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Bromide-assisted catalytic oxidation of lead(II) solids by chlorine in drinking water distribution systems†

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This study investigated the effect of bromide on the oxidation of three lead(II) solids by chlorine – a redox process critical to the control of lead release in drinking water distribution systems. Bromide had a strong catalytic effect on the oxidation of lead(II) carbonate solids, but had a limited impact on the oxidation of lead(II) phosphate.

Lead (Pb) is a toxic metal with severely adverse health effects.[1–3] Pb-Containing plumbing materials are still widely present in water distribution infrastructure in the U.S.[4] The recent crisis in Flint, Michigan has shown that controlling lead release in drinking water is an urgent challenge.[5,6] Water distribution infrastructure has historically been considered as a simple means of transmitting water, but it is a complex chemical system with interactions among many reactive components including pipe materials and residual disinfectants.[7,8] Much of the existing water infrastructure in the U.S. is near or beyond its design life.[9] Corrosion of the drinking water infrastructure results in elevated levels of metals, causing aesthetic and health problems and costing approximately 0.5% of America's GDP.[10,11]

Lead release in drinking water distribution systems is controlled by the redox chemistry of Pb(II) and Pb(IV) solids. As Pb-containing pipe materials corrode, a variety of Pb(II) minerals are produced, with cerussite $PbCO_{3(s)}$ and hydrocerussite $Pb_3(CO_3)_2(OH)_{2(s)}$ being the most commonly observed.[12,13] In the presence of residual disinfectant chlorine, both cerussite and hydrocerussite are oxidized to Pb(IV) solids, *i.e.*, lead dioxide $PbO_{2(s)}$.[14–16] Compared to Pb(II) minerals, $PbO_{2(s)}$ has a much lower solubility, but it can undergo colloidal mobilization and reductive dissolution to release lead.[17–19] To minimize lead release, phosphate is typically added to drinking water prior to its entry into water distribution systems. The presence of phosphate promotes the formation of highly insoluble hydroxylpyromorphite $Pb_5(PO_4)_3OH_{(s)}$ in corrosion scales, and prevents the formation of $PbO_{2(s)}$.[13] Therefore, understanding the conversion between Pb(II) and $PbO_{2(s)}$ is critical to the effective management of water infrastructure and prevent lead release.

As water reuse and desalination become more common to mitigate water scarcity, more recycled and desalinated water will be blended into existing distribution systems.[20] However, these alternative water resources often contain higher levels of bromide than conventional surface or groundwater.[21–23] Furthermore, seawater intrusion and brine discharge from alternative energy production (*e.g.*, shale gas) are projected to increase bromide level in drinking water by as much as 20 times in the future.[24] Recent studies showed that bromide catalyses the oxidation of transitional metals including chromium and manganese by chlorine,[25,26] and promotes the reaction between organics and chlorine to from toxic disinfection by-products.[27] However, the impact of bromide on the transformation of Pb(II) solids to $PbO_{2(s)}$ by chlorine in drinking water still remains unknown.

Considering the importance of Pb redox chemistry on the control of lead release and the risks associate with bromide in alternative water resources, it is urgent to understand the impact of bromide on the oxidation of Pb(II) solids by chlorine under chemical conditions of drinking water distribution systems.[28,29] The objective of this study was to investigate the kinetics and mechanism of bromide-assisted oxidation of representative Pb(II) solid phase oxidation by chlorine, and examine the inhibitive effects of phosphate on the redox reactivity of Pb(II) solids co-existing with bromide.

$Pb_3(CO_3)_2(OH)_{2(s)}$ and $PbCO_{3(s)}$ were purchased from Sigma-Aldrich. $Pb_5(PO_4)_3OH_{(s)}$ was synthesized based on an established method and confirmed using X-ray diffraction (Fig. S1 in the ESI†).[30] A 14 mM free chlorine solution was prepared from a 5% NaOCl solution. A 14 mM bromine (HOBr) stock solution was prepared by mixing free chlorine and NaBr with 15% molar excess of the latter for one hour.[31] In each experiment, a targeted dosage of one Pb(II) solid with 2.1 mM of total Pb was added into a completely mixed batch reactor. The concentration of bromide ranged from 0 to 20 mg L^{-1}. The dosage of chlorine or bromine

