

Calcium peroxide (CaO₂) for use in modified Fenton chemistry

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Abstract

The use of calcium peroxide (CaO₂) powder as a source of H₂O₂ to promote modified Fenton (MF) chemistry was studied. First, the rate of production and yield of H₂O₂ from CaO₂ dissolving in water at pH 6–9, and 12–13 (i.e., unbuffered CaO₂) was measured. The rate of CaO₂ dissolution increased as pH decreased, from 62 h for complete dissolution at pH 12–13 to only 4 h at pH 6. The yield of H₂O₂ also increased with decreasing pH, from zero at pH 12–13 to 82% at pH 6. The ability of CaO₂ to promote MF oxidation of PCE was demonstrated with a hydroxyl radical (•OH) scavenger (2-propanol) at pH 8. The scavenger inhibited PCE oxidation, but 97% of the PCE was oxidized without it. Release of Cl[−] showed that PCE was mineralized. Finally, PCE oxidation was compared with liquid H₂O₂ (pH 7) and with CaO₂ (pH 6, 7, 8, 9). Liquid H₂O₂ showed the lowest efficiency (mol H₂O₂ consumed/mol PCE oxidized) and the greatest temperature increase, disproportionation to O₂, and PCE volatilization. CaO₂ was a more efficient oxidant than liquid H₂O₂ at all pH values because it only releases H₂O₂ upon dissolution, reducing the loss to O₂ and volatilization. CaO₂ performed optimally at pH 8.

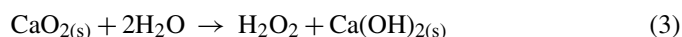
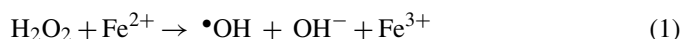
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1. Introduction

Fenton chemistry involves the catalyzed decomposition of H₂O₂ by Fe²⁺ to form the hydroxyl radical (•OH) (reaction (1)), a strong and relatively indiscriminate oxidant that reacts with most contaminants at near diffusion-limited rates [1]. Conventional Fenton chemistry, used primarily to treat waters and wastewaters, uses excess Fe²⁺ and meters in limiting amounts of H₂O₂, which results in nearly stoichiometric (1:1) conversion of H₂O₂ to •OH. Conventional Fenton chemistry also maintains a pH below 3, which is impractical in the subsurface because of the buffering capacity of geologic materials. As a result, *in situ* chemical oxidation (ISCO) applications typically use modified Fenton (MF), or Fenton-like chemistry, which operates at circum-neutral pH [2]. In MF-ISCO, iron can be added as salts of Fe²⁺ or Fe³⁺ [3], or native iron-containing minerals (e.g., goethite, ferrihydrite) can be used [4,5]. If insufficient Fe²⁺ is added, or if only Fe³⁺ is originally present, the Fe²⁺ in reaction 1 is regenerated by various reactions [6]. The low solubility of Fe³⁺ at neutral pH requires chelants (e.g., EDTA) to increase

Fe³⁺ in the aqueous phase [7,8]. High concentrations of H₂O₂ are injected during MF-ISCO to ensure a sufficient radius of influence [2]. As such, MF-ISCO is conducted under conditions of limiting Fe and excess H₂O₂, the opposite of conventional Fenton chemistry.



The instability of H₂O₂ in the subsurface is the most serious limitation of MF-ISCO. Liquid H₂O₂ (2–12%) is typically injected in ISCO [2], but its half-life is only minutes to hours [9]. Disproportionation (reaction (2)) constitutes the major loss of H₂O₂ at neutral pH [10,11]. It consumes H₂O₂ without producing •OH, and releases O₂ gas which clogs pores around injection wells and promotes contaminant volatilization [12,13]. Reaction (2) is catalyzed by metals, catalase and peroxidase enzymes, and native organic matter [2]. Reaction 2 is quite exothermic ($\Delta G^\circ = -119.2 \text{ kJ/mol}$) [14], and as temperature rises it is favored over reaction (1) [15]. This positive feedback cycle can rapidly degrade all available H₂O₂ to O₂. Phosphate is often used as a stabilizer [16], and supposedly works by

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precipitating metals and forming stable complexes with H_2O_2 [17]. However, even high phosphate concentrations do little to reduce the loss of H_2O_2 to O_2 in the presence of Fe(III) at pH 7 [11,17].

