Depassivation of Aged Fe\(^0\) by Inorganic Salts: Implications to Contaminant Degradation in Seawater

Tongxu Liu,†‡ Xiaomin Li,† and T. David Waite*†

†School of Civil and Environmental Engineering, University of New South Wales, Sydney, NSW, Australia 2052
‡Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou, P. R. China 510650

Supporting Information

ABSTRACT: In this study, aged (iron oxide coated) Fe\(^0\) was applied to the degradation of trichloroethylene (TCE) in seawater. It was found that while the aged Fe\(^0\) was inactive with regard to TCE degradation in Milli-Q water, more than 95% of the TCE present was degraded in real and synthetic seawater solutions after exposure to aged Fe\(^0\) for 21 days. Results with individual salts from the synthetic seawater revealed that no significant TCE degradation was observed in the presence of Na\(_2\)SO\(_4\), CaCl\(_2\), and NaHCO\(_3\). Partial TCE degradation (28.4%) was observed in 500 mM NaCl after 21 days, while a similar extent of degradation to that found in the seawater solutions was observed in 50 mM solutions of magnesium salts (MgCl\(_2\) and MgSO\(_4\)). Results of open circuit potential analysis suggested that the Fe\(^0\) corrosion potential was not a key determinant of extent of TCE reduction since the corrosion potential decreased to levels similar to that of Fe\(^+/\)Fe\(^2+\) in the presence of all salts examined. Lower final pH values and higher dissolved Fe(II) concentrations were observed in the presence of magnesium salts compared to other salts. Formation of the surface complex >FeOMg\(^+\) was identified as being critical to protonation of surface sites, reductive dissolution of the passivating Fe(III) oxyhydroxide layer coating the underlying Fe\(^0\) and enhancement in extent of TCE reduction. These findings provide insight into the molecular-scale mechanism of depassivation of aged Fe\(^0\) by inorganic salts with particular implications for the Fe\(^0\)-mediated degradation of contaminants in saline natural waters such as seawater and saline groundwaters.

INTRODUCTION

Many estuarine waters and coastal water bodies adjacent to industrial sites are known to harbor severe contamination, often by highly carcinogenic chlorinated compounds resident in sediments, as a result of historic contamination of groundwaters.\(^1,2\) Dredging and on-land treatment of sediments is being adopted at the most contaminated sites, but the cost of this remediation approach is too expensive to be applied on a wide scale.

Application of zerovalent iron (Fe\(^0\)) would appear to be an environmentally friendly approach of in situ remediation of contaminated sediments because it is inexpensive and readily available and can degrade or transform a wide range of contaminants including chlorinated organics,\(^3\) heavy metals,\(^4\) nitroaromatics,\(^5\) and nitrate.\(^6\) Permeable reactive barriers of Fe\(^0\) have been successfully employed for the remediation of contaminated groundwater.\(^7\) However, several laboratory and field studies involving the long-term performance of Fe\(^0\) have shown that the contaminant degradation rates decrease with time,\(^8\) because of the formation and accumulation of iron oxides on the outer layer of aged Fe\(^0\).\(^9\) Even though the Fe\(^0\) reactivity can be sustained when Fe(II)/Fe(III) hydroxides such as magnetite (Fe\(_3\)O\(_4\)) and green rust are present, the formation of Fe(III) hydroxides such as goethite (α-FeOOH), maghemite (γ-Fe\(_2\)O\(_3\)), and hematite (α-Fe\(_2\)O\(_3\)) can decrease the Fe\(^0\) reactivity.\(^10,11\) Passivation of the Fe\(^0\) surface occurs when reactive sites are covered with these iron(III) oxides, resulting in significant reduction in efficiency of electron transfer from Fe\(^0\) to the contaminant.

Chloride and bromide salts are known pitting and crevice corrosion promoters, the presence of which can destroy the passive oxide coatings and help to maintain the degradation efficiency of Fe\(^0\) in contaminated waters.\(^12−14\) When applying Fe\(^0\) in organochlorine-contaminated waters, chloride is a product of the reaction of Fe\(^0\) with the chlorinated organic contaminants and pitting corrosion as a result of the release of chloride considered to be the cause of an observed increase over time in the degradation rates of chlorinated contaminants.\(^15−17\) Hernandez et al.\(^18\) also reported that the addition of chloride accelerated trinitrotoluene degradation during treatment of contaminated water with Fe\(^0\) and Johnson et al.\(^19\) observed an almost linear increase in rate constant for carbon tetrachloride dechlorination on increase in chloride.

