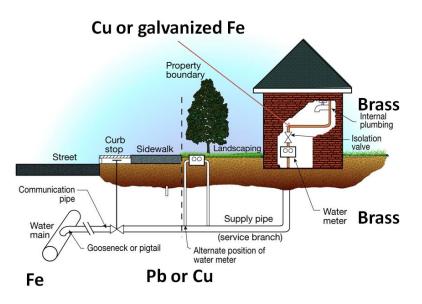# Iron Scales as a Source of Lead Contamination in Drinking Water

JB Maynard   January 2018

Household Plumbing Components

Plumbing materials commonly used in homes are made from copper, brass, lead, and iron, plus, in recent years, plastic. All are subject to deterioration. Normally, the array of pipes, valves, fittings, etc. that make up the plumbing system in a home will last for many years, but there are circumstances that cause premature failure, and these failures can occur in any part of the system. The diagram below illustrates the typical configuration of metal components. Notice that at various points along the flow path of the water, dissimilar metals are in contact. These can be sites of accelerated corrosion leading to failure of one of the parts.

Typical arrangement of the components of household plumbing.
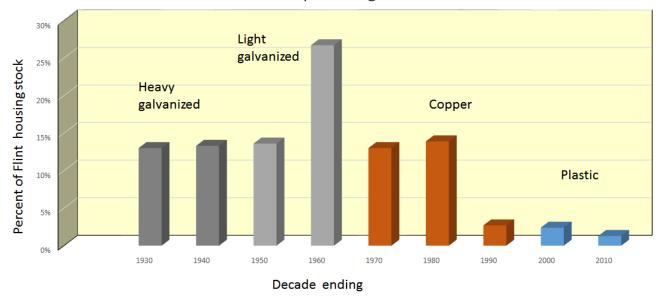
Metals used in household plumbing

Copper (Cu). Probably the dominant material in use today, it has the virtues of strength and durability plus can be installed quickly and repaired fairly easily. It is subject to two kinds of corrosion – uniform corrosion, where a thin layer of copper oxide or copper carbonate forms a protective layer on the surface, and pitting corrosion, in which a small pit is etched into the metal and grows until it breaks through the pipe wall, creating a "pinhole" leak. This style of attack on the metal surface is likely initiated by bacteria.

Lead (Pb). Once highly favored for service lines, lead has proven to be extremely toxic even at low levels and so vigorous efforts are being made to remove it. Where present it normally will be coated with a somewhat protective layer of lead carbonate. In waters with a very high oxidation state, that is with a high, stable chlorine residual, the pipes are protected by a very insoluble lead oxide, plattnerite. A change in disinfection or source water, can, however, destabilize this type of coating. Treatment of the water with phosphate leads to the formation of another very insoluble lead compound, pyromorphite.

Brass (Cu, Pb, Sn, Zn). Brass is an alloy mostly of copper and zinc, with a few percent lead and tin. A large range of compositions exists. For drinking water applications, the diagram below shows the range of zinc contents commonly found. Failure of brass components occurs via leaching of the zinc component, so called "dezincing" of the brass. Much controversy has developed over the causes of premature failures and the role of the Zn/Cu ratio in brass stability as opposed to the constituents of the water to which it is exposed.

Iron (Fe). Pure iron pipes are widely used for water mains but not commonly for premise plumbing. Instead zinc-coated steel ("galvanized) pipes and fittings are used. In the 1920s and 30s, galvanized was the most popular plumbing material for interiors. After World War II, plumbing practices changed: copper replaced lead for service lines and began to compete successfully with galvanized for interior plumbing. Copper had a higher materials cost but was faster to install so labor costs were less. In response, lower quality material began to be marketed for galvanized use and therefore homes built in the 1950s and 60s are likely to have galvanized plumbing components inferior to older homes. By the 1970s, copper had largely displaced galvanized in most applications, but plumbing supply houses still sell lots of galvanized, and it can commonly be found inserted into copper-brass plumbing runs.

