Unsolved Problems with Corrosion and Distribution System Inorganics

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Arrangement of Problems

- Source water inorganics issues
- Distribution system
- Domestic/building service & internal

Some Nagging Source Issues

- Regulated and likely-to-be regulated contaminants
- Unregulated contaminants

Regulated and Likely...

- Antimony (Sb)
  - Proven difficult to remove below about 15-25 ppb
  - No breakthroughs yet
- Perchlorate
  - Lots of active research
  - Difficulty depends on level and secondary impacts
  - Biological treatment is very promising
  - Membranes, IX currently most known
  - Need good monitoring data for secondary impacts

Regulated and Likely…

- Arsenic
  - Lots of active research
  - Very widespread
  - Often co-occurs with other problem children
    - Metals, especially if source was anoxic mineral assemblage (many aresenosulfides and sorbs easily)
    - U and some other radionuclides
    - Sometimes Rn
  - Cost is still big issue
  - Residuals/waste disposal sometimes constrains removal approach

Iron & Manganese

- Widely distributed
- Readily accumulates on all types of pipes
  - Slow oxidation at low pH; faster at high pH
  - Improvements in disinfection may raise DS ORP
- Strong surface binding properties for metals, phosphate and metals that form oxyanions
- Could be both aesthetic and contamination headache

New Simultaneous Compliance Nightmare: New case study going on now....

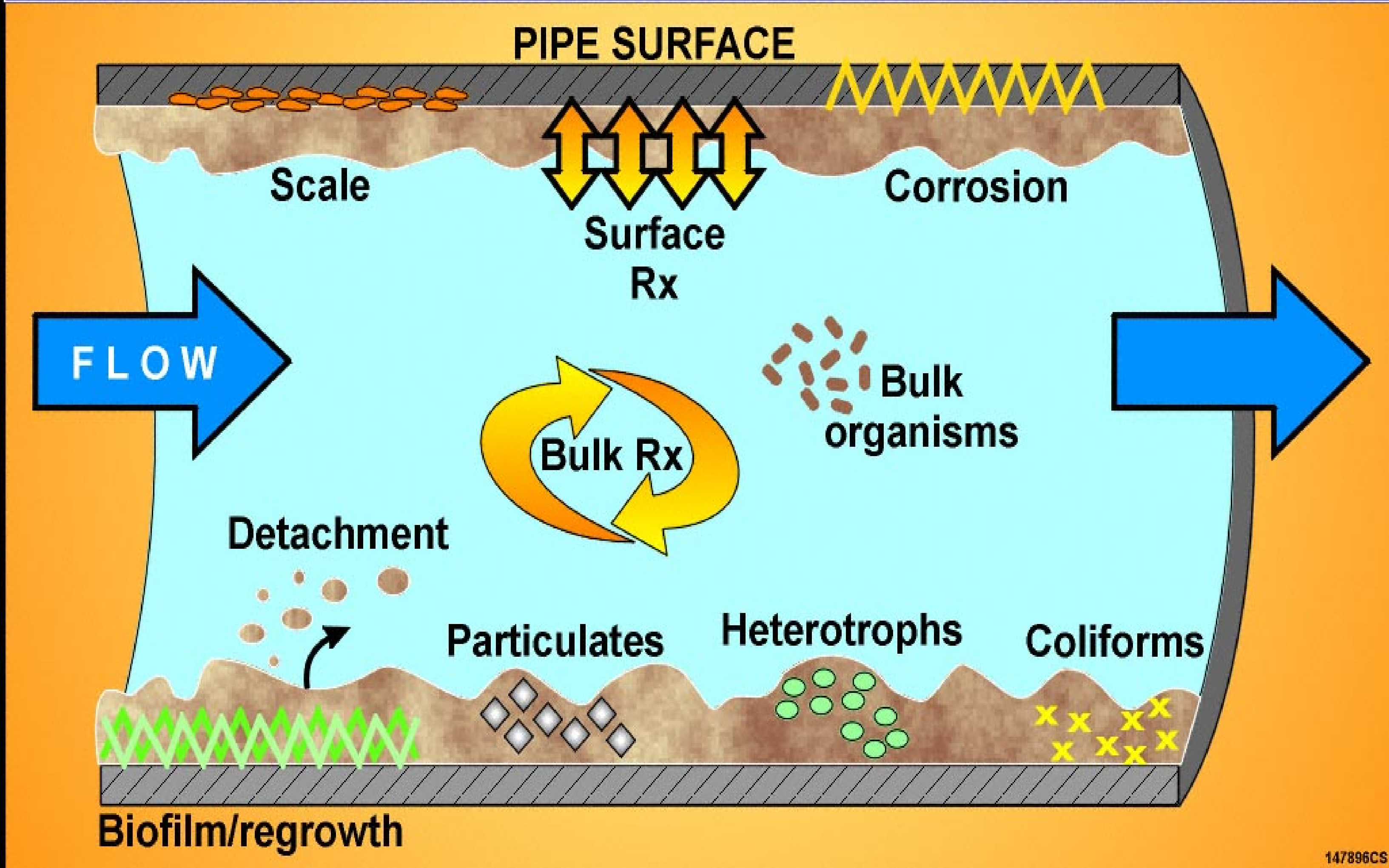
- Perfect storm of conflicts
  - Proactive very small system
  - Restrictive point-source waste discharge constraints
  - Co-occurring contaminants: U, Rn
  - Domestic plumbing with normal Pb and Cu sources
  - Slightly acidic ground water
  - Gravity fed after well & storage, variable demand
  - Local engineer with limited knowledge of big picture on proper application of technologies

