



Persulfate activation by naturally occurring trace minerals

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ABSTRACT

The potential for 13 naturally occurring minerals to mediate the decomposition of persulfate and generate a range of reactive oxygen species was investigated to provide fundamental information on activation mechanisms when persulfate is used for in situ chemical oxidation (ISCO). Only four of the minerals (cobaltite, ilmenite, pyrite, and siderite) promoted the decomposition of persulfate more rapidly than persulfate–deionized water control systems. The other nine minerals decomposed persulfate at the same rate or more slowly than the control systems. Mineral-mediated persulfate activation was conducted with the addition of one of three probe compounds to detect the generation of reactive oxygen species: anisole (sulfate + hydroxyl radical), nitrobenzene (hydroxyl radical), and hexachloroethane (reductants and nucleophiles). The reduced mineral pyrite promoted rapid generation of sulfate + hydroxyl radical. However, the remainder of the minerals provided minimal potential for the generation of reactive oxygen species. The results of this research demonstrate that the majority of naturally occurring trace minerals do not activate persulfate to generate reactive oxygen species, and other mechanisms of activation are necessary to promote contaminant destruction in the subsurface during persulfate ISCO.

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1. Introduction

In situ chemical oxidation (ISCO) has become a dominant technology for the remediation of contaminated soils and groundwater. Of the three common ISCO processes, permanganate, catalyzed H_2O_2 propagations (CHP), and activated persulfate, activated persulfate is the least mature and least understood technology. Nonetheless, persulfate appears to have many advantages as an ISCO reagent. Although the persulfate anion ($\text{S}_2\text{O}_8^{2-}$) is a strong oxidant ($E^0 = +2.01 \text{ V}$), it is usually activated by heat, transition metals, or base to generate sulfate radical ($\text{SO}_4^{\bullet-}$), a stronger oxidant ($E^0 = +2.6 \text{ V}$) [1,2]. Sulfate radical can then react with water to form another oxidant, hydroxyl radical (OH^{\bullet}) [3].

Numerous investigators have focused on the activation of persulfate. Thermal activation of persulfate has been studied for treating methyl tert-butyl ether (MTBE) [4] and trichloroethylene (TCE) [5]. Persulfate activation by iron has been approached from several perspectives. Liang et al. [6] found that iron (II), but not iron (III), activates persulfate, and proposed using thiosulfate to regenerate iron (II) after it was oxidized by persulfate activation. Anipsitakis and Dionysiou [7] demonstrated that out of nine transition metals tested, only three activated persulfate to promote degradation of 2,4-dichlorophenol: silver (I), iron (II), and iron (III),

with silver (I) providing the most activation and iron (III) the least. Killian et al. [8] and Rastogi et al. [9] subsequently demonstrated that iron chelates are more effective than iron (II) in activating persulfate. Furman et al. [10] recently elucidated the mechanism of base activation of persulfate, which involves the base-catalyzed hydrolysis of persulfate to hydroperoxide anion. The hydroperoxide anion then reduces another persulfate molecule, generating sulfate radical and sulfate anion. High ratios of base to persulfate are often required for effective persulfate activation [11].

Although a modicum of fundamental information is known about persulfate activation in relatively simple aqueous systems, its chemistry in the subsurface has received little attention. Subsurface chemistry has been shown to be a dominant factor in the effectiveness of other ISCO technologies [12]. For example, minerals decompose hydrogen peroxide leading to the formation of reactive oxygen species and resulting in rapid decomposition of hydrogen peroxide in the subsurface [13,14]. Subsurface minerals decompose H_2O_2 effectively enough that the addition of soluble iron is usually not required for CHP ISCO [15].

In contrast to research on CHP, minimal attention has been given to the possible activation of persulfate by naturally occurring minerals found in surface and subsurface soils. Liang et al. [16] studied TCE destruction in columns packed with a sandy soil; however, the authors did not investigate the potential for the minerals in the soil to activate persulfate. Costanza et al. [17] studied perchloroethylene (PCE) destruction by thermally activated persulfate in batch reactors containing several solids and soils, but they did not investigate the effect of soil minerals on persulfate activation.

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Similarly, Johnson et al. [18] studied the effect of soil natural oxidant demand, but not soil minerals, on persulfate decomposition. Ahmad et al. [19] investigated the potential for major soil minerals (e.g., goethite, birnessite) found in surface and subsurface soils to activate persulfate. They found that most of the dominant soil minerals, such as goethite and ferrihydrite, did not activate persulfate. Birnessite activated persulfate, but only at concentrations significantly greater than typically found in soils. Many trace minerals are characterized by surface charge couples significantly different from the dominant iron and manganese oxides found in soils. However, the potential for trace minerals, such as ilmenite, cuprite, etc., to activate persulfate has not been investigated to date. The objective of this research was to investigate the potential for soil trace minerals to promote the decomposition of persulfate and activate it to generate reactive oxygen species.

