# Crystallography of the Hydrates of Calcium Nitrate

**A. WILLIAM FRAZIER, R. C. MULLINS, and JAMES P. SMITH**

**Division of Chemical Development, Tennessee Valley Authority, Wilson Dam, Ala.**

*Methods of preparation, morphological and optical properties, and x-ray powder diffraction spectra of the hydrates of calcium nitrate are reported.*

CALCIUM NITRATE and its di-, tri-, and tetrahydrates occur as solid phases in the systems $Ca(NO_3)_2$–$H_2O$ and $Ca(NO_3)_2$–$HNO_3$–$H_2O$ (*1*, *2*). The crystallographic properties of the cubic anhydride were described by Retgers (*7*), but those of the hydrates have not been described completely. Shepard (*8*) and Marignac (*5*) reported certain properties of the monoclinic tetrahydrate (nitrocalcite), and Larsen (*3*) ascribed to the tetrahydrate properties of the trihydrate that he had determined on a laboratory preparation. Published x-ray diffraction spectra include only those of the anhydride and the tetrahydrate (ASTM 7-204 and 1-0229).

The crystallographic properties reported here of the hydrates of calcium nitrate were determined during the preparation of fertilizers by treatment of phosphate rock with nitric acid.

**Table I. Typical Preparations of Calcium Nitrate**

| Compound | Composition, % Ca | CaO | N | $N_2O_5$ | $H_2O$ (diff.) | Moles/Mole $N_2O_5$ CaO | $H_2O$ | Moles/Mole N Ca | $H_2O$ |
|---|---|---|---|---|---|---|---|---|---|
| Tetrahydrate | 17.1 | 24.0 | 11.8 | 45.4 | 30.6 | 1.02 | 4.05 | 0.51 | 2.03 |
| | 16.9 | 23.7 | 11.8 | 45.5 | 30.8 | 1.00 | 4.06 | 0.50 | 2.03 |
| Theory | 17.0 | 23.75 | 11.86 | 45.74 | 30.51 | 1.00 | 4.00 | 0.50 | 2.00 |
| Trihydrate | 18.2 | 25.5 | 12.7 | 48.9 | 25.6 | 1.01 | 3.14 | 0.50 | 1.57 |
| | 18.2 | 25.5 | 12.6 | 48.6 | 25.9 | 1.01 | 3.20 | 0.51 | 1.60 |
| Theory | 18.4 | 25.71 | 12.85 | 49.52 | 24.78 | 1.00 | 3.00 | 0.50 | 1.50 |
| Dihydrate | 20.1 | 28.2 | 13.9 | 53.6 | 18.2 | 1.02 | 2.05 | 0.51 | 1.03 |
| | 19.9 | 27.9 | 14.0 | 53.8 | 18.3 | 1.00 | 2.05 | 0.50 | 1.02 |
| Theory | 20.0 | 28.02 | 14.00 | 53.97 | 18.00 | 1.00 | 2.00 | 0.50 | 1.00 |
| Anhydrous | 24.4 | 34.1 | 16.9 | 65.3 | 0.6 | 1.01 | 0.06 | 0.51 | 0.03 |
| Theory | 24.4 | 34.17 | 17.08 | 65.83 | 0.00 | 1.00 | 0.00 | 0.50 | 0.00 |

**Table II. Morphological and Optical Properties of Calcium Nitrates**

| Property | $Ca(NO_3)_2 \cdot 2H_2O$ | $Ca(NO_3)_2 \cdot 3H_2O$ | $Ca(NO_3)_2 \cdot 4H_2O$ |
|---|---|---|---|
| Crystal system | Orthorhombic | Orthorhombic | Monoclinic |
| Symmetry class | mmm | mmm | 2/m |
| Morphology | Bipyramids of form {111}, modified by {100}. | Tabular on Ny – Nz, beveled by a pyramid {hkl} form. | Tabular on (100), elongated along *c*; modified by {111}, {110}, and {101}; beta = 98°. |
| Refractive indices | | | |
| Nx | 1.488 | 1.465 | 1.406 |
| Ny | 1.538 | 1.493 | 1.538 |
| Nz | 1.577 | 1.502 | 1.553 |
| Birefringence | 0.089 | 0.037 | 0.147 |
| Optic sign | Biaxial (–) | Biaxial (–) | Biaxial (–) |
| Optic axial angle 2V | | | |
| Calcd. | 80.5° | 58° | 35° |
| Observed | ~75° | 60° | 35° |
| Orientation of OAP | OAP = (100); Bxa = Nx = *c*; a:b:c = 0.809:1:0.716. | OAP (and Nx) ⊥ to tabular plane | OAP = (010); Nx $\wedge c$ = 19° in obtuse beta on (010). |
| Density,[a] grams per cc. | 2.10 | 1.87 | 1.87<br>1.90[b] |

