

Introduction

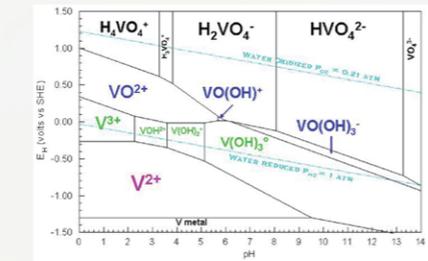
Vanadium can be either beneficial or toxic to humans, depending on its oxidation state and concentration, and its toxicity increases with increasing oxidation state. Under environmental conditions in natural and drinking water, vanadium dominantly exists in either the +4 or +5 oxidation state as aquatic species of vanadyl (VO_3^{2-}) or vanadate (VO_4^{3-}), respectively. Under somewhat reducing conditions, vanadyl (V^{IV}) species may be stable depending upon pH (Wehrli and Stumm, 1989), under oxidizing conditions, V^V (vanadate) is stable across almost the entire pH range and both ions can coexist depending on the redox potential and pH of the water and their concentrations.

The California Department of Public Health, Drinking Water Program posted a notification level for vanadium in drinking water of 5 micrograms/L in 2007 (<http://www.cdph.ca.gov/drinkingwater/Pages/default.aspx>) because of the growing body of evidence regarding its toxicity to humans from ingestion of drinking water. Recently, the accumulation of vanadium, up to as much as 2% by weight, has been reported for corrosion deposits in lead drinking water pipes from numerous United States public drinking water systems. Thus, there is a potential reservoir for human exposure, should vanadium mobilize as a result of drinking water treatment changes to meet new or more stringent regulations.

This study presents the first detailed look at vanadium speciation and distribution in lead drinking water pipe corrosion by-products. Diverse synchrotron-based techniques, including bulk XANES (X-ray absorption near edge spectroscopy), μ -XANES, μ -XRD (X-ray diffraction), and μ -XRF (X-ray fluorescence) mapping along with scanning electron microscopy - energy dispersive X-ray analysis (SEM-EDX), and wet chemical analyses were utilized in this study.

Thirty-two layers from 15 lead pipe corrosion by-products from eight different municipal drinking water distribution systems representing a wide range of water chemistries in the Northeastern and Midwestern portions of the United States were obtained for this study.

