

# Hygroscopicity of Complex Fertilizers

## Effect of Calcium Nitrate and Water Concentrations on Critical Relative Humidity of Ammonium Nitrate–Limestone

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Vacuum line techniques were used to measure the hygroscopicity of ammonium nitrate–limestone under typical storage conditions of low water and calcium nitrate concentrations. The results show that the critical relative humidity of samples with constant calcium nitrate content increases with increasing water content above a minimum water level. This water level increases with increasing

calcium nitrate concentration. Similarly, the critical relative humidity of samples with constant water decreases with increasing calcium nitrate concentration. Temperature did not greatly affect the critical relative humidity of a sample with constant water and calcium nitrate concentrations in the range of 25° to 40° C. A solubility phase diagram is used to explain these experimental results.

Ammonium nitrate–limestone (AN-L) is a fertilizer consisting mainly of ammonium nitrate and calcium carbonate. Commercially it is formed by the physical mixing in some manner of these two compounds or by the reaction of calcium nitrate with ammonium carbonate. Even small amounts of calcium nitrate in such fertilizers markedly increase their hygroscopicity. However, up to the present time the effect of small calcium nitrate concentrations on the critical relative humidity of AN-L has not been quantitatively determined. In this report, critical relative humidity is defined as that equilibrium relative humidity above which a given fertilizer will absorb water from the atmosphere. Novak (1967) studied the hygroscopicity of this system over the entire range of 0 to 100% calcium nitrate by a method based on the gross absorption of water in desiccators at several different relative humidities. This latter work presents only one data point in the range 0 to 2% calcium nitrate and ignores the effect of water on the critical relative humidity of this system, which the present work showed to be an important factor. The purpose of this work was to determine the critical relative humidity of AN-L fertilizers under the typical storage conditions of low water and calcium nitrate concentrations.

### EXPERIMENTAL PROCEDURE

The calcium nitrate content of several commercial AN-L samples was determined by the method of Roy and Bhatnagar (1964). Calcium nitrate was extracted with ammoniacal methanol solution and the calcium content of this extract determined gravimetrically. Just prior to measuring the critical relative humidity of these samples, their free water content was determined by vacuum oven methods. After the determination of the critical relative humidity of these samples according to the vacuum line method described by Geissler (1968), their gain or loss of

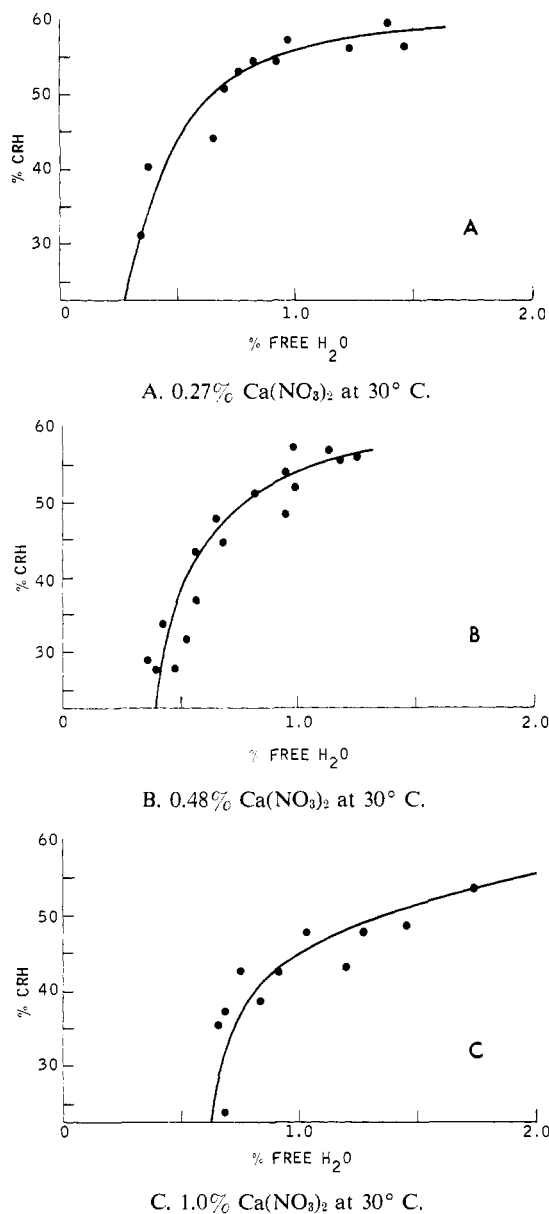
water was measured by weighing. This change in water was then combined with the free water content determined by the vacuum oven method to give a total free water content of the AN-L for which the critical relative humidity was measured.