Received: January 23, 2013
Revised: May 28, 2013
Accepted: June 10, 2013
concentration to 60 μM (but a decrease thereafter). Nurmi et al.\(^1\) suggested that substantial variations in the limiting values of corrosion potentials \(E_{corr}\) may be responsible for the significant variability in rates of contaminant reduction observed in previous studies. Generally, the concentrations of major ions in seawater are much higher than those in the contaminated waters reported in the above-mentioned literature.\(^2\) However, data are not yet available to systematically test the effects of seawater salts on the properties and performance of Fe\(^0\) with regard to organochlorine degradation.

In addition, while most research on nanosized ZVI is conducted using freshly synthesized materials, micrometer-sized ZVI in its “as purchased” state is relatively unreactive and is typically used in laboratory studies after either acid washing or depassivating in some other way. As removal of the passivating layer is likely to be difficult in full-scale applications, a real need exists to either understand the reactivity of the “as purchased” material in particular environments or to find cost-effective methods of depassivating large quantities of micrometer-sized ZVI prior to application. Based on the aforementioned reports concerning the ability of particular ions to enhance the degradation of chlorinated contaminants by Fe\(^0\),\(^10,17,18\) some of the salts present in seawater may be expected to destroy the passive film on the surface of aged Fe\(^0\) and improve the reactivity of the aged Fe\(^0\) for contaminant degradation. However, there does not appear to be any published studies regarding the application of aged Fe\(^0\) for organochlorine degradation in seawater.

In this study, aged Fe\(^0\) was used as a potential remediation material for trichloroethylene (TCE) reduction in seawater, and the effects of individual salts present in seawater on TCE reduction kinetics were investigated. The \(E_{corr}\) of aged Fe\(^0\) were also evaluated using open circuit chronopotentiometric analysis in the presence of individual salts as were changes in pH and also evaluated using open circuit chronopotentiometric analysis. The passivating layer is likely to be di or depassivating in some other way. As removal of the passivating layer is difficult in full-scale applications, a real need exists to either understand the reactivity of the “as purchased” material in particular environments or to find cost-effective methods of depassivating large quantities of micrometer-sized ZVI prior to application. Based on the aforementioned reports concerning the ability of particular ions to enhance the degradation of chlorinated contaminants by Fe\(^0\),\(^10,17,18\) some of the salts present in seawater may be expected to destroy the passive film on the surface of aged Fe\(^0\) and improve the reactivity of the aged Fe\(^0\) for contaminant degradation. However, there does not appear to be any published studies regarding the application of aged Fe\(^0\) for organochlorine degradation in seawater.

In this study, aged Fe\(^0\) was used as a potential remediation material for trichloroethylene (TCE) reduction in seawater, and the effects of individual salts present in seawater on TCE reduction kinetics were investigated. The \(E_{corr}\) of aged Fe\(^0\) were also evaluated using open circuit chronopotentiometric analysis in the presence of individual salts as were changes in pH and extent of Fe\(^0\) dissolution. Results obtained have enabled elucidation of the mechanism responsible for depassivation of aged Fe\(^0\) by inorganic salts present in saline natural waters such as seawater with new insights obtained of value in predicting the likely performance of Fe\(^0\) as a dechlorination technology in such environments.

