

Preventing leaching from lead water pipes with electrochemistry: an exploratory study

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Estimating the polarization potential for the electrochemical formation of Pb(II) or Pb(IV) corrosion products

The potentials at which Pb is oxidized to Pb(II) and Pb(IV) in a given electrolyte may be estimated using the Nernst equation (Eq S1):

$$E = E^0 - \frac{RT}{zF} \ln \frac{\alpha_{Red}}{\alpha_{Ox}} \quad \text{Eq (S1)}$$

Where E is the potential at which oxidation (or reduction) occurs (V), E^0 is the standard electrode potential for a given redox reaction (V), R is the universal gas constant ($\text{J K}^{-1} \text{mol}^{-1}$), T is the temperature (K), z is the number of electrons transferred in the half-cell reaction and α_{Red} and α_{Ox} are the chemical activities of the relevant species that are being reduced and oxidized, respectively. Assuming a constant temperature and that the chemical activities of the relevant species may be estimated using their respective concentrations allows the construction of Pourbaix Diagrams. These diagrams represent the oxidation state and predominant species of a redox-active chemical as a function of pH and potential and are thus useful for predicting the predominant species under different electrolyte conditions. A Pourbaix diagram for Pb in a 0.05 M phosphate electrolyte is shown in Figure S1.

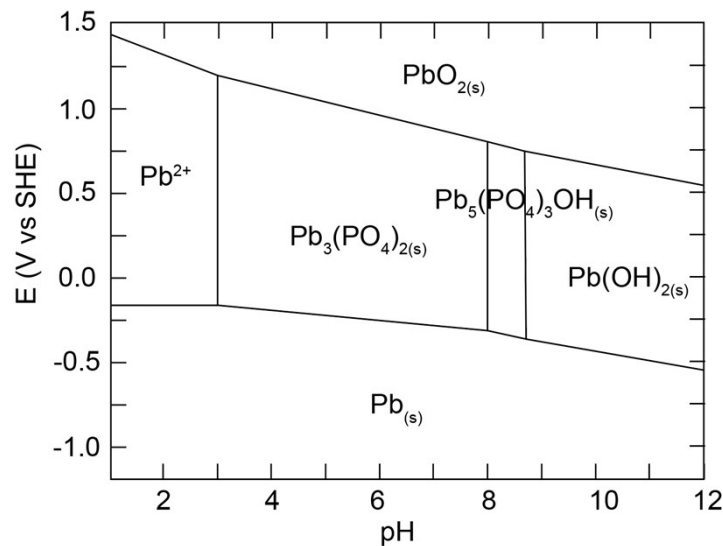


Figure S1. Pourbaix diagram of pure Pb in a 0.05 M phosphate electrolyte and a temperature of 25 C

The Pourbaix diagram shown in Fig. S1 may be used to estimate the polarization potential and pH at which $\text{Pb}_3(\text{PO}_4)_2$ or PbO_2 are the predominant Pb corrosion product; however, the estimated value is only a reference based on thermodynamics. The actual polarization potentials may be obtained experimentally using cyclic voltammetry. This technique was used on a pure Pb coupon using phosphate electrolytes with various phosphate concentrations (0.5, 0.05, 0.005 and 0.0005 M) and pH (1, 4, 10, 13) and the results are presented in Fig. S2.

