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Preventing the colloidal dispersion of Pb(IV) corrosion scales and lead release in drinking water distribution systems†

Gregory Korshin^a and Haizhou Liu  ^{*b}

Lead(IV) oxide PbO₂ is one dominant solid phase in lead corrosion scales of drinking water distribution systems. Understanding the colloidal dispersion of PbO₂ is important for lead control in drinking water, especially under scenarios of switching the residual disinfectant from chlorine to chloramine. This study investigated the changes in lead release and colloidal dispersion from PbO_{2(s)} associated with the presence of natural organic matter (NOM), the introduction of chloramine, and the addition of a phosphate corrosion inhibitor in drinking water distribution systems. Experimental data showed that when NOM was present, the surface charges of PbO₂ exhibited a prominent negative shift, leading to colloidal dispersion of Pb(IV) particles. The presence of chloramine did not significantly change the detrimental effects of NOM on the colloidal behavior of PbO₂. In contrast, the addition of phosphate greatly reduced colloidal lead release in the size range between 0.1 and 0.45 μm, and limited lead release with colloidal sizes less than 0.1 μm to below 15 μg L⁻¹, i.e., the U.S. EPA regulatory standard. The beneficial effects of phosphate addition are mainly attributed to the suppression in colloidal dispersion of Pb(IV) particles. Meanwhile, the presence of phosphate also limits the reductive dissolution of PbO₂ via the formation of hydroxypyromorphite Pb₅(PO₄)₃OH particles. Results from this study suggest that phosphate limits the dispersion of PbO_{2(s)} by NOM and prevented the release of Pb(IV) colloids into drinking water.

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Water impact

Lead release and colloidal dispersion from pre-existing PbO_{2(s)} corrosion scales in drinking water distribution systems are associated with the introduction of chloramine and presence of residual natural organic matter. Addition of a phosphate corrosion inhibitor minimizes the risks of colloidal lead release from Pb(IV) mobilization.

Introduction

Lead is one of the most dangerous contaminants commonly found in drinking water. Here we can refer to the most recent lead crisis in Flint, Michigan, where the chemical stability of lead minerals in the corrosion scales of drinking water distribution systems was dramatically disturbed after the switch of source water without a corrosion inhibitor.^{1–3} Another example is the dramatic increase of lead release in Washington DC drinking water in 2002–2004 when the residual disinfectant was switched from chlorine to chloramine.^{4,5} Because in-

gestion of lead-containing drinking water elevated blood lead levels and adversely affects human health, especially that of children,⁶ its maximum contaminant level (MCL) established by the U.S. Environmental Protection Agency is 15 μg L⁻¹.

Despite that, diverse lead-containing materials (lead pipe, lead/tin solder, lead-containing brasses and bronzes) still widely exist in water distribution systems. Although a few cities in the U.S. implemented a complete lead service line replacement for their drinking water distribution systems,^{2,7} it is logistically and economically inhibitive to eradicate all lead-containing materials from distribution networks nationwide. For example, lead-containing brass and lead-tin solder are still widely present in many premise plumbing systems and essentially exist as non-point sources of lead, which are very difficult to locate and control.^{8,9}

When inevitable lead corrosion naturally takes place in drinking water distribution systems, a variety of lead(II) solid phases are generated, notably cerussite PbCO₃ and hydrocerussite Pb₃(CO₃)₂(OH)₂. The suppression of lead release can

^a Department of Civil and Environmental Engineering, University of Washington, Seattle, 98195 USA

^b Department of Chemical and Environmental Engineering, University of California, Riverside, California, 92521 USA. E-mail: haizhou@engr.ucr.edu; Fax: +951 827 9656; Tel: +951 827 2076

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be achieved based on the minimization of equilibrium lead(II) solubility, including the adjustment of pH and alkalinity to limit Pb solubility, and the addition of a phosphate corrosion inhibitor to convert Pb(II) carbonate solids into Pb(II) phosphate solids that are much less soluble.^{1,10–12} In addition, free residual chlorine is typically maintained in drinking water distribution systems to prevent pathogen intrusion. Residual chlorine creates a favorable redox potential to promote the formation of lead(IV) oxides, *i.e.*, scrutinyite α -PbO_{2(s)} or plattnerite β -PbO_{2(s)}, *via* the oxidation of Pb(II) solid phases by chlorine.^{13–19} PbO₂ has a much lower solubility than Pb(II) carbonate solids, and theoretically should ensure a minimal risk of lead leaching into drinking water.^{13,17,20} Prior studies show that lead(IV) oxides widely existed in corrosion scales of chlorine-containing drinking water distribution systems, although other lead mineral phases were also observed.^{21,22}

Although lead(IV) oxides have low solubility, their stability is impacted by a variety of water chemical parameters. For example, the use of chloramine to replace chlorine induces destabilization of PbO₂ by changing the redox ladder,^{23,24} and was responsible for the lead crisis in Washington D.C. in the early 2000s. The presence of reductants including manganese, ferrous ions, iodide, bromide and natural organic matter (NOM) also inadvertently converts lead(IV) oxides to more soluble Pb(II) species and results in undesirable lead release.^{25–31} In particular, reactive phenolic and carboxylic moieties in NOM molecules have been found to induce reductive transformations of PbO₂.²⁸ Furthermore, NOM can enhance the colloidal mobilization of PbO₂ *via* surface complexation reactions and contribute to a possibly major fraction of particulate lead exposure.^{32,33}

