# ENVIRONMENTAL AGEING OF BASIC COPPER NITRATE

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## I. Introduction

Industries that require highly reliable technologies depend on precisely engineered materials and processes to ensure consistent performance. [1] For example, in the world's leading pyrotechnic airbag technology, a rapid reaction between Basic Copper Nitrate ($Cu_2(OH)_3(NO_3)$, BCN) and guanidine nitrate produces nitrogen gas, which inflates the airbag—producing life-saving results. [2] The reaction between BCN and guanidine nitrate can be impacted by the physical properties of the two reactive components, such as particle size, surface area, porosity, density, and moisture content. [3] Changes in these particle parameters could cause undesired changes in performance. Modern manufacturing and engineering practices such as Six Sigma and PFMEA have drastically improved our ability to hone the properties of these manufactured particles. However, the challenge is understanding how the materials will age over time through exposure to environmental conditions after the point of manufacturing. The focus of this study is to better understand how different environmental conditions will impact the physical properties of BCN and other related materials over time.

The results herein provide a framework for understanding how humidity and temperature impact the physical properties of BCN such as surface area, particle size, density, pH, and moisture content. We offer interpretation of these results under theories of particle evolution, including ostwald ripening. For perspective, we have also looked at the effects of temperature and humidity on the morphology of related materials, including copper oxide, copper nitrate crystals, and ammonium nitrate. Finally, we'll present initial results on how packaging and changes in particle preparation can impede the effects of temperature and humidity on critical parameters like surface area.

## II. Methods

Samples of BCN, copper nitrate crystals ($Cu(NO_3)_2.3H_2O$), and copper oxide ($CuO$) were prepared by proprietary manufacturing methods of The Shepherd Chemical Company. Ammonium nitrate was purchased from Aldrich. Samples were aged in a CSZ ZP-8-2-H/AC Temperature/Humidity Test Chamber with a relative humidity (RH) range of 5 to 98 ± 3% and a Temperature range of -34 to 190 ± 0.5 °C. For testing purposes, samples were stored in the chamber for 5 days at the designated conditions unless specified otherwise. Scanning electron microscopy (SEM) analysis was performed using a Hitachi SU5000. Samples were coated with gold using a Cressington 108Auto Sputter Coater for 60 seconds to limit charging. XRD measurements were conducted using a Rigaku Miniflex 600. Unless otherwise noted, x-ray powder diffractograms were recorded from 5 to 90 degree 2-theta with 40 kV voltage and 15 mA current. The instrument step size 0.05 degrees at a rate of 5 degrees/min. For BET measurements samples were degassed using a Micromeritics SmartPrep degasser and subsequent analysis was conducted using a Micromeritics Tristar 3020 surface analyzer. Bulk density was measured using a 50 mL graduated cylinder. Tap density was measured by tapping the sample 1000 times using a PharmaAlliance Group Tap Density Tester TD-12. Moisture content was measured at 80 and 105 °C using a Mettler HX204 moisture balance. pH measurements were conducted on a solution composed of 17.5 grams of the product in 20 mL of deionized water. Particle size analysis was conducted on either a Microtrac S3500 or Microtrac X100 analyzer.

## III. RESULTS & DISCUSSION

### 5 Day BCN Ageing

**Table 1.**

BCN Surface Area ($m^2/g$)

| Relative Humidity (%-RH) | 8 °C | 25 °C | 50 °C | 65 °C | 85 °C |
|---|---|---|---|---|---|
| 95%-RH | 3.28 | | 2.55 | 2.60 | 2.05 |
| 75%-RH | | 2.83 | 2.26 | 2.06 | 1.90 |
| 50%-RH | 4.15 | 3.87 | 3.16 | 2.99 | 2.18 |
| 25%-RH | | 4.22 | 4.18 | 4.00 | |
| 5%-RH | 4.56 | | 4.54 | | 4.10 |
| 0 | | | | | |

Temperature (°C)

**Figure 1.** Change in BCN Surface Area (5 Day Exposure)

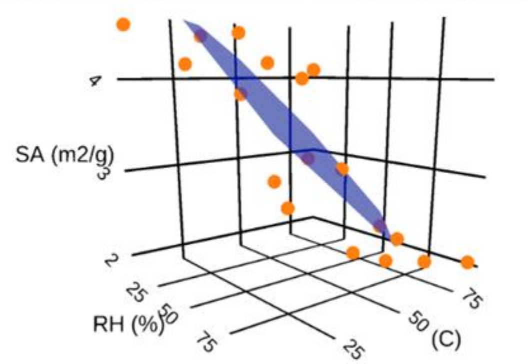


**Table 1 and Figure 1.** BCN Surface Area Measurements as a Function of Relative Humidity and Temperature (left); 3D scatter Plot of BCN Surface Area (SA) Measurements Over 5 Days of Exposure to Temperature (C) and Humidity (RH%), and the Corresponding Best Fit Plane (right)