2. Materials and methods

2.1. Materials

The minerals anatase, bauxite, calcite, cobaltite, cuprite, hematite, ilmenite, magnesite, malachite, pyrite, pyrolusite, siderite, and willemite were purchased from D.J. Minerals (Butte, MT). They were received as cubes approximately 1 cm³ and were crushed to a fine powder using a 150 mL capacity Spex shatter box with hardened steel as a grinder. Mineral surface areas were determined by Brunauer–Emmett–Teller (BET) analysis under liquid nitrogen on a Coulter SA 3100 [20]. The surface areas of the minerals and their chemical formulas are listed in Table 1. The minerals were analyzed for impurities by digesting the samples using EPA Method 3050 followed by inductively coupled plasma/mass spectrometry (ICP/MS); undetectable concentrations were found for metals exclusive of those expected in the minerals. The trace minerals were also evaluated for metals potentially released into persulfate solutions. Aqueous phases of mineral–persulfate slurries were analyzed for 15 elements and metals by ICP/MS.

Sodium persulfate ($\geq 98\%$), anisole (99%), and hexachloroethane (99.9%) were purchased from Sigma–Aldrich (Milwaukee, WI). Nitrobenzene (99%) was obtained from J.T. Baker (Phillipsburg, NJ). HPLC grade hexane was purchased from Fisher Scientific (Fair Lawn, NJ). Double-deionized water ($>18 \text{ M}\Omega \text{ cm}$) was purified using a Barnstead Nanopure II Ultrapure system.

2.2. Probe compounds

Anisole was used as a probe compound for the total flux of sulfate radical + hydroxyl radical because of its high reactivity with both hydroxyl radical and sulfate radical ($k_{\text{OH}\cdot} = 5.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$; $k_{\text{SO}_4^{\cdot-}} = 4.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [21,22]. A suitable probe compound

Table 1
Mineral formulas and surface areas.

Mineral	Formula	Surface area (m ² /g)	SE ^a
Anatase	TiO ₂	11.7	0.2
Bauxite	Al(OH) ₃	28.8	0.2
Calcite	CaCO ₃	38.0	0.2
Cobaltite	CoAsS	2.21	0.03
Cuprite	Cu ₂ O	49.5	0.08
Hematite	Fe ₂ O ₃	28.2	0.2
Ilmenite	FeTiO ₃	1.70	0.04
Magnesite	MgCO ₃	38.0	0.3
Malachite	Cu ₂ (CO ₃)(OH) ₂	3.65	0.03
Pyrite	FeS ₂	2.12	0.01
Pyrolusite	MnO ₂	1.39	0.04
Siderite	FeCO ₃	6.80	0.4
Willemite	Zn ₂ SiO ₄	1.80	0.02

^a Standard error of the mean of three replicates for surface area analysis.

specific to sulfate radical was not identified because all potential sulfate radical probes directly activated persulfate [23]. Nitrobenzene (NB) was used as a hydroxyl radical-specific probe because of its high reactivity with hydroxyl radical ($k_{\text{OH}\cdot} = 3.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) but low reactivity with sulfate radical ($k_{\text{SO}_4^{\cdot-}} = \leq 10^6$), allowing a comparison between the two radicals [22,23]. Hexachloroethane, which is unreactive with hydroxyl radical ($k_{\text{OH}\cdot} \leq 10^6 \text{ M}^{-1} \text{ s}^{-1}$), was used as a reductant probe because it is readily degraded by the reductant superoxide in the presence of electrolytes such as hydrogen peroxide and persulfate [24] and in the presence of mineral surfaces [25]; hexachloroethane is also reduced by alkyl radicals. Hexachloroethane has previously been used as probe for superoxide in CHP and persulfate systems [19,26].

2.3. Experimental procedures

All reactions were conducted in triplicate at $20 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ in 20 mL borosilicate volatile organic analysis (VOA) vials fitted with polytetrafluoroethylene (PTFE) lined caps. Reactions contained 2 g of mineral and 5 mL of 0.5 M sodium persulfate. This concentration of persulfate was chosen because it is commonly employed in ISCO field applications [10]; the relatively high concentration of trace minerals was used to evaluate the maximum potential effect of the trace mineral on persulfate activity. Reactions investigating total sulfate + hydroxyl radical, hydroxyl radical alone, and reductants contained 1 mM of anisole, nitrobenzene, and hexachloroethane, respectively. The pH of the reactions was allowed to drift downward as it would in a natural groundwater system during ISCO; the pH decreased to a range of 4–5 in all of the reactions. Positive control reactions containing 5 mL of 0.5 M persulfate and no mineral were conducted in parallel to all reactions. In addition, control reactions consisting of 2 g mineral and 5 mL of deionized water in place of persulfate were conducted in parallel to reactions containing probe compounds, to control for any direct effect of the minerals on the probe compounds. At selected time points, a triplicate set of reactors was analyzed for persulfate or probe compound residual concentrations. Reactors analyzed for probe compound residuals were extracted with hexane followed by analysis of the probe compounds by gas chromatography.

2.4. Analysis

Persulfate concentrations were quantified using iodometric titration with 0.01 N sodium thiosulfate [27]. Solution pH was measured using with a Fisher Accumet 900 pH meter.