Nightmare Cont'd

- Anion exchange installed for As removal
- Regenerated frequently to minimize waste As discharge
- Results:
  - Copper >> 1.3 mg/L
  - High Pb (hundreds to thousands of ppb
  - Erratic pH control
- Solution will be combination of anion exchange, sorptive media, aeration (phosphate if necessary)

Distribution Systems

The Distribution System as Reactor



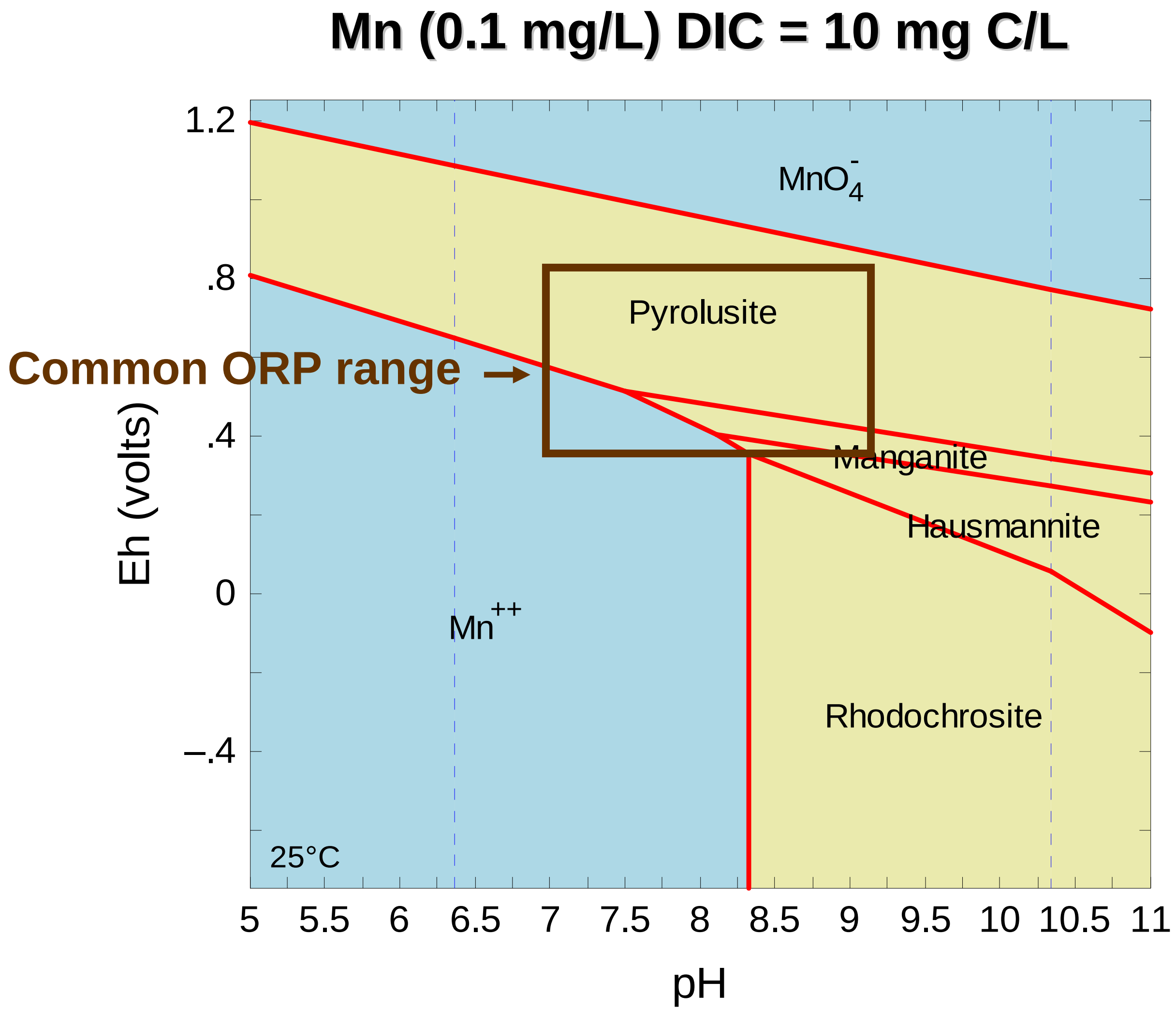
General Nature of Metallic Pipe Surfaces