Unlike copper and brass, corrosion of iron produces large volumes of scale that deposit in irregular masses on pipe interiors, referred to as "tubercles". These proliferate until they occlude most of the volume of the pipe. Their growth is similar to pitting corrosion in copper in that it begins at specific spots and eats into the pipe as well as building up a scale mass. Bacteria are likely participants. Penetration into the pipe continues until there is a breach and the pipe fails. The oxidation state of the water is crucial in iron reactions, including especially microbial processes, so the nature of the source water and steps taken to treat it have a great impact on pipe corrosion.

Predominant plumbing material

Date of home construction with likely composition of original plumbing

Impacts of Changing Water Quality on Corrosion

A water distribution system consists of an array of parts, mostly metal, and the water flowing through them. Over time, the metals oxidize (corrode) and corrosion by products (scales) deposit on the inner surfaces of the system. These scales consist of an array of compounds that evolve towards a stable mixture that is compatible with the water the system is carrying. This array confers stability on the system by isolating the raw metal from the water, which slows corrosion and limits transfer of metals to the tap. This equilibrium state is readily disrupted, however. For example, if there is a strong seasonal fluctuation in water quality parameters, the scales oscillate in and out of stability, never properly adjusting. The same is true if the water treatment plant does not strictly control variations parameters like pH and chlorine residual. More serious are abrupt treatment changes, for example shifting disinfectants. A change in water source can be especially damaging to a well-established system, if the new water is substantially different, because the old set of scales can be largely swept away, exposing bare metal to accelerated corrosion.

Effects of changing water quality on infrastructure: Iron components

In recent years, concerns have been raised about an additional lead source: galvanized plumbing components. This is distinct from the galvanic corrosion referenced above. "Galvanized" refers to the process of plating steel with zinc to improve corrosion resistance. Galvanized plumbing includes service lines as well as household plumbing, and have been implicated in cases of high lead exposures (for example see McFadden and others 2011; Clark and others 2015; Masters and Edwards 2015). Up until World War II, homes were commonly plumbed with galvanized iron. After the war, copper became common and began to dominate in the 1970s, but galvanized iron is widely available (sold in most hardware stores), and is often found inserted in place of brass fittings in many newer homes where repairs have been made. There is some evidence that galvanized pipes installed in the post-war years were thinner and had less coating, so there is a possibility that homes built in the 50s and 60s would have a greater susceptibility to plumbing failures than would be expected for their age.

Lead concentrations at the tap in homes with galvanized plumbing can remain high even after removal of a lead service line. In fact, the DC Water and authority states on their website

> **WHAT DO I DO IF MY HOME HAS GALVANIZED PIPES?**
> The only way to fully ensure that lead is not mobilized from galvanized plumbing in a home is to fully replace the galvanized plumbing.
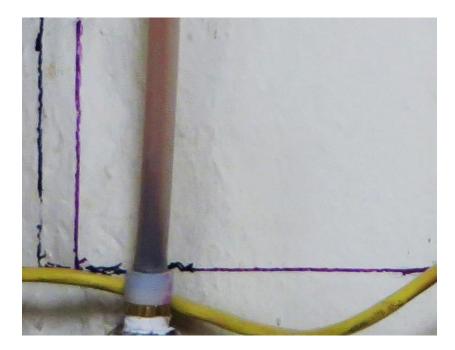> https://www.dcwater.com/faq-page/15#t15n901

Most researchers attribute this lead to particulates dislodged from the service line that became attached to the iron scales in the household plumbing.

Particulates are of critical importance in assessing risk from lead exposure. For example, Sandvig and others (2008) report for 53 tap water samples from one utility that on average particulate lead was 65% of total lead. Particulate material is mobile, or potentially mobile. It can be suspended in

water and move as the water flows, then settle out again as the water slows. Particles can be physically deposited, subject to later re-suspension and mobilization as flow rate changes and surges. Or they can become embedded in existing corrosion scales. Furthermore, like scale, a particle can also dissolve and become soluble lead. Particulate lead, once formed, can dissolve and become soluble lead, or it can be transported as particulates to the customer tap. The water the customer is exposed to can contain soluble lead or any particulate material transported from sources near and far to the tap. Variations in the above described relationship between particles and scale could include (Brown and others, 2015):
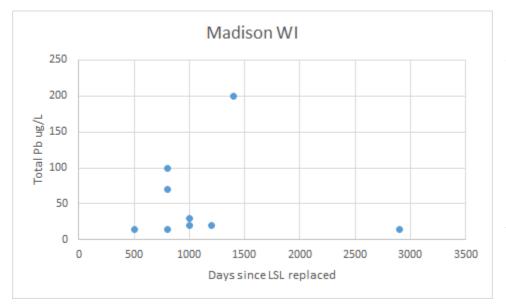
- particulate matter physically deposited on a surface can become embedded as scales deposit over it,
- soluble lead could chemically precipitate as scale on a particle surface (even a particle that does not contain lead),
- lead in particulate matter could dissolve in water then later chemically precipitate as scale
- scale can chemically precipitate onto a previously deposited scale, including scale deposited onto or co-deposited with scale of a different composition