Hexane extracts containing probe compounds were analyzed using Hewlett–Packard 5890 series II gas chromatographs (GC). For anisole and nitrobenzene analysis, the GC was fitted with a 15 m \times 0.53 mm (i.d.) SPB-5 capillary column and flame ionization detection (FID) was employed. The injector port temperature was 250 $^\circ\text{C}$, the detector port temperature was 200 $^\circ\text{C}$, the initial oven temperature was 70 $^\circ\text{C}$, the program rate was 20 $^\circ\text{C min}^{-1}$, and the final temperature was 210 $^\circ\text{C}$. For hexachloroethane analysis the GC was fitted with a 15 m \times 0.53 mm (i.d.) Equity-5 capillary column and electron capture detection (ECD) was used. The injector port temperature was 220 $^\circ\text{C}$, the detector port temperature was 270 $^\circ\text{C}$, the initial oven temperature was 100 $^\circ\text{C}$, the program rate was 30 $^\circ\text{C min}^{-1}$, and the final temperature was 240 $^\circ\text{C}$.

ICP/MS analysis of minerals by EPA Method 3050 and the aqueous phase of mineral–persulfate slurries was performed using an Agilent 7500cx ICP/MS system. Triplicate samples were analyzed for each mineral system. Conditions included Rf-power 1450 W; carrier gas flow rate 0.80 L/min; make-up gas flow rate 0.34 L/min; sample uptake 0.5 mL/min; sampling depth 7.5 mm; 1.0 mm Pt sampler; 0.4 mm Pt skimmer.

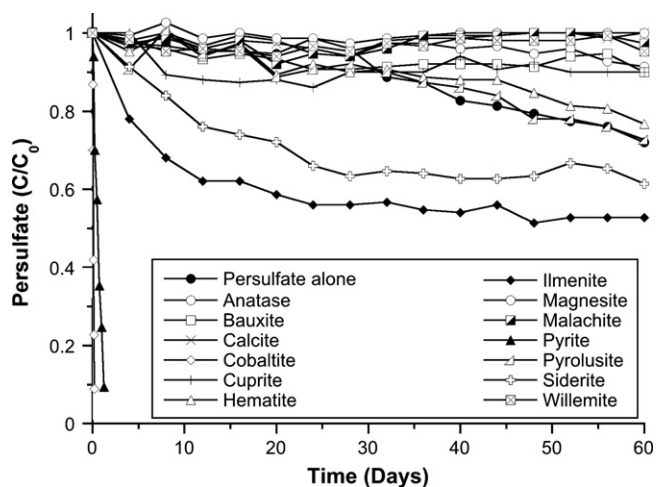


Fig. 1. Decomposition of persulfate alone and in the presence of 13 trace minerals. Reactors: 5 mL of 0.5 M persulfate and 2 g of mineral; $T=25^{\circ}\text{C} \pm 1^{\circ}\text{C}$.

3. Results and discussion

3.1. Mineral-mediated decomposition of persulfate

The decomposition of persulfate in the presence of 13 trace minerals is shown in Fig. 1. The rates of mineral-mediated persulfate decomposition varied substantially; therefore, the minerals were classified into four distinct groups based on their potential to decompose persulfate. The minerals that promoted rapid persulfate decomposition were cobaltite and pyrite with >90% of the persulfate decomposed within 5 h and 30 h, respectively. The minerals classified as slowly decomposing persulfate were ilmenite and siderite, which mediated 48% and 39% persulfate decomposition, respectively, over 60 d. The minerals termed the control group were pyrolusite and hematite, which were characterized by an undetectable difference in persulfate decomposition compared to aqueous controls containing persulfate with no minerals. The scavenging group of minerals (calcite, anatase, bauxite, cuprite, magnesite, malachite, and willemite) promoted persulfate decomposition at rates slower than in aqueous controls with no minerals. Therefore, nine of the 13 minerals either slowed or had minimal effect on the rate of persulfate decomposition, while four minerals (pyrite, cobaltite, ilmenite, and siderite) increased the rate of persulfate decomposition compared to control systems containing persulfate without minerals. These results are consistent with the findings of Johnson et al. [18] and Costanza et al. [17]; they documented that different subsurface solids had wide-ranging effects on persulfate decomposition rates in thermally activated persulfate systems. Possible mechanisms for the decrease in persulfate decomposition rate in the presence of some trace minerals include differences in redox potential or pH in the microenvironment at the surface of the trace mineral [28]. Alternatively, some functional groups on the surfaces of minerals may scavenge reactive oxygen species that might otherwise decompose persulfate [8,29,30].