- Oxides, hydroxides, hydroxycarbonates, carbonates, hydroxysulfates, etc. from corrosion
- Similar compounds from deposition or post-precipitation (particularly Fe, Mn, Al), may include silicates
- Phosphates from corrosion control
- All may be mixed with NOM
- Biofilms present in some areas and some materials

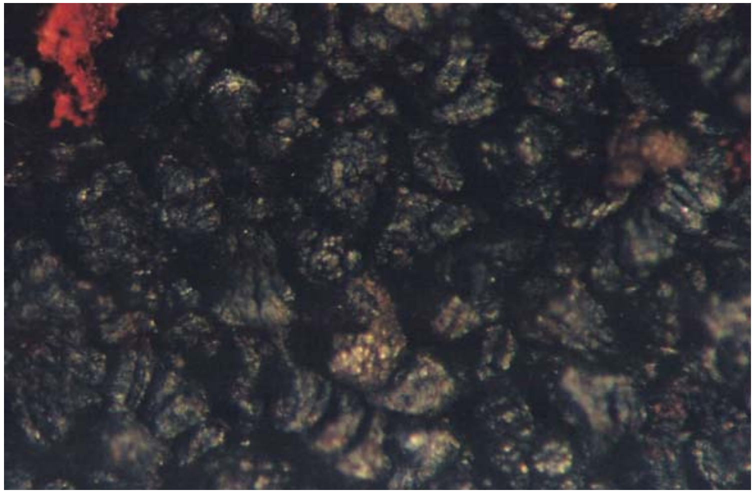
Iron Corrosion

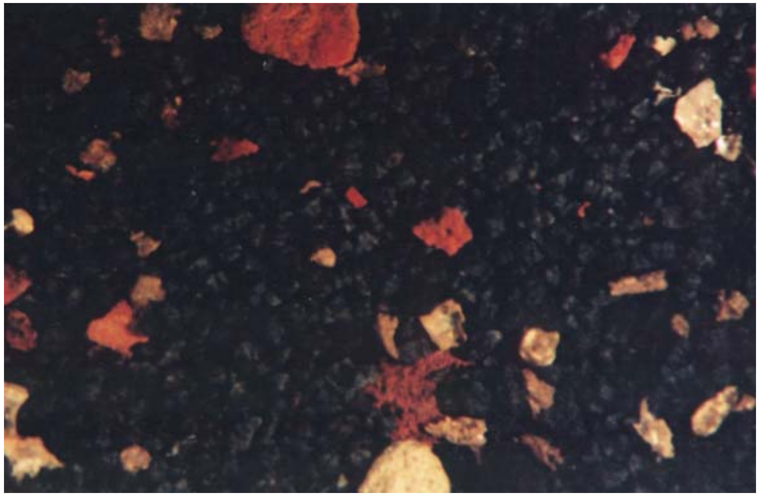
- What water qualities really inhibit tuberculation?
- What is the mechanism for impact of chloride, sulfate, bicarbonate, silicate, phosphate and calcium on scale
  - Thickness
  - Tenacity
  - Permeability
  - Reversibility (reductive dissolution)

