THE AMERICAN MINERALOGIST, VOL. 55, SEPTEMBER-OCTOBER, 1970

RANDOM CLAY POWDERS PREPARED BY SPRAY-DRYING

RANDALL HUGHES AND BRUCE BOHOR, *Illinois State Geological Survey, Urbana, Illinois 61801.*

ABSTRACT

A simple and efficient method for spray-drying clay powders has been developed. In conjuction with an examination of kaolinite crystallinity, the sprayer has been tested and shown to be useful in preparing samples for X-ray, electron microscope, and infrared analyses. Samples of illite, smectite, attapulgite, vermiculite and halloysite also were spray-dried and examined in lesser detail by X-ray diffraction and scanning electron microscopy. As shown by X-ray and/or scanning electron microscopy, all of the samples examined were randomized by spray-drying. Individual crystallites may either be arranged randomly within and/or tangentially to the fine-sized spherical droplets produced in spraying. Regardless of the individual aggregate fabric, the large numbers of spheres involved in the total powder diffraction are responsible for the randomization effects attained.

INTRODUCTION

Martin (1966) and Niskanen (1964) have proposed various solutions to problems of orientation in clay powders prepared for X-ray analysis, such as extensive grinding, modified sample holders, and various liquid media to randomize clays. Several of these methods were tested and rejected because (1) they required too much preparation time, (2) they altered the basic properties of the materials studied, or (3) reliable data could not be obtained at the extremes of clay mineral particle charge and shape.

Jonas and Kuykendall (1966) designed a laboratory-sized electrostatic precipitator (spray-dryer) to collect smectite powders for X-ray diffraction and analysis. They showed that the electrostatic precipitator thoroughly randomized smectites which have highly charged, thin, platy particles. Their method was tested by us and gave adequate results, but we found that their equipment lacked efficiency and responded differentially to degrees of clay particle charge (surface charge density).

We tested their equipment to see if both low and high charge clay minerals, having elongate as well as equant crystallites, could be randomized by this method. We found Jonas and Kuykendall's original equipment had to be modified in order to speed the preparation of the large number and volumes of samples involved in geological problems. The prepared samples were examined by X-ray diffraction and the scanning electron microscope (SEM) to determine the extent of randomization. The samples chosen to evaluate shape and charge effects on spray-drying represent the limits of those properties available within clay materials.

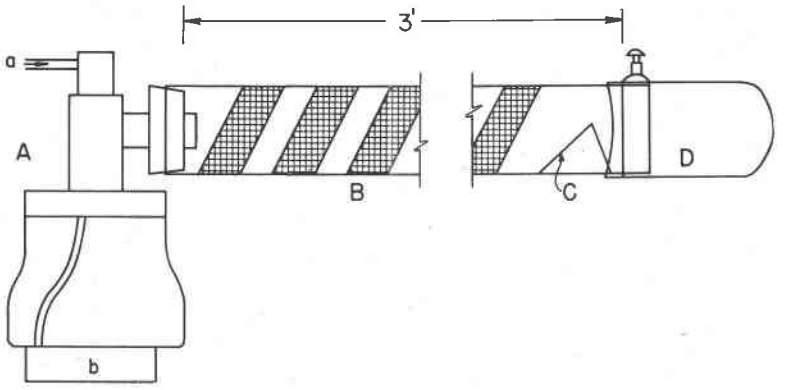

FIG. 1. Schematic drawing of the spray-dryer used in this study showing large volume nebulizer (A), drying tube (B), SEM sample foil (C), paper collector tube (D), compressed air (a), and magnetic stirrer (b).

EQUIPMENT

We have designed our spray-dryer as shown in Figure 1. The efficiency is increased by using a paper extraction thimble collector in place of the electrostatic precipitator used by Jonas and Kuykendall, and by mounting a foil in the air stream to deposit a SEM sample at the same time as the main volume of powder is collected.