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was controlled at a value between 2 and 50 mg L^{-1} as Cl_2. This range of concentrations was chosen to develop a kinetic model that is still relevant under typical drinking water conditions.[32,33]

The solution pH was maintained at a targeted value between 7.0 and 9.8 using a Eutech Instrument Alpha pH200 controller with 50 mM $HClO_4$ and 50 mM NaOH, which did not interfere with lead redox chemistry and have been widely used for pH control purposes.[17] The concentration of total inorganic carbon ($TOTCO_3$) was controlled at 1 mM using $NaHCO_3$, and ionic strength at 10 mM using $NaClO_4$. Natural organic matter was not considered in this study, because its low concentration in drinking water has a negligible effect on chlorine consumption compared to the reaction between Pb(II) and chlorine.[34,35] All experiments were conducted at 22 °C in the dark. At pre-determined time intervals, samples were taken from the Pb(II)/oxidant suspension and filtered using 0.2 μm Millipore filters. The filtered samples were analysed for chlorine or bromine concentration using the standard DPD method.[36]

Results showed that the presence of bromide significantly impacted the oxidation of $Pb_3(CO_3)_2(OH)_{2(s)}$ and $PbCO_{3(s)}$, respectively (Fig. 1 and Fig. S2, ESI†). The oxidation kinetics exhibited a lag phase followed by a rapid oxidation phase. This two-phase behaviour was associated with an autocatalytic effect of the oxidation product, $PbO_{2(s)}$.[14,17,37] As $PbO_{2(s)}$ was freshly generated, it catalysed the electron transfer of heterogamous Pb(II) oxidation by chlorine. This is likely associated with the semiconducting nature of $PbO_{2(s)}$ that facilitates electron transfer.[17,38]

Furthermore, the presence of bromide impacted the oxidation kinetics in two considerable ways. First, the duration of lag phase decreased with increasing bromide level. For example, during $Pb_3(CO_3)_2(OH)_{2(s)}$ oxidation, the duration of lag phase decreased from approximately 4 hours to less than 2 hours as the concentration of bromide increased from 0 to 20 mg L^{-1} (Fig. 1).

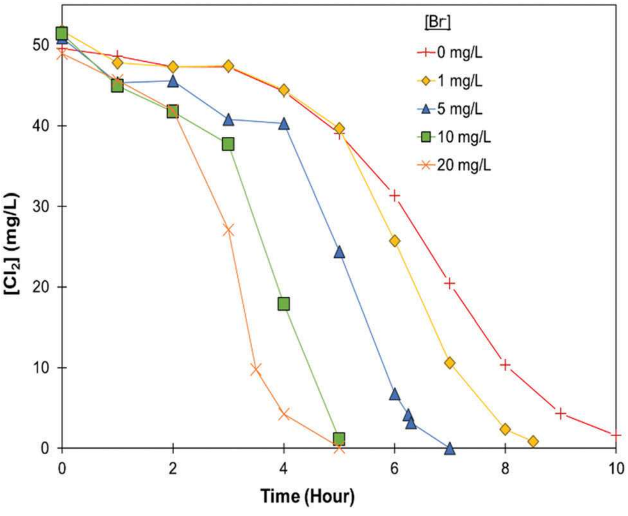


Fig. 1 Oxidation of $Pb_3(CO_3)_2(OH)_{2(s)}$ by chlorine at varying bromide concentrations. pH = 7.3, initial $[Cl_2]$ = 50 mg L^{-1}, initial $[Pb_3(CO_3)_2(OH)_{2(s)}]$ = 1.5 g L^{-1}, molar ratio of Pb(II) : Cl_2 = 8.3 : 1, ionic strength = 10 mM, $TOTCO_3$ = 1 mM.

A similar effect of bromide was observed for $PbCO_{3(s)}$ oxidation (Fig. S2, ESI†). Second, the reaction rate during the rapid oxidation phase also accelerated with higher bromide.

