



Properties of calcium peroxide for release of hydrogen peroxide and oxygen: A kinetics study



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HIGHLIGHTS

- CaO₂ can react with water to form O₂ directly without the intermediate of H₂O₂.
- The release kinetic pattern for H₂O₂ was pseudo-zero-order.
- The release kinetic pattern for O₂ was pseudo-first order.
- Increasing temperature and decreasing pH accelerate both O₂ and H₂O₂ release rates.
- Increasing temperature and pH decrease the H₂O₂ yield and increase the O₂ yield.

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ABSTRACT

Calcium peroxide (CaO₂), as one of the solid peroxides, has been increasingly used in contaminated site remediation due to its ability to release oxygen (O₂) and hydrogen peroxide (H₂O₂). Biodegradation can be enhanced by the existence of O₂. Hydrogen peroxide can be used to for *in situ* chemical oxidation via the modified Fenton. Previous studies show inconsistent results about O₂ and H₂O₂ release during CaO₂ decomposition. Additionally, the release characteristics of O₂ and H₂O₂ are not evaluated in detail.

A series of batch experiments was conducted to investigate the properties of CaO₂ decomposition and the release kinetics of O₂ and H₂O₂. O₂ and H₂O₂ were released directly from CaO₂ dissolution and H₂O₂ was not an essential intermediate in the conversion of CaO₂ to O₂. The two release paths formed a parallel reaction system, with a competitive relationship between the two paths. The release of H₂O₂ and O₂ followed a pseudo-zero-order kinetics pattern and a pseudo-first-order kinetics pattern, respectively. Increasing temperature and decreasing pH could accelerate both O₂ and H₂O₂ release rate. However, increasing temperature could decrease the H₂O₂ yield and increase the O₂ yield, which were similar to the impact of increasing pH.

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1. Introduction

With the rapid economic development in recent years, soil and groundwater pollution has frequently occurred all over the world due to waste transportation, leakage and discharge. Contaminants, including as total petroleum hydrocarbons (TPH) [1], polychloro biphenyls (PCBs) [2], polycyclic aromatic hydrocarbons (PAHs) [3], heavy metals [4], and pesticides [5] pose serious threats to human health and the environment due to their harmful characteristics such as high carcinogenicity and toxicity [6,7]. In response to a growing need to address environmental contamination, remedial

amendments have been developed. Calcium peroxide (CaO₂) is increasingly used for treating contaminated soil and ground water remediation by providing O₂ and H₂O₂ [8,9].

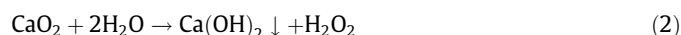
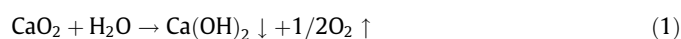
Previously, CaO₂ was used as an oxygen release compound (ORC) which can slowly decompose to release oxygen in contact with water (Eq. (1)) [10]. CaO₂ is one of the most versatile and safest solid inorganic peroxy compounds that can be considered as a solid form of oxygen [8,11]. The released oxygen can promote contaminant oxidation and enhance *in situ* aerobic microbial degradation [12–15]. Therefore, CaO₂ has been used for the remediation of many contaminated sites in US and in other developed countries [16]. White et al. [12] reported that CaO₂ greatly stimulated microbial growth in an arctic soil contaminated by crude oil. Cassidy and Irvine [14] found that CaO₂ promoted aerobic bioremediation of a water-saturated silty loam contaminated by

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bis-(2-ethylhexyl) phthalate (BEHP). Liu et al. [13] used an oxygen-releasing material (CaO_2) to construct permeable reactive barrier system and successfully removed methyl tert-butyl ether (MTBE) from groundwater. More studies have been conducted to use CaO_2 as a cost-efficient source of controlled-release oxygen to aid and enhance bioremediation [17,18].

In recent years, CaO_2 is found to be a more effective source of H_2O_2 than liquid H_2O_2 for modified Fenton *in situ* chemical oxidation (MF-ISCO) [19–21]. As is well-known, modified Fenton chemistry in subsurface involves the catalyzed decomposition of H_2O_2 by Fe^{2+} or Fe^{3+} , or native iron-containing minerals [22–24] (e.g., goethite, ferrihydrite) to form hydroxyl radicals ($\cdot\text{OH}$), which are strong and relatively indiscriminate oxidants that react with most contaminants at nearly diffusion-limited rates [25]. However, the instability of liquid H_2O_2 in the subsurface is the most serious limitation of MF-ISCO [26]. Compared with H_2O_2 , CaO_2 is relatively stable and can slowly release H_2O_2 by controlling its dissolution rate in water [27]. CaO_2 can liberate a maximum of 0.47 g H_2O_2 /g CaO_2 (Eq. (2)) and react for relatively long time and reduce disproportionation of H_2O_2 to O_2 [19,20,28,29]. Several studies have reported that adding CaO_2 to saturated soils and ground water was suitable when using MF-ISCO to remove organic contaminants [11,30]. Ndjou'ou and Cassidy [1] applied a commercially available CaO_2 -based oxidant to the treat soils contaminated with total petroleum hydrocarbons (TPH) and found that CaO_2 removed 96% of TPH. Bogan et al. [27] reported that CaO_2 performed better than liquid H_2O_2 for removing PAH from soil. Furthermore, other simulated experiments and engineering practices indicated that the application of CaO_2 was more effective for the chemical oxidation of contaminants in soils and ground water [16,19,30].