**EXPERIMENTAL SECTION**

**Materials.** Aged zerovalent iron (Fe\(^0\), powder, ~70 mesh, 99%) was obtained from Acros Organics (Product No. 197815000) and aged in air for around three months prior to use. Preliminary experiments indicated minimal change in reactivity after this aging time though, for consistency, any set of studies was undertaken on material that had been aged for the same period.\(^22\) Analysis of particle size using a Malvern Mastersizer 2000C indicated a very broad particle size distribution (Figure S1a) with an average size of around 167 μm. X-ray diffraction (XRD) analysis (Figure S1b) confirmed that the material was principally Fe\(^0\) but with traces of oxides (FeO\(_4\) and FeO) present, presumably as a surface layer. Scanning electron micrographs (SEM) of the particles (Figure S1c) suggested the presence of surface deposits or coatings with electron dispersive spectroscopic (EDS) (Figure S1d) analysis indicating that these deposits contain oxygen and well as iron atoms. Trichloroethylene (TCE), NaCl, Na\(_2\)SO\(_4\), MgCl\(_2\), MgSO\(_4\), CaCl\(_2\), and NaHCO\(_3\) were obtained from Sigma-Aldrich in Australia. Seawater was obtained from the Sydney Offshore Reference Station (pH\(_{NBS}\) 8.1) and aged in air for around three months prior to use. The aged Fe\(^0\) (1 g) was preweighed in each test serum bottle (120 mL) with the serum bottles then filled with 40 mL of either Milli-Q water (as control), seawater, synthetic seawater, or solutions of salts used to prepare the synthetic seawater. The synthetic seawater was prepared using the recipe 500 mM NaCl, 50 mM MgSO\(_4\), 10 mM CaCl\(_2\), and 2 mM NaHCO\(_3\).\(^23\) Accordingly, solutions of individual salts were prepared with concentrations in the following ranges: (a) NaCl (0−1000 mM), (b) Na\(_2\)SO\(_4\) (0−100 mM), (c) MgSO\(_4\) (0−100 mM), (d) MgCl\(_2\) (0−100 mM), (e) CaCl\(_2\) (0−20 mM), and (f) NaHCO\(_3\) (0−5 mM). The real seawater, synthetic seawater, and stock solutions of each salt were purged with O\(_2\)-free argon gas for 60 min before being transferred to an anaerobic chamber in which standard anaerobic techniques were used in the following experimental procedure. TCE in the methanol stock solution was added to the reaction solution at a final concentration of 0.22 mM before the serum bottles were sealed with Teflon-coated butyl rubber stoppers and crimp seals. All studies were conducted in duplicate with vials incubated in a shaker at 180 rpm at 25 °C. Sampling intervals were arranged on days 1, 2, 3, 5, 7, 10, 14, and 21.

**Analytical Methods.** Samples (0.15 mL) were extracted with 1.5 mL of n-hexane for TCE determination, which was carried out using a gas chromatograph (Agilent 6890) equipped with an ECD detector and Trace TR-5MS silica fused capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The injector temperature was 250 °C, and the helium flow rate was 1.0 mL min\(^{-1}\). The column temperature was set at 100 °C for 2 min, increased at a rate of 15 °C min\(^{-1}\) to 160 °C, and then switched to a rate of 5 °C min\(^{-1}\). The temperature was finally increased to 250 °C and maintained isothermally for 10 min. TCE external standards were prepared in n-hexane with standard curves found to be linear. The average of duplicate determinations of concentration is reported with relative percent differences found to be typically less than 10%. As TCE is volatile and partitions between the liquid and gas phases, the total moles of TCE remaining in both liquid and gas phases were calculated using a Henry’s Law constant for TCE of 0.00937 atm m\(^3\) mol\(^{-1}\) (the proportion of moles of TCE in the liquid phase was typically on the order of 0.54).

For determination of dissolved Fe(II) and Fe(III) concentrations, the samples were centrifuged at 1000 × g for 5 min at 25 °C, and the supernatant was filtered using a 0.22-μm syringe filter before analysis. Dissolved Fe(II) was measured colorimetrically by the 1,10-phenathroline colorimetric method, and total dissolved Fe was determined in the same manner after adding 10% hydroxylamine hydrochloride to reduce all Fe(III)(aq) to Fe(II)(aq). Dissolved Fe(III) concentration was obtained from the difference between total dissolved Fe and dissolved Fe(II). All manipulations related to preparing the samples for Fe(II) determination by 1,10-phenathroline were conducted inside the anaerobic chamber prior to colorimetric measurement.