The oxidation of Pb(II) solids, *e.g.*, $PbCO_{3(s)}$ by chlorine proceeded with the following reaction:

$$HOCl + PbCO_{3(s)} + H_2O \xrightarrow{PbO_{2(s)}} PbO_{2(s)} + H^+ + Cl^- + H_2CO_3 \quad \text{(R1)}$$

When bromide is present in drinking water, hypobromous acid (HOBr) is generated *via* bromide–chlorine reaction:

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad \text{(R2)}$$

HOBr is a weaker oxidant than HOCl, but it possesses a faster reaction kinetics with Pb(II) solids *via* the following reaction:

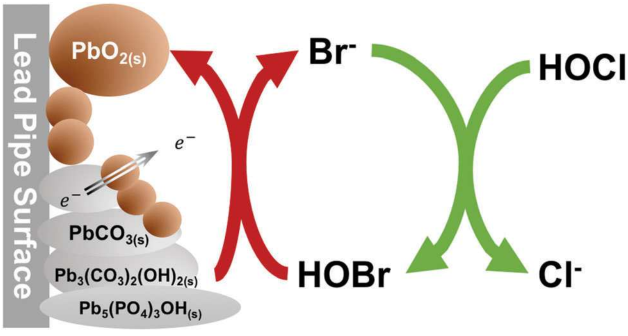
$$HOBr + PbCO_{3(s)} + H_2O \xrightarrow{PbO_{2(s)}} PbO_{2(s)} + H^+ + Br^- + H_2CO_3 \quad \text{(R3)}$$

Reaction (3) releases bromide, which participates in reaction (2) again. Therefore, bromide acts as an electron shuttle *via* the HOBr/Br^- redox pair to catalyse the oxidation of Pb(II) solids by chlorine (Scheme 1). The discovery of this novel catalytic pathway is critical to the control of lead release in distribution systems, *e.g.*, by managing halide and salt content in source water.

To quantitatively describe the bromide-assisted catalytic oxidation of hydrocerussite and cerussite, an autocatalytic reaction kinetics was employed:

$$-\frac{d[HOX]}{dt} = k_1[Pb(II)][HOX] + k_2[Pb(II)][HOX](M_{PbO_{2(s)}}) \quad \text{(E1)}$$

The first term on the right-hand side of eqn (1) represents the non-catalytic reaction mechanism, where k_1 is the surface area-normalized rate constant, [Pb(II)] is the surface area-normalized concentration of lead(II) on the solid surface, and [HOX] is the free halogen concentration. Free total halogen was used in the model because the DPD method cannot differentiate between free chlorine and bromine. Due to the low solubility of lead(II) minerals, the reaction proceeded as a heterogeneous oxidation reaction involving Pb(II) surface complexes. The second



Scheme 1 Electron shuttle mechanism of bromide-assisted catalytic oxidation of Pb(II) solids by chlorine.

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Table 1 Reaction rate constants for cerussite and hydrocerussite oxidation by chlorine in the presence of different levels of bromide

Pb(II) solid	Br^- (mg L^{-1})	k_1 (L mol^{-1} h^{-1})	k_2 ($\times 10^5$ L^2 mol^{-2} h^{-1})
$Pb_3(CO_3)_2(OH)_{2(s)}$	0	1.8	20.0
	1	2.0	23.3
	5	4.4	34.3
	10	17.4	38.5
	20	22.8	38.7
$PbCO_{3(s)}$	0	0.8	4.1
	0.5	1.7	5.7
	1	6.3	6.2
	2	7.3	6.5
	5	21.0	6.6

term corresponds to the autocatalytic oxidation accelerated by the product of $PbO_{2(s)}$, where k_2 is the rate coefficient and $M_{PbO_{2(s)}}$ is molar concentration of $PbO_{2(s)}$.

Values of k_1 and k_2 were obtained by fitting the experimental data with the model ($R^2 > 0.99$). For chlorine-driven hydrocerussite and cerussite oxidation, both k_1 and k_2 increased with the concentration of bromide (Table 1). The value of k_1 increased almost linearly with the increase of bromide concentrate. In contrast, k_2 exhibited a different trend with bromide. Its value initially increased with the bromide concentration but plateaued at bromide levels higher than 2 mg L^{-1} (Table 1).