This pathway of lead exposure from left-over particulates can be termed as "legacy contamination." It is especially severe in homes with interior plumbing that contains galvanized iron. According to Sandvig and others (2008), it also occurs to some extent in homes with copper plumbing as well as galvanized. An accumulation of iron particulates is shown in plastic pipes from utility 5. See also Salehi and others (2017) for plastic plumbing.

Before and After LSL Replacement: 4 Cities

data of Sandvig et al. 2008

How prevalent is this legacy contamination and how long does it persist? Sandvig et al (2008) report data from several cities making service line replacements. The results show improvement in 1st draw lead two months after complete service line replacement, but that significant lead remains.

A longer-term study conducted in Madison WI (Cantor, 2006) showed that some houses continued to exhibit high particulate lead for years after LSL replacement:

Some homes continue to exceed LCR limits long after replacement of lead services (only 1st draw samples with >15 µg/L shown)

Iron Scales in Distribution Systems as Agents for Lead Transport

Iron compounds are likely culprits in the persistence of lead in a house after removal of a lead service line. Iron can either be from upstream of the service line, for example in cast iron water mains (see Little and others 2014) or downstream, for example as galvanized steel pipes and fittings inside the house (Clark and others, 2015).

Toxic Substances in Upstream Iron Scales

There is good coverage for the upstream situation, which includes both surveys of a few samples from many distribution systems and intensive studies of a single system. An example of survey data is summarized in the paper by Peng and others (2010):

mg/kg	n	Al	Ba	Ca	Cr	Mg	Fe	Mn	Ni	P	Pb	S	Si	V	
Survey of elements in iron scales of U.S. distribution systems (Peng et al. 2010)															
Cast iron	22	1771	350	4702	14	1306	309091	1052	39	157	20	1.7	2172	29	
ductile iron	5	5022	162	766	7.0	152	311200	866	9	132	5	1.1	1154	27	
galvanized	4	938	80	6649	109	270	346500	1913	253	32	1199	0.4	1839	228	

Regulated elements (Cr, Pb, V) are quite low, except in galvanized pipes, although the sample set is small for that category. A study of a single system was presented by Gerke and others (2008). The aim of this paper was to test the range of variation within a single system, but it also shows quite low values for potentially toxic elements.

	Ca	Fe	Mn	P	Cr	Cu	Pb	Sr	V	Zn	Sr/Ca
Chemistry of multiple tubercles from one pipe - Utility 2 (Gerke et al. 2008)											
	%	%	%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
FeOOH-rich textures											
Surface	3.90	50.2	0.11	0.09	26	13	25	38	11.9	13	9.7
Core	0.56	59.2	0.04	0.17	27	7	96	9	3.2	8	13.4
avg	2.23	54.7	0.07	0.13	26	10	61	23	7.6	11	11.5
Fe_3O_4-rich textures											
Shell	4.82	50.8	0.11	0.05	19	6	11	30	8.4	9	8.0
Veins	0.81	56.6	0.04	0.12	28	6	159	7	2.3	7	10.2
avg	2.82	53.7	0.07	0.08	23	6	85	19	5.4	8	9.1
overall avg	2.52	54.2	0.07	0.11	25	8	73	21	6.5	9	10.3

In another study of scales from a single utility, Jones (2013) reported on water mains (flowing water) v fire hydrants (stagnant water). Again, regulated substances are low, except Ba. Notably enriched in the hydrant scales are Ca and especially Sr. See Gerke and others (2013) for a discussion of Sr in iron corrosion scales.