pH & ORP Impact on Manganese



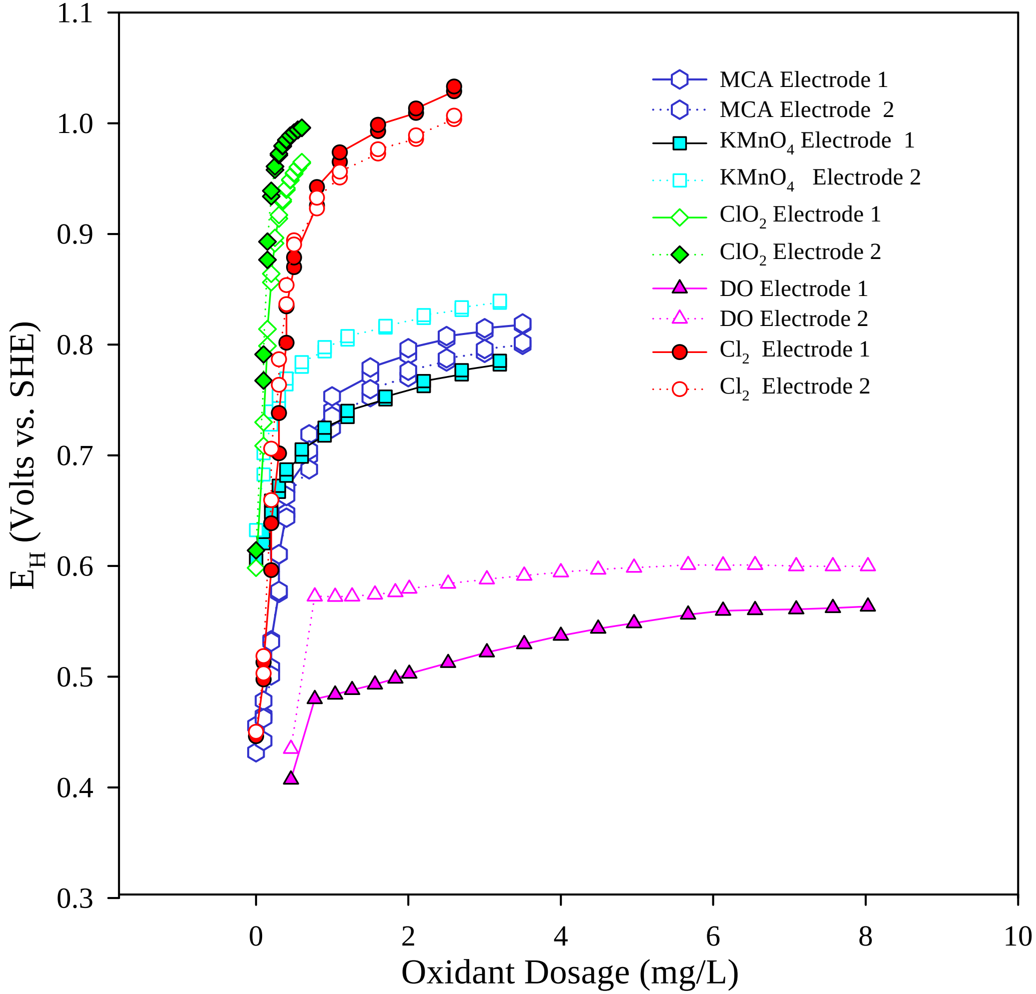
Mn Deposit from Northeastern US DS





Redox Potential of Several Oxidants

(pH 7, 10 mg C/L, 25°C)



Oxidant Research

- Go beyond kinetics of "decay" that are often system specific
- Equilibrium chemical potentials in the bulk water from different disinfectants and treatments
- Understand and quantify factors of "oxidant demand" in bulk water and corrosion byproduct materials
- Develop realistic general models to predict oxidant transformations of metals on and in scales

Practical Issues of Contaminant Accumulation

- What contaminants are involved (health risk?)
- What is the "equilibrium" mass of deposit?
- Where are the contaminants located
  - Relative to consumer ingestion?
  - Relative to regulatory monitoring locations?
  - Relative to types of mains/pipes?

Practical Issues of Contaminant Accumulation

- How easily is it destabilized?
  - How is the contaminant bound?
    - Solid phase, e.g. vanadinite?
    - Sorbed?
  - Phosphates: Do they
    - "Seal" the surfaces?
    - Dissolve or displace the surface compounds and layers?
    - Mobilize sediment particles?
    - Any or all of the above?
  - Hydraulic factors: pressure or flow changes

Nitrification Issues

- Expected to be more prevalent with
  - Increased use of chloramines in combination with phosphate corrosion inhibitors (optimum pH)
  - Disinfection of ground waters with natural NH_3 & NH_4^+
- Manifestations
  - pH drop in low-carbonate systems
    - Increased corrosion
    - Metal release from scales
  - Nitrite levels exceeding 0.5-1 mg/L as N, causing health danger