The metal composition of the minerals did not correlate with their potential to decompose persulfate. For example, ilmenite, pyrite, and siderite are Fe (II) minerals, yet ilmenite and siderite were relatively slow in decomposing persulfate, while pyrite-mediated decomposition of persulfate was very rapid. Furthermore, persulfate decomposition mediated by the Fe (II) minerals was more rapid than that promoted by the Fe (III) mineral hematite, while the copper-based minerals showed no significant difference in persulfate decomposition rates between the Cu (I) of cuprite and the Cu (II) of malachite. The absence of correlation between mineral composition and reactivity with persulfate may

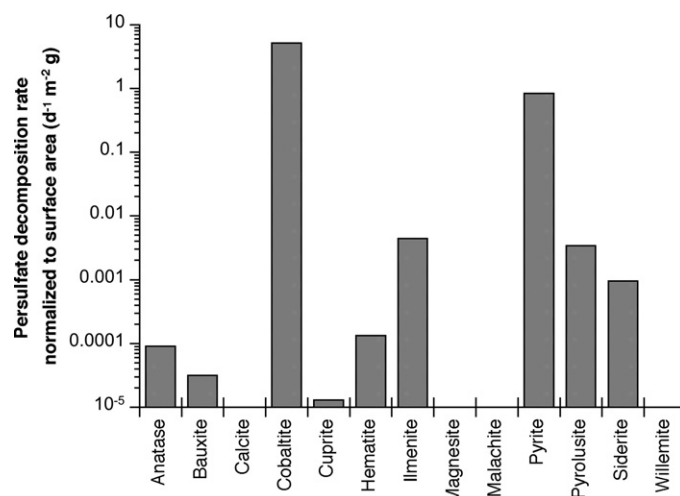


Fig. 2. Pseudo first order rate constants for persulfate decomposition in the presence of thirteen minerals, normalized to mineral surface area. Rate constants for calcite, magnesite, malachite, and willemite were zero.

be a function of the nature of persulfate activation; the decomposition of persulfate may be affected by the nature of the mineral surface, or alternatively it may be related to the release of soluble metals into the aqueous phase. Just as hydrogen peroxide is decomposed both by soluble metals and through heterogeneous catalysis by minerals [12], persulfate decomposition in these mineral systems may be due to dissolved metals from the minerals. Iron pyrite dissolves rapidly in mildly acidic water, providing a source of iron (II) for persulfate activation [31,32]. ICP/MS analysis of the aqueous phase of the pyrite–persulfate reactions confirmed the release of soluble iron (II); after 12 h of reaction, the soluble iron (II) concentration in the system was 3.4 mg/L.

Pseudo first order rate constants for reactions with minerals were calculated using the data of Fig. 1, and the rate constants were then normalized to the surface area of each mineral (Fig. 2). The trends in persulfate decomposition when normalized to mineral surface area were very similar to the trends seen in Fig. 1, with cobaltite and pyrite promoting the highest rates of persulfate decomposition. However, the normalized pyrolusite-mediated decomposition rate of persulfate increased relative to the normalized rates of the other systems. Manganese oxides are characterized by high surface areas, which likely has a significant influence on their potential to decompose persulfate. A similar trend was noted by Ahmad et al. [19] with the manganese oxide birnessite.

Based on the results of Figs. 1 and 2, calcite, ilmenite, and pyrite were used as representative minerals of three groups: (1) those that provided less persulfate decomposition than control systems, (2) those that slowly decomposed persulfate, and (3) those that rapidly decomposed persulfate. The three minerals were used for detailed investigation of reactive oxygen species generation in mineral–persulfate systems.

3.2. Sulfate + hydroxyl radical activity

Anisole was used as a probe compound to quantify relative generation rates of sulfate + hydroxyl radical in persulfate systems containing the three representative minerals. The degradation of anisole in persulfate systems containing calcite, ilmenite, and pyrite is shown in Fig. 3(a)–(c). Loss of anisole in the calcite–persulfate system was not significantly different from the persulfate-only control (Fig. 3(a)). These data indicate that calcite does not activate persulfate to generate additional sulfate + hydroxyl radical beyond that generated in persulfate–water systems, which is expected

