LETTER

A nanoscopic approach to the kinetics of anhydrite (100) surface growth in the range of temperatures between 60 and 120 °C

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ABSTRACT

In situ observations of the growth of the anhydrite (100) surface in contact with supersaturated aqueous solutions under conditions within the stability field of this mineral (60–120°C) were conducted using a hydrothermal atomic force microscope (HAFM). Advancement rates were measured for [001] steps, the most stable ones on the anhydrite (100) surface. Isothermal data fit well to linear correlations between step advancement rate and supersaturation; the activation energy for step advancement is 73 ± 5 kJ/mol. This is not significantly higher than activation energies reported for the growth of gypsum (60–70 kJ/mol) and does not support that slow dehydration rates of aqueous calcium is responsible for the well-known difficulty to precipitate anhydrite crystals from supersaturated aqueous solutions at temperatures well above the anhydrite-gypsum equilibrium temperature. The role of structural factors that could inhibit the growth of anhydrite is discussed.

Keywords: Anhydrite, kinetics, activation energy, HAFM

INTRODUCTION

Gypsum (CaSO4·2H2O) and anhydrite (CaSO4) are very important components of evaporites. While gypsum forms through primary precipitation at temperatures close to ambient, anhydrite is stable above 60 °C, and its origin in evaporitic rocks is commonly regarded as secondary after gypsum (Freyer and Voigt 2003). Anhydrite also is an important phase in modern submarine hydrothermal fields, where anhydrite dissolution/precipitation cycles influence the permeability of hydrothermal structures (Kuhn et al. 2003). Both gypsum and anhydrite are common scalants (Amjad et al. 1988), whose precipitation can reduce efficiency and production capacity in various industrial processes, such as waste water treatment, desalination, gas/oil production, neutralization of free sulfuric acid in hydrometallurgical processes, and sulfur dioxide removal from coal-fired power plants flue gas (Azimi and Papangelakis 2011 and references therein). The kinetics of gypsum nucleation and growth are relatively well understood, as numerous researchers have conducted studies exploring a wide range of physicochemical conditions, following both macroscopic (Liu and Nancollas 1970; Nancollas et al. 1973; Gill and Nancollas 1980; Fan et al. 2010; Sheikholeslami and Lau 2011) and microscopic approaches (Boshach et al. 1995; Jordan and Astilleros 2006; Van Driessche et al. 2010). Despite the importance of anhydrite in nature and industry, little information on the kinetics of anhydrite crystallization is available so far. This is due to the well-known difficulty of directly precipitating anhydrite crystals from supersaturated aqueous solutions in the absence of NaCl and/or organics, even when the experiments are conducted at temperatures well above 60 °C and anhydrite seeds are added to the solution (J. Morales, unpublished results). This difficulty has been related to a high activation energy associated with dehydration of the calcium ion (Nancollas et al. 1973), which would inhibit both the formation of anhydrite critical nuclei and the growth of anhydrite seeds, thereby favoring the formation of gypsum. Alternatively, the application of atomic force microscopy (AFM) techniques enables direct observations of processes occurring at the mineral/aqueous solution interface (Gratz et al. 1993; Jordan et al. 2001; Astilleros et al. 2006; Fan and Teng 2007). Microscopic growth rates can be derived from the observation of the lateral movement of steps (Teng et al. 2000; Pérez-Garrido et al. 2007). From sets of isothermal microscopic step spread rates at different supersaturations, the activation energy for the growth process can be estimated.

This study is concerned with the kinetics of the anhydrite (100) surface growth from supersaturated solutions in a range of temperatures within the stability field of this phase, using nanoscopic measurements. Molecular scale observations yield highly reproducible results, in marked contrast to studies involving macroscopic measurements of the growth of anhydrite (J. Morales, unpublished results). This study focuses on anhydrite (100) surfaces that are, along with (010), the most important ones in the habit of natural anhydrite crystals (Shindo et al. 1992, 2010). To our knowledge, this study is the first to directly apply atomic force microscopy to investigate the molecular-scale growth kinetics of the anhydrite (100) surface as a function of temperature and to derive the activation energy for the growth process. Although the applicability of this activation energy to the overall description of anhydrite growth can be a controversial topic, it can be regarded as a reference value that can help to better understand crystallization in the CaSO4·H2O system while accurate macroscopic data are not available.

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