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Dissolution kinetics of granular calcium carbonate in concentrated aqueous sodium dichromate solution at pH 6.0–7.0 and 110–130 °C

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Abstract

An understanding of the factors controlling calcite dissolution is important for modeling geochemical cycles and impacts of greenhouse gases on climate, diagenesis of sediments, and sedimentary rocks. It also has practical significance in the investigation of behavior of carbonates in petroleum and natural gas reservoirs and in the preservation of buildings and monuments constructed from limestone and marble. A large number of papers have been published on dissolution kinetics of calcium carbonate in aqueous solutions. But few involved the near-equilibrium region, especially at elevated temperatures and in concentrated solutions. In this paper, the dissolution kinetics of calcium carbonate in concentrated aqueous sodium dichromate solutions at pH 6.0–7.0 and 110–130 °C were studied in a 2-L autoclave. The results indicate that the dissolution reaction is mix-controlled, with surface reaction as the prevailing factor. The concentration of calcium ions in solution hardly affects the dissolution rate, but carbon dioxide in the vapor phase inhibits the dissolution reaction. The dissolution rate can be expressed by $R = k_1 a_{\mathrm{H}^+}^2 + k_2$, and the apparent activation energy is 55–84 kJ mol^{-1}.

Keywords: Dissolution kinetics; Calcium carbonate; Aqueous sodium dichromate solution; Elevated temperature

1. Introduction

The dissolution kinetics of calcium carbonate in aqueous solutions has been widely studied for many years. A large number of papers have been published over the last half century. Morse and Arvidson [1,2] summarized some important findings. Numerous studies have demonstrated that in the case of extreme undersaturation the diffusion-controlled dissolution kinetics is prevailing. As equilibrium is approached, there is a region of transition toward surface-controlled dissolution kinetics, and a changing surface-reaction-controlled region exists until equilibrium is reached. However, the reaction mechanisms could not be clearly determined because of the complexity of the carbonic acid system. For example, the dissolution reaction can be written in the following ways:

$$\mathrm{CaCO_3} \rightarrow \mathrm{Ca^{2+}} + \mathrm{CO_3^{2-}}$$

$$\mathrm{CaCO_3} + \mathrm{H^+} \rightarrow \mathrm{Ca^{2+}} + \mathrm{HCO_3^-},$$

$$\mathrm{CaCO_3} + 2\mathrm{H^+} \rightarrow \mathrm{Ca^{2+}} + \mathrm{H_2CO_3},$$

$$\mathrm{CaCO_3} + \mathrm{H_2CO_3} \rightarrow \mathrm{Ca^{2+}} + 2\mathrm{HCO_3^-},$$

$$\mathrm{CaCO_3} + \mathrm{H_2O} + \mathrm{CO_2} \rightarrow \mathrm{Ca^{2+}} + 2\mathrm{HCO_3^-}.$$

Plummer et al. [3] extensively studied this problem and put forth a group of reactions and a complex rate equation to describe their results:

$$\mathrm{CaCO_3} + \mathrm{H^+} \Leftrightarrow \mathrm{Ca^{2+}} + \mathrm{HCO_3^-},$$

$$\mathrm{CaCO_3} + \mathrm{H_2CO_3^0} \Leftrightarrow \mathrm{Ca^{2+}} + 2\mathrm{HCO_3^-},$$

$$\mathrm{CaCO_3} + \mathrm{H_2O} \Leftrightarrow \mathrm{Ca^{2+}} + \mathrm{HCO_3^-} + \mathrm{OH^-},$$

$$R = k_1 a_{\mathrm{H}^+} + k_2 a_{\mathrm{H_2CO_3}} + k_3 a_{\mathrm{H_2O}} - k_4 a_{\mathrm{Ca}^{2+}} a_{\mathrm{HCO_3^-}}.$$

Arakaki and Mucci [4] obtained a general equation for dissolution and precipitation of calcite in simple solutions by combining the experimental data of their own with those of

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others and the surface complexation model of Van Cappellen et al. [5] (* denotes a surface complex):

$$*CO_3^- + 2H^+ \underset{k_5}{\overset{k_1}{\rightleftarrows}} *Ca^+ + H_2CO_3,$$

$$*Ca^+ + H_2CO_3 \underset{k_6}{\overset{k_2}{\rightleftarrows}} *CO_3H^0 + CaHCO_3^+,$$

$$*CO_3H^0 + CaHCO_3^+ \underset{k_7}{\overset{k_3}{\rightleftarrows}} *Ca^+ + H_2CO_3 + CaCO_3^0,$$

$$CaCO_3\ (\text{solid}) \underset{k_8}{\overset{k_4}{\rightleftarrows}} CaCO_3^0,$$

$$\begin{aligned} R = {} & k_1 {*CO_3^-} (a_{H^+})^2 + (k_2 - k_5){*Ca^+} a_{H_2CO_3} + k_4 \\ & - (k_6 - k_3){*CO_3H^0} a_{CaHCO_3^+} - k_7 {*Ca^+} a_{H_2CO_3} a_{CaCO_3^0} \\ & - k_8 a_{CaCO_3^0}. \end{aligned}$$