Chemistry of tubercles from individual pipes and hydrants - Utility 2 (Jones, 2013)													
Major elements by tubercle region (wt. %)							Trace elements (mg/kg)						
	Fe	Mn	Si	Al	Ca	P	S	Ba	Co	Cr	Cu	Pb	Sr	Zn
Mains													
FeOOH-rich textures													
Surface	44.3	0.19	6.63	3.50	5.18	0.22	1.31	2505	28	25	31	12	62	20
Core	59.1	0.03	1.27	1.32	0.56	0.17	1.82	2118	29	27	7	96	9	8
Fe$_3$O$_4$-rich textures													
Shell	51.8	0.10	1.31	1.40	3.84	0.05	0.95	2287	31	17	7	19	31	9
Veins	56.5	0.04	1.13	1.26	0.81	0.12	1.79	2453	29	27	6	159	7	7
overall avg	52.9	0.09	2.59	1.87	2.60	0.14	1.47	2341	29	24	13	71	27	11
Hydrants													
FeOOH-rich textures													
Surface	25.6	0.06	1.18	1.27	20.9	0.01	0.62	4560	12	46	11	12	391	9
Core	57.8	0.05	1.56	1.35	1.35	0.08	0.34	1622	34	40	3	11	21	6
Fe$_3$O$_4$-rich textures													
Shell	34.8	0.07	1.55	1.40	15.8	0.04	0.68	3981	17	33	10	12	243	9
Veins	57.7	0.02	1.30	1.64	0.74	0.05	0.78	2919	36	50	14	9	15	8
overall avg	44.0	0.05	1.40	1.42	9.68	0.05	0.60	3271	25	42	9	11	168	8

It would seem that there is little reason to consider the upstream source as a direct contributor to lead in household plumbing despite the fact that there exists a huge reservoir of potentially mobile iron particles in this position. These particles could, however, lodge in premise plumbing to become traps for lead coming from the service line.

Toxic Substances in Downstream Iron Scales

There is more limited data available on downstream iron. We have analyzed galvanized premise plumbing from three cities:

Concentration of selected elements in iron corrosion scales on galvanized pipes										
	n	Ca %	Cd mg/kg	Cr mg/kg	Cu mg/kg	Fe %	Mn %	Pb mg/kg	S %	V mg/kg
Utility 1	4	0.86	55	34	4222	38.5	2.45	4646	0.47	335
Utility 2	13	2.16	429	73	701	19.1	0.11	2549	0.41	10
Utility 5	15	0.39	272	63	4748	39.3	0.10	3349	0.10	62
n is the number of individual pipes. Multiple samples were taken from each pipe; total of samples was 72. Some of our results for Utility 1 are included in McFadden et al. 2011. Some results were presented by Maynard & Wasserstrom 2017										

It is striking in these numbers that lead and copper are very strongly enriched compared to values from upstream iron corrosion scales. Particles detached from the downstream scales would be major contributors to lead exposure from tap water. Among the three cities, the water supplied by Utility 1 has the highest lead, and also the highest manganese. Manganese is an even better trap for lead than is iron, and could play a role in lead exposure (see Gerke and others 2015).

A question remains of whether the lead measured is derived from the service line or derived from the galvanized pipes themselves. Trussell and Wagner (1996) report that the most commonly used source of zinc for galvanizing, Prime Western, contains up to 1.4 % lead. We made 8 measurements of scrapings from the exterior of galvanized pipes in the service area of Utility 5, obtaining an average Pb content of 0.7 %. Clark and others (2015) measured 0.8 to 1.7 % Pb in zinc plating on pipes. Thus, the upstream pipes themselves can be a source of lead.

As it happens, galvanic coatings are also enriched in cadmium as well as lead, whereas other lead sources in distribution systems are Cd free (Clark and others, 2015). In our survey of galvanized pipes, Utility 1 is low in Cd, whereas pipes from utilities 2 and 5 are considerably higher. It is reasonable to conclude that the lead found in the homes supplied by Utility 1 came from the original lead service lines as particulates that then lodged in the premise plumbing, whereas it is predominantly from the downstream

galvanized pipe itself in the other two cases. Therefore, both lead sources can come into play.

An example shows how legacy contamination manifests itself in houses that have iron scales in premise plumbing.

