Preventing the Colloidal Dispersion of Pb(IV) Corrosion Scales and Lead Release in Drinking Water Distribution Systems

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Water Impact Statement

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 phosphate corrosion inhibitor minimizes the risks of colloidal lead release from Pb(IV) mobilization.

Preventing the Colloidal Dispersion of Pb(IV) Corrosion Scales and Lead Release in Drinking Water Distribution Systems

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Abstract

Lead(IV) oxide PbO_2 is one dominant solid phase in lead corrosion scales of drinking water distribution systems. Understanding the colloidal dispersion of PbO_2 is important for lead control in drinking water, especially under scenarios of switching residual disinfectant from chlorine to chloramine. This study investigated changes of lead release and colloidal dispersion from $PbO_{2(s)}$ associated with presence of natural organic matter (NOM), the introduction of chloramine, and the addition of phosphate corrosion inhibitor in drinking water distribution systems. Experimental data showed that when NOM was present, the surface charges of PbO_2 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 PbO_2. 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, *i.e.*, the U.S. EPA regulatory standard. The beneficial effects of phosphate addition is mainly attributed to the suppression in colloidal dispersion of Pb(IV) particles. Meanwhile, the presence of phosphate also limits the reductive dissolution of PbO_2 via the formation of hydroxypyromorphite $Pb_5(PO_4)_3OH$ particles. Results from this study suggest that phosphate limits the dispersion of $PbO_{2(s)}$ by NOM and prevented release of Pb(IV) colloids into drinking water.

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 a dramatic increase of lead release in Washington DC drinking water in 2002-2004 when the residual disinfectant was switch from chlorine to chloramine.[4,5] Because ingestion 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.

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, leading-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 $PbCO_3$ and hydrocerussite $Pb_3(CO_3)_2(OH)_2$. The suppression of lead release can 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 phosphate corrosion inhibitor to convert Pb(II) carbonate solids into Pb(II) phosphate solids that are much less soluble.[1,10-12] In addition, a free chlorine residual 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] PbO_2 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 a low solubility, their stability is impacted by a variety of water chemical parameters. For example, the use of chloramine to replace chlorine induces a destabilization of PbO_2 by changing the redox ladder,[23,24] and was responsible for the lead crisis in Washington D.C. in early 2000s. The presence of reductants including manganese, ferrous ion, iodide, bromide and natural organic matter (NOM) also inadvertently converts lead(IV) oxides to more soluble Pb(II) species and results in an undesirable lead release.[25-31] In particular, reactive phenolic and carboxylic moieties in NOM molecules have been found to induce reductive transformations of PbO_2.[28] Furthermore, NOM can enhance the colloidal mobilization of PbO_2 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 corrosion inhibitors (*i.e.*, phosphate) and residual disinfectant with NOM are 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 PbO_2 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 PbO_2. Similarly, the application of phosphate as a corrosion inhibitor co-existing with NOM and chloramine can affect $PbO_{2(s)}$ stability as well.

The objective of this study was to investigate lead release from 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 PbO_2 was prepared via the oxidation of 1.5 g/L hydrocerussite by 7 mM chlorine in a total volume of 500 mL at a controlled pH of 7.5 and total carbonate concentration of 1 mM (Pb(II)/chlorine molar ratio 0.83 and reaction time 1 day). After the oxidation was complete, the suspension had a dark brown color and was treated with $HClO_4$ at pH 2.0 to isolate PbO_2 formed during the reaction. The suspension of PbO_2 was deposited by filtration onto a 0.45-μm filter, washed with deionized water, then removed from the filter and freeze dried for one day. Final processed particles were identified as α-PbO_2 (scrutinyite) Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD), shown in Figure S1 of the Supporting Information (SI). Hydroxypyromorphite $Pb_5(PO_4)_3(OH)$ was synthesized by mixing 50 mM $Pb(ClO_4)_2$ with 30 mM Na_3PO_4 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 NH_2Cl was freshly prepared by mixing ammonium chloride with chlorine at a N:Cl_2 ratio of 2:1.