Open circuit chronopotentiometric measurements were carried out in a conventional two-electrode electrochemical cell using a CHI 650D Electrochemical Workstation (Texas, USA). A platinum electrode (2 mm in diameter) was used as the working electrode, with a Ag/AgCl electrode as the reference electrode.\(^5\) Unless otherwise stated, all the reported
voltage were versus Ag/AgCl. Prior to each measurement, the Pt disc electrode was polished with emery paper followed by Al2O3 powders of 1 and 0.06 mm particle sizes and was thoroughly rinsed with Milli-Q water between the two polishing steps. The Pt electrode was then cleaned successively with Milli-Q water. The aged Fe0 (1 mg) was dispersed in a dilute NaF solution (0.5 wt.% 100 μL) in an ultrasonic bath for 1 min. An aliquot (2 μL) of the above suspension was then coated on the clean Pt electrode using a microsyringe and air-dried for 3 min before being placed in the O2-free salt solution (10 mL). The sampling rate for open circuit chronopotentiometry was 1 s⁻¹, but the data in the reported figures are presented with markers spaced every 1000 data points for visual clarity. While the use of NaF and zinc to bind ZVI to the surface of the Pt disk electrode differs from the packed powder electrode approach used by Tratnyek and colleagues,24,25 NaF is recognized to be highly conductive and has been used in a similar manner to that adopted here by other investigators.26

Equilibrium speciation of salt ions and surface complexes was carried out using the thermodynamic package Visual MINTEQ 3.0 with speciation modeling also used in experimental design to ensure that mineral precipitation was avoided at the salt concentrations used. While the systems under investigation here are not at equilibrium in all aspects, speciation modeling is restricted to conditions where an iron oxhydroxide surface coating is present on the Fe0 surface and pseudoequilibrium for major ions and iron species can be reasonably assumed.

## RESULTS AND DISCUSSION

### TCE Reduction by Fe0 in Seawater

While no significant TCE degradation was observed with aged Fe0 in Milli-Q water, the TCE concentrations decreased over time with more than 90% of initial TCE degraded by day 21 in both real and synthetic seawaters (Figure 1). These results indicate that the commercial aged Fe0 was inactive in Milli-Q water but could be activated in real and synthetic seawater. The TCE concentration decreased exponentially in both cases with the pseudo-first-order rate constants (k) found to be very similar in both the synthetic seawater (0.115 d⁻¹) and the real seawater (0.118 d⁻¹). Since chloride salt has been demonstrated to increase the degradation rates of chlorinated contaminants by Fe0,27 the high concentration of Cl⁻ in the seawater may contribute to the activation of aged Fe0 for TCE reduction in this study. Besides Cl⁻ however, seawater contains both anions (i.e., SO₄²⁻ and HCO₃⁻) and cations (i.e., Na⁺, Mg²⁺, and Ca²⁺) which may contribute to the activation process. The role of particular ions in the activation of aged Fe0 is discussed further below.

### TCE Reduction by Fe0 in the Presence of Various Salts

Results of studies of TCE degradation by aged Fe0 in solutions of six different salts are shown in Figure S2 as are the results of control studies showing no TCE degradation in salt solutions in the absence of Fe0. No significant degradation of TCE by aged Fe0 was observed in the presence of Na₂SO₄, CaCl₂, and NaHCO₃ even with concentrations as high as that in seawater (Figures S2b, S2e, and S2f). These results suggest that the aged Fe0 cannot be activated by the ions SO₄²⁻, HCO₃⁻, Na⁺, and Ca²⁺, while the presence of Cl⁻ (≥50 mM) slightly facilitates TCE reduction (Figure S2a). The pseudo-first-order rate constants (k) are plotted in Figure 2. The values increased with an increase in NaCl concentration, but even the highest k value at 1000 mM NaCl (0.012 d⁻¹) was still far less than that for seawater. As such, it is clear that the high TCE removal efficiency by aged Fe0 evident in seawater is not particularly dependent on the presence of Cl⁻.