The difference in the observed effects of bromide on k_1 and k_2 was likely associated with the autocatalytic nature of heterogeneous Pb(II) oxidation by chlorine. k_1 represents the contribution from the non-catalytic oxidation of Pb(II) solids. An increase of bromide concentration significantly enhances the electron shuttle process, and consequently accelerates the non-catalytic oxidation (Scheme 1). On the other hand, k_2 represents the contribution from the autocatalytic oxidation of Pb(II) solids catalysed by $PbO_{2(s)}$. It is likely that the electron shuttle-induced effect by bromide is less significant than the catalysis by $PbO_{2(s)}$. This indicates that the introduction of bromide preferentially accelerates the non-catalytic step of the reaction, while the oxidation product of $PbO_{2(s)}$ promotes the catalytic step of the reaction.

To further investigate reaction kinetics involving bromine species, additional experiments of $PbCO_{3(s)}$ oxidation directly by HOBr were conducted (Fig. 2). The results showed that the rate of HOBr oxidation is dramatically faster than HOCl oxidation. With 50 mg L^{-1} of oxidant as chlorine, the lag phase of HOBr oxidation was approximately 5 minutes compared to 15 hours with HOCl oxidation, and the rate of oxidation was much faster with HOBr than with HOCl (Fig. 2 *vs.* Fig. 1). The catalytic reactivity of bromine species was also pH-dependent (Fig. 3). The rate of $PbCO_{3(s)}$ oxidation by bromine correlated with the speciation of HOBr at pHs ranging between 7 and 10, *i.e.*, ±1.5 pH units of p*K* values (Fig. 3). This observation strongly suggested that the electron shuttle effect of bromide was associated with the protonated species of HOBr (p*K* = 8.6). At pHs higher than the p*K* value (*i.e.*, 8.6), OBr^- instead of HOBr became predominant, and the rate of reaction dramatically decreased. This pH-dependent nature was also supported by the same pH effects observed during the oxidation of $Pb_3(CO_3)_2(OH)_{2(s)}$ by chlorine in the presence of bromide (Fig. 4). These data suggested that HOBr is much more reactive than OBr^-. Although the redox potential of $HOBr/Br^-$ pair decreases with increasing pH, it only dictates the thermodynamic likelihood of the reaction rather than the kinetics.

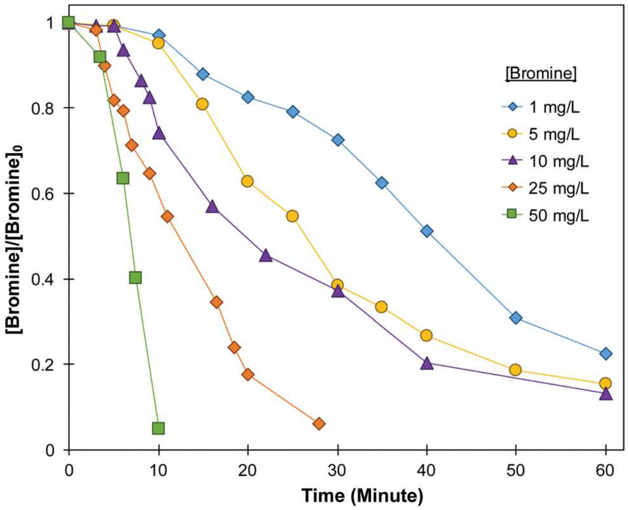

Fig. 2 Oxidation of $PbCO_{3(s)}$ by bromine with different initial concentrations of bromine. pH = 7.0, initial [$PbCO_{3(s)}$] = 0.56 g L^{-1}, ionic strength = 10 mM, $TOTCO_3$ = 1 mM.