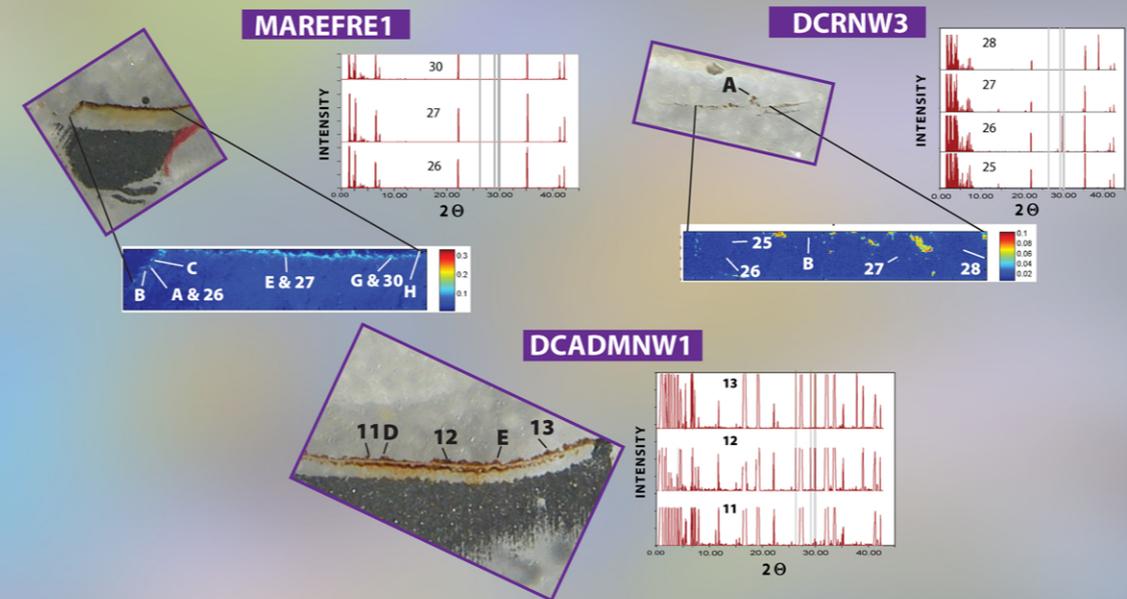
Eh-pH Diagram for Vanadium



Eh-pH diagram showing the predominance areas of the aqueous vanadium species following the Wehrli and Stumm (1989) model, computed assuming dissolved vanadium species activities of 0.1 mg/L, 25°C, and an ionic strength of zero.

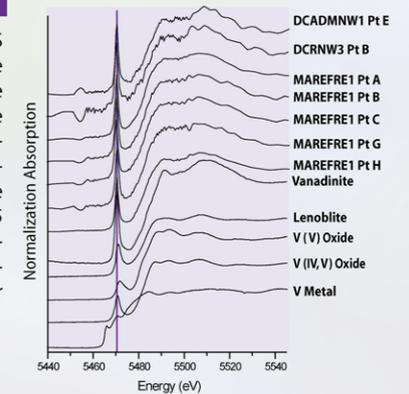
Twenty seven of the 32 corrosion by-product layers had sufficient material for ICP-OES analysis. The vanadium concentrations ranged from <40 to 8,5000 ppm with an average concentration of 2756 ppm. Ten of the corrosion by-product layers were previously analyzed by ICP-OES (Schock et al., 2008) and 16 additional corrosion by-product layers were analyzed for this study by the USGS.

Three of the lead pipe samples with their in-situ corrosion by-products from two DWDS's were analyzed with μ -XRD, μ -XRF, and μ -XANES to identify vanadium-rich phases and their location within the corrosion by-products. Two samples (DCADMNW1 and DCRNW3) are from a DWDS supplied by surface water and the other (MAREFRE1) by groundwater. Micro-XRF mapping of DCRNW3 and MAREFRE1 determined regions of discrete high vanadium concentrations. Vanadium appears to be mainly in the outer most portions of the corrosion by-products. One location, in sample DCRNW3 and three locations in DCADMNW1 produced μ -XRD traces that support the identification of vanadinite.



In-Situ XANES

The μ -XANES spectra for these samples were very similar to the bulk XANES spectra with distinct pre-edge peaks at 5469.5 eV thus vanadinite is the primary species for the in-situ samples.



CONCLUSIONS

- 1) This study presents the first known identification of vanadinite in lead pipe corrosion by-product that form in DWDS.
- 2) The overall distribution of vanadinite in lead corrosion by-products was predominantly in the surface layers (n = 8 of 13) however it was present in four of the intermediate and two of the basal layers. The intermediate and basal layers where vanadinite is present are from samples that are from the same DWDS. This water utility implemented a treatment change in 2004 which resulted in a system-wide destabilization of the lead corrosion by-products. As the corrosion by-products were re-stabilizing, they may have been exposed to bulk waters which contained vanadium and lead ions that appear to have precipitated out as vanadinite.
- 3) Based on the growing body of information indicating the adverse impacts of vanadyl (VO_3^{2-}) and vanadate (VO_4^{3-}) on human health lead corrosion by-products in any DWDS should be evaluated to ascertain if vanadinite is present. Dislodgement of pieces of these corrosion by-products or their chemical breakdown could mobilize vanadium to provide an unexpected and unmonitored detrimental human exposure event.
- 4) Conceivably vanadate and other V oxyanions may sorb to other distribution system surfaces, particularly those with iron or manganese oxyhydroxides, which are often present as pipe surfaces or post-treatment deposits and are more prevalent than lead service lines. The extent to which V has accumulated in or on those materials has not been assessed, but logically it should also be investigated to determine occurrence and consequently the level of concern.