In addition, prior studies on the effects of NOM consider a model system without the presence of other competing chemicals. For example, the co-existence of a corrosion inhibitor (*i.e.*, phosphate) and residual disinfectant with NOM is ubiquitous in drinking water distribution systems, but the combined effects of these constituents on the colloidal dispersion of PbO_{2(s)} are unknown. This aspect of lead release is all the more important given that more water utilities tend to switch the residual disinfectant from chlorine to chloramine in the long term to control disinfection by-products (DBPs).^{34,35} Compared to chlorine, chloramine reacts more slowly with NOM (*i.e.*, DBP precursors), but the pre-existence of chlorine drives the formation of PbO₂ corrosion scales in lead-containing drinking water distribution systems. Therefore, under the scenario of switching to chloramine in drinking water distribution systems, the presence of NOM is almost universally concurrent with the occurrence of chloramine and the existence of PbO₂. Similarly, the application of phosphate as a corrosion inhibitor co-existing with NOM and chloramine can affect the PbO_{2(s)} stability as well.

The objective of this study was to investigate lead release from PbO₂ and surface mechanisms associated with the colloidal mobilization of PbO_{2(s)} under water chemistry conditions relevant to drinking water distribution systems, with

special emphasis on the effects of NOM co-existing with residual disinfectant chloramine and corrosion inhibitor phosphate.

Materials and methods

Synthesized PbO₂ was prepared *via* the oxidation of 1.5 g L⁻¹ hydrocerussite with 7 mM chlorine in a total volume of 500 mL at a controlled pH of 7.5 and a total carbonate concentration of 1 mM (Pb(II)/chlorine molar ratio of 0.83 and reaction time of 1 day). After the oxidation was complete, the suspension had a dark brown color and was treated with HClO₄ at pH 2.0 to isolate PbO₂ formed during the reaction. The PbO₂ suspension was deposited by filtration onto a 0.45 μ m filter, washed with deionized water, then removed from the filter and freeze dried for one day. Final processed particles were identified as α -PbO₂ (scrutinyite) by scanning electron microscopy (SEM) and X-ray diffraction (XRD), as shown in Fig. S1 in the ESI.† Hydroxypyromorphite Pb₅(PO₄)₃(OH) was synthesized by mixing 50 mM Pb(ClO₄)₂ with 30 mM Na₃PO₄ solution and raising the pH to 8.5. The white-color precipitate was filtered, washed with DI water, freeze dried and utilized in experiments with chloramine. Suwannee River standard fulvic acid purchased from the International Humic Substances Society was used as a NOM surrogate. Fulvic acid was chosen for its phenolic and carboxylic moieties as a reactive model organic constituent. Chloramine in the form of monochloramine NH₂Cl was freshly prepared by mixing ammonium chloride with chlorine at a N:Cl₂ ratio of 2:1.

To start a dispersion reaction, 50–140 mg L⁻¹ of synthesized PbO₂ was suspended in water with a desirable concentration of NOM (0–5 mg C L⁻¹), chloramine (0–10 mg L⁻¹ as Cl₂) and phosphate (0–2 mg L⁻¹ as PO₄). The pH of the suspension was controlled at 7.5 using a requisite amount of HClO₄ or NaOH, bicarbonate concentration was fixed at 1 mM, chloride concentration was controlled at 1 mM, and ionic strength of the suspension was controlled at 10 mM. These background electrolyte levels are typical of drinking water chemical conditions. The samples were taken at predetermined time points from PbO₂ suspensions and filtered through 0.45 μ m Millipore filters. This filtration cut-off pore size was chosen because it is conventionally considered as the “operationally defined” dissolved fraction.

Lead concentration measured in the 0.45 μ m filtered samples is defined as “total lead release” in this study. To further understand the colloidal size distribution, additional 0.45 μ m filtered samples were subsequently filtered through 0.1 μ m filters and analyzed for lead concentration. Filtered solutions were immediately acidified with concentrated HNO₃ and analyzed using a Perkin-Elmer Elan DRC-e ICP-MS instrument. To measure the surface charge of lead(IV) particles, aliquots of PbO₂ suspension were taken to determine the zeta potential of PbO₂ particles using a Brookhaven Instruments zeta potential analyzer. For each sample, ten measurements of zeta potential were carried out to determine its mean value and standard deviation.

Results and discussion

Colloidal mobilization of PbO₂ in the presence of NOM

To determine the effects of NOM on the colloidal properties of PbO₂, the surface charges of PbO₂ at different pH values and NOM concentrations were first measured using zeta potential quantification. In the absence of NOM, a pronounced decrease of zeta potential with increasing pH was observed (Fig. 1). The protonation-active PbO₂ surface acquired charge as more negatively charged Pb(IV) hydroxo surface species were formed at a higher pH, which was consistent with prior observations.¹³ When a small amount of NOM was present (0.1 mg C L⁻¹), the surface charge of PbO₂ exhibited *ca.* 20 mV negative shift in the entire pH range (Fig. 1). The decrease suggested the occurrence of a competitive adsorption of NOM molecules whose charges, together with those of the hydroxo surface complexes present on the PbO₂ surface, caused the zeta potential to decrease. When the NOM concentration was increased to 0.5 mg L⁻¹ and above, the zeta potential of PbO₂ decreased to a level more negative than -60 mV and became insensitive to pH changes (Fig. 1). This trend indicates that the surface of PbO₂ particles became saturated with adsorbed NOM molecules, and its surface was dominated by Pb(IV)-NOM complexes instead of Pb(IV)-hydroxo complexes.