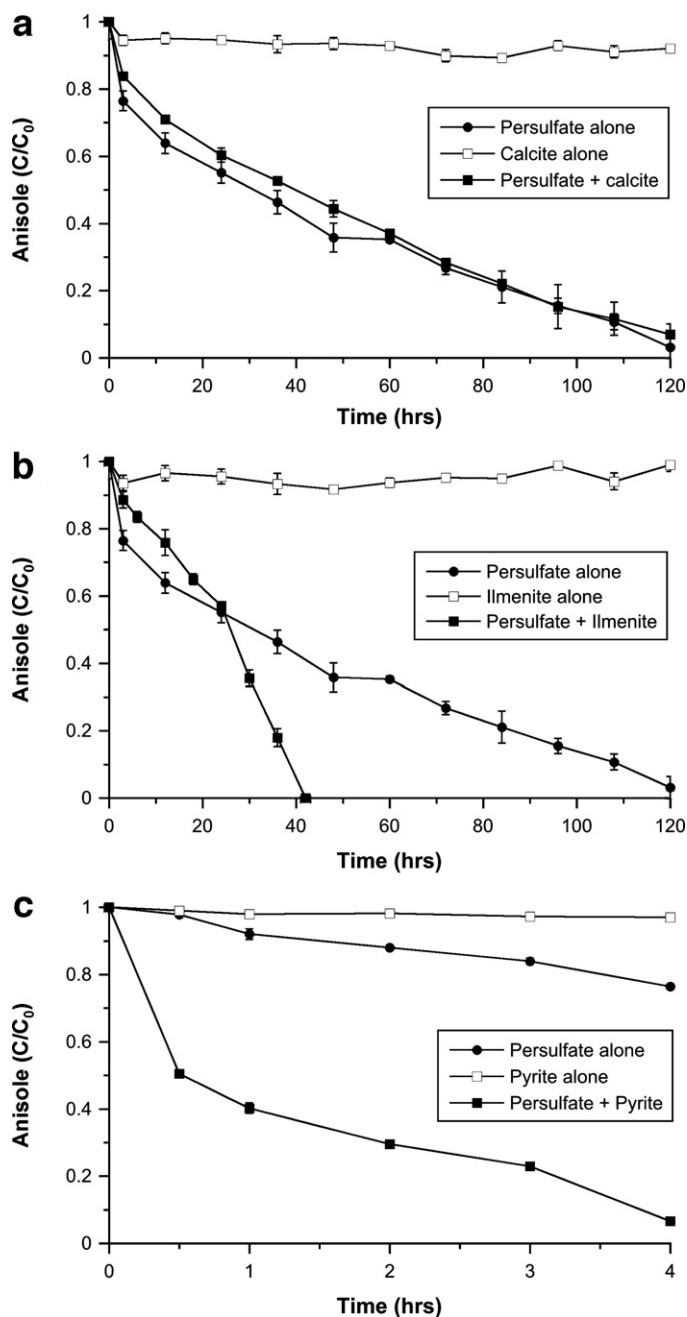


Fig. 3. Degradation of the combined sulfate + hydroxyl radical probe anisole by trace mineral–persulfate systems at $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$. (a) Calcite; (b) Ilmenite; (c) Pyrite.

based on the minimal persulfate decomposition promoted by calcite (Fig. 1). In the ilmenite–persulfate system (Fig. 3(b)), anisole degraded 99% within 42 h, demonstrating significant generation of sulfate + hydroxyl radical relative to the persulfate–water control. Anisole degraded even more rapidly in the pyrite–persulfate system (Fig. 3(c)), with >95% degradation over 4 h compared to <20% in the persulfate–water control. These results indicate that rapid decomposition of persulfate in the presence of pyrite (Fig. 1) mediates a corresponding high rate of sulfate + hydroxyl radical generation.

3.3. Hydroxyl radical activity

Hydroxyl radical generation, quantified by oxidation of the hydroxyl radical probe nitrobenzene, in persulfate systems

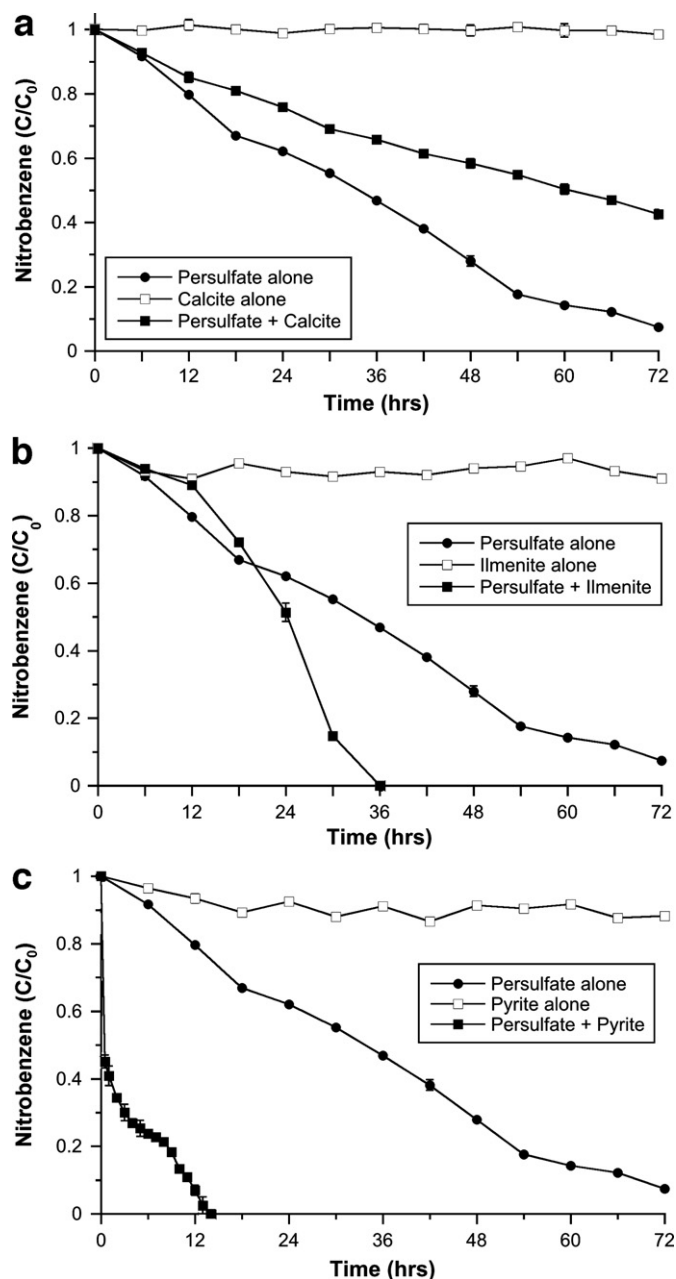


Fig. 4. Degradation of the hydroxyl radical probe nitrobenzene by trace mineral–persulfate systems at $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$. (a) Calcite; (b) Ilmenite; (c) Pyrite.