ACKNOWLEDGEMENTS

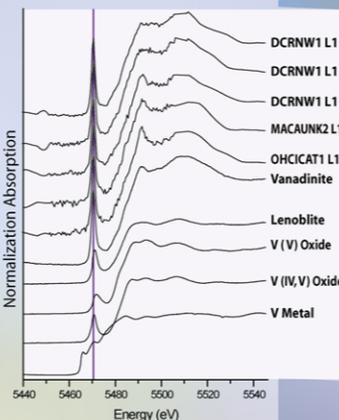
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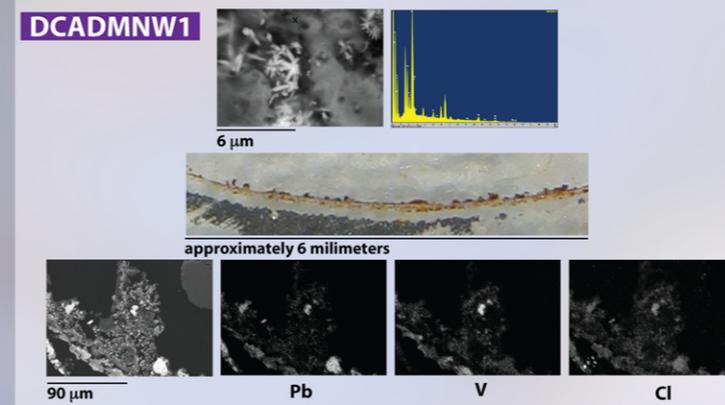
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Bulk XANES

Vanadium-rich minerals when examined by XANES yield very distinct pre-edge peaks (position and intensity; Wong et al., 1984). Five representative XANES spectra of thirteen bulk samples are presented. All have very distinct pre-edge vanadium peaks at 5469.5 eV coupled with dominant derivative peak positions at 5468.9 eV, and a normalized pre-edge peak intensities of approximately one. These characteristics are indicative of the vanadium-rich phase, vanadinite ($Pb_5(VO_4)Cl$) (Wong et al., 1984; Chaurand et al.,



Secondary Electron images and EDAX spectra for In-situ pipe scale



Acicular and fibrous crystals were identified in secondary electron images and confirmed by SEM-EDAX spectra and elemental maps (Jeol 5800) that these grains consist of only lead (Pb), vanadium (V), and chlorine (Cl). These findings indicate that the SEM-EDAX may be utilized as a screening tool for lead corrosion by-products to determine if vanadinite is present.

Sample ID	Source Water	Corrosion Treatment	Layer	Bulk XANES	μ -XRD	μ -XANES
DCHENW1	S	OP	L1	X		
DCHENW2	S	OP	L1			
DC39NW1	S	OP	L1	X		
DCLNE1	S	OP	L1	X		
DCRNW1	S	OP	L1	X		
MADORCH1	S	CP	whole	X		
MAFRUNK1	S	CP	L1	X		
MACAUNK2	GW	CP	L1	X		
CTNHHA1	S	BP	L1	X		
OHICAT1	S	P	L1	X		
KYLOSL1	S	CP	L1	X		
DCRNW3	S	OP	L1		X	X
DCADMNW1	S	OP	L1		X	X
MAREFRE1	GW	CP	L1		X	X

KEY:
 S = surface water
 GW = ground water
 OP = orthophosphate
 BP = blended phosphate
 CP = carbonate passivation

Sample ID	Layer	V (ppm)	Pb (ppm)
DCHENW1	L1	2760	69000
DCHENW2	L1	1900	752000
DC39NW1	L1	6540	676000
DCLNE1	L1	4310	814000
DCRNW1	L1	6330	406000
MADORCH1	whole	<40	722000
MAFRUNK1	L1	323	472000
MACAUNK2	L1	2630	417000
CTBFEM3	L1	330	703000
CTNHHA1	L1	1900	438000
OHICAT1	L1	2200	737000
KYLOSL1	L1	2200	426000
DCRNW3	L1	8500	522000
DCADMNW1	L1	5480	406100
MAREFRE1	L1	237	86000