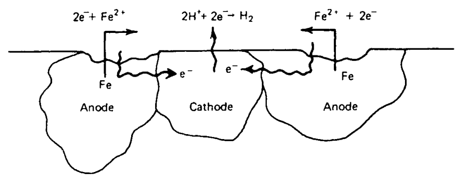


FIGURE 17.1 Adjoining anodes and cathodes during the corrosion of iron in acidic solution. (*Source: Water Chemistry,* V. L. Snoeyink and D. Jenkins. Copyright © 1980, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

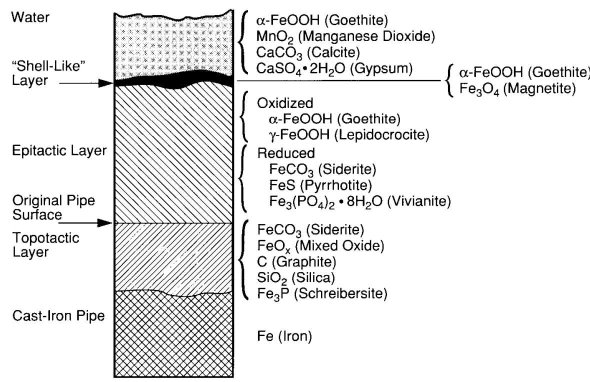
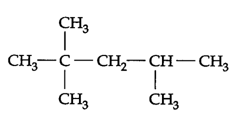
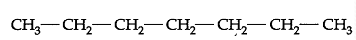


Figure 2-6 Schematic of scale on a cast-iron distribution pipe

Background: Other Sources



2,2,4- Trimethylpentane, known as "octane" or "isooctane", a highly branched alkane, shows little tendency to knock. Octane rating = 100.



n-Heptane, a straight-chain, unbranched alkane, knocks readily, even under moderate conditions. Octane rating = 0.

Figure 8.6
A combination of 2,2,4-trimethylpentane and heptane is used to evaluate octane ratings.

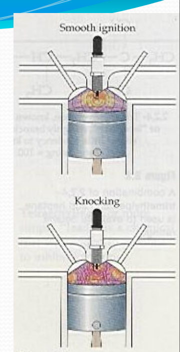
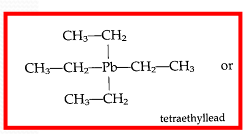


Figure 8.5
Smooth ignition and knocking.

TABLE 8.3 Octane Ratings

	Approximate Octane Rating
n-Octane	−20
n-Heptane	0
n-Pentane	60
Regular gasoline	87
Premium gasoline	93
2,2,4-Trimethylpentane	100
Ethanol	105
Methanol	105
Benzene	105
Methyl *tert*-butyl ether	115



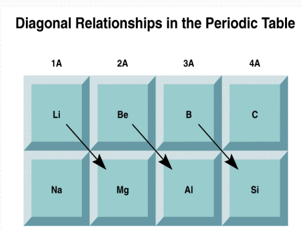
From: The Extraordinary Chemistry of Ordinary Things, C.H. Snyder

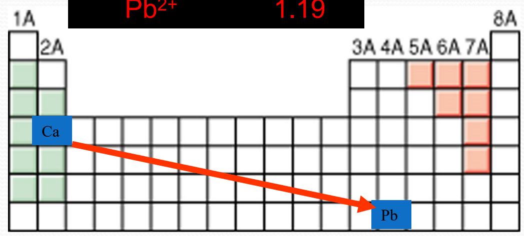
Why is Pb^{2+} Toxic

Diagonal Relationships in the Periodic Table

- There is a chemical resemblance between an element and the element one down and to the right
- Diagonal relationships result from similarity in charge density (ratio of charge to ion size)
- Because of the lanthanide contraction Ca^{2+} and Pb^{2+} have similar sizes.
- So Pb^{2+} can interfere with Ca^{2+} metabolism, particularly in neuronal signaling.

Ion	Ionic Radius (Å)
Ca^{2+}	1.14
Pb^{2+}	1.19





Important Biological Properties

- Lead bioaccumulates in bones, teeth, nails, and hair.
- Pb doesn't degrade.
- Transferrable across the placental and blood-brain barriers.
- Multiple ingestion routes – by eating, drinking and breathing.
- Treatable with chelation therapy

Chronic Exposure

- Long term, low dose
  - Reproductive and early development
    - Various studies suggest fetal toxicity (birth outcome, growth, mental development) starts at a relatively low blood concentration, 8-20 μg/dL in the mother.
  - Cognitive and other neurobehavioral effects
    - CDC and the EPA have proposed a 10 μg/dL blood concentration limit.