The sprayer (A) at the left in Figure 1 is a standard metal, high-volume De Vilbiss nebulizer which operates by passing a stream of compressed air (a) over the open end of a capillary tube. Due to the increased pressure in the chamber, the fine mist moves out through the glass tube (B). Drying is achieved by wrapping a standard heat tape spirally around the length of the tube. Drying is completed within the first two-thirds of the length of the tube (B), and the measured temperature of the exiting air flow is below 150°C. When an SEM sample is needed, it is deposited on a small foil (C) placed at a 45° angle to the air stream near the exit. The dried powder sample is collected in the paper extraction thimble (D) and is easily removed with a camel hair brush. The ease of sample collection and removal is one of the main attributes of the modified equipment. Since many clay processing methods are centered around water suspensions, the spray-dryer can easily be used in sequential testing without loss of efficiency.

SAMPLE PREPARATION

The samples for this study were sized to either <1 μm or <2 μm by settling or centrifuge methods. Normally the fine fraction was flocculated and then redispersed at a higher solids-to-water ratio. Unless the suspension became thixotropic, the high solids suspensions were proportionately more efficient for spray-drying. As shown in Figure 1, a magnetic stirrer (b) placed under the reservoir was used to homogenize the samples and keep them in suspension during spraying.

RESULTS

Definitive estimates of randomization by X-ray powder analysis have several inherent difficulties. Theoretical intensity ratios are valid only to

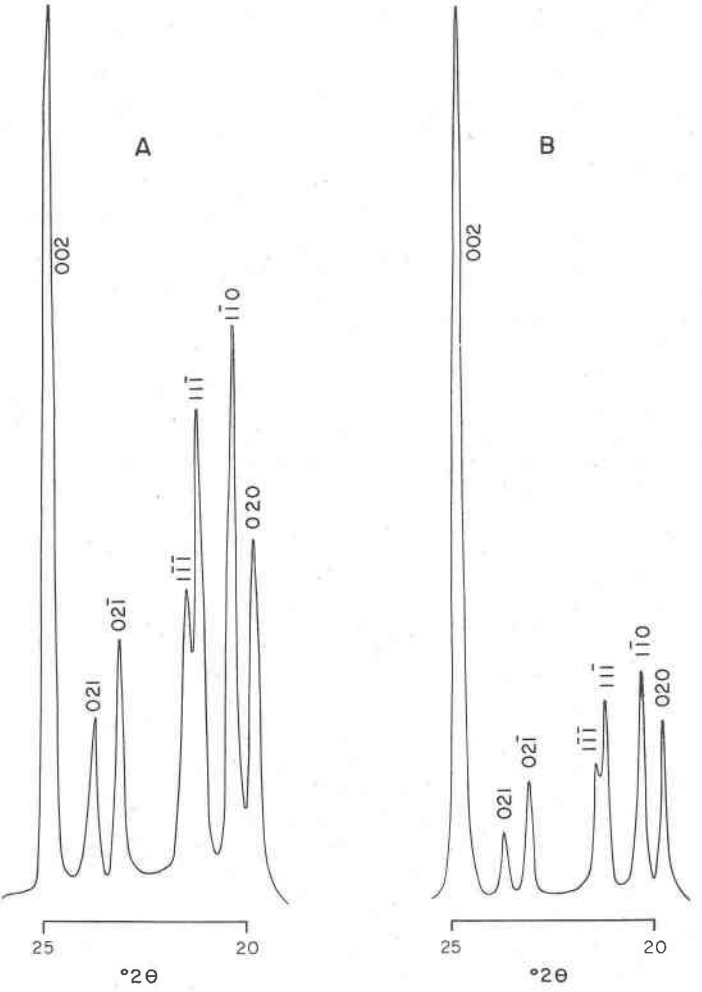

FIG. 2. Comparison of selected interval X-ray diffractograms of samples of spray-dried (A) and mortar-ground (B) kaolinite. Samples were packed in a standard Norelco backloading sampe holder.

the extent that the sample under investigation has the same structural characteristics as the "standard structure." Because published clay mineral structural determinations usually lack the accuracy necessary to calculate absolute intensities, at least two of the following three methods of evaluation should be used in combination for determining randomization: (1) a sample can be compared to the experimental X-ray ratios derived from a similar sample, (2) the sample can be compared to the