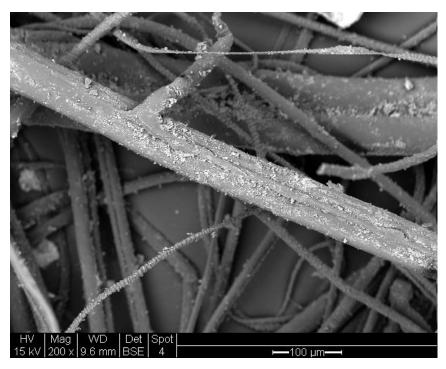### Particulate lead trapped by iron compounds

A house served by utility 2 was studied for Pb and Cu capture by point-of-use carbon filters (Cantor, 2013) One of the houses studied had a complete lead service line with copper internal plumbing. There was at the point-of-entry a sediment filter which had not been exchanged for several years. It was heavily coated with iron compounds:

Sediment filter clogged with iron oxide. Has percent level lead as well.

Xrf pellets prepared by melting plastic fabric

Fe = 9.1 %   Pb = 4.7 %
Mn = 0.8 %   Cu = 0.6 %

Moreover, considerable lead was also contained in the filter. SEM imaging shows a dense coating of lead on top of iron-impregnated filter fibers.

Sediment filter made up of polyester fibers coated with iron (the dull gray in the image) to which particles of Pb (white specks) have attached or onto which lead has precipitated from solution

Iron hydroxides, especially goethite – FeOOH – have long been known to have a high affinity for adsorbing heavy metals from solution (Cornell & Schwertmann, 2003, provide a good review). The sequence at this house appears to have been, first, the accumulation of iron corrosion by products, derived from cast iron water mains upstream, followed by attachment of lead derived from the service line to the pre-existing iron compounds, both in dissolved and particulate form. This lead might have been sequestered indefinitely inside the filter. On the other hand, some disturbance, whether physical jarring or a change in water chemistry, might send a wave of lead-bearing particles downstream to be consumed by the residents. Thus, the iron on this filter can act as a sink or a source for lead, depending on changing conditions.

The experience from this house points to the importance of particulate lead in domestic plumbing. It shows that this lead moves through the system, accumulating in quiet areas along the flow path or sticking to iron oxide-hydroxide scales on pipe interiors along the way. This accumulation of legacy lead particles can lie dormant, especially if the system is not properly flushed, until some disturbance occurs, when a large reservoir of lead suddenly becomes available.

Factors Promoting Destabilization of Iron Scales with Consequent Lead Exposure

From the case study, it can be seen that (1) lead can be transported into homes as particulates to lodge in the domestic plumbing; (2) that lead has a high affinity for iron
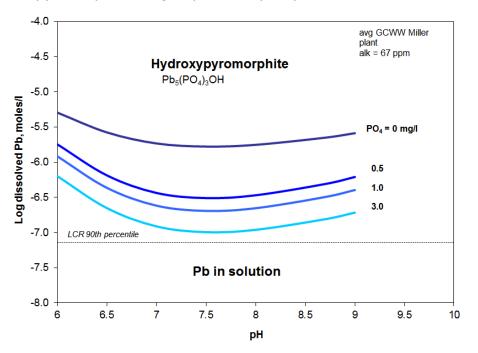
hydroxide surfaces. From survey data, lead is not found in significant amounts attached to iron corrosion scales upstream of lead services, but can be highly elevated downstream. In addition, lead can be released from the zinc coatings on galvanized iron to be reprecipitated in iron corrosion byproducts within the home. So, there are two sources of iron particles, the upstream water mains and the downstream plumbing if it contains galvanized iron pipe. There are also two sources of lead, the service line and galvanized premise plumbing. Note that upstream iron particles, originally very low in lead, will acquire it over time, so all iron scales within the home have the potential to be carriers of lead.