Nitrification Issues-pH, NO_2^-

Assume:

pH entering system = 7.5

DIC = 2 mg C/L

PO_4 = 3 mg/L

0.5 mg/L NH_4^+-N converted to NO_2N

(only partial completion)

$$dpH = -\frac{dC_A}{\beta} = -\frac{0.036 meq/L}{0.039 meq/L/pH} = -0.92\,pH$$

Aluminum Interactions

- 1991-2 studies in Wales
  - Destabilization of Al scales when alum stopped
  - High levels of Pb, Sb, Sn, Cu and Zn associated with particles
- Various UK studies: high Al leaching from cement relining
- Berend & Trouwborst (1999) documented Al poisoning & deaths of kidney dialysis patients from desalinated water and polyphosphates fed into cement-lined pipes

Aluminum Interactions

- Some health concerns expressed
- Recent research documented widespread occurrence of Al-containing solids in Pb pipe scales from alum-using systems
  - Sometimes protective against Pb release
  - Adverse interaction with phosphates
  - Serious hydraulic problems from phosphates and hydroxides
- Consumption of phosphate inhibitor
- Pre-dosing of P can reduce (Frommel & Snoeyink)

LSL Examples (ppm unless noted)

Al %	Fe %	Mn %	As	Ba	Bi	Co	Cr	Ni	Sn	V
2.3	2.3	1.8	64	142	100	472	72	455	48	6690
3.0	2.9	1.5	71	160	nr	140	180	223	170	4440
1.7	1.2	0.8	42	150	nr	26	280	58	16	6540
0.9	0.7	1.0	43	62	nr	25	110	56	<8	4280
1.3	0.6	0.5	<200	57	<200	40	96	56	170	2760
0.8	0.2	0.2	<200	35	<200	<20	64	<40	220	1900
1.3	1.6	1.3	34	184	35	76	36	50	159	2910
1.0	1.3	0.6	46	120	nr	40	130	78	<10	4310
3.6	2.4	0.3	<200	160	<200	130	210	69	210	3900
4.1	8.0	1.9	150	320	<50	93	230	190	130	6330
1.8	1.6	1.4	<30	124	45	62	49	116	<20	2560

Related Issues

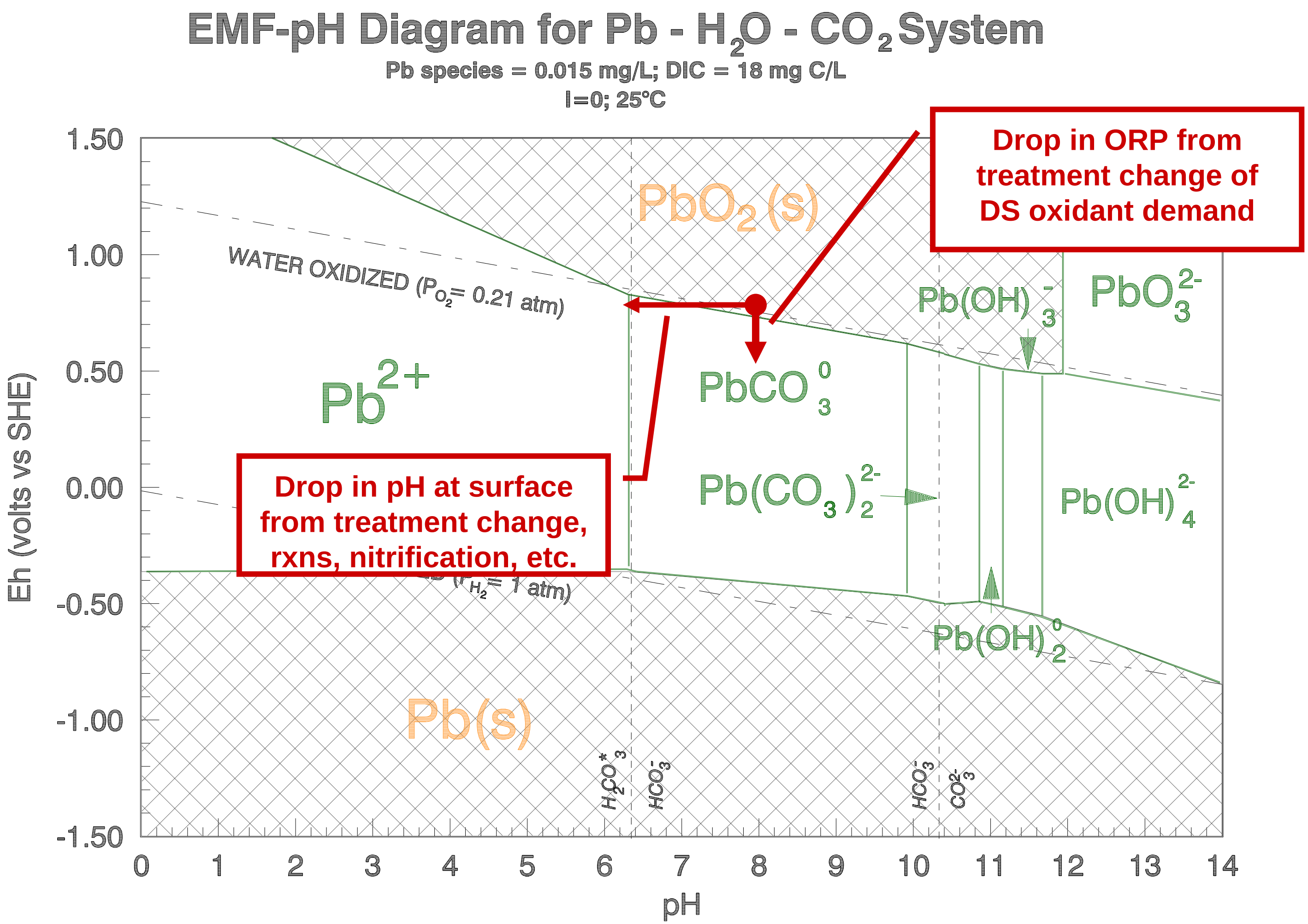
- Rn given off from accumulated Ra
- Persistence of As at or above MCL after As removal processes successfully installed (Lytle, 2007)
- Control of post-precipitation from coagulation
- Severe pH increase from cement lining
  - Adversely affects phosphate inhibitor treatment
  - Turbid water including metals