As the surface charge of PbO₂ increased to a more negative value in the presence of NOM, PbO₂ particles exhibited a higher extent of colloidal dispersion due to a stronger repulsive force exerted among the surfaces of the particles, and consequently resulted in an increase in total lead release. Total lead release from PbO₂ increased dramatically with increasing NOM concentration after different days of reaction (Fig. 2A). Lead release increases quasi-linearly with a NOM concentration of up to 1 mg L⁻¹, albeit somewhat slower as the NOM concentration increased from 1 to 5 mg L⁻¹. A cor-

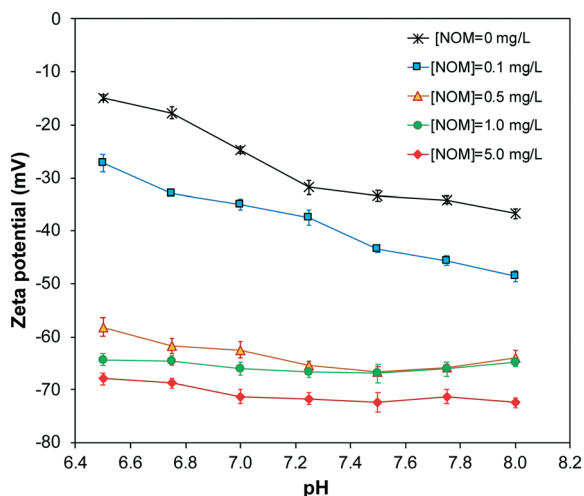


Fig. 1 Impact of Suwannee River fulvic acid concentrations on the zeta potential of PbO₂. Ionic strength = 10 mM, [PbO₂] = 140 mg L⁻¹, TOTCO₃ = 1 mM, [Cl⁻] = 1 mM. The solid lines are trendlines connecting the data points.

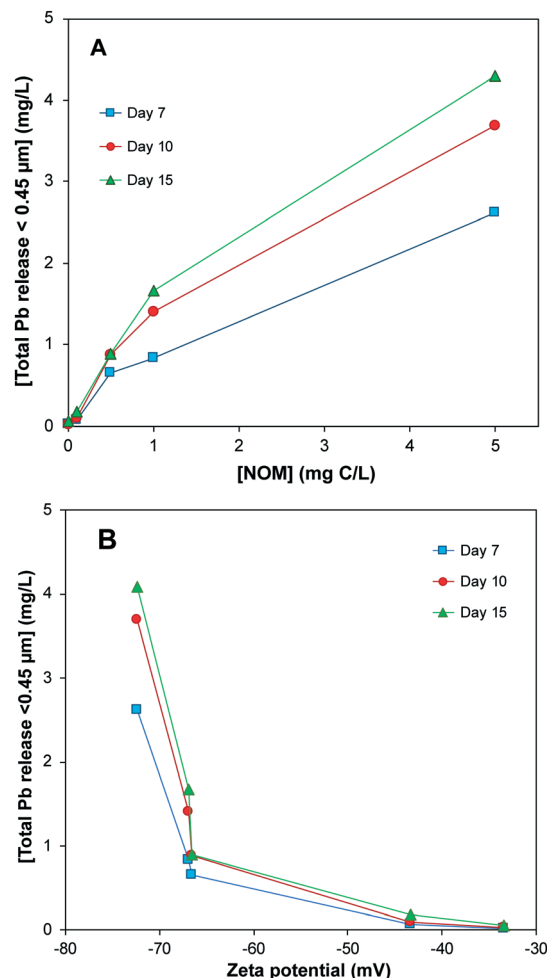


Fig. 2 Impact of Suwannee River fulvic acid NOM concentrations on lead release (<0.45 μ m) from PbO₂ particles. (A) Lead release; (B) correlation with zeta potential. PbO₂ = 140 mg L⁻¹, TOTCO₃ = 1 mM, Cl⁻ = 1 mM, pH = 7.5, [NOM] = 0–5 mg C L⁻¹. The solid lines are trendlines connecting the data points.

relation between the zeta potential of PbO₂ particles and lead release data shows an inverse relationship, in which total lead release was highly impacted by the negative surface charge of PbO₂ (Fig. 2B). Total lead release increased as the surface of the PbO₂ particles becomes more negative, but it increased dramatically as the zeta potential became more negative than *ca.* -65 mV, a threshold beyond which the surface charge-induced colloidal dispersion accelerated.

In addition, colloidal lead release associated with particle sizes between 0.1 and 0.45 μ m increased almost linearly with time up to 7 days, and the fraction of colloidal lead release with sizes less than 0.1 μ m also increased with NOM levels (Fig. S2†). Overall, less than 10% of lead release was contributed by particles with sizes less than 0.1 μ m, indicating that the truly “dissolved” lead fraction was small, and the majority of lead release was contributed by colloids with sizes between 0.1 and 0.45 μ m. The filtered samples had a visually discernible light yellow to brownish color and were somewhat opaque, indicating that colloidal PbO₂ was released and

contributed to the total lead release. These particles are likely to be Pb(IV) nanoparticles released from the morphologically complex PbO₂ substrate primarily formed by very small (<100 nm) coalesced nuclei. These nano-scale components of the PbO₂ substrate apparently were susceptible to dispersion at highly negative surface charges induced by adsorbed NOM molecules.