If these lead-bearing particles simply stayed in place, they would provide little threat to the home's residents. What events might be responsible for dislodging this material? The three most critical water quality variables in controlling corrosion scale behavior are pH, phosphate content and redox level. Decreases in any of the three can destabilize existing scales. The pH of the water is normally controlled at the treatment plant and varies only modestly through the distribution system. In the same way, systems that use phosphate for corrosion control normally keep a constant level in the whole system. Systems with constant chlorine residual will have constant redox levels in flowing water, although not in stagnant. Therefore, normal water utility practice will promote stability in corrosion scales. However, water utilities often blend different source waters in different proportions, may change disinfection procedures, or may change their approach to corrosion control. Any of these events may have a disastrous effect on existing scales. The usual effect is to cause sloughing of scale from the pipe walls, which has two effects: first obvious particulates appear at the tap (red water) and second fresh metal surfaces are exposed to corrosive attack. This causes rapid reaction between metals and the water, resulting in elevated dissolved lead and copper, but also weakens the metal and can produce structural failures and considerable water and mold damage from leaking pipes and fixtures.

Of the three factors mentioned, redox levels are the most difficult to control, which has been the source of serious problems with lead exposure. Redox in distribution systems is affected by disinfectant type and levels and by the amount of organic matter in the water and in the corrosion scales. Systems using chlorine have a high initial redox level, and if organic matter is low, they tend to maintain a high chlorine residual throughout. Systems using chloramine have a lower initial redox level, and the nitrogen added to the system can promote bacterial growth that further lowers redox levels. Finally, organic matter itself can lower redox levels, through stimulating growth of bacteria.

Destabilization of iron - effect of phosphates

Phosphate addition is the normal first line of defense for a utility experiencing rising lead levels. The theoretical underpinning for this strategy is the very low solubility of the pyromorphites, a group of lead phosphate minerals:

The addition of phosphate favors the formation of pyromorphite, which is very insoluble and so passivates lead on lead or brass surfaces

The added phosphate can be in the form of the simple monomer, orthophosphate, or can be one of many polyphosphates, the most common being hexametaphosphate. Often the chemical applied will be a proprietary blend of phosphates, making it difficult to interpret results across different utilities. For example, Cantor and others (2000) found that in some circumstances polyphosphates actually increased the amount of lead or copper released. Likely this effect results from varying ratios of ortho- to poly-phosphate. Too much poly- may lead to stabilization of the metal in solution rather than in the solid, and therefore increase rather than decrease exposure to lead. The authors also concluded that it was necessary for a utility contemplating the use of polyphosphates to run tests for 6 months to 1 year to obtain stable results for predicting effects out in the system. Further, Cantor (2017) stressed that phosphate treatment seems to be effective only against release of dissolved lead and has no benefit for particulate lead.

Although phosphate addition has a good track record in reducing dissolved lead release from lead pipes, the situation is not so clear for cast iron and galvanized iron pipes. Polyphosphates have long been used to control the appearance of high iron in drinking water, so called "red water" complaints. It is important, however, not to confuse the problem of colored water with the problem of iron corrosion (McNeill and Edwards, 2000, 2001). The polyphosphate forms a complex with soluble iron that prevents it from

precipitating and therefore generating turbidity and red color. As a consequence, polyphosphate dosing may cure the red water complaint but actually enhance iron corrosion.

Some information about orthophosphate effects on lead attached to iron is available in Wasserstrom (2016). She used synthetic scales, prepared by the precipitation of monomineralic iron oxyhydroxides onto fiber filters. These filters were then exposed to lead doped tap water in a flow-through faucet rig, and the amount of lead absorbed measured from the volume used and the incurrent and excurrent lead concentrations. A parallel control, using a filter without added iron was run at the same time. Once the lead solution was exhausted, a new solution doped with orthophosphate was run through the filters. Subsequent lead leaching was suppressed by the added phosphate, but only at relatively high phosphate levels.

Effect of phosphate on Pb attached to FeOOH (lepidocrocite)					
Test run	Step 1 - Fe addition	Step 2- Pb addition		Step 3 - PO$_4$ addition	
	Fe mass (g)	Pb conc (ug/L)	Pb retained (mg)	PO$_4$ conc (mg/L)	Pb released (mg)
Run 7	7	40	3.8	1.8	1.3
Control	0	40	0.2	1.8	0.4
Run 8	7	40	5.4	3.5	0.3
Control	0	40	0.5	3.5	0.2
Run 9	7	40	5.5	11.6	0
Control	0	40	0.01	11.6	0.1