Domestic/Commercial Plumbing

Major Issues

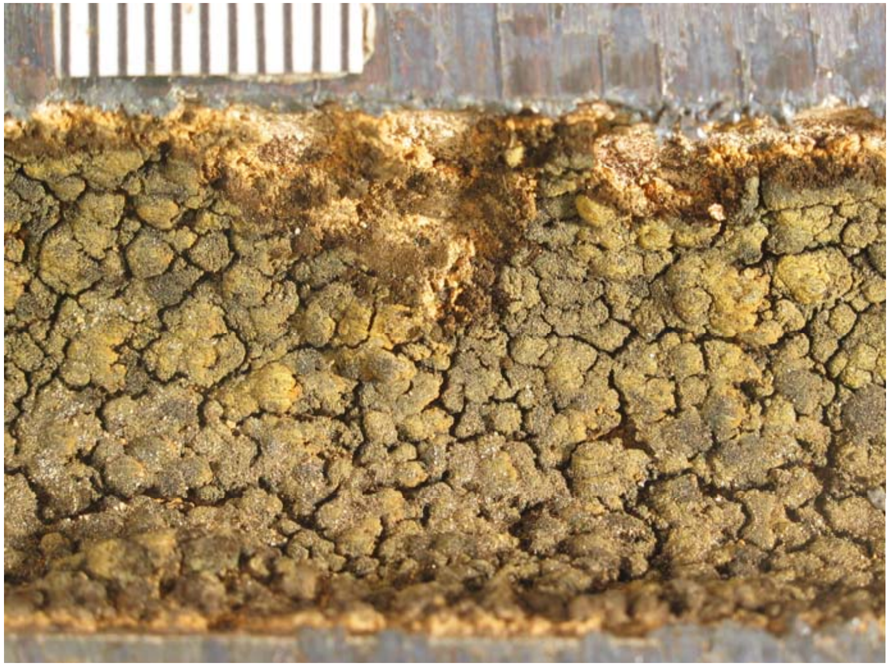
- Prevalence and stability of PbO_2 deposits
  - More prevalent than originally thought
  - Present in 3 modes
    - Nearly uniform scale
    - Mixed scales, multiple minerals, occurs as patches
    - Distinct layer over Pb(II) solids
  - Exact relationship of stability to pH, DIC, type and residual of disinfectant
  - Kinetics of formation and dissolution
  - Refinement of solubility estimates