To start a dispersion reaction, 50-140 mg/L of synthesized PbO_2 was suspended in water with a desirable concentration of NOM (0-5 mg C/L), chloramine (0-10 mg/L as Cl_2) and phosphate (0-2 mg/L as PO_4). pH of the suspension was controlled at 7.5 using a requisite amount of $HClO_4$ 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 10mM. These background electrolyte levels are typical of drinking water chemical conditions. Samples were taken at predetermined time points from PbO_2 suspensions and filtered through 0.45-μm 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-μm filtered samples are defined as "total lead release" in this study. To further understand the colloidal size distribution, additional 0.45-μm filtered samples were subsequently filtered through 0.1-μm filters and analyzed for lead concentration. Filtered solutions were immediately acidified with concentrated HNO_3 and analyzed using a Perkin-Elmer Elan DRC-e ICP-MS instrument. To measure the surface charge of lead(IV) particles, aliquots of PbO_2 suspension were taken to determine the zeta potential of PbO_2 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 PbO_2 in the presence of NOM

To determine the effects of NOM on the colloidal properties of PbO_2, surface charges of PbO_2 at different pHs 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 (Figure 1). The protonation-active PbO_2 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), the surface charge of PbO_2 exhibited *ca.* 20 mV negative shift in the entire pH range (Figure 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 PbO_2 surface, caused the zeta potential to decrease. When NOM concentration was increased to 0.5 mg/L and above, the zeta potential of PbO_2 decreased to a level more negative than -60 mV and became insensitive to pH changes (Figure 1). This trend indicates that the surface of PbO_2 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 PbO_2 increased to a more negative value in the presence of NOM, PbO_2 particles exhibited a higher extent of colloidal dispersion due to a stronger repulsive force exerted among the surfaces of particles, and with attendant increases of total lead release. Total lead released from PbO_2 increased dramatically with increasing NOM concentration after different days of reaction (Figure 2A). Lead release increases quasi-linearly with NOM concentration up to 1 mg/L, albeit somewhat slower as NOM concentration increased from 1 to 5 mg/L. A correlation between zeta potential of PbO_2 particles and lead release data shows an inverse relationship, in which total lead release was highly impacted by the negative surface charge of PbO_2 (Figure 2B). Total lead release increased as the surface of PbO_2 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 μm increased almost linearly with time up to 7 days, and the fraction of colloidal lead release with sizes less than 0.1 μm also increased with NOM levels (Figure S2). Overall, less than 10% of lead release was contributed by particles with sizes less than 0.1 μm, indicating that the truly “dissolved” lead fraction was small, and a majority of lead release was contributed by colloids with sizes between 0.1 and 0.45 μm. The filtered samples had a visually discernible light yellow to brownish color and were somewhat opaque, indicating that colloidal PbO_2 was release and contributed to the total lead release. These particles are likely to be Pb(IV) nanoparticles released from the morphologically complex PbO_2 substrate primarily formed by very small (<100 nm) coalesced nuclei. These nano-scale components of the PbO_2 substrate apparently were susceptible to dispersion at highly negative surface charges induced by adsorbed NOM molecules.

Impact of chloramine on lead release from PbO_2

Chloramine *per se* has a discernible but insignificant impact on the surface charges of PbO_2. For example, in the absence of NOM, the introduction of up to 2 mg/L of chloramine shifted the zeta potential of PbO_2 by *ca.* 10 to 20 mV more negatively compared to the conditions without chloramine (Figure 3A). The negative shift of surface charge of PbO_2 by chloramine alone was likely due to the adsorption of chloramine or its degradation intermediates on the surface of PbO_2. However, when a considerable level of NOM was present (*e.g.*, 0.5 mg C/L), the presence of varying chloramine concentrations had a largely insignificant effect on the zeta potential of PbO_2 particles which was consistently in the range of *ca*. -60 to -65 mV (Figure 3A). This behavior of PbO_2 indicates that its surface properties are predominantly controlled by adsorption of NOM, and chloramine negligibly affects the interaction of NOM with PbO_2 particles.

Lead release data also show that NOM is the single most important factor determining the stability of PbO_2 in the presence of chloramine. Lead release data at two NOM levels (0.5 and 5.0 mg/L) show that despite some variations, for a constant NOM concentration, the amount of lead release were similar regardless of chloramine concentrations, and a change of NOM from 0.5 to 5.0 mg/L increases lead release by more than 8 times (Figure 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 (Figure S3 *vs*. Figure 2B). These results demonstrate that NOM is the dominant factor that largely defines the surface 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-μm filtered samples observed in this study. In addition, intermediate products from chloramine auto-decay reactions can reduce PbO_2 to Pb(II) and mobilize lease release.[24,30]