Impact of chloramine on lead release from PbO₂

Chloramine *per se* has a discernible but insignificant impact on the surface charges of PbO₂. For example, in the absence of NOM, the introduction of up to 2 mg L⁻¹ of chloramine shifted the zeta potential of PbO₂ by *ca.* 10 to 20 mV more negatively compared to the conditions without chloramine (Fig. 3A). The negative shift of the surface charge of PbO₂ by chloramine alone was likely due to the adsorption of chloramine or its degradation intermediates on the surface of PbO₂. However, when a considerable level of NOM was pres-

ent (*e.g.*, 0.5 mg C L⁻¹), the presence of varying chloramine concentrations had a largely insignificant effect on the zeta potential of PbO₂ particles which was consistently in the range of *ca.* -60 to -65 mV (Fig. 3A). This behavior of PbO₂ indicates that its surface properties are predominantly controlled by adsorption of NOM, and chloramine negligibly affects the interaction of NOM with PbO₂ particles.

Lead release data also show that NOM is the single most important factor determining the stability of PbO₂ in the presence of chloramine. Lead release data at two NOM levels (0.5 and 5.0 mg L⁻¹) show that despite some variations, for a constant NOM concentration, the amount of lead release was similar regardless of chloramine concentrations, and a change of NOM from 0.5 to 5.0 mg L⁻¹ increases lead release by more than 8 times (Fig. 3B). A correlation of zeta potentials and total lead release in the presence of chloramine exhibited a trend that was similar to that in the absence of chloramine (Fig. S3† vs. 2B). These results demonstrate that NOM is the dominant factor that largely defines the surface

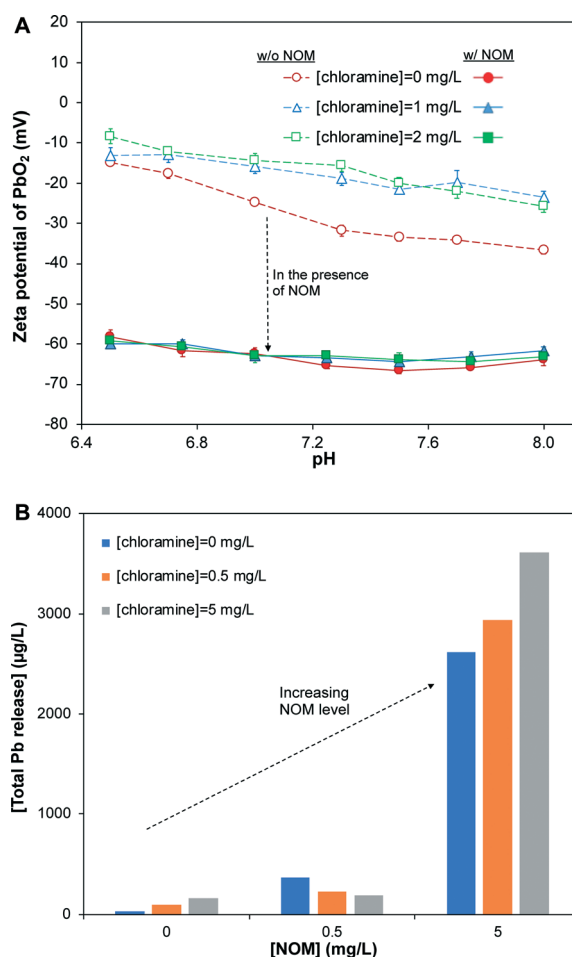


Fig. 3 Impact of chloramine on the lead release from PbO₂ in the presence of Suwannee River NOM. (A) Zeta potential, [NOM] = 0 and 0.5 mg C L⁻¹; both solid and dash lines are trendlines connecting the data points. (B) Lead release after 5 days of reaction. Ionic strength = 10 mM, [NOM] = 0.5 and 5 mg L⁻¹, PbO₂ = 140 mg L⁻¹, TOTCO₃ = 1 mM, Cl⁻ = 1 mM.

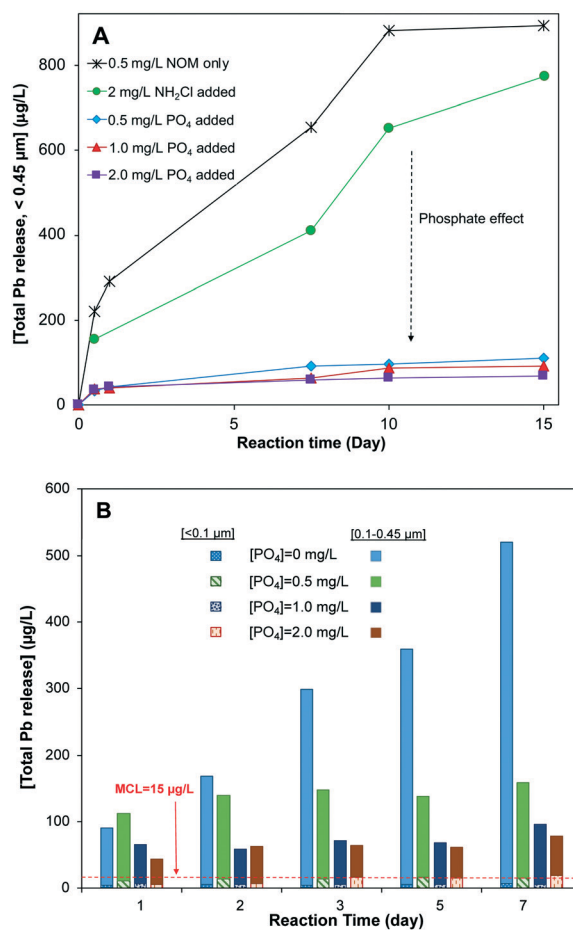


Fig. 4 Impact of phosphate on the lead release from PbO₂ in the presence of Suwannee River NOM and chloramine. (A) Total lead release; the solid lines are trendlines connecting the data points. (B) Size distribution of total lead release. Ionic strength = 10 mM, NOM = 0.5 mg L⁻¹, PbO₂ = 140 mg L⁻¹, chloramine = 2 mg L⁻¹, TOTCO₃ = 1 mM, Cl⁻ = 1 mM.