### RESULTS AND DISCUSSION

Figure 1A shows the effect of the per cent free water on the critical relative humidity of AN-L samples containing 0.27 wt. % calcium nitrate at a constant temperature of 30° C. No significant differences in critical relative humidity were observed between samples containing equal amounts of calcium nitrate obtained from separate commercial sources. All samples used in this study contained 26% nitrogen. However, the concepts discussed here apply equally as well for both 21 and 26% AN-L. The critical relative humidity at very low water concentrations is constant at 23% and increases rapidly with further increase in water above 0.3% free water. It begins to level off at 1% free water, when the critical relative humidity of pure ammonium nitrate, equal to 59%, is approached. Figure 1B shows the effect of per cent water on critical relative humidity of AN-L samples with 0.48% calcium nitrate. Again, the critical relative humidity at low water concentrations is 23% and increases rapidly with increasing free water content until the critical relative humidity of pure ammonium nitrate is approached. However, in this case, the threshold for increasing critical relative humidity is at a higher free water content. Figure 1C shows similar results for AN-L samples containing 1.0% calcium nitrate. As before, a sharp increase in critical relative humidity with increasing water is observed, with its threshold at a still higher water content of about 0.6%. At these higher calcium nitrate concentrations, the approach of the critical relative humidity of the system to that of pure ammonium nitrate is much more gradual with increasing water, with concentrations of greater than 2% water needed to give a critical relative humidity of more than 55%. Other curves were obtained for commercial samples with different calcium nitrate contents. These are not presented because in general they had similar shapes and were all displaced toward lower critical relative humidity values and higher

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**Figure 1. Critical relative humidity of ammonium nitrate-limestone**

moisture contents with increasing calcium nitrate contents.

These observed experimental results are most easily explained with solubility or phase rule concepts. Lamberger and Paris (1948) established the phase diagrams for the water-calcium nitrate-ammonium nitrate system at 10°, 20°, and 30° C. A portion of their diagram at 30° C. is shown in Figure 2. Ammonium nitrate-limestone can be considered as a binary mixture of ammonium nitrate and calcium nitrate. The latter is formed during production or storage by the reaction of ammonium nitrate and calcium carbonate. This binary treatment ignores the presence of calcium carbonate, and is valid because the critical relative humidity of the system is not influenced by calcium carbonate due to its insolubility in water. In the lower portion of the triangle of Figure 2 bounded by the points calcium nitrate-ammonium nitrate dihydrate, ammonium nitrate, and point *M*, all compositions exist as vary-

ing proportions of three phases—that is, solid ammonium nitrate, solid double salt, and a saturated solution whose composition is given by the coordinates of point *M*. Since the critical relative humidity of any such system is determined by the vapor pressure of this saturated solution, all points within this triangular area must have a unique critical relative humidity. In the fan-shaped area bounded by ammonium nitrate and points *N* and *M*, all compositions exist in two phases—that is, solid ammonium nitrate and saturated solutions whose compositions are given by the solubility curve connecting points *N* and *M*. The saturated solution for such a given over-all composition is given by that point on the saturation curve *M-N* which lies on the end of the tie-line passing through the over-all composition point and the ammonium nitrate corner. The critical relative humidity of this over-all composition point would then be determined by the saturated solution and would lie somewhere between the value for pure ammonium nitrate and the unique value exhibited by all the compositions in the lower triangular area.

