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CEE 371
Water and Wastewater Systems

Lecture #22

Drinking Water Treatment: Fe/Mn removal, corrosion & stabilization

Reading: Chapter 7, pp.255-259

Why remove Fe/Mn

- No known adverse health effects associated with typical levels of Fe or Mn in drinking water
- "High" (relative) levels can lead to water discoloration complaints and staining of laundry & fixtures
- US Treated Water Standards
  - (recommended goals address chronic water quality problems)

	IRON (mg/L)	MANGANESE (mg/L)
EPA Secondary MCLs	0.3	0.05
Recommended Goals	0.1	0.015

Based on: J.E. Tobiason

Sources of Fe & Mn

Based on: J.E. Tobiason

- Groundwater:
  - **mineral dissolution under reducing (anoxic) conditions**
  - **concentration relatively stable over time, but can vary widely between different wells in same "well field" (aquifer location)**
- Surface Waters:
  - **occurrence of reducing conditions in influent waters**
  - **i.e., thermal stratification leading to anoxic hypolimnion in lakes or reservoirs (possible control via multiple depth intake options)**
  - **significant seasonal variations in concentrations likely**
  - **Fe or Mn in river sources is usually in particulate form**
- Treatment Plant Sources
  - **Anoxic sludge blankets in clarifiers (i.e., if solids not continuously removed from clarifier)**
  - **Recyle flows from backwash lagoons, dewatering systems, etc**
  - **Mn as contaminant in Fe coagulants (might add 20 to 50 µg/L)**
- Other: acid mine drainage, landfill leachate

Treatment Approaches

Based on: J.E. Tobiason

- Oxidation & Precipitation
  - **Strong Oxidants ($KMnO_4$, ClO_2, O_3)**
  - **Weak Oxidants - Fe only (O_2, Cl_2)**
- Greensand Filtration
  - **naturally occurring or manufactured zeolite**
  - **adsorption & oxidation**
- Oxide-Coated Filter Media
  - **coatings on normal media; adsorption & oxidation**
- Biological Oxidation
- Membrane Filtration (RO, NF; if dissolved)

Oxidation & Precipitation

Based on: J.E. Tobiason

- *Stoichiometry:*
  - **need to add sufficient oxidant to react with metal**
  - **see Tables for reactions with various oxidants**
  - **must also satisfy competing oxidant demand (NOM, other reduced species), so add in excess of stochiometric amount**
- *Rate of reaction (kinetics):*
  - **need sufficient time for oxidation**
  - **rate can be affected by pH, temperature, etc.**
- *Removal of precipitated (oxidized) metals*:
  - **Use various solid/liquid separation processes**
  - **Clarification (often preceded by coagulation)**
  - **Media filtration: requires destabilized particles/colloids**
  - **MF/UF membrane filtration**

Stoichiometry of Fe Oxidation

Based on: J.E. Tobiason

Oxidant	**Reaction for Oxidation of Fe(II) to Fe(III)**	**Stoichiometry (mg ox/mg Fe)**
O_2 (aq)	$2Fe^{2+} + \frac{1}{2} O_2 + 5H_2O \rightarrow 2Fe(OH)_3(s) + 4H^+$	0.14
$O_3 \rightarrow O_2$ (aq)	$2Fe^{2+} + O_3 + 5H_2O \rightarrow 2Fe(OH)_3(s) + O_2 + 4H^+$	0.43
Cl_2 (HOCl)	$2Fe^{2+} + HOCl + 5H_2O \rightarrow 2Fe(OH)_3(s) + Cl^- + 5H^+$	0.64
$ClO_2 \rightarrow ClO_2^-$	$Fe^{2+} + ClO_2 + 3H_2O \rightarrow Fe(OH)_3(s) + ClO_2^- + 3H^+$	1.20
MnO_4^-	$3Fe^{2+} + MnO_4^- + 7H_2O \rightarrow 3Fe(OH)_3(s) + 2MnO_2(s) + 5H^+$	1.41

Iron Control

Based on: J.E. Tobiason

- ☐ Fe^{2+} is rapidly oxidized by dissolved oxygen (a very weak oxidant) at pH > 7 (if not complexed with natural organic matter (NOM))
- ☐ *For groundwater, often have Fe(II) oxidation along with aeration to strip elevated CO_2 (this raises pH as well)*
- ☐ Strong oxidants result in almost instantaneous oxidation of Fe(II)
- ☐ *Oxidants always react much faster with Fe(II) than Mn(II); impacts on sequencing of oxidant addition*
- ☐ Usually Fe removal is very good if Mn removal is done well