Dreybrodt and co-workers [6,7] investigated the dissolution of granular calcite in the H_2O–CO_2–$CaCO_3$ system, and concluded that the dissolution rate depends critically on the ratio of solution volume to the surface area of reacting minerals, V/A. For $V/A < 10^{-3}$ cm, the dissolution is controlled entirely by conversion of CO_2 into H^+ and HCO_3^-, whereas in the range of V/A from 10^{-3} cm to 10^{-1} cm both CO_2 conversion and molecular diffusion are rate-controlling factors.

Recently, new approaches for studying surface reaction processes, e.g., atomic force microscopy and optical interferometry, have also been applied to investigate calcite dissolution [8–17]. However, there remains a major challenge in integrating these new means into meaningful and practical methods. A general theory of surface dissolution mechanisms that is required to satisfactorily correlate observations of mineral surfaces with concentrations of dissolved components is currently lacking. As Morse and Arvidson pointed out, “there is no general equation that can be applied to all calcites and simply correlate surface area with solution composition.” Moreover, little is known about the influences of temperature on calcite dissolution kinetics in the surface-reaction-controlled near-equilibrium region that commonly exists in natural systems.

In this paper we studied the dissolution kinetics of granular calcium carbonate in concentrated aqueous sodium dichromate solution at pH 6.0–7.0 and 110–130 °C, which is a part of the key project entitled “Optimization Integration of the 10 kt/a Cleaner Production Technology for Chromium Salts,” supported by the National Natural Science Foundation of China and the Chinese Academy of Sciences.

The aqueous sodium dichromate solution possesses buffering capacity according to the following hydrolysis reaction:

$$Cr_2O_7^{2-} + H_2O \Leftrightarrow 2HCrO_4^- \Leftrightarrow 2CrO_4^{2-} + 2H^+.$$

The concentrations of dichromate and chromate and/or their molar ratio in solution can vary in a wide range within a narrow pH region. In the solution of pH $\geqslant 6$ and below 100 °C, calcium carbonate hardly dissolves. This makes it possible for us to study the dissolution kinetics of calcite in the near-equilibrium region at elevated temperatures.

2. Materials and procedures

2.1. Materials

Both calcium carbonate (purity $\geqslant$99.0 mass%, mean size 20 µm, B.E.T. (Brunauer Emmett Teller procedure) surface area 0.2–0.5 m^2/g) and sodium dichromate dehydrate (purity $\geqslant$99.5 mass%) are analytical grade reagent.

2.2. Procedures

Experiments were conducted in a two-liter autoclave (Model WHFK-2, Weihai Automation Control Autoclave Co. Ltd., China) with a temperature control unit and a backflow condenser to ensure a constant reaction volume. According to the preset plan, given amounts of calcium carbonate, sodium dichromate dihydrate and water were put into the autoclave, then the autoclave was closed, heated, and stirred. When the temperature reached the predetermined value, the outlet of carbon dioxide was opened slowly with the temperature kept constant. After the temperature and pressure were steady, the first sample was taken. Samples were taken at a given time interval and filtered with 0.22-µm membrane filters. Dichromate in the filtrates was determined by adding aqueous barium chloride solution and the produced hydrochloric acid was titrated by sodium hydroxide with phenolphthalein as indicator. The total Cr^{6+} in the filtrates was determined by ammonium ferrous sulfate titration with N-phenylanthranilic acid as indicator and calcium in the filtrates by EDTA (ethylene diamine tetraacetic acid) titration with calcium carboxylate as indicator. The conversion (x) of dichromate and dissolved fraction of calcium carbonate were calculated as follows:

$$x = (C_0 - C)/C_0.$$

The dissolved fraction of calcium carbonate $= bx$, where C_0 and C are the concentrations of dichromate in the initial solution and in samples, respectively. b is the molar ratio of dichromate to calcium carbonate in the initial solution.

3. Results and discussions

Figs. 1a–1c and Figs. 2a–2c show the relationship between the dissolved fraction of calcium carbonate and reaction time (t) and that between dx/dt and $1 - x$ at 110, 120, and 130 °C. It can be found that dx/dt and $1 - x$ have an excellent linear relationship and the slopes of the lines