Recent studies suggest that calcium peroxide (CaO_2) is a more effective source of H_2O_2 for ISCO than liquid H_2O_2 [18,19]. Although other compounds exist which can release H_2O_2 (e.g., Na_2CO_3 , MgO_2), CaO_2 was chosen for these studies because it is relatively inexpensive and has a long history of application to site remediation, mostly as an oxygen releasing compound. CaO_2 dissolves to form H_2O_2 and $\text{Ca}(\text{OH})_2$ via reaction (3), liberating a maximum of 0.47 g H_2O_2 /g CaO_2 [20] and heat ($\Delta G^\circ = -20.7$ kJ/mol) [21]. The advantage is that H_2O_2 release is auto-regulated by the rate of CaO_2 dissolution, reducing disproportionation since not all the H_2O_2 is available at once as with liquid H_2O_2 . Technical grade CaO_2 powder (50% CaO_2 /50% $\text{Ca}(\text{OH})_2$) is the least expensive form, and is injected as a slurry in water. Aquifers are less permeable to solids than liquids, but this may not be a disadvantage relative to liquid H_2O_2 because disproportionation also clogs pores [12].

Evaluating the utility of CaO_2 in MF chemistry is difficult because the literature is lacking in controlled studies on the rate of dissolution of CaO_2 in water and the yield of H_2O_2 . Because CaO_2 has been used mostly to release O_2 for bioremediation there is confusion in the literature about its behavior with regard to H_2O_2 production, and it has even been postulated that O_2 is formed directly from CaO_2 instead of H_2O_2 [22]. Varying pH is the main reason for the conflicting information. Unless a buffer is added the pH increases to 12–13. However, the rate of CaO_2 dissolution and the stability of H_2O_2 increase with decreasing pH. Arienzo [23] reported that the concentration of H_2O_2 in a 0.2% slurry of CaO_2 increased from 380 mg/L to 1200 mg/L as the pH was decreased from 11 to 3. Rates of dissolution were not reported. White et al. [24] and Cassidy and Irvine [25] measured O_2 release for 2 months in soils with unbuffered CaO_2 , but Ndjou'ou and Cassidy [19] showed that CaO_2 was exhausted within 2 days at pH 8. The instability of H_2O_2 at high pH makes it impossible to identify as an intermediate. It is also difficult to distinguish biological from chemical oxidation of contaminants since both are oxidative processes with the same products. This difficulty is exacerbated by recent findings that aerobic biodegradation co-exists with MF oxidation of contaminants in soils, even at high doses of liquid H_2O_2 [26].

The ability of CaO_2 to produce $\bullet\text{OH}$ has not yet been demonstrated. Ndjou'ou and Cassidy [19] compared the treatment of a soil contaminated with petroleum hydrocarbons using a commercially available CaO_2 -based oxidant and liquid H_2O_2 at pH of 8. CaO_2 removed 96% of total petroleum hydrocarbons (TPH), compared with 74% using liquid H_2O_2 . Since a biological control showed only 30% reduction, they concluded that the TPH removal in the test reactors was due to MF oxidation. This study indicated that CaO_2 was a more efficient source of H_2O_2 for MF chemistry than liquid H_2O_2 . Bogan et al. [18] also reported that CaO_2 performed better than liquid H_2O_2 in removing polycyclic aromatic hydrocarbons (PAH) from soil. However, these two studies did not demonstrate $\bullet\text{OH}$ -mediated MF oxidation.

This research is the first to demonstrate that CaO_2 can promote MF oxidation of contaminants. First, the yield of H_2O_2 from CaO_2 and the time required for dissolution was determined at various pH values. Second, a $\bullet\text{OH}$ scavenger (2-propanol) was used to show that the observed oxidation of tetrachloroethene (PCE) by CaO_2 at pH 8 was due to the production of $\bullet\text{OH}$. Finally, the performance of MF oxidation of PCE using liquid H_2O_2 (pH=7) and CaO_2 (pH=6, 7, 8, and 9) was compared in closed reactors. Temperature was monitored, and PCE volatilization and disproportionation of H_2O_2 to O_2 were quantified. Oxidant efficiency (mmol H_2O_2 consumed/mmol PCE oxidized) was calculated directly for H_2O_2 , and estimated for CaO_2 using the yield of H_2O_2 measured at each pH value in the first set of experiments.

2. Materials and methods

2.1. Materials

Technical grade CaO_2 (50% CaO_2 /50% $\text{Ca}(\text{OH})_2$) and liquid H_2O_2 (50%) were provided by Nippon (Tokyo, Japan). Tetrachloroethene (PCE) (99.9%), 2-propanol (99.9%), and hexane (99.9%) were purchased from Acros Organics (Pittsburgh, PA). Anhydrous disodium ethylenediaminetetraacetate (EDTA) (99%) ($\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2\text{Na}_2$), anhydrous ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$), monosodium phosphate monohydrate ($\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$) and disodium phosphate heptahydrate ($\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from Aldrich (Milwaukee, WI).