Ways to Destabilize PbO_2



High Fe, Mn & Al on Lead

$Pb_9(PO_4)_6$ + residual $PbCO_3$



$PbCO_3 + Pb_3(CO_3)_2(OH)_2$

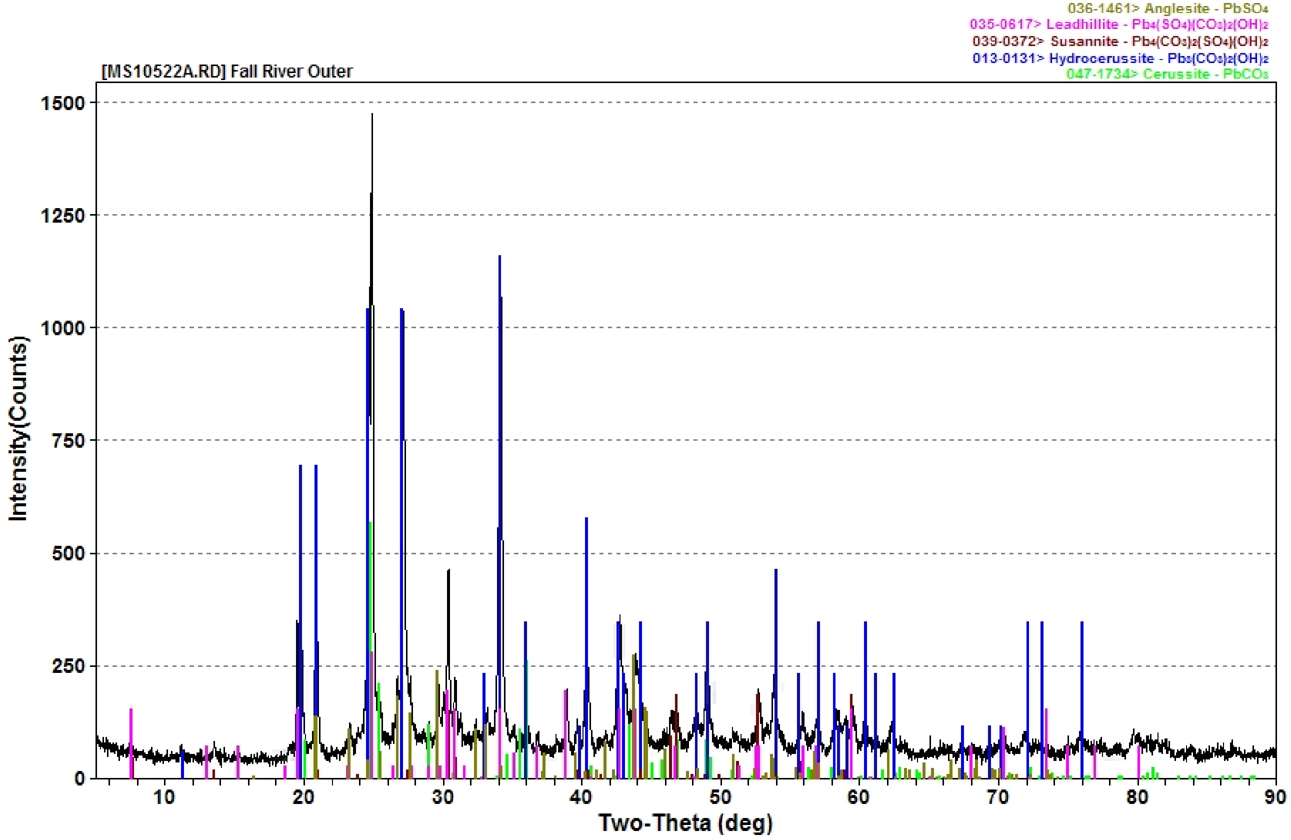
Major Issues

- Serious gaps in knowledge of phosphate solids
  - Critically important for Pb, Cu control
  - May adversely interact with Al, Fe, Mn
- Gaps remain for Pb hydroxycarbonate solubility
  - Especially high pH (> 9)
    - Plumbonacrite identified in scales
    - Need to refine aqueous complexes of Pb(II)
    - Better prediction of phase boundaries of carbonates
  - No usable data for Hydroxycarbonate/sulfate phases
- Long-term leaching characteristics and physical stability of non-Pb alloys
- Factors responsible for copper pinhole leaks

