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AN X-RAY DIFFRACTION SYSTEM WITH CONTROLLED RELATIVE HUMIDITY AND TEMPERATURE

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Asystem enabling X--ray diffraction patterns under controlled conditions of relative humidity and temperature has been devised and combined with an X--ray powder diffractometer. Relative humidity in the sample space is controlled by mixing dry N2 gas with saturated water vapor. Temperatures of the sample and inner wall of the sample chamber are monitored by two attached thermocouples and the information was fed back to the control unit. Relative humidity between 0% and the 95%, and temperature between room temperature and 60°C can be controlled. All parameters including those for XRD are programmable and the system runs automatically. The function of the system was checked by recording the XRD patterns of montmorillonite (a clay mineral) and NaCl under increasing and decreasing relative humidity.

Key words: relative humidity control, temperature control, X--ray diffraction

I. Introduction

The XRD measurements should be carried out at a controlled relative humidity especially for samples that are susceptible to a hydration, dehydration, and deliquescence. For example, the interlayer spacing of the clay mineral montmorillonite is known to vary with water vapor pressure. Similarly, some organic compounds such as amorphous cyclodextrin with ketoprofen or nifedipine (Kawano et al., 1985) and α-lactose monohydrate (Mikura et al, 1975) are sensitive to water vapor hydration. For materials, it is essential to obtain XRD patterns under controlled relative humidity and temperature.

An X-ray diffraction apparatus with a relative humidity control system was reported by Watanabe and Sato (1988). In their system, relative humidity was varied by mixing of saturated water vapor with dry air using manual valves with flow meters. The temperature and relative humidity of the sample chamber was fixed at 25°C. Their system was well suited for XRD analysis of montmorillonite at different relative humidity, as a constant temperature. Iwasaki and Torii (1991) designed a different system in which the sample space for XRD and a chamber for generating saturated water vapor were connected by a thermally insulated pipe. Because the pressure of the saturated water vapor at any temperature is known, the relative humidity of the sample space was indirectly controlled by varying the temperature of both the sample space and the water vapor generator. This system is elegant and has the capability of being computerized. The geometry of the X-ray diffractometer, however, requires a long piping distance from the chamber of the water vapor generator to the sample space. As this may cause instability of the thermal insulation, the indirect control of the relative humidity is not entirely reliable.

Here, we describe an improved system for XRD analysis under controlled temperature and relative humidity. The system is based on the two systems described above, but without their intrinsic limitations. The system runs automatically and may be of wide use. To demonstrate the functions of the system, we measured basal spacing of montmorillonite at varying relative humidity, and crystal collapse of NaCl due to deliquescence.

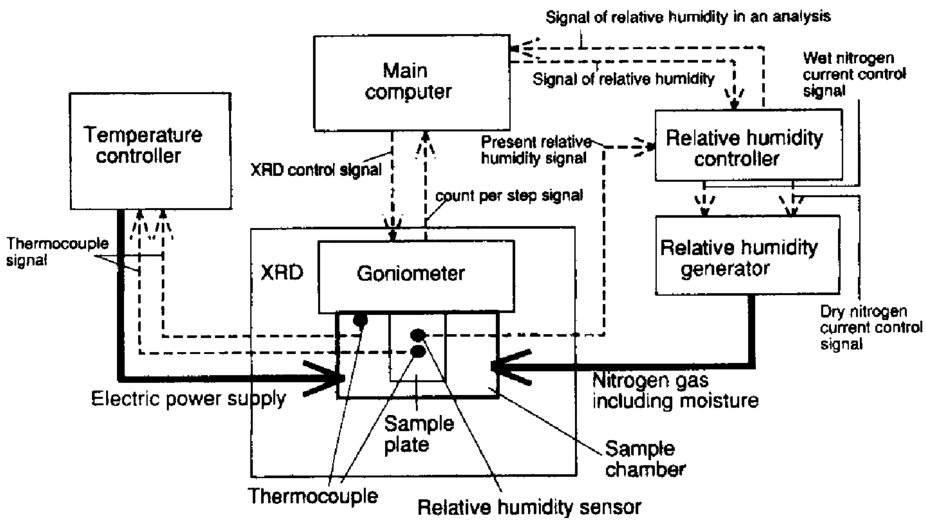

Fig. 1 Block diagram of the present system for XRD analysis under controlled relative humidity and temperature

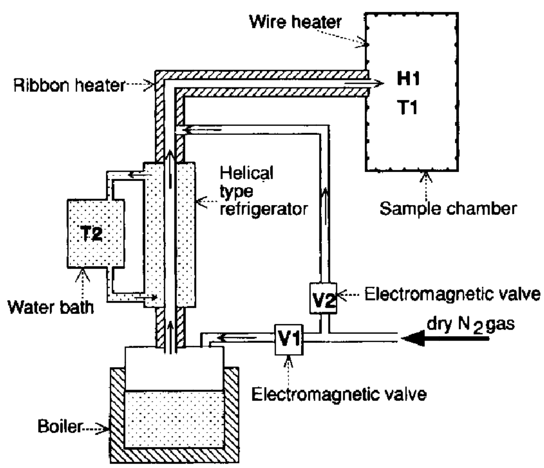

Fig. 2 Schematic illustration of the relative humidity generator.

II. X-Ray Diffractometer with a Relative Humidity and Temperature Control System

The design principle of the present system is shown in Fig. 1. Some details are given in Fig. 2. The X-ray diffractometer used is a commercial model fixed horizontal with a sample holder, and the diffraction angle 2θ is varied by rotating the X-ray tube and the detector (RIGAKU, RINT2100S). The sample holder is placed in an air-tight chamber provided with an inlet and outlet for gas at a controlled humidity (Figs. 1 and 2). The chamber is equipped with a wire heater on the inner wall and is thermally insulated.