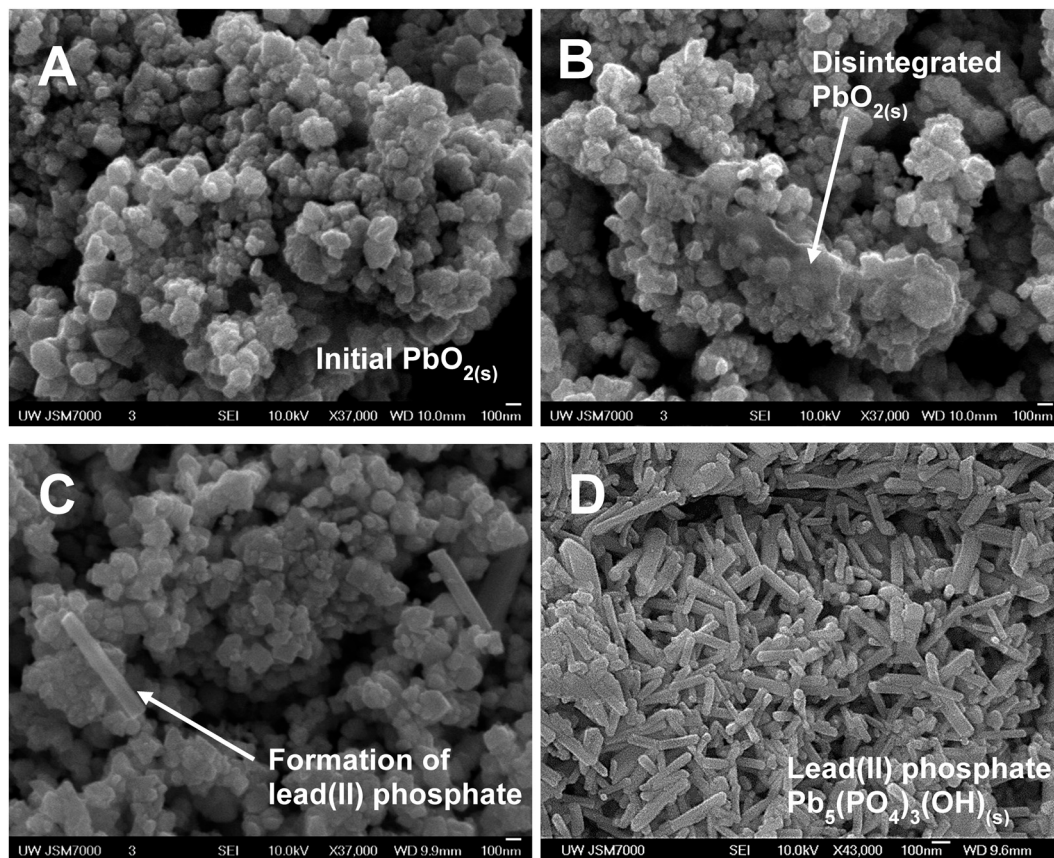


Fig. 5 Morphology of PbO_2 particles in different chemical conditions after 16 days of reaction. PbO_2 140 mg L^{-1} , ionic strength 10 mM . (A) PbO_2 particles in 0.25 mg L^{-1} NOM with 2 mg L^{-1} chloramine; (B) PbO_2 particles in 2 mg L^{-1} NOM with 2 mg L^{-1} chloramine; (C) PbO_2 particles with the formation of lead(II) phosphate in 0.25 mg L^{-1} NOM with 2 mg L^{-1} chloramine and 1 mg L^{-1} phosphate; (D) hydroxypyromorphite $\text{Pb}_5(\text{PO}_4)_3\text{OH}_{(\text{s})}$.

properties of PbO_2 in the presence of varying levels of chloramine.

There are several mechanisms involving lead release from PbO_2 by NOM and chloramine. First, redox active functional groups of NOM can reductively dissolve PbO_2 to soluble Pb(II) .^{26,28} Second, the zeta potential data presented in this study show that NOM can also interact with Pb(IV) by colloidal dispersion and release of submicron Pb(IV) particles. This is also evidenced by the yellowish color of $0.45 \mu\text{m}$ filtered samples observed in this study. In addition, intermediate products from chloramine auto-decay reactions can reduce PbO_2 to Pb(II) and mobilize lead release.^{24,30}

Additional size fractionation measurements carried out in the presence of chloramine suggest that a majority of lead release in the presence of NOM came from colloidal particles with the size ranging from 0.1 to $0.45 \mu\text{m}$ (Fig. S4†). This is consistent with the observation in the absence of chloramine (Fig. S2†). Therefore, compared to NOM, chloramine does not appear to have a decisive role in affecting the colloidal behavior of PbO_2 .