Additional size fractionation measurements carried out in the presence of chloramine suggest a majority of lead release in the presence of NOM came from colloidal particles with the size ranging from 0.1 to 0.45 μm (Figure S4). This is consistent with the observation in the absence of chloramine (Figure 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 $Pb_5(PO_4)_3OH$. However, the effect of phosphate on inhibiting lead release from PbO_2 co-existing with 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 as PO_4) were added into the PbO_2/NOM/chloramine system. Results shows that when 0.5 mg/L phosphate was added to the system, lead release from PbO_2 was reduced by more than 90% from 510 to 140 μg/L after 7 days of reaction (Figure 4A). Adding 1 and 2 mg/L phosphate suppressed lead concentration to below 90 and 60 μg/L 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 μm (Figure 4B). The first 0.5 mg/L addition of phosphate is most beneficial than the subsequent incremental addition of phosphate in suppressing colloidal lead release. For instance, adding 0.5 mg/L phosphate decreased total colloidal lead concentration with sizes between 0.1 and 0.45 μm from 550 to 180 μg/L after 7 days of reaction. Furthermore, in all cases with the addition of phosphate, lead release in the colloidal fraction with size less than 0.1 μm was effectively below 15 mg/L, *i.e.,* the lead maximum contamination level (MCL) set by U.S. EPA. This trend strongly suggests that the addition of phosphate inhibitor is effective to suppress 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 exposures to phosphate, NOM and chloramine visualize the mechanism of lead release. The crystals of initial PbO_2 exhibited a cubic shape, with relatively sharp edges and an intact crystalline structure (Figure 5A). When exposed to 2 mg/L 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 (Figure 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 (Figure 2). When 1 mg/L of phosphate was added to the system, PbO_2 crystals remained intact crystalline structures with sharp edges. Meanwhile, small needle-shape crystals with a length of several hundred nm developed on the surface of PbO_2 particles (Figure 5C). These crystals had morphological features closely resembling those of hydroxypyromorphite $Pb_5(PO_4)_3OH_{(s)}$ (Figure 5D). The formation of hydroxypyromorphite likely resulted from heterogeneous lead phosphate nucleation,[36] and in this case, an interaction between Pb(II) released from reductive dissolution of PbO_2 and phosphate present in the suspension.

The above results of SEM analyses ascertain that NOM affects PbO_2 particles to be 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 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 μm. This trend is different from prior observation on Pb(II) solids, where phosphate adsorption increased the risk of colloidal dispersion from Pb(II) solids.[39] In addition, phosphate addition minimizes the reductive dissolution of PbO_2 via the precipitation of $Pb_5(PO_4)_3OH_{(s)}$, however, this is of secondary importance compared to the PbO_2 dispersion inhibition effect. Separate control experiments demonstrated that total lead release from $Pb_5(PO_4)_3OH_{(s)}$ was very low (< 15 μg/L) either in the absence or presence of chloramine (Figure S5), which is consistent with the effect of phosphate on $PbO_{2(s)}$ stability (Figure 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 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 μm. As an effective control strategy, phosphate addition is beneficial in preventing the destabilization of Pb(IV) oxides in corrosion scales under reducing chemical conditions. While phosphate is known to suppress lead release caused the electrochemically-driven oxidation of Pb(0)-containing plumbing materials, results of this study point to an added benefit of phosphate in controlling the chemical stability of Pb(IV)-containing corrosion scales in drinking water distributions 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 Pb(IV) corrosion scales by NOM.

Acknowledgements

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Supporting Information Section

Figures showing lead release from and zeta potential profiles of PbO_2 under different chemical conditions are provided in the SI section.