Stoichiometry of Mn Oxidation

Based on: J.E. Tobiason's notes

Oxidant	**Reaction for Oxidation of Mn(II) to Mn(IV)**	**Stoichiometry (mg ox/mg Mn)**
O_2 (aq)	$Mn^{2+} + \frac{1}{2} O_2 + H_2O \rightarrow MnO_2(s) + 2H^+$	0.29
$O_3 \rightarrow O_2$ (aq)	$2Mn^{2+} + O_3 + H_2O \rightarrow MnO_2(s) + O_2 + 2H^+$	0.88
Cl_2 (HOCl)	$Mn^{2+} + HOCl + H_2O \rightarrow MnO_2(s) + Cl^- + 3H^+$	1.30
$ClO_2 \rightarrow ClO_2^-$	$Mn^{2+} + 2ClO_2 + 2H_2O \rightarrow MnO_2(s) + 2ClO_2^- + 4H^+$	2.45
MnO_4^-	$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2(s) + 4H^+$	1.44

Mn Control with $KMnO_4$

- Fast oxidation rates for pH > 6.0 to 6.5
  - **Mn(II) to Mn(IV), precipitate as MnO_2 (s)**
  - **rate increases as pH increases**
  - **rate and extent decrease as DOC level increase (competitive oxidant demand)**
  - **produces colloidal (submicron size) particles**
- *Need to remove colloidal MnO_2 formed by oxidation (may need destabilization (coagulation))*
- Permanganate relatively easy to feed, store on site

Based on: J.E. Tobiason's notes

Mn Control with Free Chlorine

- Slow rate of oxidation unless pH > 8.5-9
- *Rate of oxidation much slower than for Fe^{2+}*
- Slow oxidation of Mn^{2+} in water distribution system with free chlorine residual can cause aesthetic problems
- *Free chlorine is very important for Mn removal via oxide-coated media process (see later notes)*

Based on: J.E. Tobiason's notes

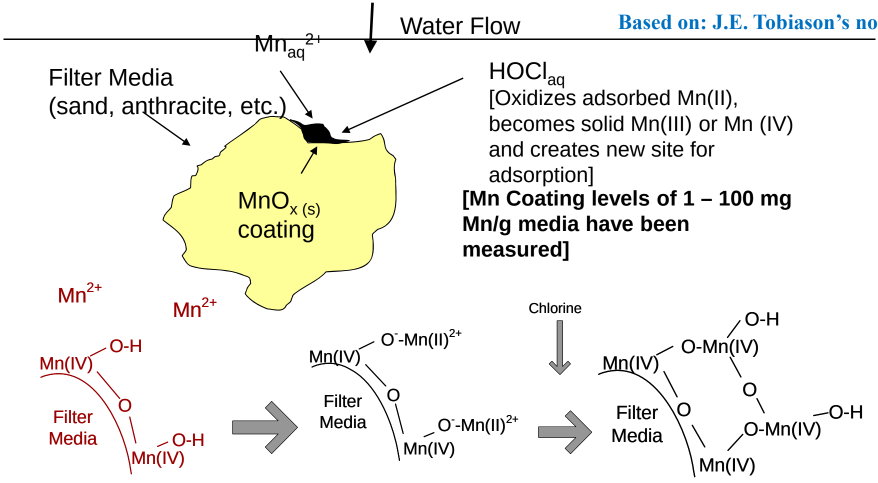
Mn Control via Oxide-Coated Media

- Use of Mn-oxide coating on typical granular media in filters to remove dissolved Mn(II)
- *Similar concept as commercial greensand filtration, but media is larger size (better for lower headloss)*
- Key: adsorption & oxidation of soluble Mn^{2+}
  - **media coated with Mn oxide, naturally or intentionally (add $KMnO_4$ to water within media, allow to react)**
  - **Mn^{2+} forms surface complex and is then oxidized by free chlorine from solution**
  - **Regenerates oxidized MnO_x (s) coating for additional uptake of reduced Mn**

Based on: J.E. Tobiason's notes

Mn removal by Oxide-coated media

Based on: J.E. Tobiason's notes



HOCl$_{aq}$
[Oxidizes adsorbed Mn(II), becomes solid Mn(III) or Mn (IV) and creates new site for adsorption]