Surprisingly, very effective TCE removal by aged Fe0 was observed in solutions of MgSO₄ and MgCl₂. In correspondence with the extent of TCE degradation in both real and synthetic seawaters, approximately 90% of the initial TCE was removed in the treatments with MgSO₄ (5–100 mM) and MgCl₂ (10–100 mM) after reaction for 21 days (Figures S2c and S2d). The k values (Figure 2) for the treatments with MgCl₂ and MgSO₄ were much higher than those with the other salts; additionally, the k values for the treatments with 50 mM MgSO₄ (0.122 d⁻¹) and MgCl₂ (0.101 d⁻¹) were close to those for real (0.118 d⁻¹) and synthetic seawater (0.115 d⁻¹). These results suggest that the activation of aged Fe0 in seawater is mainly attributed to the presence of the magnesium cation. While the ability of chloride to accelerate the degradation of contaminants by Fe0 has been widely documented, little has been reported on the ability or the mechanism of deactivation of aged Fe0 by magnesium.

### Corrosion Potential of Fe0 in the Presence of Various Salts

The Ecorr of Fe0, which can be characterized using open circuit chronopotentiometry, is a mixed potential reflecting the equilibrium potential of the dominant redox couple, the kinetics of charge transfer between these species and the electrode, and mass transport of species into the pore space and across the passive film.20,24,28 The open circuit chronopotentiograms

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**Figure 1.** Kinetics of TCE reduction by aged Fe0 in different media, including control (Milli-Q water), synthetic seawater (500 mM NaCl, 50 mM MgSO₄, 10 mM CaCl₂, and 2 mM NaHCO₃), and real seawater.

**Figure 2.** Pseudo-first-order rate constants (k) of TCE reduction by aged Fe0 in solutions of different inorganic salts, including NaCl (0–1000 mM), Na₂SO₄ (0–100 mM), MgSO₄ (0–100 mM), MgCl₂ (0–100 mM), CaCl₂ (0–20 mM), and NaHCO₃ (0–5 mM).
provide a sensitive indication of changes in redox reactions at the surface of the Fe$^0$ deposited on the platinum disk electrode.$^{20,24,28}$ The $E_{\text{corr}}$ value in Milli-Q water (Figure S3) was initially determined to be around $-0.2$ V vs Ag/AgCl and then increased to a relative plateau at around $-0.05$ V vs Ag/AgCl after 2 h, indicating that the commercial aged Fe$^0$ is fully passivated.

With the addition of different types of salts, the $E_{\text{corr}}$ (Figure S3) decreased dramatically to a value of $-0.6$ to $-0.8$ V vs Ag/AgCl after 2 h. A similar effect of salt addition on $E_{\text{corr}}$ has been observed by other investigators$^{20,24,28}$ and (in addition to confirming the robustness of the electrochemical methods used here) suggests a breakdown of the passivating film on the surface of aged Fe$^0$. The final values of $E_{\text{corr}}$ after 4 h residence in the various salt solutions (Figure 3) were similar to the typical value of fresh Fe$^0$ in the active state ($-0.7$ to $-0.8$ V vs Ag/AgCl).$^{20}$ As can be seen from Figure S3, $E_{\text{corr}}$ decreased more slowly when the Fe$^0$-coated electrode was placed in NaHCO$_3$ solution than was the case for the other salt solutions and a relatively low $E_{\text{corr}}$ of about $-0.6$ V vs Ag/AgCl after 4 h was obtained for aged Fe$^0$ in 1 mM sodium bicarbonate, suggesting a degree of passivation of the Fe$^0$, possibly due to precipitation of carbonate phases, a phenomenon observed previously with micro-Fe$^0$.20

In addition to Cl$^-$ and SO$_4^{2-}$ anions,$^{20}$ other ions present in seawater (i.e., Na$^+$, Mg$^{2+}$, Ca$^{2+}$, and HCO$_3^-$) appear to induce the decrease of $E_{\text{corr}}$; however, such an observation is not consistent with the significant difference in kinetics for TCE reduction by aged Fe$^0$ in the different salt solutions. The effects of different salts on the $E_{\text{corr}}$ values appear to be decoupled from the effects of these salts on TCE reduction. It is clear that some other mechanism(s) need to be considered. Particular consideration is given below to the possibility of the generation of localized acidity from proton release as a result of either hydrolysis or surface complexation processes at the surface of aged Fe$^0$.

