



Phosphate adsorption and precipitation on calcite under calco-carbonic equilibrium condition



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HIGHLIGHTS

- PO_4^{3-} adsorption and precipitation were separated according to experimental factor.
- PO_4^{3-} precipitation can be anticipated by saturation index of Ca-P precipitate.
- Result of PO_4^{3-} removal percentage change indicates PO_4^{3-} precipitation.
- CD-MUSIC model calculation shows occurrence of PO_4^{3-} precipitation.

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ABSTRACT

Phosphate (PO_4^{3-}) removal on calcite often entails two processes: adsorption and precipitation. Separating these two processes is of great importance for assessment of PO_4^{3-} stability after removal. Thus, this study was aimed at finding a critical range of conditions for separating these two processes in calco-carbonic equilibrium, by adjusting PO_4^{3-} concentration, reaction time and pH. PO_4^{3-} removal kinetic results showed that: (I) At pH7.7, PO_4^{3-} removal was mainly by adsorption at initial PO_4^{3-} concentration $\leq 2.2 \text{ mg L}^{-1}$ and reaction time $\leq 24 \text{ h}$, with dominant precipitation occurring at initial PO_4^{3-} concentration $\geq 3 \text{ mg L}^{-1}$ after 24 h reaction; (II) At pH8.3, adsorption was the key removal process at initial PO_4^{3-} concentration $\leq 7.5 \text{ mg L}^{-1}$ and reaction time $\leq 24 \text{ h}$, whereas precipitation was observed at initial PO_4^{3-} concentration of 10 mg L^{-1} after 24 h reaction, (III) At pH 9.1 and 10.1, PO_4^{3-} removal mechanism was mainly by adsorption at initial PO_4^{3-} concentration $\leq 10 \text{ mg L}^{-1}$ within 24 h reaction. Based on the kinetic results, it is suggested that PO_4^{3-} precipitation will occur after 24 h reaction when saturation index of amorphous calcium phosphate is between 1.97 and 2.19. Besides, increasing PO_4^{3-} concentration does not cause a continuous decline of PO_4^{3-} removal percentage. Moreover, experimental removal data deviated largely from the theoretical adsorption value by CD-MUSIC model. These indicate occurrence of precipitation which is in agreement with the kinetic result. Therefore our study will provide fundamental reference information for better understanding of phosphorous stabilization after removal by calcite.

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1. Introduction

Phosphate (PO_4^{3-}) is recognized as one of the key elements that

impair the aquatic environmental quality since excess of phosphorous (P) supply can cause eutrophication to water body (Lin et al., 2011; Liu et al., 2016; Li et al., 2016; Murphy et al., 1983). Calcite (CaCO_3) is a common mineral in the hydrosphere and lithosphere (Hamilton et al., 2009) and has the potential to retain PO_4^{3-} , thereby reducing its mobility. Considering the importance of calcite in P control, the interaction between PO_4^{3-} and calcite surface has

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been widely studied (House and Donaldson, 1986; Kleiner, 1988; Liu et al., 2012; Sindelar et al., 2015; Song et al., 2006; Wang et al., 2012; Xu et al., 2014). These studies generally have shown the following common features: the initial rapid uptake of phosphate onto calcite occurs through surface adsorption, which is then followed by a slow transformation of amorphous calcium phosphate prior to nucleation or precipitation of calcium phosphate on calcite. Briefly, it refers to two main mechanisms: adsorption and precipitation.

Often times, adsorbed phosphate would be released completely in less than 0.5 h during experimental phase of desorption (Sø et al., 2011), whereas the precipitated phosphate would be incorporated onto calcite surface and is supposed to remain stable despite changes in solution chemistry (Naidu and Scherer, 2014). Therefore, finding the critical range that distinguishes these two mechanisms in P removal behavior is of great importance for the assessment of P stability after its removal. However, to our knowledge, few studies have been conducted in this regard. For example, studies by Karageorgiou et al. (2007) and Sø et al. (2011) strictly confine to conditions that could avoid precipitation and reasonably explain the adsorption results, while others have just paid attention to P removal efficiency without precise interpretation of the removal mechanism (Liu et al., 2012).

To better understand the distinction between the adsorption and precipitation mechanism sufficient knowledge of the influencing factors is paramount. In general, factors such as the initial PO_4^{3-} concentration, reaction time and pH are most known to influence the PO_4^{3-} fixation mechanism (Griffin and Jurinak, 1973; Liu et al., 2012; Millero et al., 2001; Xu et al., 2014). Particularly, when initial PO_4^{3-} concentration is lower than the required concentration for the precipitation of Ca-P solid compounds, it is theoretically impossible for precipitation to take place. Conceptually, PO_4^{3-} retention on calcite can be attributed to surface adsorption at low concentration and precipitation at high concentration (Perassi and Borgnino, 2014). Secondly, adsorption and precipitation with prerequisite of over saturation are time-depend processes. Usually, adsorption is known to occur earlier than precipitation, though they may coexist in later reaction. Meanwhile, reports have shown that about 80% of the adsorption could be realized in just within 10 s (Kuo et al., 1972), while precipitation may happen after several hours or even days (Griffin and Jurinak, 1973). Besides, another important indicator in calcite surface reaction study is pH. For example, pH could affect the net charge of calcite surface (Van Cappellen et al., 1993). In addition, solubility of calcite and solution ion concentration such as Ca^{2+} , OH^- , HCO_3^- and CO_3^{2-} (Suzuki et al., 1986) are determined by pH. Both adsorption and precipitation are influenced by the surface and solution chemistry; therefore pH could have important impact on the formation of these two processes (Sø et al., 2011).