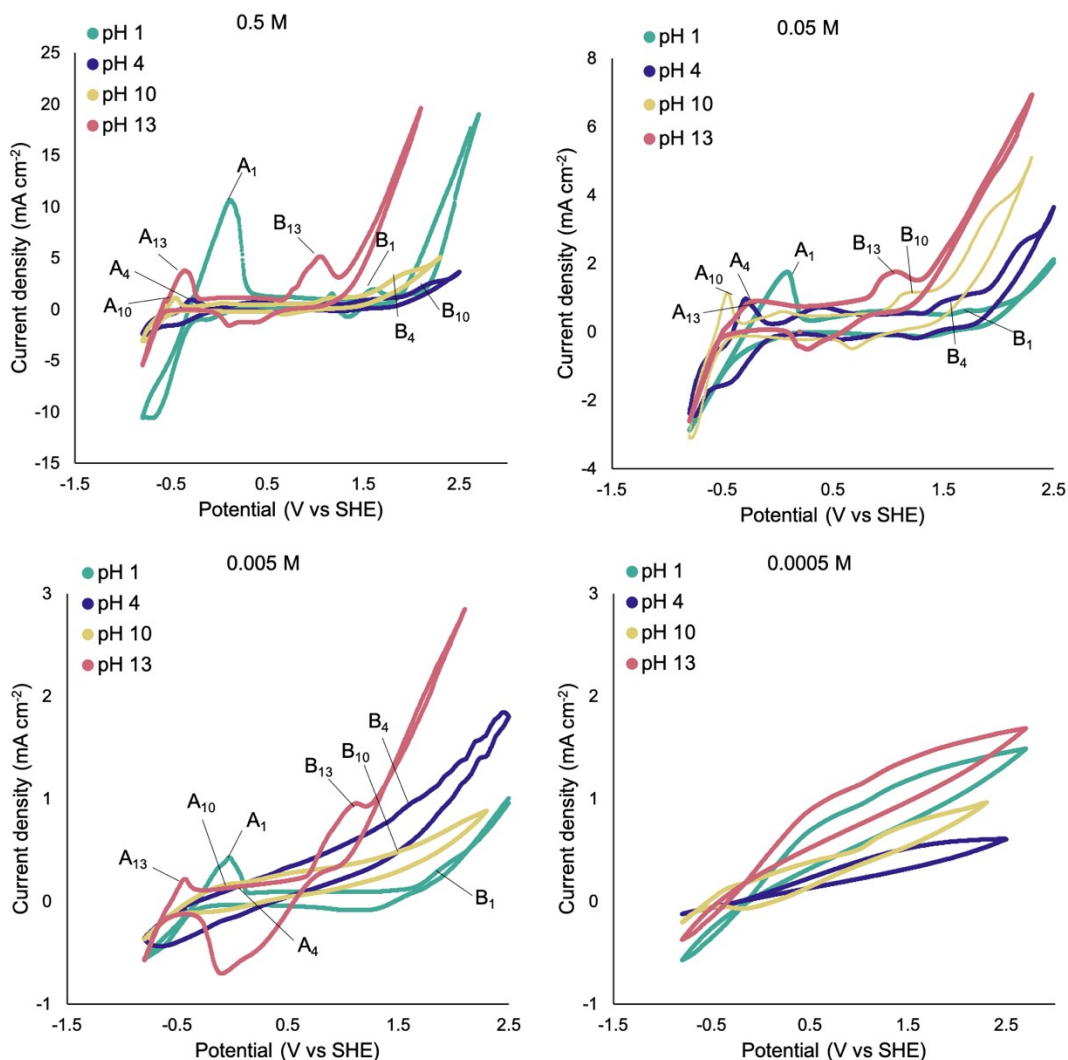


Figure S2. Cyclic voltammetry of a Pb coupon in a various phosphate solution at different pH values. The letters A_{XX} and B_{XX} show the potentials at which Pb(0) is oxidized to Pb(II), and Pb(II) is oxidized to Pb(IV), respectively, where XX is the pH of the electrolyte (1, 4, 10 and 13).

When using dilute phosphate solutions (0.005 and 0.0005 M) as the electrolyte, it becomes harder to identify the potentials at which Pb is oxidized to Pb(II) and Pb(IV) (points Axx and Bxx in Fig. S2). In dilute electrolytes the Pb oxidation process becomes diffusion-controlled and thus the voltammograms do not show any peaks.

Chronoamperometric polarization of Pb coupons to yield Pb(II) and Pb(IV) corrosion products

The potentials identified in Fig. S2 represent the potentials at which Pb(0) is oxidized to Pb(II), and Pb(II) is oxidized to Pb(IV) under different electrolytes. We will refer to these potentials, for brevity, as Pb^{0/2+} and Pb^{2+/4+} potentials. The Pb coupons were polarized chronoamperometrically at the corresponding Pb^{0/2+} and Pb^{2+/4+} potentials according to the electrolyte characteristics for 2 h. The chronoamperometry curves are shown in Fig. S3. In the cases where the Pb^{0/2+} and Pb^{2+/4+} potentials could not be identified (when using a 0.0005 M phosphate solution), the potentials used were + 0.2 V above those used for the 0.005 M solution. This increase in potential was used to account for the increased overpotential due to the lower conductivity of the electrolyte.