[a] Calculated from Gladstone-Dale relationship (*4*).
[b] Reported by Marignac (*5*).

## *Preparation of Test Material*

The three hydrates of calcium nitrate were crystallized from appropriate solutions, prepared with reagent chemicals, in the system $Ca(NO_3)_2$–$HNO_3$–$H_2O$ (*1*, *2*). All products were coarsely crystalline; they were filtered by suction on coarse, fritted-glass plates, and dried at room temperature in a current of dry air. The preparations used in the characterization studies were shown petrographically to be clean and homogeneous. The compositions of typical preparations are shown in Table I.

Other methods were used to prepare larger quantities of the salt and its hydrates. Anhydrous calcium nitrate was prepared by heating the tetrahydrate at 150° to 190° C. until the viscous melt dehydrated to a dry, white powder. The dihydrate was crystallized from a solution of the anhydrous salt in 95%

**Table III. Powder X-Ray Diffraction Patterns[a]**

| $Ca(NO_3)_2 \cdot 2H_2O$ d, A. | $I/I_1$ | $Ca(NO_3)_2 \cdot 3H_2O$ d, A. | $I/I_1$ |
|---|---|---|---|
| 6.34 | 100 | 6.19 | 100 |
| 4.84 | 22 | 5.90 | 7 |
| 4.53 | 22 | 5.27 | 15 |
| 3.85 | 31 | 4.23 | 7 |
| 3.69 | 9 | 3.91 | 9 |
| 3.17 | 58 | 3.40 | 11 |
| 3.12 | 11 | 3.34 | 7 |
| 2.97 | 11 | 3.29 | 8 |
| 2.86 | 13 | 3.17 | 8 |
| 2.65 | 50 | 3.08 | 59 |
| 2.56 | 17 | 3.00 | 14 |
| 2.50 | 10 | 2.90 | 8 |
| 2.46 | 9 | 2.66 | 8 |
| 2.33 | 16 | 2.61 | 10 |
| 2.26 | 67 | 2.58 | 9 |
| 2.17 | 33 | 2.53 | 7 |
| 2.11 | 68 | 2.45 | 9 |
| 1.96 | 9 | | |
| 1.94 | 19 | | |
| 1.92 | 33 | | |
| 1.88 | 9 | | |

[a] Patterns obtained with a Geiger counter x-ray diffractometer, CuK$\alpha$ radiation, $\lambda$ = 1.5405 A. The intensities of each pattern were measured as peak heights above background and expressed as percentages of the strongest line.

ethyl alcohol. The trihydrate was prepared by addition of the anhydrous salt to a melt of the tetrahydrate until the liquid was saturated at 50° C. The supernatant liquid was decanted off, cooled to 45° C., and seeded, whereupon the mass solidified as the trihydrate. The tetrahydrate was crystallized from its solution in water through use of published data on the system $Ca(NO_3)_2$–$H_2O$ (*1*).

### Properties of the Compounds

The morphological and optical properties of the hydrates of calcium nitrate, summarized in Table II, were observed on several preparations of each hydrate; these properties are sufficient for identification, even when the hydrate is still in its mother liquor. The bipyramidal form of the dihydrate is a useful distinguishing feature, and the birefringence of the dihydrate is more than double that of the trihydrate. Both the tri- and the tetrahydrate usually form highly modified, thick, tabular crystals that are not readily distinguished morphologically, but the extreme birefringence of the tetrahydrate, its low Nx (below that of the mother liquor), and its monoclinic symmetry serve to distinguish it from the trihydrate. Anhydrous calcium nitrate is cubic and has a refractive index of 1.602.