2.2. Reactor set-up

The 4 L Pyrex reaction vessels used in these studies had a maximum liquid volume of 2 L. The contents were mixed with a magnetic stirrer at maximum speed. The reactors were kept in a temperature controlled room at 10 °C to simulate groundwater temperatures in northern climates [27]. No thermal insulation was used around the reactors. Each reactor had a custom-fitted lid with four ports. Three of the ports housed dedicated probes to measure pH, temperature, and dissolved O_2 (DO). The use of the fourth port was different for each study. During the studies on H_2O_2 yield from CaO_2 , the fourth port was open. In the $\bullet\text{OH}$ scavenging study of PCE oxidation, the fourth port vented to the atmosphere and was fitted Supleco ORBO[®] (activated carbon) tubes to trap and quantify PCE volatilized. Three tubes were placed in series to ensure that PCE did not breakthrough. For the studies comparing MF oxidation of PCE with H_2O_2 and CaO_2 the ORBO[®] tubes were again used to capture PCE, but they were connected to a 1 L Tedlar[®] gas sampling bag to collect and quantify the O_2 released. Each gas sampling bag had a polypropylene valve and septum fitting to measure air pressure and draw samples. The gas bags were vacuum-emptied before being fitted on the reactors. The reactor set-up was pressure tested by injecting air into the bags, and was capable of maintaining a pressure of 2 atm for 3 months. Since the highest pressure measured in the studies was 1.24 atm, the reactor set-up was deemed suitable for capturing and quantifying O_2 released.

Table 1
Concentrations of buffers used to maintain the desired pH values during testing with CaO_2 and H_2O_2

| pH | $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (g/L) | $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ (g/L) | Buffer strength (mM) |
|--------------------|---|--|-------------------------|
| 6 | 12.1432 | 3.2176 | 100 |
| 7 | 2.9181 | 7.733 | 50 |
| 8 | 0.1884 | 4.994 | 20 |
| 9 | 0.01 | 2.6605 | 10 |
| 12–13 ^a | None | None | None |

^a The pH of a 0.2% (w/v) slurry of unbuffered technical grade CaO_2 in water.

2.3. Buffer solutions and doses of modified Fenton reagents

Buffer solutions used in the reactors were made in de-ionized water using $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$. Table 1 shows the pH values tested, the doses of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ used (in g/L), and the buffer strength (in mM). Each reactor had a 2 L of the appropriate buffer. Preliminary testing verified that each buffer solution was able to maintain the desired pH with the dose of CaO_2 and other reagents used. The dose of CaO_2 for all reactors was 4 g technical grade powder, resulting in a 0.2% slurry (w/v). With a purity of 50%, the actual mass of CaO_2 added to each reactor was 2 g, or 1 g CaO_2/L . According to Eqs. (2) and (3), the 2 g of CaO_2 added per reactor contain a maximum theoretical mass of O_2 of 444.0 mg (13.88 mmol O_2), and a maximum theoretical mass of H_2O_2 of 943.4 mg (27.76 mmol H_2O_2), or 472 mg $\text{H}_2\text{O}_2/\text{L}$ (13.88 mM H_2O_2). In the experiments on H_2O_2 yield only CaO_2 was added to the buffers. In the studies with PCE, each reactor also received 80 mg of Fe(III) to promote MF chemistry via reaction (1), and 40 mg EDTA to chelate the Fe so that it will be more available to participate in reaction 1. The reactor testing liquid H_2O_2 in the comparative studies received a dose of 27.76 mmol H_2O_2 (13.88 mM), the maximum theoretical amount contained in the 2 g dose of CaO_2 .

2.4. Sample handling and preparation for PCE analyses

PCE was extracted from duplicate 10 mL unfiltered samples of reactor liquid with 2 mL of hexane by mixing in 25 mL screw-cap test tubes on a wrist action shaker for 6 h. After centrifuging, the hexane was extracted with a syringe and placed in 2 mL vials for PCE analyses. PCE trapped in the ORBO[®] tubes was extracted in the same fashion by sacrificing each tube in 2 mL of hexane and 10 mL of added de-ionized water.

2.5. Analyses

All analyses were done in duplicate. H_2O_2 was only measured in the aqueous phase, which is justified by its complete miscibility in water and low volatility (W.T. Hess, 1995). H_2O_2 was measured in the filtrate from 10 mL samples from the reactors passed through a 0.45 μm filter. The H_2O_2 was quantified using a Hach DR5000 spectrophotometer after color was developed with titanium sulfate [15]. The detection limit for H_2O_2 was 0.04 mM. The pH was monitored continuously with an

Orion probe and meter. Temperature was also measured continuously with a Vernier stainless steel probe. The DO was measured before oxidant addition and after oxidation was complete using a YSI Instruments probe. A water manometer was used to measure air pressure in the gas bags after chemical oxidation was complete. Duplicate 25 mL gas samples were then taken from the sampling bags and injected into an Illinois Instruments-3600 O_2 Analyzer to measure O_2 . The O_2 analyzer was calibrated between 20% and 30% O_2 . Cl^- was measured in samples of reactor filtrate with a Thermo Orion specific probe.