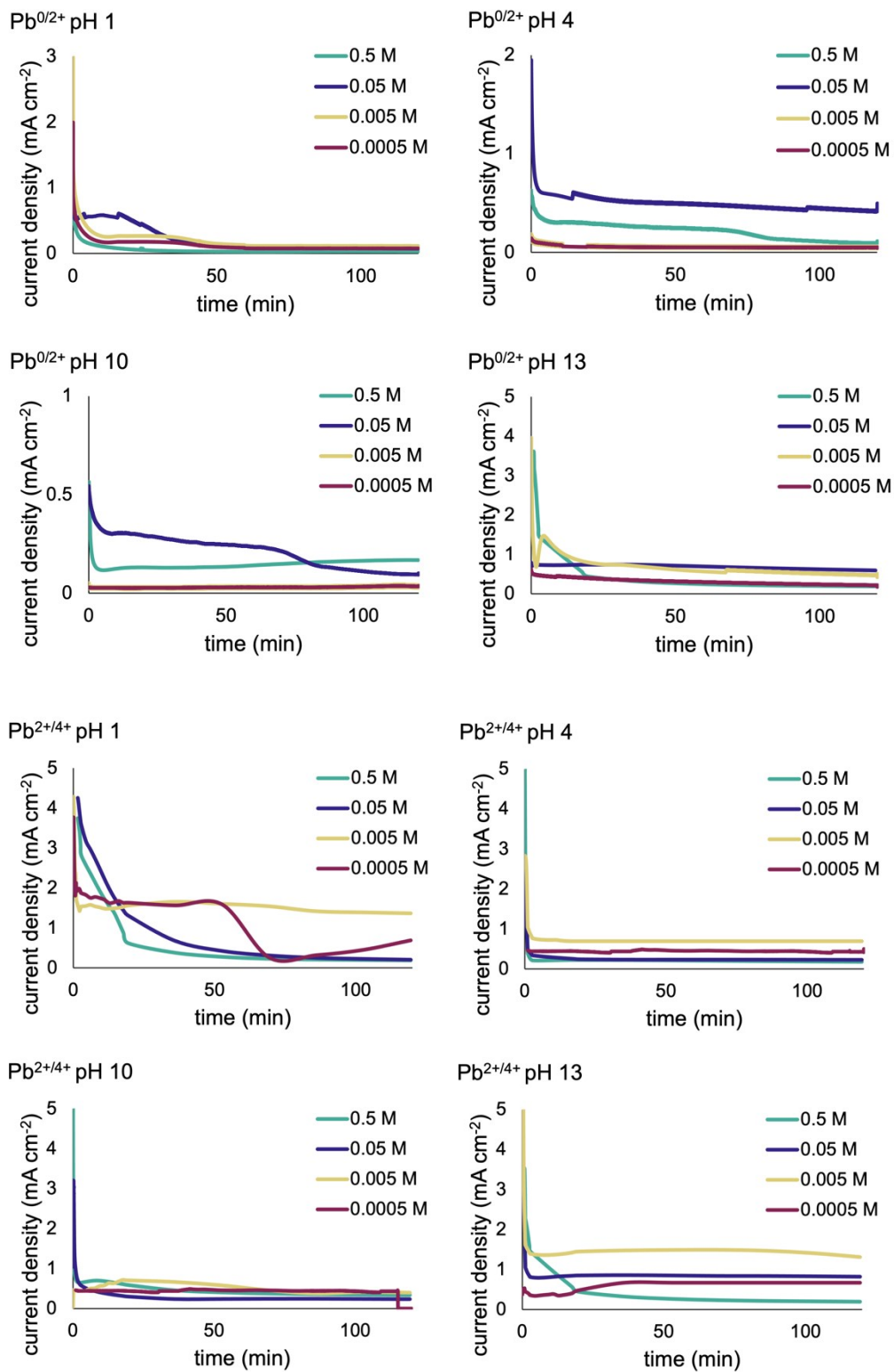


Figure S3. Polarization curves for a Pb anode polarized at the $Pb^{0/2+}$ potential and at the $Pb^{2+/4+}$ potential using a phosphate solution of varying concentrations at various pH values. As shown,

higher phosphate concentrations generally result in higher initial current densities; however, over time the current declines with the formation of a passive film on the Pb electrode