containing the representative minerals calcite, ilmenite, and pyrite is shown in Fig. 4(a)–(c). Nitrobenzene was oxidized more slowly in the presence of calcite than in the persulfate–water control system (Fig. 4(a)), with 60% nitrobenzene loss in the calcite–persulfate system compared to 90% in the persulfate–water control system over 72 h. These results suggest that calcite inhibited hydroxyl radical generation, and are consistent with the inhibitory effect of calcite on persulfate decomposition. In contrast, a greater flux of hydroxyl radical was promoted in the ilmenite–persulfate system; >99% of the nitrobenzene was oxidized over 36 h, with only 50% of the nitrobenzene lost in the persulfate–water control system over the same time period (Fig. 4(b)). Hydroxyl radical generation was rapid in the pyrite–persulfate system (Fig. 4(c)), with >99% nitrobenzene loss over 14 h in the presence of pyrite while 25% of the nitrobenzene was lost in the persulfate–water control system. The rapid generation of hydroxyl radical in pyrite–persulfate systems may

have been due to dissolution of the pyrite, providing soluble iron (II) to activate persulfate [31,32]. The results of Fig. 4(a)–(c) demonstrate that the three trace minerals calcite, ilmenite, and pyrite promote highly different rates of hydroxyl radical generation in persulfate systems, consistent with their different potential to promote persulfate decomposition.

3.4. Reductant activity

Superoxide is a weak nucleophile and reductant that is generated in CHP systems [24] and in activated persulfate systems [10]. In CHP systems superoxide is responsible for the degradation of highly oxidized organic contaminants (e.g., carbon tetrachloride) [33], for the enhanced desorption of hydrophobic organic contaminants [34], and the enhanced treatment of dense non-aqueous phase liquids (DNAPLs) [35]. HCA was used to investigate the activity of superoxide and other nucleophiles and reductants in persulfate systems containing the representative minerals calcite, ilmenite, and pyrite (Fig. 5(a)–(c)). In calcite–persulfate systems HCA loss was 27% after 72 h (Fig. 5(a)). This loss was not significantly different from the 24% loss in the persulfate–water control, demonstrating that the addition of calcite to persulfate systems did not promote the generation of nucleophiles or reductants. In contrast, reductant activity in ilmenite–persulfate systems was significantly greater than in persulfate–water control systems or in ilmenite systems with no persulfate (Fig. 5(b)) with 63% HCA degradation over 72 h. The data of Fig. 5(a) and (b) demonstrate that while some nucleophiles or reductants are generated in persulfate systems containing ilmenite, a minimal flux of these species is generated by the calcite activation of persulfate. These results are consistent with rates at which ilmenite and calcite promote persulfate decomposition (Fig. 1).

HCA loss in the pyrite–persulfate systems was 36% over 72 h (Fig. 5(c)), which was greater than the 24% loss in the persulfate–water control. However, unlike results with the other two minerals (Fig. 3(c) and Fig. 4(c)), systems containing pyrite with no persulfate rapidly degraded HCA, with 77% loss of HCA in the first 24 h and 93% lost over 72 h. Kriegman-King et al. [36] documented that pyrite directly reduces carbon tetrachloride. Because HCA is similar to carbon tetrachloride in degree of chlorination and carbon oxidation state, it was likely also directly reduced by pyrite. Direct reduction of HCA by pyrite may have been minimized in the pyrite–persulfate system due to oxidation of pyrite and Fe (II) by persulfate.

3.5. Screening of reactive oxygen species generation

In addition to the detailed analyses of hydroxyl radical, sulfate radical, and superoxide generation by the three representative minerals (calcite, ilmenite, and pyrite) shown in Figs. 3–5, a 24 h evaluation of all the minerals was conducted to provide a simple comparison of the potential for all 13 minerals to generate the three reactive oxygen species. The 24 h results using the probe compounds anisole and nitrobenzene, listed in Table 2, show wide-ranging potential for mineral activation of persulfate to generate sulfate and hydroxyl radical. Oxidation of anisole and nitrobenzene ranged from less than that of persulfate–water systems for some minerals, to >99.9% for pyrite–persulfate systems. In contrast, the generation of reductants and nucleophiles, quantified by loss of the probe compound HCA, was minimal in all mineral–persulfate systems relative to persulfate–water controls.