The effect of free water concentration on the critical relative humidity of AN-L containing a small amount of calcium nitrate (present at equilibrium as the dihydrated double salt but reported in Figure 1 as per cent calcium nitrate) can now be examined. The free water rather than total water contents are used in order to neglect the water that is tied up in this hydrated double salt. In general, better data correlations are obtained when free water rather than total water contents are used in Figure 1. In the absence of any free water, the total composition of such a fertilizer is given by point *W*. As water is added to this system the critical relative humidity is that corresponding to solution *N* or, as has been found experimentally, equal to 23%. The critical relative humidity does not change with increasing water until sufficient water is present to place the total composition within the fan-shaped area—that is, water concentrations higher than point *X*. As more water is now added to the system, the saturated solutions in equilibrium with pure ammonium nitrate change in composition along the saturation curve *M-N*, but cannot become higher in water content than point *Y*. As these change in composition, the critical relative humidity of the over-all system also changes. The change will be an increase since more dilute saturated solutions with increasing vapor pressures are formed as more water is added. If the over-all anhydrous ammonium nitrate fertilizer contains a higher percentage of calcium nitrate, then point *W* lies farther away from the ammonium nitrate corner—that is, lies farther to the left. On the addition of water to this system, the critical relative humidity of 23% applies over a larger range of water concentrations. Thus, more water is needed to place the over-all composition point within the fan-shaped area ammonium nitrate-*M-N*. However, once this water content is exceeded the critical relative humidity again increases with increasing water concentration, as the saturated solutions change in composition along the curve *M-N*. This explains why the critical relative humidity of AN-L fertilizers increases with increasing water content at constant calcium nitrate concentrations until the critical relative humidity of ammonium nitrate is approached and why the threshold for this increasing relative humidity

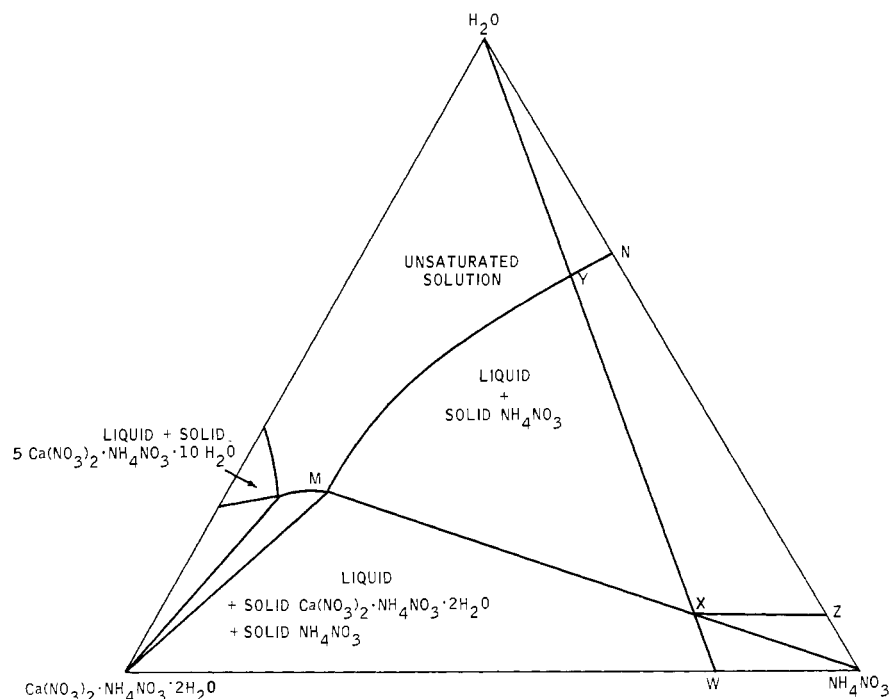


Figure 2.  $\text{Ca}(\text{NO}_3)_2 \cdot \text{NH}_4\text{NO}_3 \cdot 2\text{H}_2\text{O} - \text{NH}_4\text{NO}_3 - \text{H}_2\text{O}$  phase diagram on equivalent % basis, 30° C.

occurs at higher water concentrations with increasing calcium nitrate concentration.

The data on critical relative humidity *vs.* the per cent of water for the various AN-L samples with different calcium nitrate contents were reworked to establish the effect of calcium nitrate concentration on the critical relative humidity of AN-L samples at constant free moisture contents. From individual curves similar to those shown in Figure 1 for each of the AN-L samples tested, the critical relative humidities at definite free moisture contents were obtained for samples with varying calcium nitrate concentrations. In this manner, straight-line relationships between critical relative humidity and the per cent of calcium nitrate were generated for several water concentrations. These are shown in Figure 3. At constant moisture contents, critical relative humidity decreases from 59 to 23% with increasing calcium nitrate, with the decrease becoming less severe as the water content is increased.