PCE was analyzed in duplicate hexane extracts using a Hewlett-Packard 6890 gas chromatograph (GC) with electron capture detection and a DB-1 fused-silica capillary column (15 m \times 0.317 mm i.d., 0.25 μm film thickness). The oven was at 40 °C for 5 min, and increased 5 °C/min to 130 °C. The injector and detector were at 240 °C and 350 °C, respectively.

2.6. Measuring O_2 released from CaO_2 and H_2O_2

The total amount of O_2 released was determined by adding the amount of O_2 released from CaO_2 or H_2O_2 to the aqueous phase and the gas phase, and subtracting from this the amount of O_2 originally present in the reactor. The initial amount of aqueous-phase O_2 was calculated by multiplying the DO concentration by 2 L. The initial amount of gas-phase O_2 was calculated using the atmospheric O_2 concentration (20.9%) and the volume of headspace without the gas bag (2125 mL). After the reactions with added CaO_2 or H_2O_2 were complete, the amount of aqueous-phase O_2 was again determined by multiplying the post-reaction DO concentration by 2 L. The gas-phase release of O_2 was calculated from the O_2 in the gas sampling bag, using a headspace volume of 3125 mL (i.e., 2125 mL + 1 L from the gas bag).

3. Results and discussion

3.1. Yield of H_2O_2 from CaO_2 dissolution at different pH values

Fig. 1 shows the release of H_2O_2 with time in the reactors from dissolution of CaO_2 for the different pH values tested.

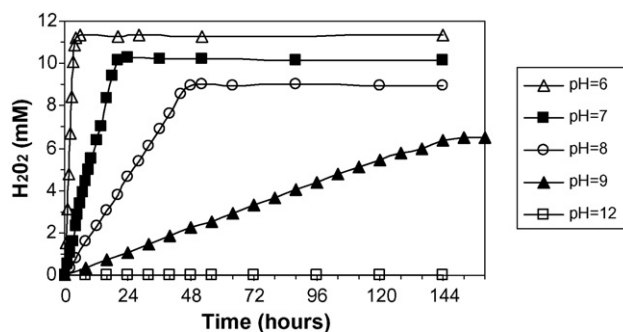


Fig. 1. Release of H_2O_2 from a 0.2% (w/v) slurry of CaO_2 in water during the first 160 h at the various pH values tested. For pH 12–13, CaO_2 dissolution had not reached completion after 160 h.

Table 2

The H₂O₂ yield from a 0.2% (w/v) slurry of CaO₂ in water, the increase in temperature, and the time required for complete CaO₂ dissolution at the pH values tested

| pH | H ₂ O ₂ yield ^a (mmol) | %H ₂ O ₂ yield ^b | %O ₂ yield ^c | Increase in temperature (°C) | Time required for dissolution |
|-------|--|---|------------------------------------|---------------------------------|----------------------------------|
| 6 | 22.75 | 82 | 18 | 8.2 | 4 h |
| 7 | 20.53 | 74 | 26 | 3.7 | 20 h |
| 8 | 18.04 | 65 | 35 | 1.8 | 52 h |
| 9 | 13.06 | 47 | 53 | 0.7 | 6 days |
| 12–13 | 0 | 0 | 100 | 0 | 62 days |

^a From the final aqueous H₂O₂ concentration measured (i.e., mM × 2L).

^b Based on a 100% theoretical yield of 27.76 mmol H₂O₂ from the 2 g CaO₂ added.

^c Calculated assuming that the CaO₂ not released as H₂O₂ was released as O₂.

Table 2 lists the % yield of H₂O₂, the associated increase in temperature and the time required for complete CaO₂ dissolution. Complete dissolution of the CaO₂ in the reactors was verified by adding concentrated HCl to a sample to reduce the pH to 2 and then measuring H₂O₂ concentration. No increase in H₂O₂ concentration after acidification indicated that all the CaO₂ had been dissolved. Although O₂ was not measured in these studies, it can be assumed that any CaO₂ not converted to H₂O₂ was released directly as O₂ [20]. The O₂ yield listed in Table 2 was calculated using this assumption. The continuously monitored pH data are not shown in Fig. 1 because the buffer solutions maintained the target pH throughout CaO₂ dissolution. The pH of the unbuffered CaO₂ remained between 12 and 13.