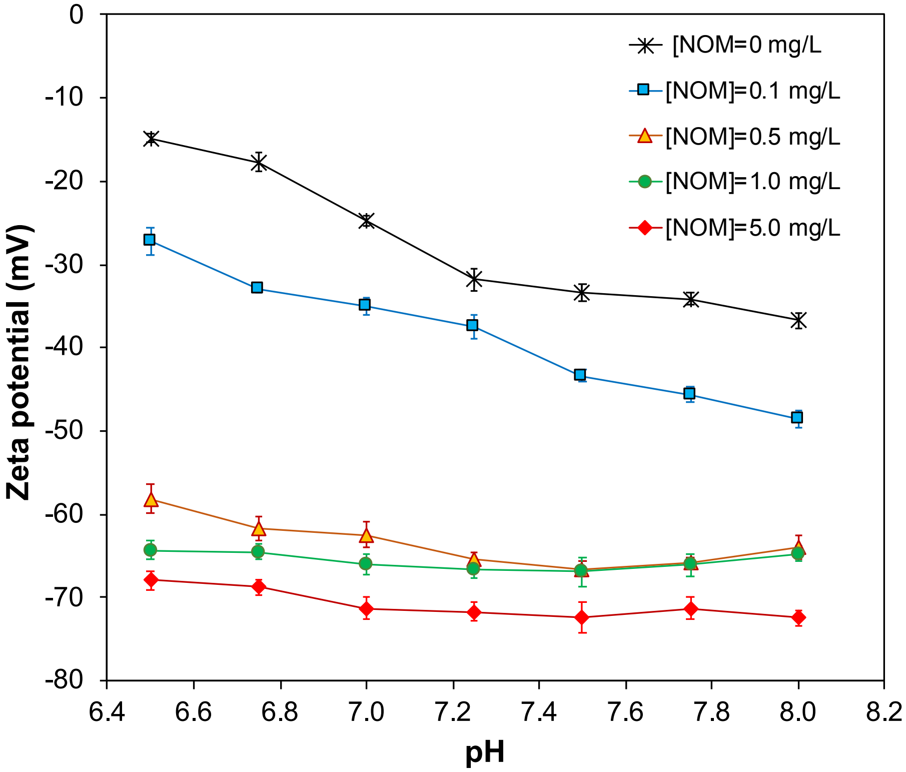

Figure 1 Impact of Suwannee River fulvic acid concentrations on the zeta potential of PbO_2. Ionic strength=10 mM, $[PbO_2]$=140 mg/L, $TOTCO_3$=1 mM, $[Cl^-]$=1 mM. The solid lines are trendlines connecting the data points.