Neurodevelopmental Toxicity Mechanisms

- Lead alters the effectiveness of the intracellular adhesion molecule in the brain, thereby affecting brain structural development.
- Lead strongly interferes with the Ca^{2+} messenger system.
  - Ca^{2+} is used throughout the body as an intracellular messenger that converts electrical impulses to hormonal signals.
  - Pb^{2+} either replaces or inhibits removal of Ca^{2+}.

Acute Pb Toxicity

Blood concentration > 50 - 100 µg/dL

- Anemia, reduced red blood cell levels.

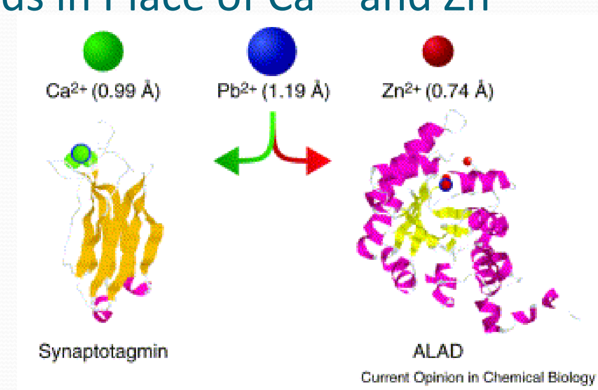
Central nervous system

- Encephalopathy: characterized by excess water in the brain.
- Mechanism: blood/brain barrier properties altered as Pb^{2+} substitutes for Ca^{2+}.

Renal (kidney) system

- Disturbs amino acid and glucose cycling.

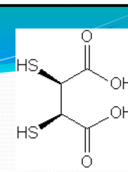
Pb^{2+} Binds in Place of Ca^{2+} and Zn^{2+}



Lead targets proteins that naturally bind calcium and zinc. Examples of proteins that are targeted by lead include synaptotagmin, which acts as a calcium sensor in neurotransmission, and ALAD, the second enzyme in the heme biosynthetic pathway. Despite its size, lead (1.19 Å, blue sphere and circles) can substitute for calcium (0.99 Å, green spheres) in synaptotagmin and zinc (0.74 Å, red spheres) in ALAD.

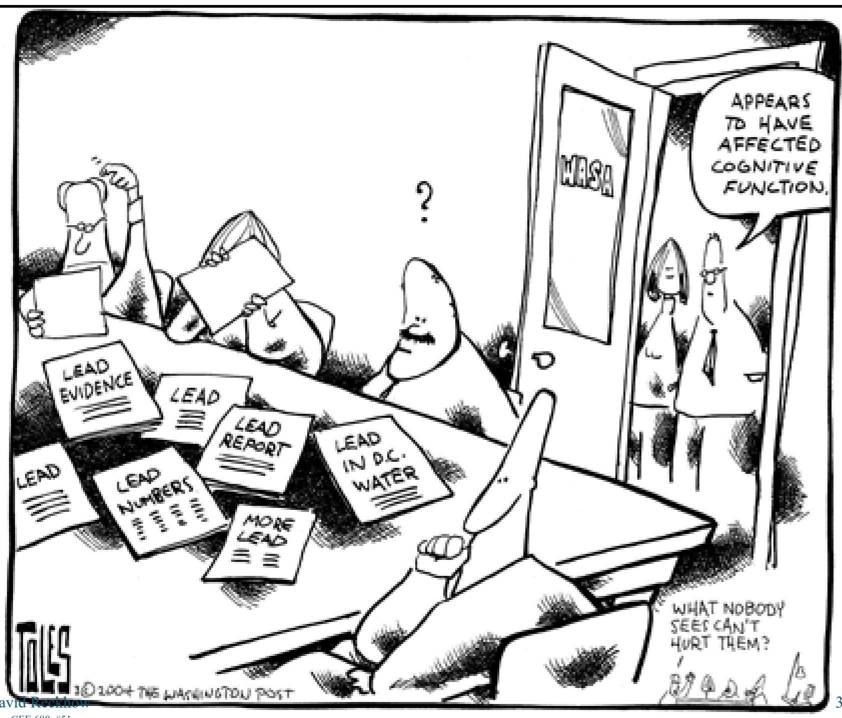
H.A. Godwin, *Current Opinion in Chemical Biology* **2001**, 5:223–227

Pb Chelation Therapy



- Succimer (*meso*-2, 3-dimercaptosuccinic acid, DMSA) is the drug of choice for Pb chelation therapy and is also recommended for asymptomatic children with blood lead levels 40 – 70 mg/dL.
- Next are $CaNa_2EDTA$
- D-penicillamine

CEE 680 #50 David Reckhow 29



David Reckhow 30
CEE 680 #51

- To next lecture