It is clear from Fig. 1 and Table 2 that the yield of H₂O₂ and the dissolution rate of CaO₂ increased with decreasing pH. Unbuffered CaO₂ (pH=12–13) had no measurable H₂O₂ production. Although only the first 160 h of data were shown in Fig. 1, unbuffered CaO₂ required more than 2 months to dissolve completely. This is consistent with rates of O₂ release in soils with unbuffered CaO₂ reported in the bioremediation literature [24,25]. In contrast, CaO₂ was dissolved within 4 h at pH 6, and within 52 days at pH 8. This is consistent with the findings of Ndjou'ou and Cassidy [19], who showed that a CaO₂-based oxidant buffered at pH 8 was exhausted within 2 days in well-mixed soil slurries. Higher rates of CaO₂ dissolution also resulted in a greater temperature increase, because the dissolution of CaO₂ is exothermic. The maximum temperature increase measured was 8.2 °C for pH 6. The temperature maxima decreased with increasing pH, despite the fact that disproportionation increased with increasing pH. This apparent inconsistency can be explained by the slower CaO₂ dissolution rate at increasing pH, which allowed more time for heat generated via exothermic reactions to escape from the reactor walls. The H₂O₂ released in these studies was stable because there was nothing added to the reactors to catalyze its decomposition (e.g., Fe and organic compounds). The % yield of H₂O₂ decreased from 83% of the theoretical maximum (27.76 mmol) at pH 6 to 47% at pH 9, and was zero with unbuffered CaO₂. Values of pH lower than 6 were not tested in these studies, because the purpose was to investigate the use of CaO₂ for MF (i.e., quasi-neutral pH) reactions. Moreover, the cost of MF-ISCO increases with decreasing pH because of increased buffer requirements (Table 1).

3.2. Scavenger studies with 2-propanol to verify •OH-mediated PCE oxidation

Fig. 2 shows the results of the study using CaO₂ at pH 8 to oxidize PCE with and without a •OH scavenger (2-propanol). A control reactor that received only PCE was also maintained for comparison. The other two reactors received PCE along with CaO₂, Fe(III), and EDTA, and one of these also received 2-propanol. The dose of CaO₂ was the same as in the previous studies (4 g). The dose of PCE in all three reactors was 6 mmol (3 mM, or 500 mg/L), and the dose of 2-propanol was 30 mM. Using 2-propanol was based on its effectiveness as a scavenger of •OH [26,28,29]. Analyses done at the end of the experiments (60 h) verified that no CaO₂ and no measurable amount of unreacted H₂O₂ remained in the MF reactors.

Fig. 2 shows that in the MF reactor without 2-propanol PCE was nearly completely removed (99%) within 52–60 h. This is consistent with the time required for CaO₂ dissolution at pH 8 in the previous studies (Fig. 1, Table 2). Extraction and analysis of the ORBO[®] tubes showed that only 2% (0.12 mmol) of the PCE removed was due to volatilization. Concentrations of Cl⁻ in this reactor increased simultaneously with PCE removal, indicating that PCE was mineralized. The final Cl⁻ concentration was approximately 11 mM, resulting in a ratio of 3.7 mmol Cl⁻ released/mmol PCE oxidized. This is similar to molar ratios observed by Ndjou'ou et al. [26] for MF oxidation of PCE in soils using liquid H₂O₂. The amount of PCE oxidized (5.83 mmol,

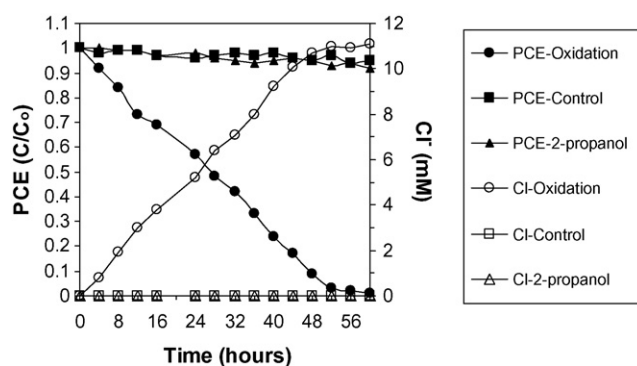


Fig. 2. PCE removal and Cl⁻ release with time in a control with no oxidants, and in reactors with CaO₂-based MF chemistry with and without a •OH scavenger (2-propanol). The conditions were pH=8, CaO₂ dose=0.2% (w/v), PCE dose=3mM, 2-propanol dose=30 mM.

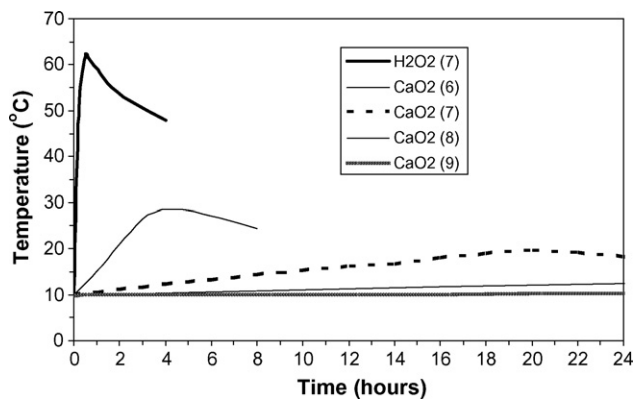


Fig. 3. Temperature variations with time in the reactors promoting MF oxidation of PCE with liquid H_2O_2 at pH 7 and with CaO_2 at pH 6, 7, 8, and 9. The dose of liquid H_2O_2 was 13.88 mM and the CaO_2 dose was 0.2% (w/v).

or 97%) was obtained by subtracting the mmol volatilized from the total mmol removed. In contrast, the reactor with 2-propanol behaved like the control, showing no PCE removal except via volatilization (3%). This reactor also showed no measurable release of Cl^- . These results indicate that the PCE oxidation in the reactor without 2-propanol was caused by $\bullet\text{OH}$ produced via reaction (1). These results, along with those of the previous study, also demonstrate that CaO_2 at quasi-neutral pH releases H_2O_2 which participates in MF oxidation.