A recently manufactured lot of BCN was sampled and aged under temperature and relative humidity conditions ranging from 8-85 °C and 5-95% RH, respectively. All samples were analyzed for changes in surface area, particle size, density, SEM, and XRD. Of the properties measured, surface area (Table 1 and Figure 1) and SEM (Figure 2) data showed the most consistent behavior across all conditions. In general, surface area tends to decrease with increasing temperature. For instance, at a constant 5% RH, increasing the temperature from 8 °C to 85 °C resulted in a surface area decrease from $4.5m^2/g$ to $4.1m^2/g$ for an approximate 9%

decrease. Similarly, but to a much greater extent, surface area decreases with increasing relative humidity. For instance, at a constant temperature of 8 °C, increasing the relative humidity from 5% to 95% resulted in a surface area decrease from 4.5m$^2$/g to 3.3m$^2$/g, an approximate 26% decrease. The largest change in surface area is observed when both temperature and humidity are increased, resulting in a surface area of 2.05 m$^2$/g at 85 °C and 95% RH—a 55% reduction in surface area. Under the most extreme conditions evaluated (i.e., low humidity/low temperature and high humidity/high temperature), the surface area levels off setting a maximum and a minimum for the experimental conditions. Data between these conditions were graphed and modeled with a best fit plane (eq. 1).

$$Surface\ Area = -0.02(\%RH) - 0.03(Temp.) + 5.73\ (eq.\ 1)$$

Although qualitatively, humidity seems to have the most significant impact on surface area, the similarity of the coefficients in this equation suggests these two factors play an equal role in the ageing process. It is important to note that the data presented above was collected on a single manufactured lot of BCN. Within the 5 samples evaluated under each condition, the average standard deviation in the surface area measurement was 0.13 m$^2$/g. Different manufactured lots of BCN evaluated in this study exhibited similar trends in surface area decrease with increasing temperature and relative humidity, however, the absolute change in surface area varied between each.

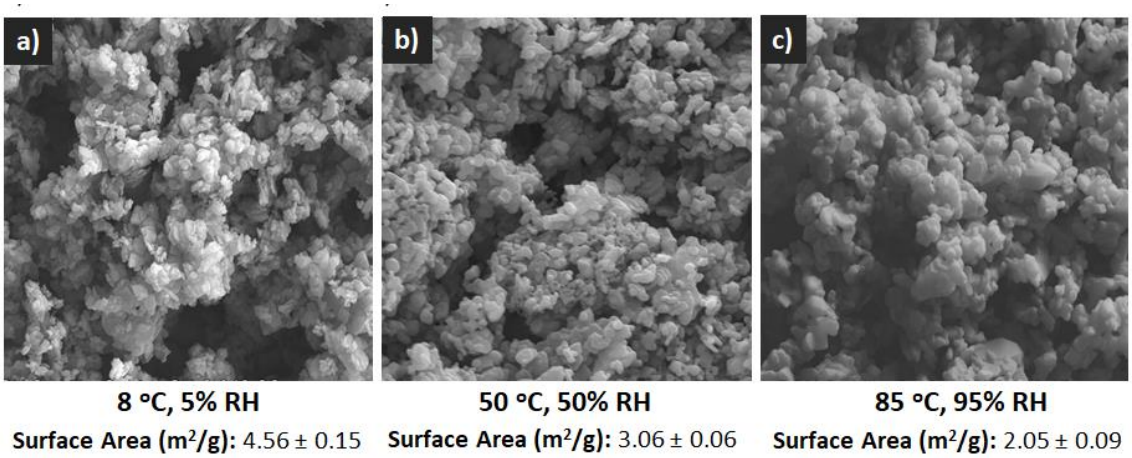


**Figure 2.** SEM Images of BCN at a) 8 °C and 5% RH, b) 50 °C and 50% RH, and c) 85 °C and 95% RH.

SEM images of BCN before and after exposure to heat and humidity reveal the physical morphology changes (Figure 2) under the given set of conditions. At low temperature and humidity, the particles can be described as aggregates of small, plate-like crystals. At 50 °C and 50% RH, the particles appear larger and smoother than they do at the lowest conditions. At 85 °C and 95% RH, the particles are starting to grow together forming larger clumps consistent with decreased surface area and an ostwald ripening-like process. Interestingly, preliminary kinetics studies show that the most significant decrease in surface area decay occurs within the first 24 hours. For instance, a sample of BCN with an initial surface area of 4.7 $m^2/g$ decreased to 2.6 $m^2/g$ within the first 24 hours of storage at 85 °C and 95% RH. The sample would continue to age over the next 4 days but only show an additional decrease of 0.4 $m^2/g$. However, BCN exposed to 50% RH and 50 °C only resulted in a final surface area of 3.2 $m^2/g$. This observation suggests that the decrease in surface area might be similar to an exponential decay process where the rate of decay is dependent on the humidity and temperature. However, more experiments are needed to elucidate this observation. Other characterization data like particle size, moisture content and density show some sample to sample variability, but nothing consistent with changes in temperature and humidity (Tables 2-7). XRD patterns of BCN showed no significant changes after exposure for 5 days, indicating that changes in surface area and particle morphology does not impact the crystalline lattice (Figure 3). In other words, although samples are showing a decrease in surface area, the observed material is still BCN.