**pH and Dissolved Fe(II) in the Presence of Various Salts.** To examine whether changes in acidity occur as a result of either salt hydrolysis or surface complexation processes, pH values after 21 days of reaction were measured with the results presented in Figure 4a. Results of pH measurements for selected salt concentrations as a function of time have also been determined with the results in Figure S4 revealing that the final pH values were reached within one day of suspension of the aged Fe$^0$ in the particular salt solution. A constant final pH value of around 10.5 was observed for the treatments with different concentrations of NaCl and Na$_2$SO$_4$, while the initial pH decreased from 10.4 to 9.8 when the CaCl$_2$ concentration increased from 0 mM to 20 mM. For the treatments in MgSO$_4$ and MgCl$_2$, the pH decreased to around 8.6 for magnesium concentrations from 0 mM to 10 mM and decreased to around 8.1 in 100 mM magnesium salt solutions. This decrease in pH was presumably associated with proton (H$^+$) release in the treatments with magnesium salts.

The increase of acidity on immersion of the aged Fe$^0$ in magnesium salt solution may well affect the surface properties of the Fe$^0$ potentially resulting in corrosion of active Fe$^0$ or dissolution of iron oxides on the aged Fe$^0$ surface resulting in the release of dissolved iron into solution. Experimental measurements showed that dissolved Fe(II) but not dissolved Fe(III) could be detected in the experiments described here. As shown in Figure 4b, less than 0.005 mM of dissolved Fe(II) was detected in the treatments with NaCl, Na$_2$SO$_4$, NaHCO$_3$, and CaCl$_2$, while an obvious increase in dissolved Fe(II) was found when the concentrations of MgSO$_4$ and MgCl$_2$ were $\geq$50 mM. The release of dissolved Fe(II) to solution confirms that the presence of magnesium salts results in the destruction of the passivating iron oxide layer on the surface of aged Fe$^0$ with Fe(II) being formed either as result of oxidative dissolution of the underlying Fe$^0$ and/or (Fe$^0$-mediated) reductive dissolution of the Fe(III) oxide passivating layer. While the presence or absence of amorphous iron oxyhydroxide coatings on the Fe$^0$ would not be detectable, XRD analysis of the Fe$^0$ particles after reaction with TCE (Figure S5) showed similar patterns in all
cases with the same crystalline products present as those observed in aged Fe0 prior to reaction (Figure S1b). Based on the results presented above, it would seem reasonable to conclude that the high rates of TCE degradation by the aged Fe0 in the presence of magnesium salts is related to the decrease in pH and increase in dissolved Fe(II) induced by magnesium ions.

Proton Release from Fe0 in the Presence of Various Salts. Total H+ concentrations were calculated using Visual MINTEQ for different concentrations of individual salts with the surface of aged Fe0 assumed to be covered by hydrous ferric oxide (HFO), an amorphous form of iron (oxy)hydroxide used widely in previous speciation calculations. While we have no conclusive evidence that HFO was present at the surface of the aged Fe0, the likelihood of this ubiquitous amorphous phase being present is high given that the Fe0 was exposed to oxygen for a significant time prior to use in the studies described here. For the purposes of the speciation calculations, the concentration and specific surface area of HFO were set at 1 g L−1 and 600 m2 g−1, respectively, and the site density assigned to be 2.26 sites nm−2 in accord with the “weak” binding sites as recommended by Dzombak and Morel (the “strong” binding sites will only be important when considering adsorption of trace contaminants). The results in Figure 5a show that the presence of Na2SO4 (0–100 mM), NaCl (0–1000 mM), and NaHCO3 (0–1000 mM) do not significantly increase the H+ concentration in the reaction solution with HFO, while the H+ concentration increased dramatically from 0.009 μM to 0.08 μM when the concentrations of CaCl2 increased from 0 mM to 2 mM and then reached a relative plateau on further increase in CaCl2 concentration. The H+ concentrations increased monotonically on increase in the concentrations of magnesium salts, with 0.216 μM and 0.253 μM of H+ predicted to be present in the aged Fe0 systems containing 50 mM of MgSO4 and MgCl2, respectively. The calculated increases in extent of proton release in the systems with various salts appear to be consistent with the detected decreases of pH in Figure 4a, confirming that the magnesium and calcium salts induce the in situ generation of H+ at the surface of aged Fe0.