Based on the two equations above, uncertainty exists regarding the decomposition behavior of CaO_2 with respect to O_2 and H_2O_2 production. It has been postulated that O_2 is directly formed from CaO_2 rather than from H_2O_2 [12,31]. However, other studies have suggested that the conversion of CaO_2 to O_2 occurs through a requisite intermediate of H_2O_2 [32]. Northup and Cassidy [20] indicated that pH variations may be responsible for the conflicting information, but further evaluation about the decomposition behavior was barely carried out, especially when considering the relationship between the two release pathways (O_2 and H_2O_2) after CaO_2 dissolution. Few literatures about the decomposition behavior of CaO_2 and yield of H_2O_2 and O_2 under different conditions have led to uncertainty regarding the application of CaO_2 and its roles in Fenton chemistry and aerobic bio-stimulation.

The release characteristics of O_2 or H_2O_2 have also attracted many researchers' attention. White et al. [12] and Cassidy and Irvine [14] measured release of O_2 for 2 months in soils with unbuffered CaO_2 , but Ndjou'ou and Cassidy [1] indicated that CaO_2 was exhausted within 2 days at pH 8. Nykanen et al. [33] reported that CaO_2 can release O_2 when it reacts with water over 5–7 months. However, Northup and Cassidy [20] showed the rate of CaO_2 dissolution increased as the pH decreased, from 62 h at pH 12–13 (for complete dissolution) to 4 h at pH 6. The above studies roughly measured the separate release rates of O_2 and H_2O_2 . Although Northup and Cassidy gave a relatively detailed evaluation of the H_2O_2 release rates at various pH values, they did not comprehensively analyze the release kinetics of both O_2 and H_2O_2 in the same experiments.

In this study, a series of batch experiments was conducted to illustrate the characteristics of CaO_2 dissolution and O_2 and H_2O_2 release. The main objectives of this study were to (1) verify the decomposition behavior of CaO_2 and determine the mechanisms

controlling the conversion of CaO_2 to H_2O_2 and O_2 ; to (2) test and study the kinetics of H_2O_2 and O_2 release under different conditions.

2. Experimental protocols

2.1. Materials

Analytical grade CaO_2 was purchased from Aladdin Reagent Co. Ltd. (Shanghai, China), and the CaO_2 content was 72.4% according to testing. A scanning electron microscope (SEM) image of CaO_2 is shown in Fig. 1. It can be seen from the image that the CaO_2 particles were uniform in size, with most particles size between 1 and 2 μm . Monosodium phosphate dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) and disodium phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$) were purchased from the Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). The buffer solutions used in this study were prepared with $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ in de-ionized water. Preliminary testing verified that the buffer solution was able to maintain the desired pH with the dose of CaO_2 and other reagents used. Liquid H_2O_2 (30%) was obtained from the Sinopharm Chemical Reagent Co. Ltd.

2.2. Experimental procedures

To explore the decomposition behavior of CaO_2 and the O_2 and H_2O_2 release kinetics, experiments were conducted at 11 pH values (6, 6.25, 6.5, 6.75, 7, 7.25, 7.5, 7.75, 8, 8.5 and 9) in combination with three temperatures (10, 22 and 35 $^\circ\text{C}$). 200 mL of the buffer solution and 0.3 g CaO_2 was used in this series of experiments with a maximum theoretical mass of 0.14 g (15.08 mM) H_2O_2 or 0.067 g (7.54 mM) O_2 released according Eqs. (1) and (2). In the study of the release kinetics of H_2O_2 , three additional experiments with 0.3, 0.4, and 0.5 g of CaO_2 were conducted at pH 7 and 10 $^\circ\text{C}$.

All experiments were conducted in 250 mL jacketed cylindrical glass reactors equipped with a sealing cap. Preliminary testing verified that each reactor could maintain a constant pressure for at least 7 days. Before beginning the experiment, the volumes of each reactor were measured to accurately calculate the gas phase. In addition, the initial contents of DO in the buffer solution were also measured. The temperatures of the system were maintained using a thermostat water bath.

First, a certain amount of CaO_2 and the buffer solution were added into the glass reactor. Then, the reactor was sealed and the contents in the reactor were mixed using a magnetic stirrer at 170 rpm. At each time interval, the O_2 (g) concentration in the

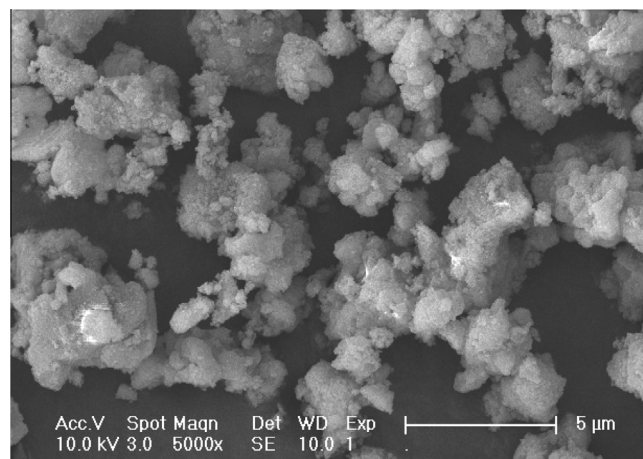


Fig. 1. Characterization of CaO_2 .

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