Low levels of PO$_4$ allowed lead to be leached, whereas at 3.5 mg/L and above, lead was effectively retained. Most utilities dose phosphate at less than 3 mg/L (as PO$_4$), which may be inadequate or poorly protective in cases where there are iron-rich scales within the premise plumbing. For example, the Detroit water treatment plants used 2-5 mg/l PO$_4$ in 2014-2015, which would have been somewhat protective of lead attached to iron scales, but not completely. Flint, Michigan was originally using Detroit water with PO$_4$, but switched to Flint River water with no added PO$_4$. A burst of lead and iron release followed, which pushed these two contaminants into premise plumbing. Flint then switched in October 2015 to a Lake Huron source, to which PO$_4$ was added at about 3 mg/l. This amount was likely inadequate to prevent further leaching of the bolus of lead that had been added to the premise plumbing.

From work at VPI (McNeill and Edwards, 2000) and in our laboratory, it seems likely that adding phosphate to distribution systems will not be of much benefit to homes that have been contaminated with lead-bearing iron particulates unless higher-than normal
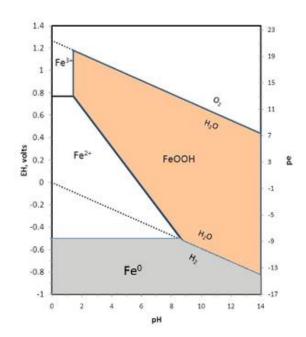
doses are applied. Moreover, lowering or eliminating phosphate could lead to catastrophic release of iron particulates. If these contain lead, as they would in galvanized pipes, they would generate extremely high lead exposures in tap water.

Destabilization of iron - Effect of changing redox

Iron is highly sensitive to the oxidation state of the system. There are various ways to express the oxidation level. In distribution systems the two most common are Eh, the potential relative to a standard hydrogen electrode, and ORP, the oxidation-reduction potential relative to a Ag/AgCl reference electrode. ORP is the field measurement usually made; Eh is used in theoretical calculations. The two are related by

Eh = ORP + 0.241volts   (Copeland and Lytle 2014)

When Eh of the system is low, iron is in the ferrous state, Fe^{2+}, and is relatively soluble. When Eh is high, iron is in the ferric state, Fe^{3+}, and is insoluble at normal pH values. Redox behavior of this kind is normally represented in Eh-pH (Pourbaix) diagrams as follows.

Eh-pH diagram for Fe + H_2O. The upper boundary is the stability limit of water, where H_2O breaks down to yield O_2; conversely the lower boundary is where H_2O breaks down to yield H_2.
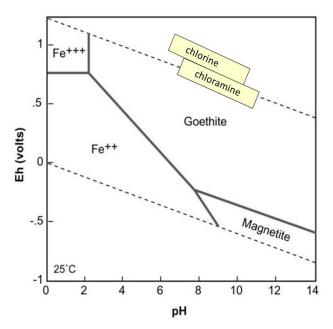
Note that metallic iron is unstable in the presence of water and will tend to oxidize, that is to rust, releasing H_2 gas. This is the fundamental process of iron pipe corrosion, which produces a variety of iron corrosion byproducts:

Ferric oxide and hydroxide minerals			
Name	Formula	Color (fine-grained)	
Goethite	α-FeOOH	Orange-yellow	Common in tubercle cores
Lepidocrocite	γ-FeOOH	Orange	Common as surface layer on tubercles
Feroxyhyte[2]	δ-FeOOH	Yellow	Converts to goethite on exposure to air
Ferrihydrite	$Fe_{10}O_{14}(OH)_2$	Yellow-brown	Common in soils; rare as pipe scale
Hematite	α-Fe_2O_3	Red	Common in soils; rare as pipe scale
Maghemite	δ-Fe_2O_3	Brown	Common in soils; rare as pipe scale
Mixed Ferrous-ferric minerals			
Green rust	$(Fe^{2+}_4Fe^{3+}_2(OH)_{12}$ $(CO_3)(H_2O)_3)$	Greenish black	Common in tubercles but quickly converts to FeOOH on drying
Magnetite	$Fe^{2+}Fe^{3+}_2O_4$	Black	Common in tubercles as a hard cap
Ferrous minerals			
Siderite	$FeCO_3$	White to purple	Common in core of tubercles
MacKinawite	FeS	Black	Likely to occur in cores, frequency unknown
Pyrite	Fe_2S	Greenish Black	Common in sediments; rare in distribution systems