Generally, the generation of acidity in the aged Fe0 system is related to the occurrence of a variety of processes including surface acid–base reactions, hydrolysis, chemisorption, and surface complexation in the presence of the various salts. The reactions related to proton release in the aged Fe0 system with various types of salts are presented below and will be used to illustrate how these salts influence proton release. Equations 1 and 2 represent the acid–base reactions that occur at surface sites of HFO expected to be present at the surface of aged Fe0. As can be seen from these equations, H+ can be generated from the dissociation of fully protonated >FeOH2+ sites for pK1 < pH < pK2 and from dissociation of >FeOH0 sites for pH > pK2.

\[ \text{>FeOH}_2^+ \rightleftharpoons \text{>FeOH}^0 + H^+ \quad \log K = -7.29 \tag{1} \]

\[ \text{>FeOH}^0 \rightleftharpoons \text{>FeO}^- + H^+ \quad \log K = -8.93 \tag{2} \]

Protons may also be generated from hydrolysis of Mg2+ (eq 3) and Ca2+ (eq 4) when MgSO4, MgCl2, and CaCl2 electrolytes are used. In addition, surface complexation of Mg2+ and Ca2+ with >FeOH0 can drive proton release as a result of the formation of >FeOMg2+ sites (eq 5) and >FeOCa2+ (eq 6).

\[ \text{Mg}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{MgOH}^+ + \text{H}^+ \quad \log K = 2.56 \tag{3} \]

\[ \text{Ca}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{CaOH}^+ + \text{H}^+ \quad \log K = 1.15 \tag{4} \]

\[ \text{Mg}^{2+} + \text{>FeOH}_0 \rightleftharpoons \text{>FeOMg}^+ + \text{H}^+ \quad \log K = -4.6 \tag{5} \]

\[ \text{Ca}^{2+} + \text{>FeOH}_0 \rightleftharpoons \text{>FeOCa}^+ + \text{H}^+ \quad \log K = -5.85 \tag{6} \]

In comparison with implementation of the dechlorination reaction in Milli-Q water, implementation of the reaction in solutions of calcium or magnesium salts (or in seawater) results in significant binding of the divalent cations Mg2+ and Ca2+ to >FeOH0 sites on the HFO surface with formation of the resultant surface complexes facilitating proton release. The predicted concentrations of all the possible species in Table S1 contributing to proton release versus individual salt concentrations are plotted in Figure S6. The increase in concentration of species such as >FeO− was negligible in the presence of NaCl (Figure S6a) and Na2SO4 (Figure S6b), indicating that no significant proton release was associated with dissociation of >FeOH0 sites. These results suggest that the presence of NaCl and Na2SO4 would be expected to have a very weak effect on proton release in the aged Fe0 system in accord with the experimental results obtained.

Low concentrations of MgOH+ or CaOH− were predicted in the presence of MgSO4, MgCl2, and CaCl2 (Figures S6c, S6d,
and Se6) with these concentrations not changing significantly with increasing salts concentrations, indicating that these species had little contribution to the total proton release. In comparison, the concentration of the surface complex $>\text{FeOMg}^+$ increased dramatically on increase in magnesium salt concentrations (Figures S6c and S6d) with concomitant extensive release of protons to solution during the formation of this surface complex (Figure 5a). Concentrations of $>\text{FeOCa}^+$ and $>\text{FeOHCa}^{2+}$ increased with increase in calcium salt concentration, while the concentrations of $>\text{FeOH}^0$ and $>\text{FeO}^-$ decreased as a result of increasing competition with the calcium surface complexes (Figure S6e). As the average concentration of CaCl2 (10 mM) in seawater is significantly lower than that of MgSO4 (50 mM), the extent of proton release as a result of formation of $>\text{FeOCa}^+$ was significantly less than that resulting from the presence of magnesium salts.