To better interpret and compare the results of Table 2, the data were normalized to the persulfate–water control systems. The relative degradation of anisole, nitrobenzene, and hexachloroethane in 13 mineral–persulfate systems normalized to corresponding persulfate–water control systems is shown in

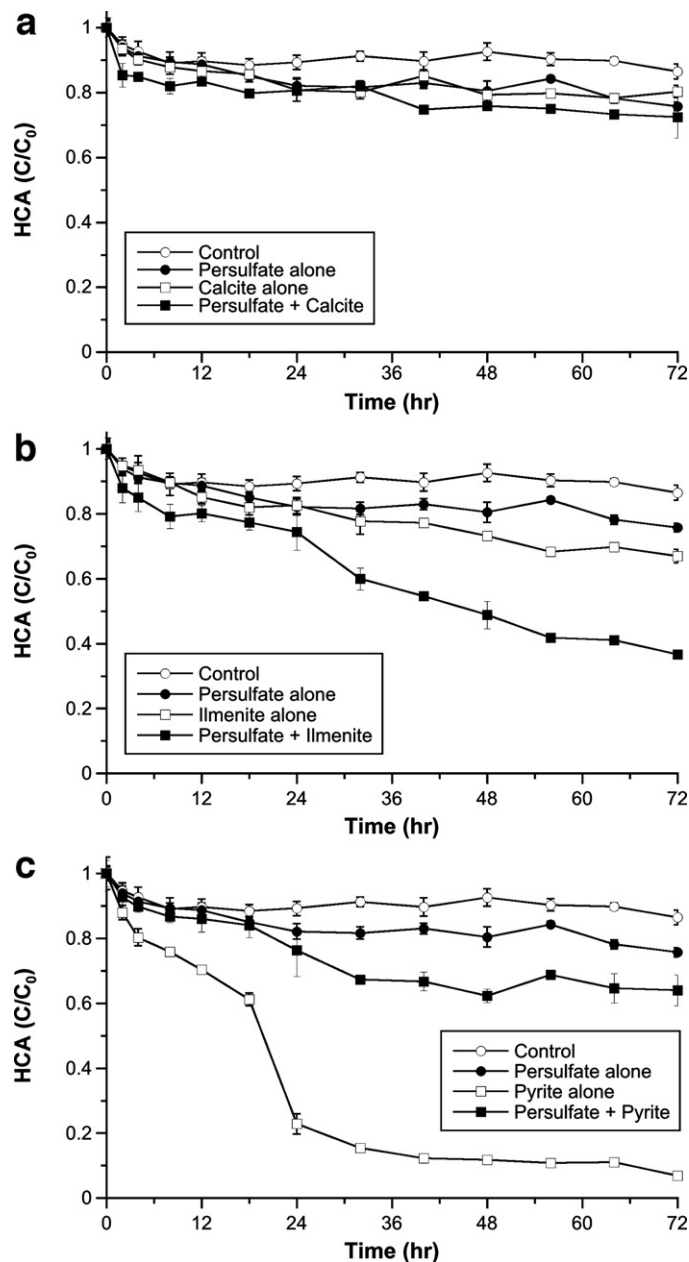


Fig. 5. Degradation of the reductant probe hexachloroethane in trace mineral–persulfate systems at 25 °C ± 1 °C. (a) Calcite; (b) Ilmenite; (c) Pyrite.

Fig. 6. The probe compounds degraded at rates similar to or slower than persulfate–water control systems in many of the mineral–persulfate systems. Furthermore, not all minerals were consistent in activation of persulfate for generation of all of the reactive oxygen species, or inhibiting generation of all of the reactive oxygen species. For example, pyrite and malachite promoted the generation of sulfate+hydroxyl radical, but did not result in significant generation of reductants and nucleophiles. Ilmenite, magnesite, and willemite provided a net increase in hydroxyl radical generation, but not sulfate radical generation, relative to the persulfate–water control systems. In contrast, cuprite and malachite promoted some generation of sulfate radical but not hydroxyl radical. Nonetheless, the majority of the 13 minerals evaluated resulted in minimal increases in generation rates of reactive oxygen species relative to persulfate–water systems. The minimal activation of persulfate by most of the trace minerals used in this study is consistent with the results of Kanwatej et al. [37], who found

Table 2
Percent degradation of the probe compounds anisole, nitrobenzene, and hexachloroethane in mineral–persulfate systems.

	Anisole		Nitrobenzene		Hexachloroethane	
	% Loss	SE ^a	% Loss	SE	% Loss	SE
Control (DI Water)	7.55	1.34	15.5	1.84	10.9	0.587
Persulfate Alone	45.4	0.321	37.2	0.405	17.9	1.03
Anatase	49.1	0.824	36.7	2.15	22.2	0.887
Bauxite	52.0	0.934	29.5	0.962	23.9	0.764
Calcite	40.3	1.73	26.4	2.00	19.4	0.538
Cobaltite	40.4	0.713	43.6	0.804	29.4	0.087
Cuprite	57.1	1.39	36.3	0.848	22.1	0.751
Hematite	66.9	3.14	47.6	0.812	20.6	0.628
Ilmenite	43.3	3.19	48.0	0.606	23.6	1.40
Pyrolusite	48.6	0.366	23.1	0.378	25.1	1.09
Pyrite	>99.9	0.0	>99.9	0.0	23.6	1.36
Malachite	83.0	2.82	43.4	0.397	19.9	0.200
Magnesite	51.2	1.07	63.0	1.04	26.0	0.893
Siderite	50.9	0.381	35.1	0.340	19.5	0.883
Willemite	43.5	1.06	50.6	0.808	19.0	2.19

^a Standard error of the mean of three replicates.