The relative humidity and temperature are controlled as follows. The temperature in the sample chamber is independently controlled by a cascade-type controller (CHINO, DP4000), which controls the wire heater on the inner wall on the base of both the temperatures of the sample and of the inner wall of the chamber. Gas of a specified humidity is formed by mixing dry N_2 (V2) (Fig. 2) and wet N_2 (Vl) (Fig. 2) saturated with water vapor at approximately the same temperature

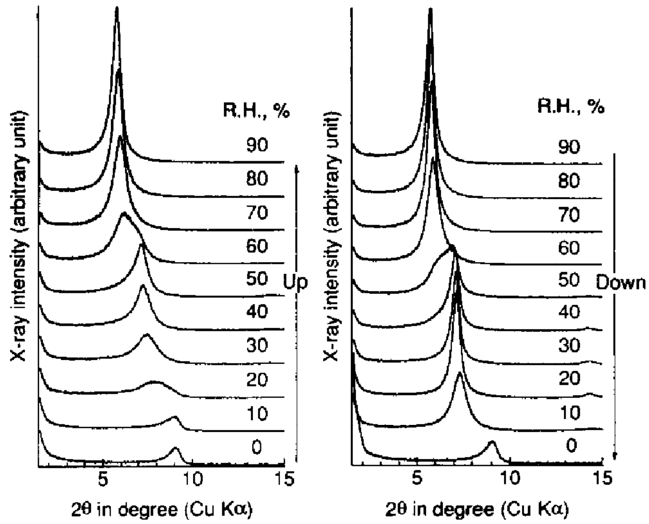

Fig. 3 The XRD patterns of Na-montmorillonite taken at increasing (0% - 90%) relative humidity and decreasing (90% - 0%) relative humidity (RH) and at 30°C. Changes are shown in basal spacing.

(T2) (Fig. 2) as that of the sample chamber (T1) (Fig. 2). The relative humidity in the chamber is monitored by a relative humidity sensor (SIN-El, HUMENT) and fed back to the relative humidity controller that operates the electromagnetic valves (Vl and V2 in Fig. 2).

All controllers are connected to a main computer that also commands the X-ray diffraction analysis. Thus all functions are programmable and XRD measurements can be carried out automatically under controlled relative humidity from 0% to 95%, and temperature from room temperature to 60°C. Deviations in relative humidity and temperatures are ±0.10C and ±0.2%, respectively.

The sample chamber has a wide open window for letting X-ray through. In order to minimize heat diffusion a double kapton $[(C_{22}H_{10}N_{2}0_{4})_{n}]$ film is used as protection,

III. Obtaining X-Ray Diffraction Patterns at Varying Relative Humidity

A. Montmorillonite

The basal spacing of Na-saturated montmorillonite is known to vary with humidity due to a gain or less of interlayer water (e.g. Watanabe and Sato, 1988). For this reason, we selected Na-montmorillonite to demonstrate the function of the present system. The changes in basal spacing under increasing from 0% to 90% and decreasing 90% to 0% relative humidity at 30°C are shown in Fig. 3. The former result was almost identical with that reported by Watanabe and Sato (1988), who carried out their measurements in the air at 25°C.

An interesting observation is the change in basal spacing with decreasing relative humidity. The change of basal spacing showed a hysteresis between increasing and decreasing relative humidity. This will be discussed in detail elsewhere.

B. NaCl

The XRD patterns of NaCi at a relative humidity of 95% are given in Fig. 4 showing crystal lattice collapse due to deliquescence.

IV. Discussion

Using the present system, XRD patterns are conveniently obtained under controlled temperature and relative humidity, each of which can be independently programmed. Moreover, uncertainties in temperature and relative humidity measurements due to imperfect thermal insulation are avoided, because the temperature and relative humidity of the

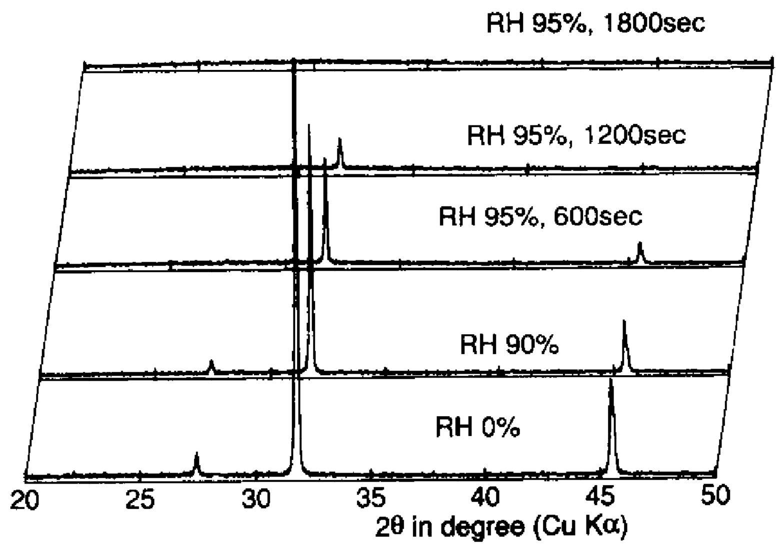

Fig. 4 X-ray pattern of Nacl at different relative humidity (RH) and 30°C. The pattern at 95% RH was obtained after the indicated time of exposure.

sample space are monitored and back-fed to the controllers. The present system is, therefore, an improvement of the previous system (Watanabe and Sato, 1988: Iwasaki and Torii , 1991).

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