3.3. Comparing MF oxidation of PCE with H_2O_2 (pH = 8) and CaO_2 (pH = 6–9)

The performance of liquid H_2O_2 (pH=7) and CaO_2 (pH=6–9) for MF oxidation of PCE was investigated. In the tables and figures, each reactor is denoted by the oxidant used followed by the pH in parentheses (e.g., CaO_2 (8) is used for the reactor with CaO_2 buffered at pH 8). Fig. 3 is a plot of temperature in the reactors during the first 24 h. Fig. 4 shows the total percentage of PCE removed in the reactors, and the percent volatilized vs. oxidized. Table 3 lists the increase in temperature, O_2 released, PCE removed via volatilization and oxidation, and calculated values of oxidant efficiency. The molar ratio of Cl^- released to PCE oxidized is not listed, but ranged from 3.6 to 3.8 for all reactors, indicating PCE mineralization. The pH data are not shown because readings did not vary from the target pH.

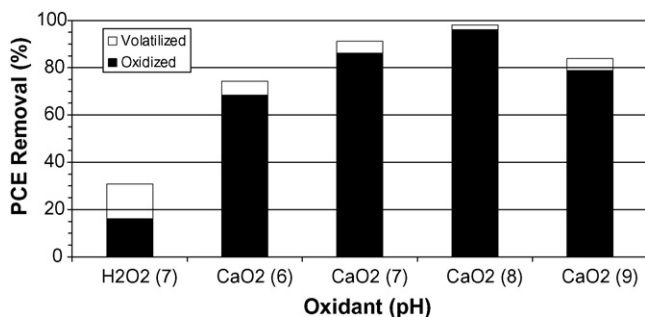


Fig. 4. Total PCE removal and percent volatilized vs. oxidized in the reactors promoting MF oxidation of PCE with liquid H_2O_2 at pH 7 and with CaO_2 at pH 6, 7, 8, and 9. The CaO_2 concentration was 0.2% (w/v).

The reactors were closed and samples of the contents were taken only after reactions were complete. The reactor with H_2O_2 was considered finished reacting after 40 min, and the reactors with CaO_2 were considered finished according to the time for CaO_2 dissolution in Table 2. Gas samples were first taken to measure O_2 and the post-reaction DO reading was taken, after which the reactors were opened for sampling. Analyses verified that no solid CaO_2 or H_2O_2 remained.

Temperature readings (Fig. 3) are an indication of the rate and time of completion of reactions promoted by CaO_2 and H_2O_2 . Because CaO_2 dissolution, H_2O_2 disproportionation, and $\bullet\text{OH}$ -mediated PCE oxidation are all exothermic, an increase in temperature indicates that one or more of these reactions is still occurring, and a decrease in temperature indicates that these reactions have ceased. The greater the rate of these reactions, the greater is the rate and extent of temperature increase. The temperature in the reactor with liquid H_2O_2 increased to 62.3 °C within 35 min and then began to decrease because H_2O_2 was depleted. In contrast, the temperature maxima in the reactors with CaO_2 were all less, and occurred later than with liquid H_2O_2 . This indicates that CaO_2 was able to maintain oxidation reactions over a longer period of time than liquid H_2O_2 . The temperature maxima in the reactors with CaO_2 , and the time at which they occurred, decreased with increasing pH, which can be explained by decreasing rates of CaO_2 dissolution with increasing pH (Fig. 1). In fact, the temperature maxima in the reactors with CaO_2 coincided with the time required for CaO_2 dissolution at each pH value (Table 2). This illustrates how the rate of CaO_2 dissolution auto-regulates the rate of release of H_2O_2 and its participation in chemical reactions, and shows that the rate of MF oxidation using CaO_2 can be controlled simply by changing the pH.

