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Analytica Chimica Acta 583 (2007) 197–201

ANALYTICA
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Determination of equilibrium humidities using temperature and humidity controlled X-ray diffraction (RH-XRD)

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Received 20 June 2006; received in revised form 21 September 2006; accepted 27 September 2006

Abstract

Confined growth of crystals in porous building materials is generally considered to be a major cause of damage. We report on the use of X-ray diffraction under controlled conditions of temperature and relative humidity (RH-XRD) for the investigation of potentially deleterious phase transition reactions. An improved procedure based on rate measurements is used for the accurate and reproducible determination of equilibrium humidities of deliquescence and hydration reactions. The deliquescence humidities of NaCl (75.4 ± 0.5% RH) and $Ca(NO_3)_2 \cdot 4H_2O$ (50.8 ± 0.7% RH) at 25 °C determined with this improved RH-XRD technique are in excellent agreement with available literature data. Measurement of the hydration of anhydrous $Ca(NO_3)_2$ to form $Ca(NO_3)_2 \cdot 2H_2O$ revealed an equilibrium humidity of 10.2 ± 0.3%, which is also in reasonable agreement with available data. In conclusion, dynamic X-ray diffraction measurements are an appropriate method for the accurate and precise determination of equilibrium humidities with a number of interesting future applications.

Keywords: X-ray diffraction; Humidity control; Kinetics; Phase transformation; Deliquescence; Hydration

1. Introduction

Crystal growth in the pores of natural rocks or porous building materials such as stone, brick, concrete, etc. is a major weathering mechanism [1,2]. Damage in such materials is caused by the pressure generated if growing crystals become confined. Crystal growth of salts and salt hydrates is the result of phase transition reactions that are usually induced by changes in ambient relative humidity (RH) and temperature. Relevant processes include crystal growth from solution or in the course of a hydration reaction. Under unfavorable climatic conditions repeated cycles of humidity and temperature can cause the rapid decay of building materials attacked by this process. X-ray diffraction is an appropriate method for the investigation of phase transition reactions. It has been shown recently [3] that deleterious reactions such as crystallization from solution or during a hydration reaction can be studied in situ using X-ray diffraction under controlled conditions of temperature and relative humidity (RH-XRD).

For the conservation of building materials it is very important to know critical environmental conditions that have to be avoided to prevent crystal growth. Therefore, the knowledge of deliquescence humidities and equilibrium humidities of hydration–dehydration reactions is particularly important [4]. In previous work [3] we have shown that it is possible to determine equilibrium humidities by using RH-XRD. In the present work, we extend our previous approach and improve the capability of RH-XRD for an accurate determination of both equilibrium humidities of hydration reactions and the deliquescence humidity of salt crystals. The procedure adopted for the determination of equilibrium humidities involves kinetic measurements. It is based on the fact that reaction rates decrease as equilibrium is approached and the rate goes to zero at equilibrium. In this report we show that the equilibrium humidity of a reaction induced by a change in RH can be determined by extrapolation from rate measurements at different values of RH. The procedure is used to determine the deliquescence humidities of NaCl and $Ca(NO_3)_2 \cdot 4H_2O$ and the equilibrium humidity of the $Ca(NO_3)_2$–$Ca(NO_3)_2 \cdot 2H_2O$ transition. Comparison with available literature data confirms the accuracy of the method, which also offers good precision.

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doi:10.1016/j.aca.2006.09.054

2. Methodology

A salt with general composition $M_{\nu_M}X_{\nu_X}\cdot\nu_0H_2O$ consists of ν_M positive ions, M, of charge z_M, ν_X negative ions, X, of charge z_X, and ν_0 molecules of water. In a deliquescence reaction of a salt

$$M_{\nu_M}X_{\nu_X}\cdot\nu_0H_2O(cr)\overset{H_2O(g)}{\rightleftharpoons}\nu_M M^{z_M+}(aq)+\nu_X X^{z_X-}(aq)$$

the crystalline solid picks up water vapor and forms a saturated solution. At relative humidities above RH_{eq}, i.e. the deliquescence humidity, the solution continues to pick up water and a more dilute solution is formed. If the relative humidity drops below the deliquescence humidity, water evaporates to dryness and the crystalline solid is formed again. At equilibrium however, according to the Gibbs phase rule, the crystalline solid and the saturated solution can coexist indefinitely. Consequently, the net reaction rate at $RH = RH_{eq}$ is zero. Approaching RH_{eq}, the rate of the transformation reaction continuously decreases.