Therefore, the purpose of this paper is (i) to work out a dominant process of adsorption or precipitation using common batch method by adjusting the initial PO_4^{3-} concentration, reaction time and pH, and (ii) to provide the corresponding critical range of influencing factors that can distinctively separate adsorption and precipitation mechanisms. Hence, this study will provide reference information for the assessment of phosphorous stability after removal by calcite.

2. Materials and methods

2.1. Materials

Calcite (>99% purity) used in this study was sourced from Xirong Chemistry Company, China.

The morphology of the calcite was confirmed by Hitachi S-3600N VP SEM (Hitachi, Japan), as shown in Fig. S1. The BET surface

area of calcite particles determined by N_2 multipoint gas adsorption (Autosorb-1-C, Quantachrome, USA), was $0.61 \text{ m}^2/\text{g}$.

2.2. Production of pre-equilibrated water

The sorption of PO_4^{3-} to calcite was studied under calco-carbonic equilibrium conditions (i.e. atmospheric CO_2 , calcite phase and the solution species are at thermodynamic equilibrium). As shown in Fig. S2, equilibrium water (EQW) was produced by the following steps: (1) 10 g of calcite was put in 8 L of ultrapure water reservoir; (2) using Visual MINTEQ 3.1 (Gustafsson, 2014), quantitative hydrochloric acid (HCl) or sodium hydroxide (NaOH) was added into the reservoir to adjust the pH; (3) water reservoir was aerated continuously by bubbling filtered and humidified air through the water at constant ambient atmospheric pressure until equilibrium was attained. pH values of 7.7, 8.3, 9.1 and 10.1 were chosen due to their closeness to that of natural calcareous environment (Marschner, 1995). Moreover, such a pH range could minimize the addition of acid or base which otherwise would increase the effects of ionic strength. After equilibrium, EQW was obtained by filtration via $0.45 \mu\text{m}$ cellulose acetate filter. The experimental and theoretical values of ionic strength, pH and aqueous Ca of EQW are listed in Table S1, as well as the details of acid or base additions.

2.3. Experimental procedure

One gram (1 g) of calcite and 40 ml EQW were introduced into 50 ml centrifuge tube. In order to ensure equilibrium between calcite and EQW, the tubes were capped and shaken in thermostated oscillator (150 rpm, at $25 \pm 1 \text{ }^\circ\text{C}$) for 24 h after which equilibrium was verified by pH measurement. The solutions (KH_2PO_4) with the total PO_4^{3-} concentration of 0.5, 1, 1.5, 1.8, 2.2, 3, 5, 7.5, and 10 mg L^{-1} were introduced into the tubes, respectively. The tube was then capped and allowed to undergo continuously shaking for PO_4^{3-} sorption at different contact time duration of 0.5, 1.5, 3, 6, 10 and 24 h. The pH was immediately measured and the tubes were centrifuged for 5 min at 4000 rpm. After centrifugation, 10 ml of super-solution was analysis for the PO_4^{3-} and Ca contents. For the sake of comparison, a tube without PO_4^{3-} addition was prepared as a blank sample, and analyzed with them at the end of experiments. All outlined experiments were repeated twice. In the process, several tubes for experiments without calcite were included in each set-up to check for the loss of PO_4^{3-} e.g., precipitation of a phosphate-containing phase or adsorption into the tube. Finally, no decrease in PO_4^{3-} concentration in any of these tubes was observed.

2.4. Analytical method

The concentration of PO_4^{3-} was analyzed spectrophotometrically using the ammonium molybdate-blue method according to DS/EN ISO 6878:2004 (2004). The amount of PO_4^{3-} removal was calculated as the differences between the initial and final aqueous concentration. The Ca concentration was analyzed by atomic absorption spectroscopy (Agilent 3150G). Calibration for Ca analysis was made with 5 standards between 0.5 and 2.5 mg L^{-1} with R^2 not less than 0.99. The limit of detection for Ca analysis was 0.2 mg L^{-1} . The pH was measured using pH meter (PHSJ-4F, Shanghai INESA).

Visual MINTEQ 3.1 was employed to calculate saturation index (SI) of Ca-P minerals and ion activity, using the default equilibrium constants in its database (Gustafsson, 2014; Zuo et al., 2015). The surface complexation model of CD-MUSIC (Charge Distribution Multisite Ion Complexation) (Hiemstra and Van Riemsdijk, 1996) was adapted by Wolthers et al. (2008) for calcite. In later work by Sø et al. (2012), a more developed version of this CD-MUSIC model is

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