Table 3 lists the maximum temperature increase in the reactors during MF oxidation of PCE. The exothermic reactions in the system (i.e., CaO_2 dissolution, disproportionation of H_2O_2 , and MF oxidation) cannot be distinguished from temperature increase alone. However, temperature increase in the CaO_2 -based MF reactors was over twice that for the corresponding pH in the CaO_2 dissolution experiments without MF chemistry (cf. Tables 2 and 3). The reason for the lower temperature maxima in the CaO_2 dissolution experiments (Table 2) is that the H_2O_2 released did not participate in MF reactions, and the chemical energy represented by the H_2O_2 in the reactors was not released, as it was in the MF oxidation experiments. This shows that the energy released by MF oxidation and/or disproportionation was slightly more than twice that from dissolution of CaO_2 . Dissolution of CaO_2 is exothermic ($\Delta G^\circ = -20.7$ kJ/mol) and Fenton oxidation of organics releases a similar amount of energy [21,30]. However, by far the most exothermic reaction in MF systems is H_2O_2 disproportionation ($\Delta G^\circ = -119.2$ kJ/mol) [14]. A direct relationship was observed between temperature increase and O_2 release (Table 3), a measure of disproportionation. The O_2 released can be assumed to have come from decomposition of H_2O_2 , or from O_2 released directly by CaO_2 that was never available as H_2O_2 . It was assumed that there was no other source of O_2 except CaO_2 or H_2O_2 and that no O_2 was consumed by biodegradation. The first assumption is supported by the common use of

Table 3

Results from the comparative studies of MF oxidation of PCE using H₂O₂ and CaO₂ at the various pH values tested

| Oxidant (pH) | Increase in temperature (°C) | O ₂ released (mmol) | Final [PCE] (mM) | PCE removed (mmol) | PCE volatilized (mmol) | PCE oxidized ^a (mmol) | Efficiency ^b (mol H ₂ O ₂ ^c /mol PCE) |
|-----------------------------------|------------------------------|--------------------------------|------------------|--------------------|------------------------|----------------------------------|---|
| H ₂ O ₂ (7) | 52.3 | 12.82 | 2.08 | 1.84 | 0.86 | 0.98 | 28.3 |
| CaO ₂ (6) | 18.5 | 7.90 | 0.77 | 4.46 | 0.36 | 4.10 | 5.5 |
| CaO ₂ (7) | 9.7 | 7.22 | 0.27 | 5.46 | 0.29 | 5.17 | 4.0 |
| CaO ₂ (8) | 4.8 | 5.64 | 0.06 | 5.88 | 0.12 | 5.76 | 3.1 |
| CaO ₂ (9) | 1.6 | 5.15 | 0.49 | 5.02 | 0.28 | 4.74 | 2.8 |

^a PCE oxidized = total mmol PCE removed – mmol PCE volatilized.^b mmol H₂O₂ consumed/mmol PCE oxidized.^c mmol H₂O₂ = 27.76 for H₂O₂ (7), and for CaO₂ the H₂O₂ yields from Table 2 were used.

O₂ to measure H₂O₂ disproportionation [11,13]. The second assumption is supported by the fact that; (1) PCE and EDTA are essentially non-biodegradable aerobically [31,32], (2) the reactors were not amended with microorganisms, and (3) the high H₂O₂ concentrations would likely inhibit any microbial activity [14].

The greatest release of O₂ (12.82 mmol) was observed in the reactor with liquid H₂O₂ (Table 3). Vigorous bubbling was also observed with liquid H₂O₂, another sign of rapid O₂ release. High losses of H₂O₂ to O₂ are characteristic of MF systems using liquid H₂O₂, even with large amounts of phosphate buffer [11,13,16]. This scavenging of H₂O₂ is the major drawback of using liquid H₂O₂ in MF-ISCO. The O₂ released from CaO₂ at pH 7 was 7.22 mmol, markedly less than with liquid H₂O₂, even though the pH and the phosphate buffer concentration were the same for both. All the CaO₂ reactors showed much less O₂ release than liquid H₂O₂, despite the fact that CaO₂ releases considerable O₂ without MF reagents (Table 2). In fact, the O₂ release from the CaO₂-based MF systems decreased with increasing pH, even though the amount of O₂ released from CaO₂ without MF reagents increases with increasing pH (Table 2), and despite the fact that the stability of H₂O₂ decreases with increasing pH (Hess, 1995). This apparently paradoxical behavior can be explained by the decreasing rate of CaO₂ dissolution and H₂O₂ release with increasing pH. These results show that CaO₂, by maintaining lower levels of H₂O₂, can reduce disproportionation losses and that these losses can be controlled by varying the pH.

CaO₂ also achieved a much greater extent of PCE oxidation than liquid H₂O₂, at all the pH values tested (Table 3, Fig. 4). Fig. 4 illustrates the % removal of PCE, and the relative contribution of volatilization vs. chemical oxidation. Only 31% of the PCE was removed in the reactor with liquid H₂O₂, and nearly half of this was due to volatilization. This is not surprising, since liquid H₂O₂ also resulted in the greatest release of O₂ and the highest temperature, both of which encourage volatilization. For CaO₂, a pH of 8 provided the greatest total removal of PCE (98%), and only 2% of this was due to volatilization, whereas 96% was attributed to chemical oxidation. These results confirm those obtained with CaO₂ at pH 8 in the •OH scavenging studies (Fig. 2), and show that CaO₂ performed optimally at pH 8.