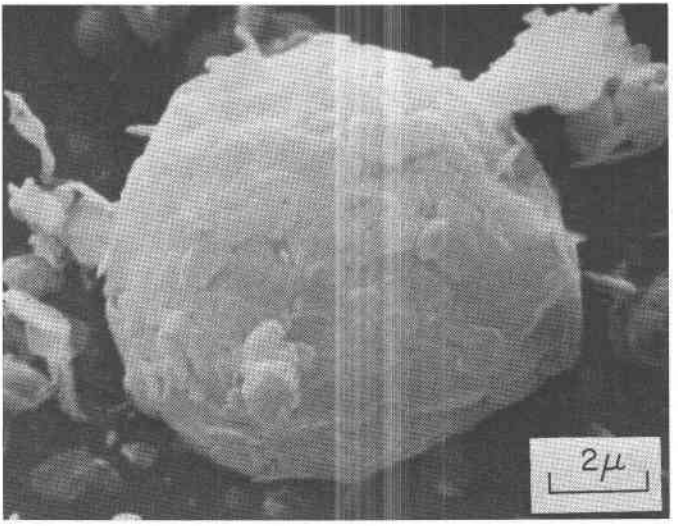

FIG. 3. Scanning electron micrograph of a spray-dried sample of authigenic kaolinite from the St. Peter Sandstone in Illinois.

theoretical intensity ratios based on the most precise structural determination available, or (3) a single peak may be shown to be unaffected by changes in crystal character and therefore comparable on different samples containing equivalent weights of the mineral. The last method is an out-growth of the work of Niskanen (1964) by which he demonstrated that pure, random, kaolinite samples generated a quantitatively uniform $0k0$ intensity without respect to their "crystallinity."

We have checked all three methods and, within the accuracy of our determinations, have shown the spray-dried samples to be random. Figure 2 shows two X-ray diffraction patterns of a well-crystallized kaolinite sample over a selected angular diffraction interval. The first pattern (A) illustrates X-ray peak ratios of the spray-dried sample that are very nearly equal to the experimental X-ray intensities as given in the ASTM X-ray Diffraction File, No. 14–164. The second pattern (B) demonstrates the tendency for accentuation of the 002 peak relative to general *hkl* intensities when a standard (mortar-ground) powder mount is used. The ratios in pattern A of distinct *hkl* indices, with respect to the 002, are comparable to the theoretical values reported by Brown (1961, p. 111–112). Finally, on an absolute scale, the 020 is maximized in this sample and gives an intensity comparable to all the other equally pure kaolinites investigated by the authors.

We also evaluated the X-ray crystallinity of a number of authigenic

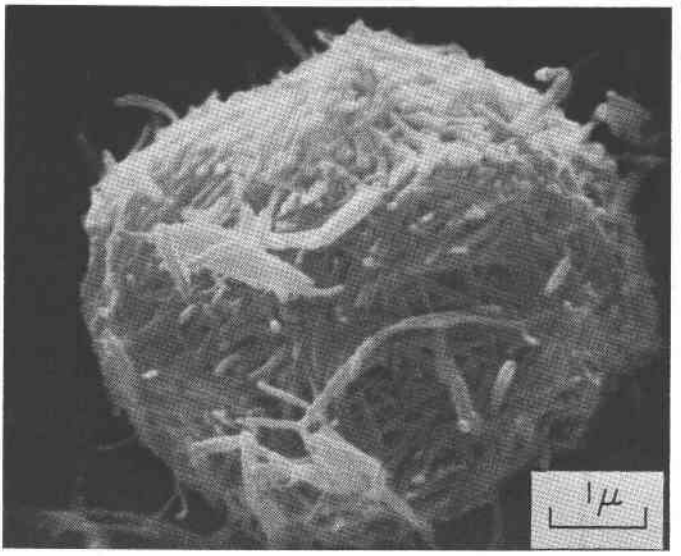

FIG. 4. SEM micrograph of spray-dried attapulgite from the Lower Tertiary of Mexico.

kaolinites. In areas where the geology of the kaolinites indicated predictable differences in crystallinity, these differences were observed in the X-ray patterns. Tests were made of repacked and surface-rubbed powder mounts of the sprayed samples, and only excessive rubbing caused any significant change in the X-ray results.