The x-ray powder diffraction pattern of the di- and trihydrates of calcium nitrate are shown in Table III. Patterns of the anhydride and tetrahydrate agree with those in the ASTM card index (7-204 and 1-0229).

The crystal morphology of calcium nitrate tetrahydrate in Table II agrees with that reported by Marignac (*5, 6*). The optical properties determined in a laboratory preparation and ascribed by Larsen (*3*) to the tetrahydrate agree with those reported here for the trihydrate. The trihydrate is orthorhombic, not triclinic as reported by Bassett and Taylor (*1*). The dimorphic form of the tetrahydrate described by Flatt and Fritz (*2*) was prepared, but its dry crystals altered so rapidly to the stable tetrahydrate that it could not be characterized.

### Literature Cited

(1) Bassett, H., Jr., Taylor, H. S., *J. Chem. Soc.* **101,** 576 (1912).
(2) Flatt, R., Fritz, P., *Helv. Chim. Acta* **33,** 2045 (1950).
(3) Larsen, E. S., *U. S. Geol. Survey Bull.* **679** (1921).
(4) Larsen, E. S., Berman, H., *Ibid.,* **848** (1934).
(5) Marignac, *Ann. des Mines* **9,** 28 (1856); quoted in (*1*), (*6*).
(6) Palache, C., Berman, H., Frondel, C., "Dana's System of Mineralogy," Vol. bf. Wiley, New York, 1951.
(7) Retgers, *Z. Kryst. Min.* **21,** 257 (1889); quoted in (*1*).
(8) Shepard, C. U., "Treatise on Mineralogy," Vol. bf. p. 84, 1835; quoted in (*6*).

*Received for review January 21, 1964. Accepted February 27, 1964.*

**FERTILIZER MATERIALS**

# Effect of Calcination on the Character of Phosphate Rock

**H. P. FREEMAN, J. H. CARO, and NORBERT HEINLY**

**U. S. Fertilizer Laboratory, Soil and Water Conservation Research Division, Agricultural Research Service, U. S. Department of Agriculture, Beltsville, Md.**

Two varieties of phosphate rock were calcined under conditions of controlled temperatures and retention times. Physical and chemical properties were measured on the laboratory calcines and on five commercially calcined rocks. Results showed that the response to calcination differs with rock variety. With increasing temperature, a Morocco rock exhibited a sharp collapse of the internal structure of the particles between 500° and 700° C., whereas a Utah rock was less affected. Solubility of phosphorus decreased in the Morocco rock but increased to a maximum at 850° C. in the Utah rock. Changes occurring in both rocks with increase in retention time were pronounced but slow, so that close control of heating time was not necessary. Reactivity of both rocks was decreased by calcination, but the decrease was frequently insignificant. The commercially calcined rocks were apparently treated under conditions corresponding to the threshold of the structural collapse, so that maximum benefits of calcination are being routinely realized.

An appreciable proportion of the phosphate rock mined throughout the world is heated in some sort of furnace before being introduced into fertilizer or animal feed. The objectives of this treatment fall into two broad categories, distinguishable by the temperatures used. In general, processes conducted above 1000° to 1100° C. remove the fluorine and, with use of additives, allow chemical reactions to occur that make the phosphate in the rock available (*16*). Treatments below 1000° C. are carried out to increase the grade of the mineral, remove objectionable organic matter and carbonate, and improve acidulation characteristics, with accompanying economic advantages. Other effects include improvement in grindability and decrease in bulk density (*13*).

The higher temperature treatments bring about gross changes, such as sintering or fusion, that are readily apparent on examination of individual particles of the rock. The changes occurring at the lower temperatures, on the other hand, are not well defined. This paper reports the results of a systematic examination of the character of rocks from different geographic deposits as affected by low-temperature calcination.

### Scope of Investigation

The study was designed to allow description of the changes in phosphate rock effected by variation in both