The oxidant efficiency (mmol H₂O₂ consumed/mmol PCE oxidized) was calculated directly for H₂O₂ using the dose applied (27.76 mmol), and was estimated for CaO₂ using the

yield of H₂O₂ measured at each pH value in the experiments on CaO₂ dissolution (Table 2). It is not certain that the H₂O₂ yield from CaO₂ was the same in the MF system as in the system without Fe, EDTA and PCE. However, attempts in previous experiments to directly measure H₂O₂ released from CaO₂ (data not shown) showed that the H₂O₂ was too short-lived to be measured. CaO₂ and H₂O₂ were completely consumed in all the reactors. The values of oxidant efficiency in Table 3 are comparable to those reported by Crimi and Siegrist [33]. There was an inverse relationship between oxidant efficiency and loss of oxidant to O₂ released, because H₂O₂ lost to disproportionation cannot form •OH and chemically oxidize PCE. Liquid H₂O₂ showed an oxidant efficiency of 28.3 mmol H₂O₂ consumed/mmol PCE oxidized. This is far greater than values obtained for CaO₂, even though CaO₂ released considerably less than the theoretical maximum of 27.76 mmol H₂O₂ (Fig. 1, Table 2), which was the dose of liquid H₂O₂ used. This clearly shows that liquid H₂O₂ was an inefficient MF oxidant compared with CaO₂ at any pH. The efficiency of CaO₂ as a MF oxidant increased with increasing pH, from 5.5 at pH 6 to 2.8 at pH 9, even though the yield of H₂O₂ decreases with increasing pH (Fig. 1, Table 2). As with O₂ release, this trend can be explained by the lower rate of H₂O₂ release from CaO₂ with increasing pH. The efficiency at pH 9 was slightly lower than at pH 8, even though pH 8 resulted in more PCE oxidation and less volatilization. This is a result of the lower yield H₂O₂ for pH 9 (Table 2).

The results from these studies suggest that regulating the rate of availability of H₂O₂ using CaO₂ increases the efficiency of MF oxidation relative to using liquid H₂O₂ by reducing losses of H₂O₂ to disproportionation. Liquid H₂O₂ proved quite unstable and inefficient, even with a strong phosphate buffer. Furthermore, the results of these studies indicate that the optimal pH for CaO₂ in MF chemistry is 8. Below this pH the rate of release of H₂O₂ from CaO₂ is too fast, causing excessive disproportionation (Fig. 3, Table 3). The resulting temperature increase and O₂ release encourage contaminant volatilization. Furthermore, maintaining a CaO₂-based MF system at a pH below 8 requires considerably more phosphate buffer to be used (Table 1), which increases cost. As pH rises above pH 8, the amount of H₂O₂ released from CaO₂ decreases rapidly (Fig. 1, Table 2), and CaO₂ becomes less effective for MF treatment, and more suitable for releasing O₂ for bioremediation. Ndjou'ou and Cassidy [19] showed that a commercially available CaO₂-based MF

oxidant at pH 8 was able to promote chemical oxidation and biodegradation of petroleum hydrocarbons.

4. Conclusions

Rapid decomposition of liquid H₂O₂ in soils limits the applicability of modified Fenton (MF) chemistry for *in situ* chemical oxidation (ISCO). We conclude from these laboratory studies that CaO₂ can be a more efficient source of H₂O₂ for MF oxidation of PCE than liquid H₂O₂. The rate of release of H₂O₂ from CaO₂ is auto-regulated by the rate of CaO₂ dissolution, which can be controlled by adjusting the pH. The rate of CaO₂ dissolution increases markedly with decreasing pH. In this study, 62 days were required for complete dissolution of unbuffered CaO₂ (pH = 12–13), whereas only 4 h were required when CaO₂ was buffered at pH 6. The yield of H₂O₂ from CaO₂ also increases considerably with decreasing pH. The yield of H₂O₂ from a 0.2% (w/v) slurry of technical grade CaO₂ (50% purity) increased from 47% (13.06 mmol) at pH 9 to 82% (22.75 mmol) at pH 6. Studies of MF treatment of PCE showed that CaO₂ at all pH ranging from 6 to 9 was a more efficient source of H₂O₂ for MF oxidation of PCE than liquid H₂O₂ at pH 7. Liquid H₂O₂ showed excessive disproportionation to O₂, increasing temperature dramatically and volatilizing nearly as much PCE it oxidized. By releasing H₂O₂ only upon dissolution, CaO₂ (at pH 6–9) achieved a much greater oxidant efficiency (mmol H₂O₂ consumed/mmol PCE oxidized), and resulted in much less PCE volatilization and greater PCE oxidation than liquid H₂O₂. The optimal performance of CaO₂ was observed at pH 8, which is recommended for MF-ISCO applications. The ability of CaO₂ at pH 8 to promote MF oxidation of PCE via the production of hydroxyl radicals was demonstrated in these studies.

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