**Mechanism Responsible for Depassivation of Fe$^0$ in Seawater.** Many studies have focused on the effects of anions (such as chloride and fluoride) on the depassivation of aged Fe$^0$ but only a few have reported the effects of cations on the corrosion behavior and reducing capacity of fresh Fe$^0$ and Zn$^0$. 33-35 38 In this study, it is clear that high concentrations of chloride may facilitate the depassivation of aged Fe$^0$ thereby increasing the rate of TCE degradation in accord with previous reports. However, based on the results of studies of the effects of individual salts reported here, the contribution of chloride to the degradation of TCE by aged Fe$^0$ was far less than the contribution of magnesium ions.

Based on the speciation analysis for individual salt solutions presented above, it is apparent that formation of $>\text{FeOMg}^+$ is critical to the extent of proton release in seawater. A consequence of the resultant decrease in pH of the solution (and, perhaps even more significantly, at the HFO surface) is the resultant increase in concentration of the surface species $>\text{FeOH}^+$ (Figure 5b). This is potentially critical to depassivation as there is ample evidence that protonation of surface sites leads to enhanced tendency for dissolution of minerals such as iron oxides as it is recognized to lead to the generation of highly polarized interatomic bonds in the immediate proximity of the surface central ions which facilitates the detachment of cationic surface groups and their release to solution. 30,39,40 Indeed, the rate of dissolution of metal oxides has been shown in many instances to be directly proportional to the concentration of the fully protonated surface species. 41 While an increase in iron oxide dissolution rate is typically observed on decrease in pH, proton-mediated dissolution is recognized to be relatively slow, at least compared to that observed on reduction of surface-located Fe(III). 42 In the studies described here, the metal ion released to solution was in the form of Fe(II) with reduction of Fe(III) present in the relatively unstable $>\text{FeOH}^+$ species presumably induced by reaction with underlying Fe$^0$, i.e.

$$\text{Mg}^{2+} + >\text{FeOH}^0 \rightleftharpoons >\text{FeOMg}^+ + \text{H}^+ \tag{8}$$

$$>\text{FeOH}^0 + \text{H}^+ \rightleftharpoons >\text{FeOH}^+_2 \tag{9}$$

$$\text{Fe}^0 + >\text{FeOH}^+_2 \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{regenerated} >\text{FeOH}^0 \tag{10}$$

While these reactions are no doubt a simplification of the actual processes occurring at the surface of the passivated Fe$^0$, they do convey the key elements of the proposed depassivation process in which sorption of magnesium ions in seawater to HFO surface sites results in localized decrease in pH with concomitant increase in the concentration of relatively labile $>\text{FeOH}^+$ surface species which are prone to reduction by underlying Fe$^0$ with subsequent release of Fe$^{2+}$ to solution. The resultant removal of the iron oxyhydroxide coating from the Fe$^0$ surface results in exposure of the solution to the underlying Fe$^0$ which then enables effective dechlorination of TCE.

While detailed mechanistic aspects of the depassivation process remain to be elucidated, the recognition that major ions present in saline solutions such as seawater lead to in situ depassivation of aged Fe$^0$ highlights the likely long-term efficacy of application of Fe$^0$-mediated degradation of chlorinated contaminants in saline environments such as seawater. The findings presented in this work also provide insight into potential cost-effective approaches to depassivating aged Fe$^0$ and should assist in wider application of this interesting technology.

### ASSOCIATED CONTENT

#### Supporting Information
Additional data include characterization of raw Fe$^0$ particles before TCE reduction, kinetics of TCE transformation by aged Fe$^0$ in the solution with individual inorganic salts, open circuit potential (OCPT) vs time in the solution with different inorganic salts, pH changes during TCE reduction, XRD characterization of Fe$^0$ particles after TCE reduction, and model predicted concentrations of the species related to the H$^+$ release. This material is available free of charge via the Internet at http://pubs.acs.org.

### AUTHOR INFORMATION

**Corresponding Author**

*E-mail: d.waite@unsw.edu.au.*

**Notes**

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The author (T.X.L.) acknowledges the award of a UNSW Vice-Chancellor’s Post-Doctoral Research Fellowship with Supplementary Research Support Grant (No. RG114816). The authors also acknowledge support provided through ARC Linkage Project LP100100852.

### REFERENCES