Impact of phosphate addition on colloidal lead release from PbO_2

Phosphate has been widely used as an effective lead corrosion inhibitor. The addition of phosphate converts Pb(II)

solids into extremely insoluble lead phosphate minerals, *e.g.*, hydroxypyromorphite $\text{Pb}_5(\text{PO}_4)_3\text{OH}$. However, the effect of phosphate on inhibiting lead release from PbO_2 co-existing with a residual disinfectant and organic matter remains unknown. To investigate the effects of phosphate on the colloidal dispersion of PbO_2 , different concentrations of phosphate (expressed as mg L^{-1} as PO_4) were added into the PbO_2 /NOM/chloramine system. Results show that when 0.5 mg L^{-1} phosphate was added to the system, lead release from PbO_2 was reduced by more than 90% from 510 to $140 \mu\text{g L}^{-1}$ after 7 days of reaction (Fig. 4A). Adding 1 and 2 mg L^{-1} phosphate decreased the lead concentration to below 90 and $60 \mu\text{g L}^{-1}$ after 7 days of reaction, respectively. These data demonstrate that phosphate is very effective in minimizing lead release from PbO_2 by preventing the colloidal dispersion of PbO_2 regardless of the presence of NOM and chloramine.

Size fractionation data also confirmed that the addition of phosphate significantly reduced colloidal lead release in the size range of 0.1 to $0.45 \mu\text{m}$ (Fig. 4B). The first 0.5 mg L^{-1} addition of phosphate is most beneficial compared to the subsequent incremental addition of phosphate in suppressing colloidal lead release. For instance, adding 0.5 mg L^{-1} phosphate decreased the total colloidal lead concentration with sizes between 0.1 and $0.45 \mu\text{m}$ from 550 to $180 \mu\text{g L}^{-1}$ after 7

days of reaction. Furthermore, in all cases with the addition of phosphate, lead release in the colloidal fraction with a size less than $0.1\ \mu\text{m}$ was effectively below $15\ \text{mg L}^{-1}$, *i.e.*, the lead maximum contamination level (MCL) set by the U.S. EPA. This trend strongly suggests that the addition of a phosphate inhibitor is effective in suppressing lead release from PbO_2 under reducing conditions in the presence of humic substances and chloramine.

Morphological analyses of PbO_2 particles after 16 days of exposure to phosphate, NOM and chloramine realize the mechanism of lead release. The crystals of initial PbO_2 exhibited a cubic shape, with relatively sharp edges and an intact crystalline structure (Fig. 5A). When exposed to $2\ \text{mg L}^{-1}$ of NOM for 16 days, however, PbO_2 nano-crystals showed signs of structural change. Some PbO_2 particles formed a coalesced layer, and they had less discernible crystalline features (Fig. 5B). This transformation of the initial crystalline structure is indicative of the colloidal dispersion and reductive transformation of PbO_2 by NOM, and agrees with the observations of NOM-enhanced lead release (Fig. 2). When $1\ \text{mg L}^{-1}$ phosphate was added to the system, PbO_2 crystals retained their intact crystalline structures with sharp edges. Meanwhile, small needle-shaped crystals with a length of several hundreds of nm developed on the surface of PbO_2 particles (Fig. 5C). These crystals had morphological features closely resembling those of hydroxypyromorphite $\text{Pb}_5(\text{PO}_4)_3\text{OH}_{(\text{s})}$ (Fig. 5D). The formation of hydroxypyromorphite likely resulted from heterogeneous lead phosphate nucleation,³⁶ and in this case, an interaction between $\text{Pb}(\text{II})$ released from reductive dissolution of PbO_2 and phosphate present in the suspension.

The above results of SEM analyses ascertain that NOM makes PbO_2 particles less crystalline and enhances their susceptibility to colloidal dispersion. Similar NOM effects have been observed elsewhere including NOM interactions with copper and iron oxides.^{37,38} However, the presence of phosphate limits the colloidal dispersion of PbO_2 . It is likely that phosphate adsorbs onto the surface of PbO_2 and thus competes with the sorption of NOM, eventually weakening the association of NOM on the PbO_2 surface. The adsorption of phosphate on the surface of PbO_2 prevented the dispersion of PbO_2 particles, especially in the colloidal fraction between 0.1 and $0.45\ \mu\text{m}$. This trend is different from prior observation on $\text{Pb}(\text{II})$ solids, where phosphate adsorption increased the risk of colloidal dispersion from $\text{Pb}(\text{II})$ solids.³⁹ In addition, phosphate addition minimizes the reductive dissolution of PbO_2 *via* the precipitation of $\text{Pb}_5(\text{PO}_4)_3\text{OH}_{(\text{s})}$, however, this is of secondary importance compared to the PbO_2 dispersion inhibition effect. Separate control experiments demonstrated that total lead release from $\text{Pb}_5(\text{PO}_4)_3\text{OH}_{(\text{s})}$ was very low ($<15\ \mu\text{g L}^{-1}$) either in the absence or presence of chloramine (Fig. S5†), which is consistent with the effect of phosphate on $\text{PbO}_{2(\text{s})}$ stability (Fig. 4). Prior studies also showed that lead release was negligible when lead(II) phosphate solid was present in the system.¹¹