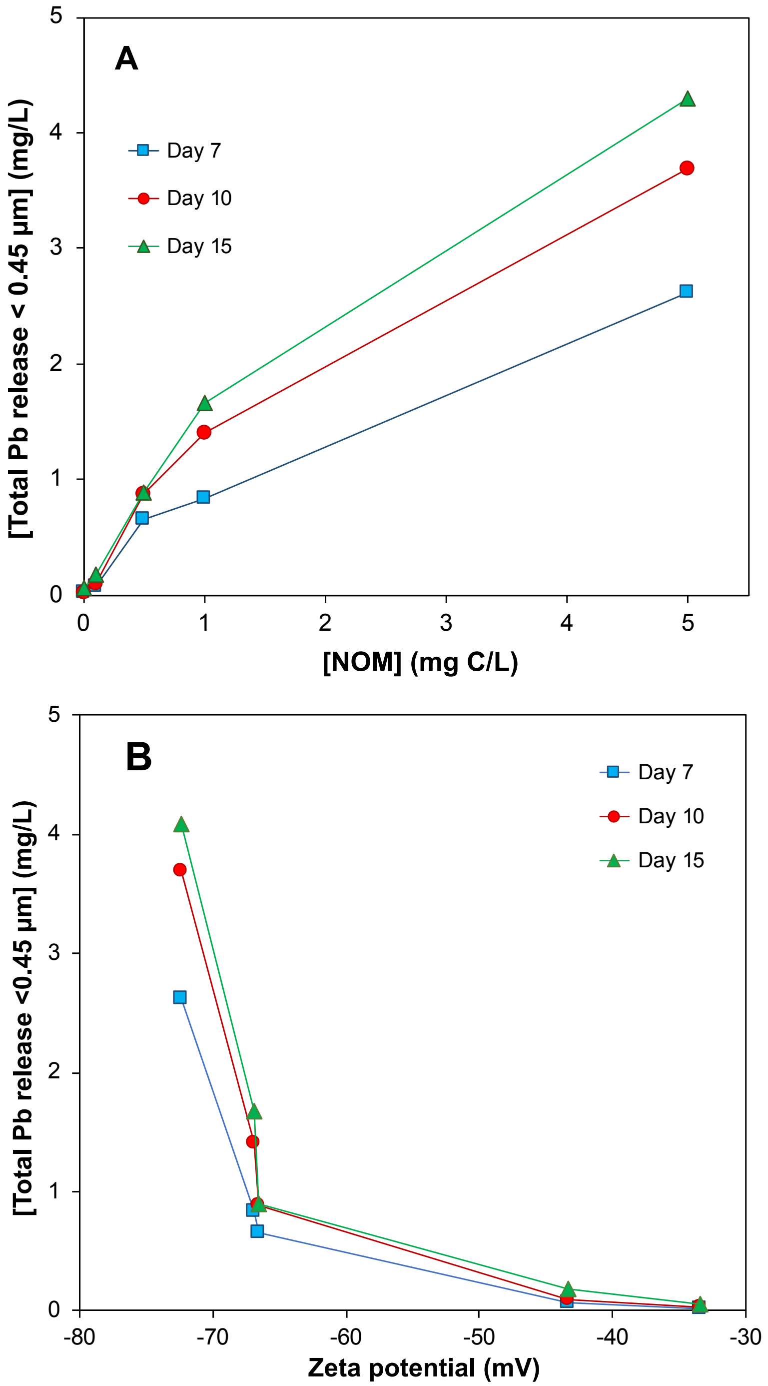

Figure 2 Impact of Suwannee River fulvic acid NOM concentrations on lead release (<0.45μm) from PbO_2 particles. (A) Lead release; (B) correlation with zeta potential. PbO_2=140 mg/L, $TOTCO_3$=1 mM, Cl^-=1 mM, pH=7.5, [NOM]=0-5 mg C/L. The solid lines are trendlines connecting the data points.