Using the current densities shown in Fig. S3 and Faraday's law it is possible to estimate the PbO₂ formation rates of the electrochemical cell. These rates are given by the currents observed during the first few seconds of polarization, after which a thin layer of PbO₂ forms and O₂ evolution becomes the predominant reaction¹. This is supported by a considerable increase in dissolved O₂ when using the Pb^{2+/4+} potentials, as shown in Figure S4 for different phosphate electrolytes at pH 10. Considering the lowest initial current density observed when using the Pb^{2+/4+} potential, 0.4 mA cm⁻², and using Faradays law, we estimate that the PbO₂ formation rate in 1 cm² of Pb(0) is at least 1.04 μmol s⁻¹ in the proposed electrochemical system. In contrast, the PbO₂ formation rates observed in water distribution systems range from 2.31 x10⁻⁵ to 4.63x10⁻⁴ μmol s⁻¹ when free chlorine is the main oxidant². Thus, scale buildup using the proposed electrochemical system is at least 4 orders of magnitude faster than the chemical scale formation that occurs naturally in water distribution systems.

To the best of our knowledge, there are no kinetic studies quantifying the formation rates of Pb₃(PO₄)₂ scales in water distribution systems (Pb₃(PO₄)₂ is rarely observed in these systems), thus, a similar comparison cannot be performed for the Pb^{0/2+} potentials. However, given that the use of orthophosphates to stop Pb leaching takes months to years³, it is safe to assume that the Pb₃(PO₄)₂ formation rates in water distribution systems are lower than those observed in the proposed electrochemical system (an average of 0.54 μmol s⁻¹ cm⁻²).

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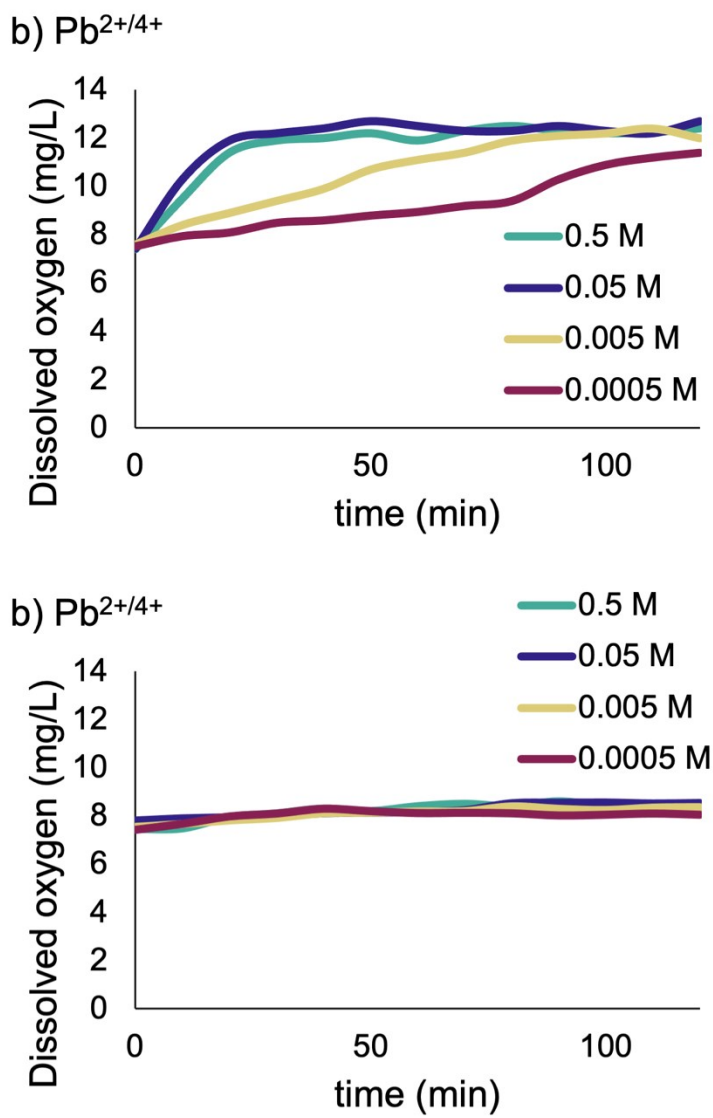


Figure S4. Dissolved O₂ during the polarization of Pb coupons at the a) Pb^{0/2+} potential and b) at the Pb^{2+/4+} potential using a phosphate solution of varying concentrations at pH 10. Dissolved O₂ levels increase from around 8 to 12 mg L⁻¹ when using the Pb^{2+/4+} potentials. On the other hand, dissolved O₂ remains at around 8.5 mg L⁻¹ when using the Pb^{0/2+} potential.