Considering a hydration reaction,

$$M_{\nu_M}X_{\nu_X}+\nu_0H_2O(g)\rightleftharpoons M_{\nu_M}X_{\nu_X}\cdot\nu_0H_2O(cr)$$

the situation is quite similar. At RH_{eq}, the two solid phases coexist in equilibrium with water vapor and the net reaction rate is equal to zero. At relative humidities either above or below RH_{eq} the hydrated and the anhydrous forms, respectively, are the only stable solids that can exist.

Several methods have been described in the literature for determining equilibrium humidities of phase transition reactions. One approach is water vapor pressure measurements at equilibrium. Methods for the determination of vapor pressure have been reviewed by Greenspan [5]. For instance, the vapor pressure over a saturated salt solution yields the deliquescence humidity of the salt at that temperature. Such experimental data exist in the literature for many salts; however, the data are usually quite scattered, particularly in the case of hydration–dehydration equilibria.

Another approach for the determination of equilibrium humidities is based on dynamic measurements. Such methods involve the measurement of a property of a condensed phase, i.e. a solid or a solution, at different relative humidities. These methods have been summarized by Yang et al. [6]. We have shown recently that X-ray diffraction, if conducted in a humidity chamber (RH-XRD), is also an appropriate technique for that purpose [3]. In that work, the equilibrium humidities RH_{eq} of phase transformation reactions were determined by a stepwise procedure. A sample of the educt phase was subjected to a stepwise increase in RH under isothermal conditions. Samples were equilibrated for 1 or 2 h at each humidity. Phase transformations induced by a change in RH were detected by sudden changes in the XRD patterns, i.e. the appearance or disappearance of characteristic peaks of the educt or the product phase. This approach requires very small step-sizes in RH variation in order to improve the uncertainty in the determination of RH_{eq}. A major problem with this approach arises from the kinetics of the transformation reaction. Usually the reaction rate strongly decreases as one approaches the equilibrium humidity of the transformation reaction. This results in very long equilibration times close to RH_{eq}. Unacceptable increases in equilibration times severely limit the applicability of the stepwise method. This problem resulted in an increased uncertainty of ±2.5% RH in the determination of the deliquescence humidity of $Na_2SO_4\cdot10H_2O$ in our previous work [3].

In the present work we present an improved dynamic method for more accurate determination of equilibrium humidities with RH-XRD. It is shown below how analysis of the rates of phase transition reactions can be successfully applied for the determination of RH_{eq}. The procedure is based on the evaluation of the total reaction time that is required until a phase transition reaction is complete. If a reaction, induced by an RH change, is carried out at different relative humidities, the total reaction times should increase as one approaches RH_{eq}. If an appropriate functional form of the RH dependence of the total reaction time can be established, the equilibrium RH can be determined by extrapolation to infinite reaction time. It is shown below that this approach can be successfully applied to determine the equilibrium humidities of deliquescence and hydration reactions.

3. Experimental

3.1. Instrumentation

Diffraction patterns were recorded on a Bragg-Brentano parafocusing reflection diffractometer (D 5000, Siemens, Germany) providing a horizontal θ:2θ configuration using Cu Kα-radiation and a position-sensitive detector (PSD). The goniometer is equipped with an environmental cell consisting of an air-tight cylindrical stainless steel chamber which is fixed to the θ-circle of the diffractometer. The window for passage of X-rays is sealed with a 6 μm Mylar film. The sample stage in the chamber is fixed with adjusting screws in the correct height of the θ:2θ alignment. A uniform temperature distribution in the chamber is achieved by circulating water through channels in both the cylindrical chamber wall and the sample stage. The front cover is equipped with drillings for temperature and humidity sensors. Inlet and outlet ports for the flows of thermostated water and air from a humid air generator are located on the backside of the chamber.

In the humid air generator compressed air is saturated with water vapor in a thermostated bubbler and passes a condensation trap at a temperature approximately 0.5 K below the final temperature. The desired relative humidity is maintained by accurately mixing dry and water-saturated air flows using automated mass-flow controllers. Appropriate mixing ratios of the wet and dry air flows are controlled by a computer program. A Pt-100 sensor and a capacitive humidity sensor (HMP 233, Vaisala, Finland) are positioned closed to the sample stage and give feedback of temperature and humidity in the chamber. The humidity control system allows variation of the relative humidity in the chamber between 3% RH and 97% RH. A more detailed description of the environmental chamber and the humidity control system is provided in Ref. [3].