[Mn Coating levels of 1 – 100 mg Mn/g media have been measured]

$$Mn^{2+} + HOCl \rightarrow MnO_2 + Cl^-$$

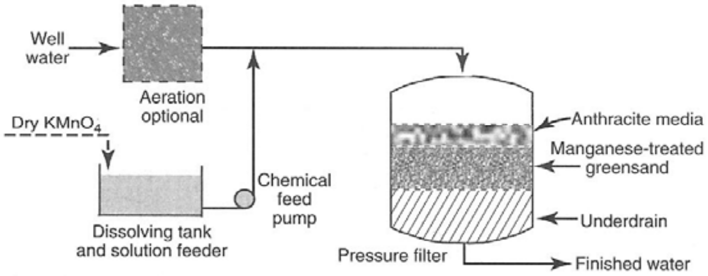
1.3 mg HOCl/mg Mn

X-section of Newport News Anthracite with ~ 40 mg Mn/g media

From: J.E. Tobiason

Pressure Filter for Mn

- ☐ Greensand: Pre-coated with MnO_x
  - Regenerated with $KMnO_4$

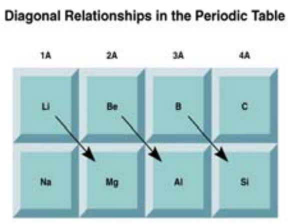


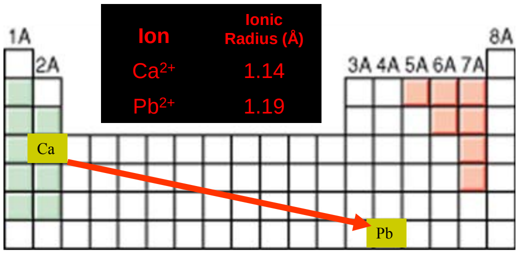
Corrosion Problems

- ☐ Damage to pipes, valves, etc
  - Pipe breaks in distribution system
  - Pinhole leaks in homes
- ☐ Contamination of drinking water
  - Fe/Cu levels
  - Pb – the big concern

Why is Pb^{2+} Toxic?

- ☐ 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.

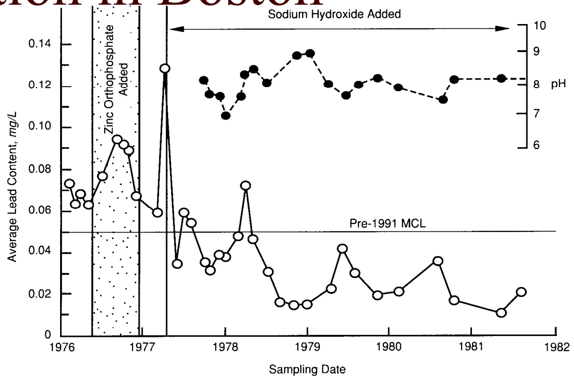




Ion	Ionic Radius (Å)
Ca^{2+}	1.14
Pb^{2+}	1.19

Pb mitigation in Boston

- ☐ Karalekas study



Source: Karalekas et al. (1983).

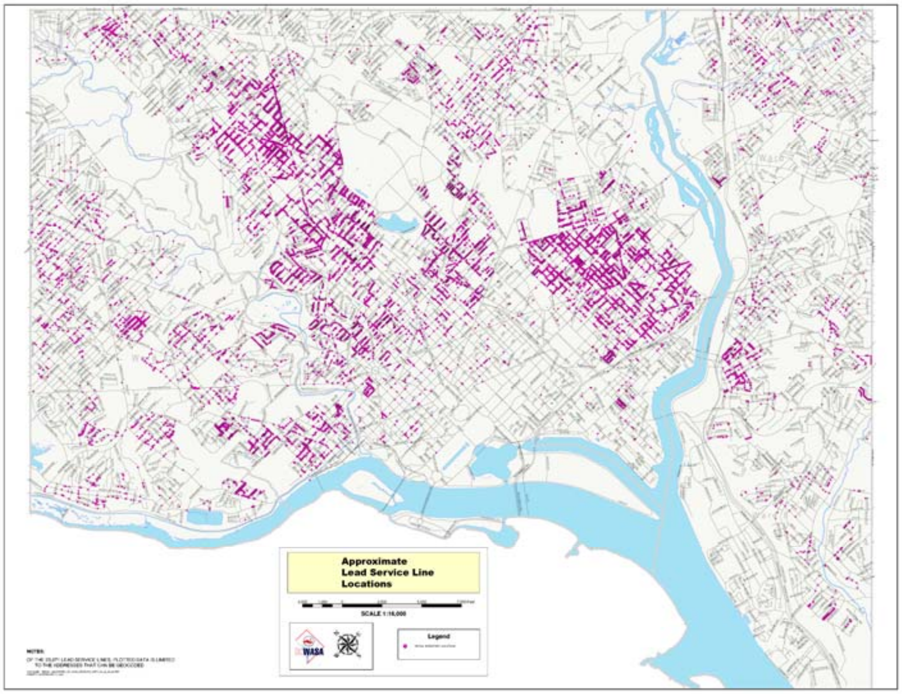
Figure 4-2 Mean levels of lead in samples taken from Boston, Massachusetts, and Somerville, Massachusetts, 1976-1981