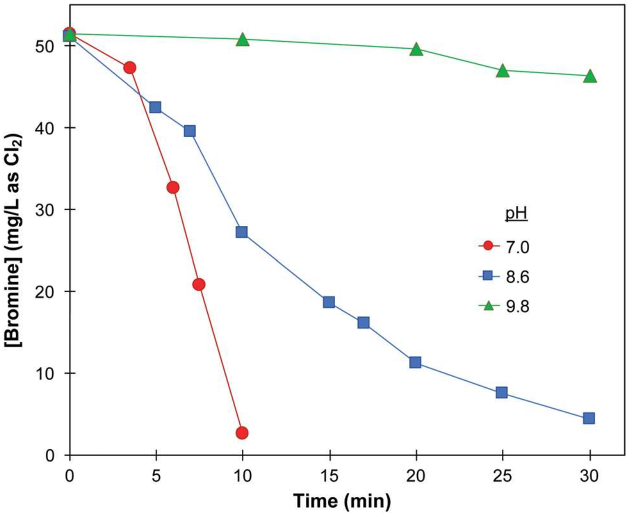

Fig. 3 Oxidation of $PbCO_{3(s)}$ by bromine at varying pH levels. Initial [bromine] = 50 mg L^{-1}, initial [$PbCO_{3(s)}$] = 0.56 g L^{-1}, ionic strength = 10 mM, $TOTCO_3$ = 1 mM.

In contrast, the bromide-assisted catalytic oxidation of Pb(II) solids by chlorine exhibited a much slower rate with $Pb_5(PO_4)_3OH_{(s)}$. The oxidation reaction was negligible within 6 days (Fig. S3, ESI†). The direct oxidation of $Pb_5(PO_4)_3OH_{(s)}$ by HOBr also exhibited extremely slow reaction kinetics compared to $PbCO_{3(s)}$ and $Pb_3(CO_3)_2(OH)_{2(s)}$ (Fig. S4, ESI†). At bromine concentrations of 50 mg L^{-1}, $PbCO_{3(s)}$ had a lag phase of about 4 minutes and chlorine was completely consumed within

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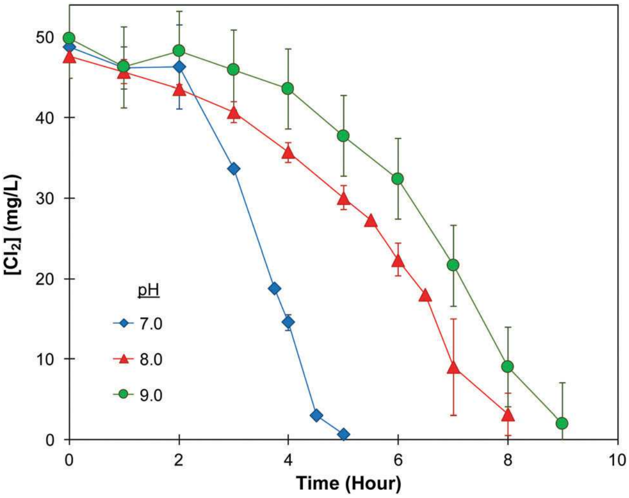

Fig. 4 Oxidation of $Pb_3(CO_3)_2(OH)_{2(s)}$ by chlorine at varying pH. Initial $[Cl_2]$ = 50 mg L^{-1}, $[Br^-]$ = 10 mg L^{-1}, initial $[Pb_3(CO_3)_2(OH)_{2(s)}]$ = 1.5 g L^{-1}, ionic strength = 10 mM, $TOTCO_3$ = 1 mM.

approximately 10 minutes. In contrast, $Pb_5(PO_4)_3OH_{(s)}$ oxidation with 50 mg L^{-1} of bromine had a lag phase of 8 hours and was completely oxidized by 22 hours. This trend indicated that the $Pb_5(PO_4)_3OH_{(s)}$ is much more resistant to bromine oxidation than $PbCO_{3(s)}$ and $Pb_3(CO_3)_2(OH)_{2(s)}$.

Because $Pb_5(PO_4)_3OH_{(s)}$ is the predominant Pb(II) solid phase in drinking water distribution systems that implement phosphate corrosion control strategy, the observed trend suggested that the addition of phosphate would be successful in mitigating the catalytic effects of bromide, and inhibit the bromine-driven oxidation of Pb(II) solids in the corrosion scales of drinking water distribution systems.

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