The key message is that processes that lower the redox level will make iron more soluble and will disrupt previously deposited iron scales. Once these scales are disturbed, direct attack on the pipe is possible and pipe failure results.
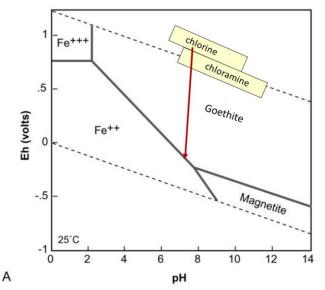
Destabilization of iron - Effect of disinfectant changes

Water utilities commonly disinfect water using chlorine or chloramine, either as the primary or as the secondary disinfectant when ozone or uv is the primary. Chlorine produces a very high redox level, higher than the stability field of water, so it is an extremely powerful and effective oxidizer of organic matter, including microbes. Chloramine is less effective but is longer-lasting, which is important in maintaining a stable total chlorine residual. The first diagram below shows the approximate position of drinking waters disinfected with chlorine and with chloramine. In either case, the oxidation state of the system is very high, as high or higher than the stability limit of water.

Eh-pH diagram for stable iron oxyhydroxides and oxides. Superimposed are the fields for measured values of Eh and pH for chlorine and chloramine disinfectants from Copeland & Lytle 2015.

Keeping some disinfectant throughout the system is key to public health, but also to the integrity of the distribution infrastructure. If there is too much organic carbon in the water, all of the chlorine or chloramine will be consumed, and the oxidation state of the water will fall. The consequence is having the system pass out of the chemical conditions that keep iron and manganese solids stable and into those that dissolve these and other metals, as shown below. We know that Flint experienced long periods of low to no chlorine residual, which would have moved the water out of the stability field of the solid iron oxides into the field of dissolution.

Predicted path for a drinking water if chlorine residual goes to zero. PHREEQC model of water with alkalinity of 85, chloride = 75, sulfate = 28.

A

Another issue with organic matter in drinking water is that it reacts with chlorine during disinfection to create toxic byproducts like chloroform. Chloramine has less tendency to form these compounds, but it drops the oxidation potential somewhat, enough to destabilize the lead[IV] oxide PbO_2. The lead crisis in Washington DC was associated with a switch from chlorine to chloramine disinfection, which dissolved long-established lead scales. A serious indirect effect of chloramine emerges from its tendency to induce nitrification by bacteria, which convert the ammonia portion of the molecule to nitrite.

$$NH^{4+} + 3O_2 = 2H_2O + 2NO_2^- + 4H^+$$

The reaction consumes oxygen and releases acid, so both the Eh and pH are lowered, driving the water towards the field of soluble iron. The situation is magnified if there is significant manganese in the scale. The redox boundary for soluble manganese is appreciably higher than that for iron, so manganese will be readily lost from the scale, making it physically less stable.

Destabilization of iron – Sulfate-reducing bacteria

Organic matter poses a serious concern for the maintenance of distribution systems, and most utilities vigorously attempt to minimize it. Cantor (2017) did a detailed investigation over several years of maintenance practices at eight utilities in Wisconsin, and found that cleaning the system, "maintaining system hygiene", was more effective at reducing lead and copper levels than chemical treatment of the water. Systems with high organic carbon will have high levels of microbial activity as microorganisms use this carbon as a food supply. In the process they reduce the oxidation state of the system, which favors dissolution of iron and consequent release of any toxic substances adsorbed to that iron.

Lytle et al (2005) showed that sulfate-reducing bacteria can be active inside iron tubercles, as measured by the degree of isotopic fractionation of the sulfur. These bacteria can produce severe corrosion of metallic iron via their production of H_2S or by direct attack on the metallic iron (Enning and Garrelfs 2014).

Corrosion rates of iron by these bacteria can be as high as 0.9 mm/year. Thus, it would take a little over three years for corrosion pits to penetrate a typical galvanized iron pipe (3mm thickness). Introduction of high sulfate, high organic water into a distribution system with little or no chlorine residual, as occurred at Flint, would lead to proliferation of these bacteria and sharply accelerated deterioration of any iron-based plumbing components.

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