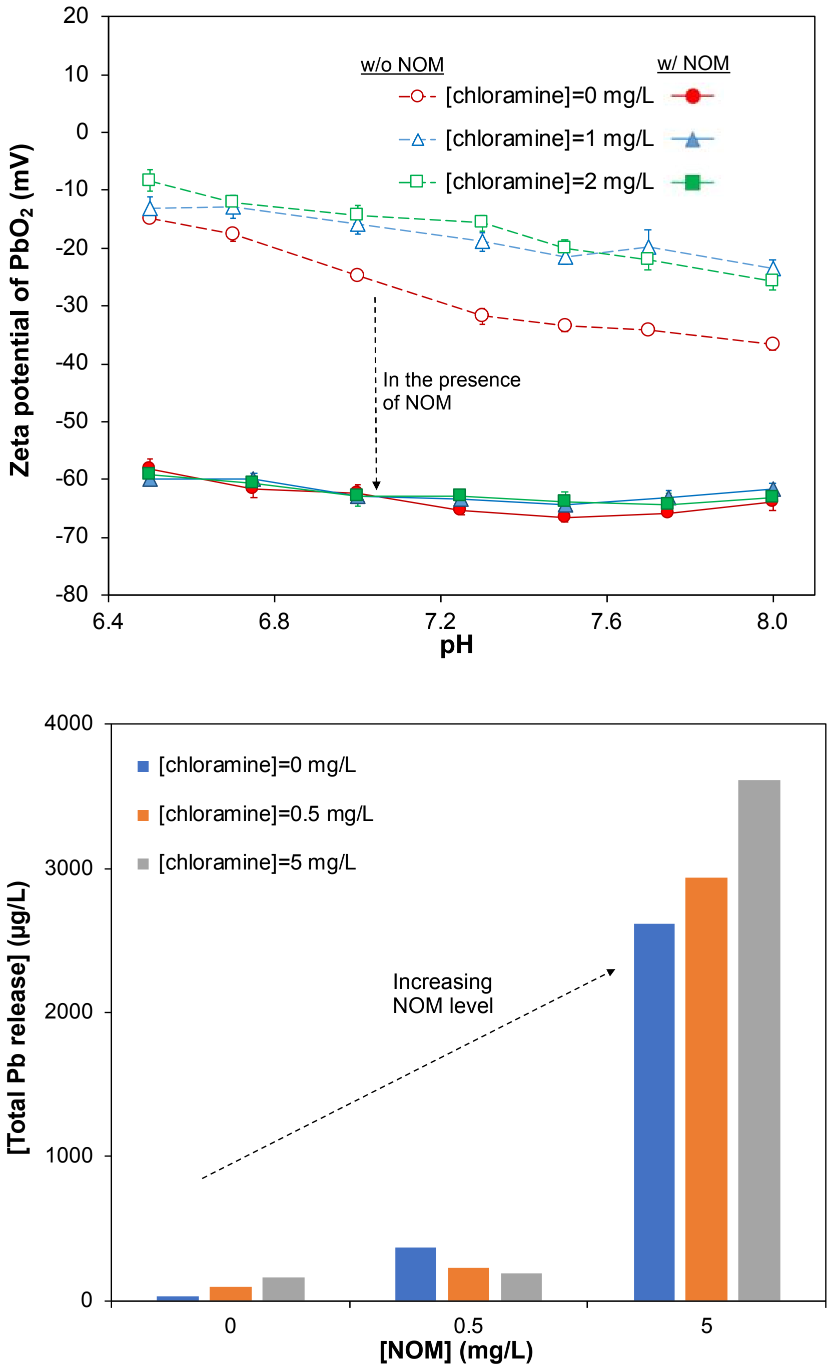

Figure 3 Impact of chloramine on the lead release from PbO_2 in the presence of Suwannee River NOM. (A) Zeta potential, [NOM]=0 and 0.5 mg C/L; both solid and dash lines are trendlines connecting the data points. (B) lead release after 5 days of reaction. Ionic strength= 10 mM, [NOM]=0.5 and 5 mg/L, PbO_2=140 mg/L, $TOTCO_3$= 1 mM, Cl^-= 1mM.

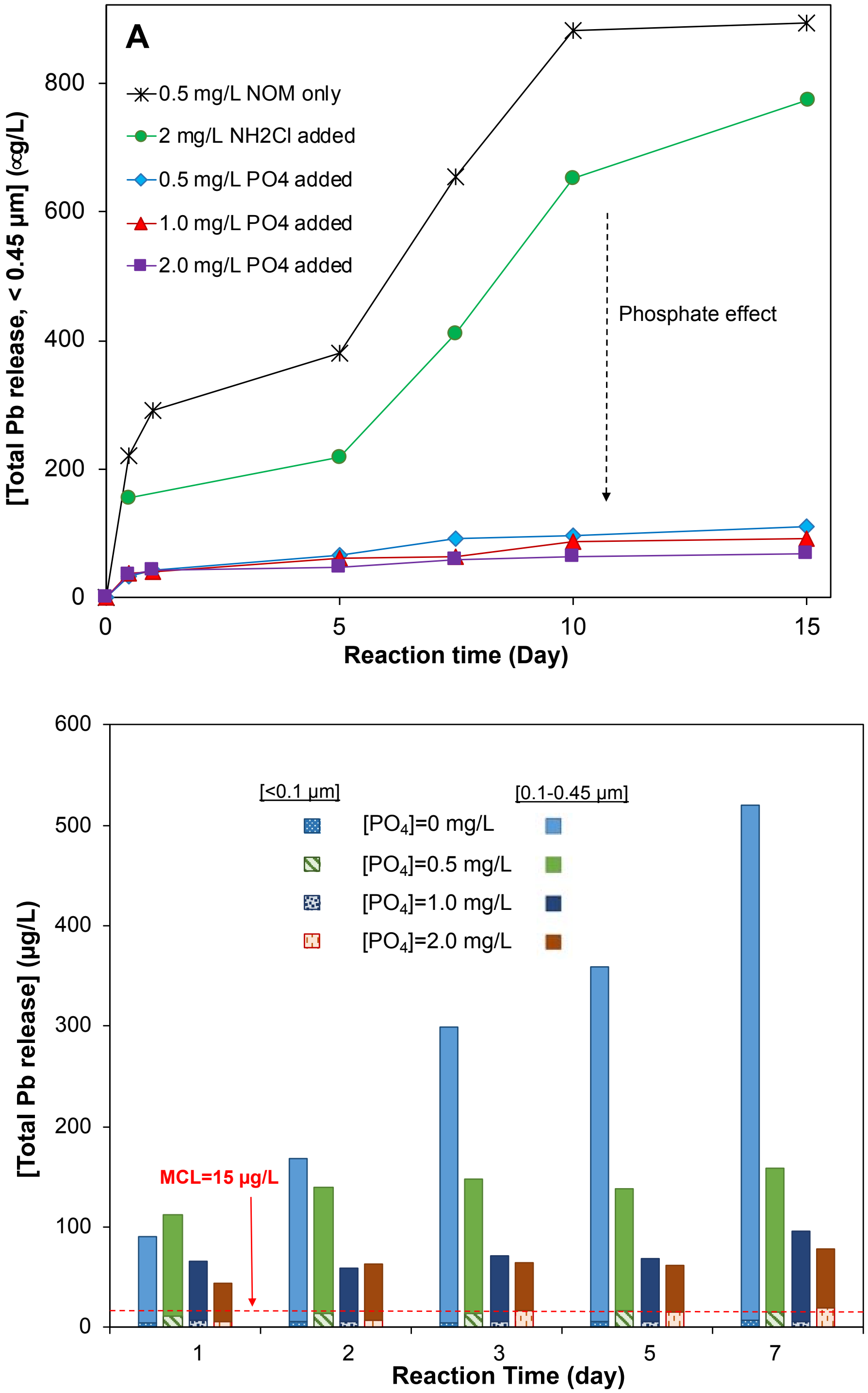

Figure 4 Impact of phosphate on the lead release from PbO_2 in the presence of Suwannee River NOM and chloramine. (A) total lead release; the solid lines are trendlines connecting the data points. (B) size distribution of total lead release. Ionic strength=10 mM, NOM=0.5 mg/L, PbO_2=140 mg/L, chloramine=2 mg/L, $TOTCO_3$=1 mM, Cl^-=1 mM.