Engineering implications

Results of this study indicate a high risk of destabilization of PbO_2 -based corrosion scales and lead release when humic substance-like natural organic matter is present and chloramine is used as a residual disinfectant. A major contribution to lead release comes in this case from the mobilization of colloidal lead in particulate sizes between 0.1 and $0.45\ \mu\text{m}$. As an effective control strategy, phosphate addition is beneficial in preventing the destabilization of $\text{Pb}(\text{IV})$ oxides in corrosion scales under reducing chemical conditions. While phosphate is known to suppress lead release caused by the electrochemically-driven oxidation of $\text{Pb}(\text{0})$ -containing plumbing materials, results of this study point to an added benefit of phosphate in controlling the chemical stability of $\text{Pb}(\text{IV})$ -containing corrosion scales in drinking water distribution systems. To predict the exact level of colloidal dispersion of PbO_2 in drinking water distribution systems, future studies need to investigate hydraulic factors and transport phenomena. For water utilities with lead-containing materials in drinking water distribution systems, phosphate addition is an effective strategy to inhibit the dispersion of $\text{Pb}(\text{IV})$ corrosion scales by NOM.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

- 1 K. J. Pieper, M. Tang and M. A. Edwards, Flint water crisis caused by interrupted corrosion control: investigating “ground zero” home, *Environ. Sci. Technol.*, 2017, 51(4), 2007–2014.
- 2 K. J. Pieper, R. Martin, M. Tang, L. Walters, J. Parks, S. Roy, C. Devine and M. A. Edwards, Evaluating water lead levels during the Flint water crisis, *Environ. Sci. Technol.*, 2018, 52(15), 8124–8132.
- 3 T. M. Olson, M. Wax, J. Yonts, K. Heidecorn, S. Haig, D. Yeoman, Z. Hayes, L. Raskin and B. R. Ellis, Forensic estimates of lead release from lead service lines during the water crisis in Flint, Michigan, *Environ. Sci. Technol. Lett.*, 2017, 4(9), 356–361.
- 4 S. Triantafyllidou and M. Edwards, Lead (Pb) in tap water and in blood: implications for lead exposure in the United States, *Crit. Rev. Environ. Sci. Technol.*, 2012, 42(13), 1297–1352.
- 5 M. Edwards and A. Dudi, Role of chlorine and chloramine in corrosion of lead-bearing materials, *J. - Am. Water Works Assoc.*, 2004, 96(10), 69–81.
- 6 B. P. Lanphear, R. Hornung, J. Khoury, K. Yolton, P. Baghurst, D. C. Bellinger, R. L. Canfield, K. N. Dietrich, R.