We concluded that the X-ray patterns of low- and high-particle charge spray-dried clay minerals were random to the accuracy of the X-ray methods used. The same basic logic applied for the evaluation of the other clay mineral groups that were tested. The results from the other clay mineral groups supported exactly the conclusions drawn from the spray-dried kaolinites.

The samples were also examined by scanning electron microscopy. Three representative micrographs are given in Figures 3, 4, and 5. Figure 3 shows the tendency for the ((001)) faces of the individual crystallites in the kaolinite sample to be tangential to the sphere. When clay size particles become more equant, the crystallites tend to randomize progressively along the surface of the sphere. The tendency to a tangential configuration increases as the crystallite's shape becomes more elongate, so that the sprayed attapulgite sphere in Figure 4 is almost totally composed of tangential crystallites.

Figure 5 is a micrograph of a sprayed sample of illite in which low

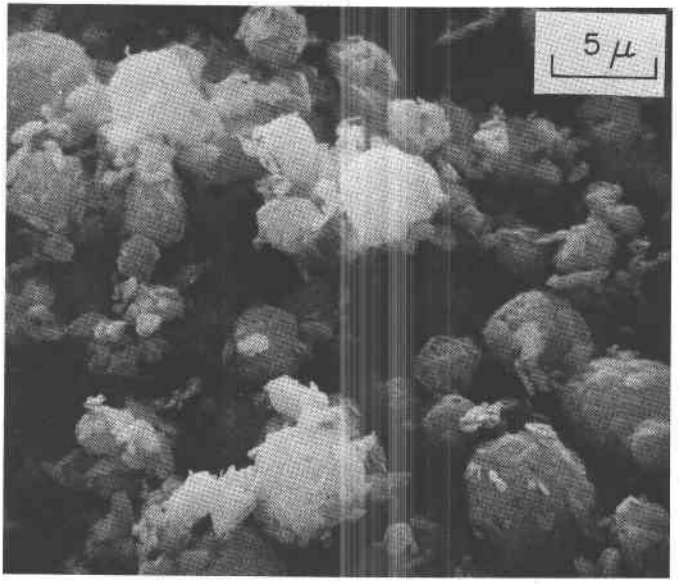

FIG. 5. SEM micrograph of a spray-dried sample of well-crystallized, Silurian illite from the Interlake Formation of Montana.

particle charge is inferred from X-ray behavior. This micrograph also demonstrates the approximate size and numerical ratio between spherical aggregates and free crystallites (dust). Samples of both kaolinite and illite having low-charged particles are shown throughout the study to be as well-randomized as the higher-charged attapulgite and expandable clay mineral groups. Estimates of the sphere size from the micrographs indicated a range of 10 μm to a few tenths of a μm with an average of about 2 μm. The confirmation by SEM of the randomization with this equipment has led to further examinations of the character of individual clay minerals themselves. These results of the SEM investigations are more fully discussed in another report (Bohor and Hughes, 1970).

In summary, spray-drying of clays and similarly-sized minerals produces a very high degree of randomization. The resultant samples can be used in X-ray, infrared and scanning electron microscope analyses with considerable gain in uniformity of results.

ACKNOWLEDGMENT

Financial support from the U.S. Department of Health, Education and Welfare, Public Health Service, National Air Pollution Control Administration, Consumer Protection and Environmental Health Service, through Research Grant No. AP00517 is gratefully acknowledged. We also wish to thank the Center for Electron Microscopy at the University of Illinois for the use of their facilities.

References

Bohor, B. F., and R. E. Hughes (1970) Scanning electron microscopy of clays and related minerals. *Clays Clay Minerals* (in press).

Brown, G. (1961) *The X-ray Identification and Crystal Structures of Clay Minerals*. The Mineralogical Society, London.

Jonas, Edward C., and J. R. Kuykendall (1966) Preparation of montmorillonites for random powder diffraction. *Clay Mineral.* **6,** 232–235.

Martin, R. Torrence (1966) Quantitative fabric of wet kaolinite. *Clays Clay Minerals Proc. Nat. Conf.* **14,** 271–287.

Niskanen, Eric (1964) Reduction of orientation effects in the quantitative X-ray diffraction analysis of kaolin minerals. *Amer. Mineral.* **49,** 705–714.

Manuscript received, March 13, 1970; accepted for publication, May 22, 1970.