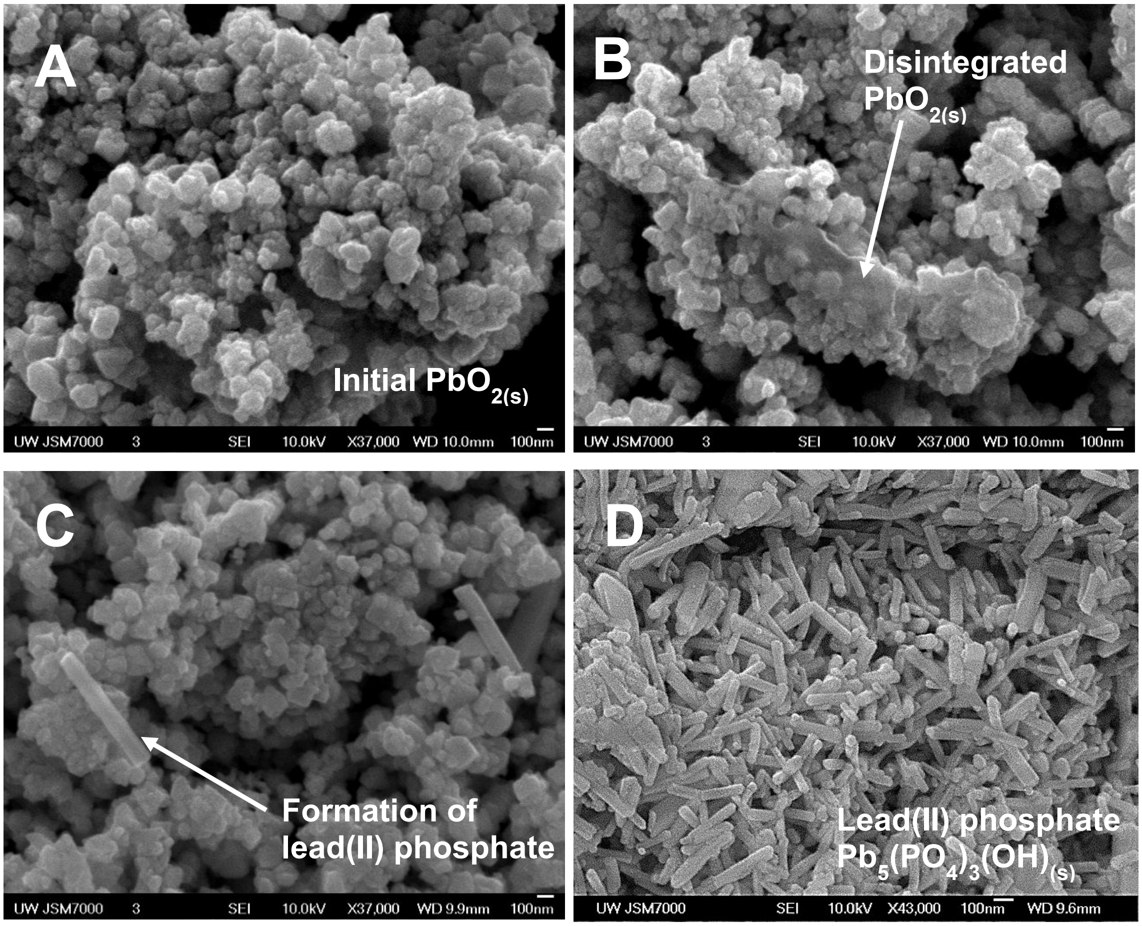

Figure 5 Morphology of PbO_2 particles in different chemical conditions after 16 days of reaction. PbO_2 140 mg/L, ionic strength 10 mM. (A) PbO_2 particles in 0.25 mg/L NOM with 2 mg/L chloramine; (B) PbO_2 particles in 2 mg/L NOM with 2 mg/L chloramine; (C) PbO_2 particles with the formation of lead(II) phosphate in 0.25 mg/L NOM with 2 mg/L chloramine and 1 mg/L phosphate; (D) hydroxypyromorphite $Pb_5(PO_4)_3OH_{(s)}$.