Fall River, MA

Unusual minerals: anglesite, susannite, and leadhillite

$Pb_3(SO_4)(CO_3)_2(OH)_2 + PbSO_4$



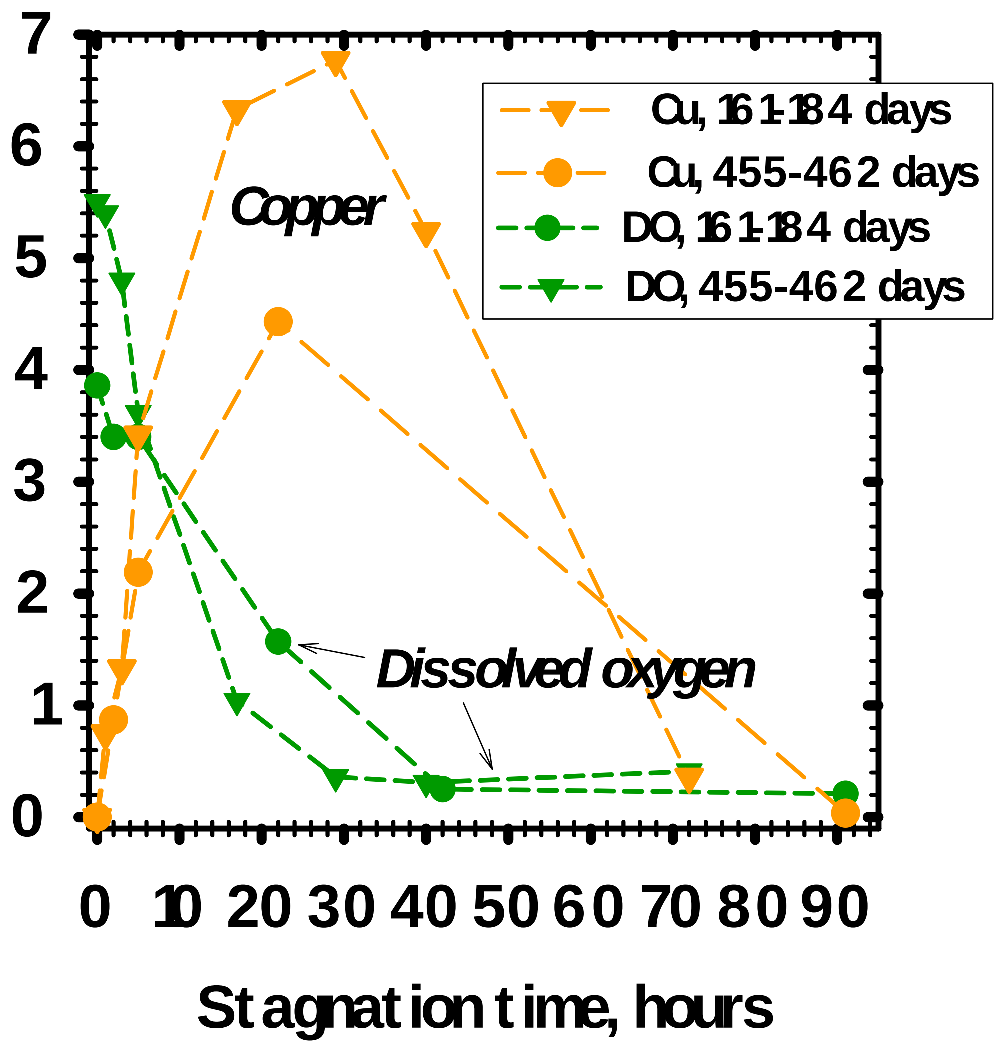
Major Issues

- Role of Mn, Fe, Al, Ca and other deposits on surface
  - Could inhibit metal release
  - Could be sink for inhibitor
  - Could promote erratic particulate release
    - Hydraulic factors
    - Chemical instability
- What is the kinetic or solubility role of non-carbonate anions, such as chloride and sulfate?

Major Issues

- Solubility and kinetics of Fe, Mn, Cu, Al, Pb silicates
- Relationship of pipe age and standing time on copper levels
  - Proper LCR targeting of copper high-risk sites could dramatically increase Cu exceedances
  - Very high dependence of passivating film solubility and mineralogy on age
  - Complex profiles of metal level vs. standing time
  - What are optimal pH & DIC combinations to accelerate passivation and "aging."

ORP in Action with Cu: Stagnation Effects



Conclusions

- Substantial research still needs to be done
  - Where and how contaminants REALLY occur
  - Many temporal variability issues beyond the plant
  - The many interactions among variables requires more emphasis on integrated corrosion/chemistry models
- Combination of fundamental and applied research needed
- "Simultaneous compliance" issues are growing
- Public health protection probably requires important new and revised regulations to realistically assess contamination

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Questions?