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

Public Outrage

- ☐ DC & elsewhere

- ☐ Conversion from chlorine to chloramines
  - Redox potential went down
  - Insoluble Pb(+IV) deposits became reduced to the more soluble Pb(+II)



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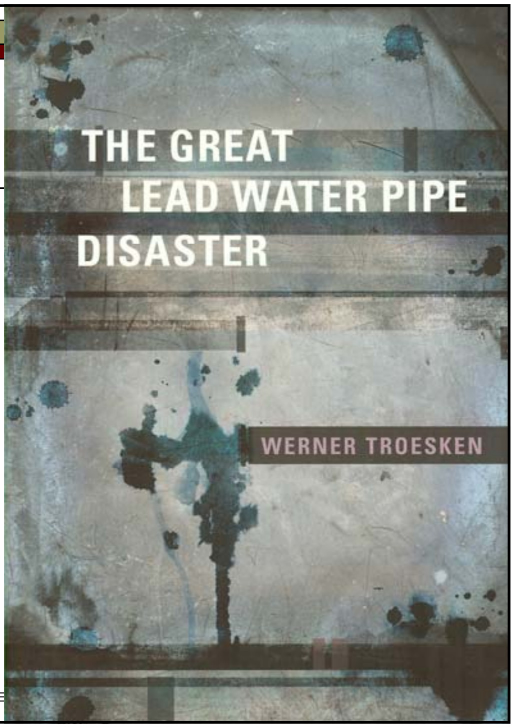
- ☐ Long history of man’s self-inflicted exposure to lead and resulting deaths, dementia, denial, etc.



Iron Scale

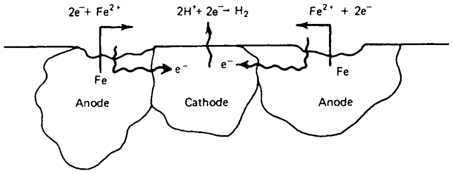


FIGURE 17.1 Adjoining anodes and cathodes during the corrosion of iron in acidic solution. (*Source: Water Chemistry,* V. L. Snoeyink and D. Jenkins. Copyright © 1980, John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

- ☐ Metallic iron “wants” to corrode in the presence of oxygen
- ☐ Lining pipes with cement can slow the process (CLDI)
- ☐ Slight precipitation may help too

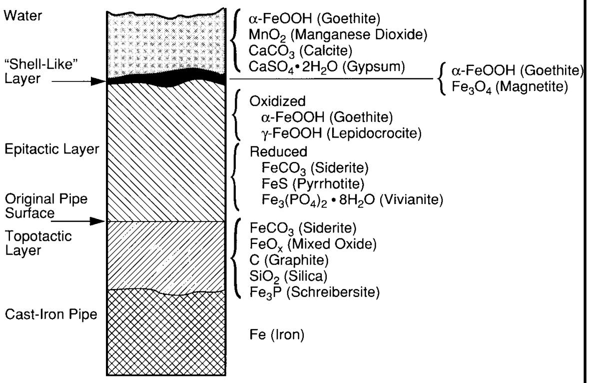


Figure 2-6 Schematic of scale on a cast-iron distribution pipe

Corrosion control

- Cathodic protection
  - Sacrificial anode: created by introduction of a more easily reduced metal (Mg or Zn), or by an imposed current
  - OK for metal steel tanks but too expensive for a distribution system
- Chemical control
  - Phosphate additives (polyphosphates, ortho-phosphates)
  - Elevation of pH, sometimes with additional alkalinity
- Special options for Pb control
  - Removal lead service connections, lead fixtures and pipes with lead solder

Question

- ☐ You’re treating a groundwater that has 0.7 mg/L iron and 0.3 mg/L manganese. How much chlorine dioxide must you add to oxidize both?
  - a) 0.78 mg/L
  - b) 1.00 mg/L
  - c) 1.21 mg/L
  - d) 1.42 mg/L
  - e) 1.57 mg/L

- ☐ To next lecture