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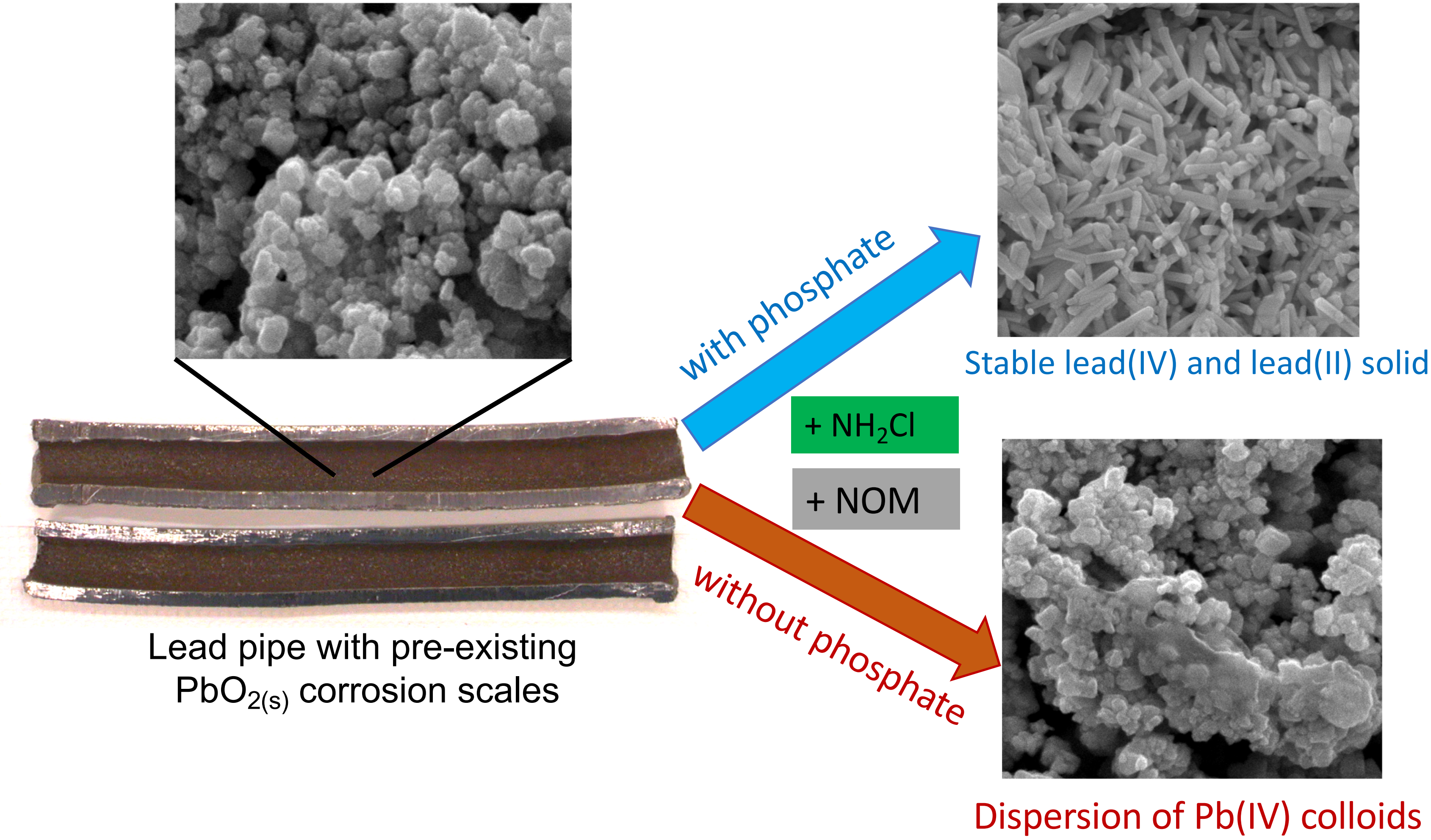

Lead pipe with pre-existing $PbO_{2(s)}$ corrosion scales

with phosphate

$+ NH_2Cl$

+ NOM

without phosphate

Stable lead(IV) and lead(II) solid

Dispersion of Pb(IV) colloids