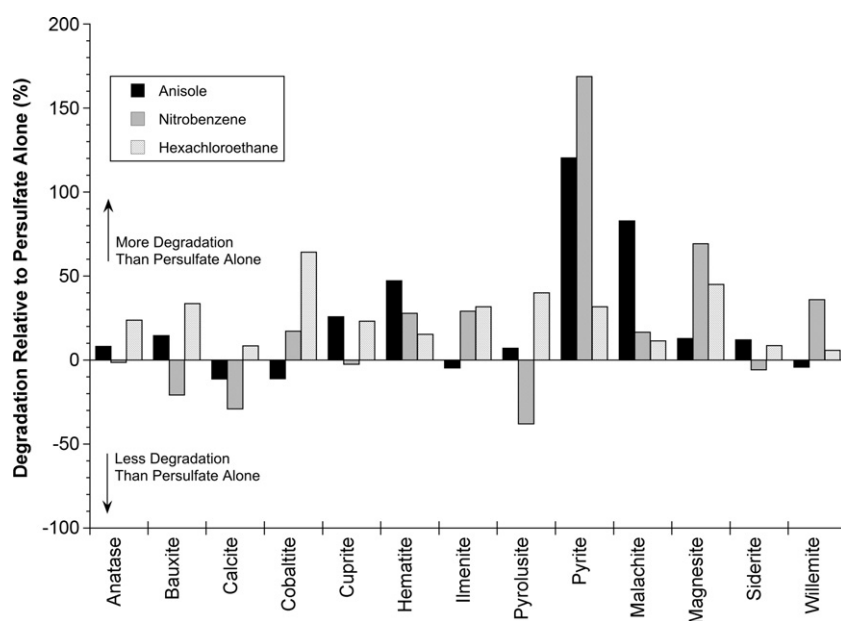


Fig. 6. Degradation of anisole, nitrobenzene, and hexachloroethane in persulfate–mineral systems over 24 h relative to the persulfate–water control.

that in the absence of added activators, the half-life of persulfate in seven aquifer materials ranged from 2 to 600 d.

Unlike CHP systems in which most major and trace minerals catalyze the decomposition of hydrogen peroxide to generate a robust mixture of reactive oxygen species, persulfate is not appreciably activated by most trace minerals; furthermore, many of the trace minerals actually decrease rates of persulfate activation and scavenge reactive oxygen species. In addition, those trace minerals that do activate persulfate are usually present in the subsurface at concentrations much lower than those used in this study. These results are consistent with those of Ahmad et al. [19], who found that typical concentrations of goethite, ferrihydrite, and birnessite, the major minerals found in soils, did not activate persulfate to generate reactive oxygen species.

Minimal persulfate reactivity has been observed at a number of activated persulfate field applications [38]. Such low reactivity may be due to scavenging of reactive oxygen species by trace minerals present in the subsurface solids. If trace minerals also significantly affect commonly used methods of persulfate activation (e.g., iron-chelate activation), then new activators may be required that are

not affected by the scavenging of reactive oxygen species by trace minerals.

4. Conclusions

Thirteen trace minerals were evaluated for their potential to promote the decomposition of persulfate and generate reactive oxygen species. Trace minerals were characterized by wide-ranging potential to promote persulfate decomposition. Seven of the minerals (anatase, bauxite, calcite, cuprite, magnesite, malachite, and willemite) mediated the decomposition of persulfate at rates slower than the persulfate–water control systems containing no minerals. Two minerals (pyrolusite and hematite) promoted persulfate decomposition at rates nearly equal to the persulfate–water control systems. Four minerals (cobaltite, ilmenite, pyrite, and siderite) decomposed persulfate at rates greater than the persulfate–water control systems. Therefore, nine of the 13 minerals either slowed or had minimal effect on the rate of persulfate decomposition.

The reaction-specific probe compounds anisole, nitrobenzene, and HCA were used to detect total sulfate+hydroxyl radical, hydroxyl radical alone, and reductants and nucleophiles, respectively. The most reactive activator of persulfate for the generation of sulfate radical and hydroxyl radical was pyrite; this result may be due to the reduced nature of pyrite. All of the other minerals provided lower rates of generation of these oxidants than pyrite, and in some cases lower rates of radical generation than the persulfate–water control systems. All of the minerals promoted a small amount of reductant or nucleophile generation relative to the persulfate–water control systems. The majority of the 13 minerals showed minimal potential to generate reactive oxygen species.

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