To explain these results, the effect of calcium nitrate impurity on the critical relative humidity of AN-L at a constant water content is followed. Pure ammonium nitrate-limestone at a finite water level is represented by a point such as Z in Figure 2. Its critical relative humidity is determined by the composition of the saturated solution in equilibrium with solid ammonium nitrate or point N, and has a value of 59%. As the calcium nitrate concentration increases and the free water content remains constant, the over-all composition varies along line Z-X. As this is done, the saturated solutions vary along the saturation curve and the critical relative humidity decreases. When sufficient calcium nitrate is present to place the over-all composition within the lower triangle bounded by the double salt, ammonium nitrate, and point M, the critical

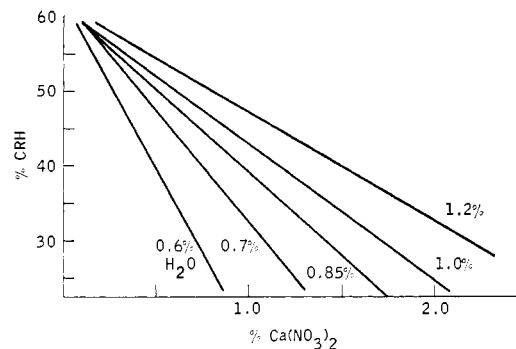


Figure 3. Critical relative humidity of ammonium nitrate-limestone at different water and  $\text{Ca}(\text{NO}_3)_2$  concentrations at 30° C.

relative humidity is equal to 23%, its lowest possible value. If the water content of the original ammonium nitrate-limestone is lower than point Z, the decrease from 59 to 23% in the critical relative humidity requires less calcium nitrate. This is in complete agreement with the experimental results.

A series of experiments was run to determine the effect of temperature on the critical relative humidity of an AN-L sample that contains constant amounts of both water and calcium nitrate. The critical relative humidity of samples with calcium nitrate concentrations of 0.5% was determined as a function of water content at several different temperatures. At each temperature the critical relative humidity at 0.5% free water was read from the curves obtained, which were similar to those shown in Figure 1B. Figure 4 shows this final data as the effect of temperature

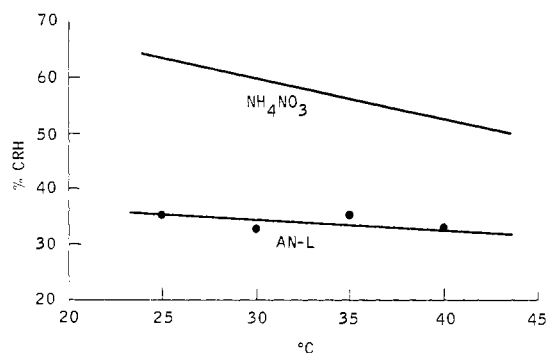


Figure 4. Critical relative humidity of ammonium nitrate-limestone at 0.5% water and 0.5%  $\text{Ca}(\text{NO}_3)_2$

on the critical relative humidity of AN-L with constant calcium nitrate and water concentrations of 0.5%. Also shown is the effect of temperature on the critical relative humidity of pure ammonium nitrate. Apparently, temperature is not a significant variable in the determination of the critical relative humidity of such systems.

Although the phase rule interpretation presented here satisfactorily explains all of the experimental data, it only does so in a qualitative manner. Up to now, there is no way of predicting the exact shape of the critical relative humidity curves, such as those experimentally determined for the ammonium nitrate-limestone system.

It is well known that the value for the critical relative humidity is independent of the weight ratio of solid components in equilibrium with the saturated solution of a multicomponent fertilizer. But, if the solution becomes saturated with newly formed components, or if any component disappears from the solid phase of the system, then the critical relative humidity of the mixture will be altered. The results of this work indicate that, in order to be meaningful, reported values for the critical relative humidity of multicomponent or complex fertilizers must be accompanied by accurate data on moisture content of the sample and on temperature of the determination. The presence in the mixture of small amounts of highly soluble components that form a eutectic can alter the critical relative humidity appreciably when slight variations occur in moisture content or temperature. Fortunately, the moisture contents of most complex fertilizers are low enough to ensure a constant critical relative humidity value over a relatively wide range of moisture values at any given temperature.

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Received for review January 2, 1968. Accepted February 21, 1968.  
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