- Bornschein, T. Greene, S. J. Rothenberg, H. L. Needleman, L. Schnaas, G. Wasserman, J. Graziano and R. Roberts, Low-level environmental lead exposure and children's intellectual function: an international pooled analysis, *Environ. Health Perspect.*, 2005, **113**(7), 894–899.
- 7 M. R. Schock, A. F. Cantor, S. Triantafyllidou, M. K. Desantis and K. G. Scheckel, Importance of pipe deposits to Lead and Copper Rule compliance, *J. - Am. Water Works Assoc.*, 2014, **106**(7), E336–E349.
 - 8 E. Deshommes, L. Laroche, D. Deveau, S. Nour and M. Prévost, Short- and long-term lead release after partial lead service line replacements in a metropolitan water distribution system, *Environ. Sci. Technol.*, 2017, **51**(17), 9507–9515.
 - 9 A. A. Abokifa and P. Biswas, Modeling soluble and particulate lead release into drinking water from full and partially replaced lead service lines, *Environ. Sci. Technol.*, 2017, **51**(6), 3318–3326.
 - 10 M. R. Schock, I. Wagner and R. J. Oliphant, Corrosion and Solubility of Lead in Drinking Water, In *Internal Corrosion of Water Distribution Systems*, American Water Works Association, Denver, CO, 1996.
 - 11 L. Xie and D. E. Giammar, Equilibrium solubility and dissolution rate of the lead phosphate chloropyromorphite, *Environ. Sci. Technol.*, 2007, **41**(23), 8050–8055.
 - 12 H. Liu, K. D. Schonberger, G. V. Korshin, J. F. Ferguson, P. Meyerhofer, E. Desormeaux and H. Luckenbach, Effects of blending of desalinated water with treated surface drinking water on copper and lead release, *Water Res.*, 2010, **44**(14), 4057–4066.
 - 13 H. Liu, G. V. Korshin and J. F. Ferguson, Interactions of Pb(II)/Pb(IV) solid phases with chlorine and their effects on lead release, *Environ. Sci. Technol.*, 2009, **43**(9), 3278–3284.
 - 14 H. Liu, G. V. Korshin and J. F. Ferguson, Investigation of the kinetics and mechanisms of the oxidation of cerussite and hydrocerussite by chlorine, *Environ. Sci. Technol.*, 2008, **42**(9), 3241–3247.
 - 15 J. Orta, S. Patton and H. Liu, Bromide-assisted catalytic oxidation of lead(II) solids by chlorine in drinking water distribution systems, *Chem. Commun.*, 2017, **53**(62), 8695–8698.
 - 16 Y. Wang, Y. Xie, W. Li, Z. Wang and D. E. Giammar, Formation of lead(IV) oxides from lead(II) compounds, *Environ. Sci. Technol.*, 2010, **44**(23), 8950–8956.
 - 17 Y. Xie, Y. Wang, V. Singhal and D. E. Giammar, Effects of pH and carbonate concentration on dissolution rates of the lead corrosion product PbO₂, *Environ. Sci. Technol.*, 2010, **44**(3), 1093–1099.
 - 18 D. A. Lytle and M. R. Schock, Formation of Pb(IV) oxides a in chlorinated water, *J. - Am. Water Works Assoc.*, 2005, **97**(11), 102–114.
 - 19 E. J. Kim and J. E. Herrera, Characteristics of lead corrosion scales formed during drinking water distribution and their potential influence on the release of lead and other contaminants, *Environ. Sci. Technol.*, 2010, **44**(16), 6054–6061.
 - 20 M. R. Schock, I. Wagner and R. J. Oliphant, Corrosion and Solubility of Lead in Drinking Water, In *Internal Corrosion of Water Distribution Systems*, American Water Works Association, Denver, CO, 1996.
 - 21 M. K. DeSantis, S. Triantafyllidou, M. R. Schock and D. A. Lytle, Mineralogical evidence of galvanic corrosion in drinking water lead pipe joints, *Environ. Sci. Technol.*, 2018, **52**(6), 3365–3374.
 - 22 S. Triantafyllidou, M. R. Schock, M. K. DeSantis and C. White, Low contribution of PbO₂-coated lead service lines to water lead contamination at the tap, *Environ. Sci. Technol.*, 2015, **49**(6), 3746–3754.
 - 23 J. A. Switzer, V. V. Rajasekharan, S. Boonsalee, E. A. Kulp and E. W. Bohannon, Evidence that monochloramine disinfectant could lead to elevated Pb levels in drinking water, *Environ. Sci. Technol.*, 2006, **40**(10), 3384–3387.
 - 24 Y. P. Lin and R. L. Valentine, Release of Pb(II) from monochloramine-mediated reduction of lead oxide (PbO₂), *Environ. Sci. Technol.*, 2008, **42**(24), 9137–9143.
 - 25 Z. Shi and A. T. Stone, PbO₂(s, Plattnerite) reductive dissolution by aqueous manganous and ferrous ions, *Environ. Sci. Technol.*, 2009, **43**(10), 3596–3603.
 - 26 Y. P. Lin, M. P. Washburn and R. L. Valentine, Reduction of lead oxide (PbO₂) by iodide and formation of iodoform in the PbO₂/I⁻/NOM System, *Environ. Sci. Technol.*, 2008, **42**(8), 2919–2924.
 - 27 Y. P. Lin and R. L. Valentine, Reductive dissolution of lead dioxide (PbO₂) in acidic bromide solution, *Environ. Sci. Technol.*, 2010, **44**(10), 3895–3900.
 - 28 D. J. Dryer and G. V. Korshin, Investigation of the reduction of lead dioxide by natural organic matter, *Environ. Sci. Technol.*, 2007, **41**(15), 5510–5514.
 - 29 Y. P. Lin and R. L. Valentine, The release of lead from the reduction of lead oxide (PbO₂) by natural organic matter, *Environ. Sci. Technol.*, 2008, **42**(3), 760–765.
 - 30 Y. P. Lin and R. L. Valentine, Reduction of lead oxide (PbO₂) and release of Pb(II) in mixtures of natural organic matter, free chlorine and monochloramine, *Environ. Sci. Technol.*, 2009, **43**(10), 3872–3877.
 - 31 Z. Shi and A. T. Stone, PbO₂(s, Plattnerite) reductive dissolution by natural organic matter: reductant and inhibitory subfractions, *Environ. Sci. Technol.*, 2009, **43**(10), 3604–3611.
 - 32 L. S. McNeill and M. Edwards, Importance of Pb and Cu particulate species for corrosion control, *J. Environ. Eng.*, 2004, **130**(2), 136–144.
 - 33 S. Triantafyllidou, J. Parks and M. Edwards, Lead particles in potable water, *J. - Am. Water Works Assoc.*, 2007, **99**(6), 107–117.
 - 34 C. J. Seidel, M. J. McGuire, R. S. Summers and S. Via, Have utilities switched to chloramines?, *J. - Am. Water Works Assoc.*, 2005, **97**(10), 87–97.
 - 35 F. Rosario-Ortiz, J. Rose, V. Speight, U. von Gunten and J. Schnoor, How do you like your tap water? Safe drinking water may not need to contain a residual disinfectant, *Science*, 2016, **351**(912), 912–914.

- 36 C. Dai, J. Zhao, D. E. Giammar, J. D. Pasteris, X. Zuo and Y. Hu, Heterogeneous lead phosphate nucleation at organic-water interfaces: implications for lead immobilization, *ACS Earth Space Chem.*, 2018, 2(9), 869–877.
- 37 G. V. Korshin, M. B. Benjamin and R. S. Sletten, Adsorption of natural organic matter (NOM) on iron oxide: effects on NOM composition and formation of organo-halide compounds during chlorination, *Water Res.*, 1997, 31(7), 1643–1650.
- 38 G. V. Korshin, J. F. Ferguson and A. N. Lancaster, Influence of natural organic matter on the corrosion of leaded brass in potable water, *Corros. Sci.*, 2000, 42(1), 53–66.
- 39 J. Zhao, D. E. Giammar, J. D. Pasteris, C. Dai, Y. Bae and Y. Hu, Formation and aggregation of lead phosphate particles: Implications for lead immobilization in water supply systems, *Environ. Sci. Technol.*, 2018, 52(21), 12612–12623.