Table 2.

BCN Tap Density (g/mL)

Relative Humidity (%-RH)

| 0 | 8 °C | 25 °C | 50 °C | 65 °C | 85 °C |
|---|---|---|---|---|---|
| 95%-RH | 0.70 | | 0.72 | 0.70 | 0.72 |
| 75%-RH | | 0.68 | 0.69 | 0.67 | 0.67 |
| 50%-RH | 0.70 | 0.70 | 0.68 | 0.68 | 0.69 |
| 25%-RH | | 0.71 | 0.70 | 0.69 | |
| 5%-RH | 0.70 | | 0.70 | | 0.72 |

Temperature (°C)

Table 3.

BCN Bulk Flow Density (g/mL)

Relative Humidity (%-RH)

| 0 | 8 °C | 25 °C | 50 °C | 65 °C | 85 °C |
|---|---|---|---|---|---|
| 95%-RH | 0.46 | | 0.51 | 0.49 | 0.52 |
| 75%-RH | | 0.45 | 0.51 | 0.46 | 0.47 |
| 50%-RH | 0.484 | 0.48 | 0.45 | 0.48 | 0.48 |
| 25%-RH | | 0.48 | 0.47 | 0.45 | |
| 5%-RH | 0.48 | | 0.47 | | 0.50 |

Temperature (°C)

Table 4.

BCN Moisture Balance at 80°C

Relative Humidity (%-RH)

| 0 | 8 °C | 25 °C | 50 °C | 65 °C | 85 °C |
|---|---|---|---|---|---|
| 95%-RH | 0.30 | | 0.32 | 0.21 | 0.29 |
| 75%-RH | | 0.27 | 0.28 | 0.20 | 0.21 |
| 50%-RH | 0.25 | 0.25 | 0.20 | 0.18 | 0.14 |
| 25%-RH | | 0.26 | 0.19 | 0.24 | |
| 5%-RH | 0.30 | | 0.16 | | 0.18 |

Temperature (°C)

Table 5.

BCN Moisture Balance at 105°C

Relative Humidity (%-RH)

| 0 | 8 °C | 25 °C | 50 °C | 65 °C | 85 °C |
|---|---|---|---|---|---|
| 95%-RH | 0.39 | | 0.42 | 0.34 | 0.34 |
| 75%-RH | | 0.39 | 0.37 | 0.29 | 0.28 |
| 50%-RH | 0.32 | 0.35 | 0.27 | 0.26 | 0.21 |
| 25%-RH | | 0.34 | 0.29 | 0.32 | |
| 5%-RH | 0.30 | | 0.26 | | 0.26 |

Temperature (°C)

Table 6.

BCN pH

Relative Humidity (%-RH)

| 0 | 8 °C | 25 °C | 50 °C | 65 °C | 85 °C |
|---|---|---|---|---|---|
| 95%-RH | 4.98 | | 5.16 | 5.05 | 4.81 |
| 75%-RH | | 5.09 | 4.71 | 5.13 | 4.96 |
| 50%-RH | 5.25 | 5.22 | 5.21 | 5.13 | 5.47 |
| 25%-RH | | 5.27 | 5.23 | 5.25 | |
| 5%-RH | 5.43 | | 5.30 | | 5.33 |

Temperature (°C)

Table 7.

BCN Particle Size Distribution ($D_{50}$)

Relative Humidity (%-RH)

| 0 | 8 °C | 25 °C | 50 °C | 65 °C | 85 °C |
|---|---|---|---|---|---|
| 95%-RH | 4.44 | | 4.12 | 4.40 | 3.74 |
| 75%-RH | | 4.36 | 4.29 | 4.48 | 4.99 |
| 50%-RH | 4.20 | 4.16 | 4.25 | 4.31 | 5.01 |
| 25%-RH | | 4.28 | 4.13 | 4.27 | |
| 5%-RH | 4.04 | | 4.30 | | 3.85 |

Temperature (°C)

**Tables 2-7.** Impact of BCN ageing on the following particle properties: Tap Density (Table 2, top left), Flow Density (Table 3, middle left), pH (Table 4, bottom left), Moisture Content at 80 °C (Table 5, top right), Moisture Content at 105 °C (Table 6, middle right), and $D_{50}$ Particle Size Distribution (Table 7, bottom right)

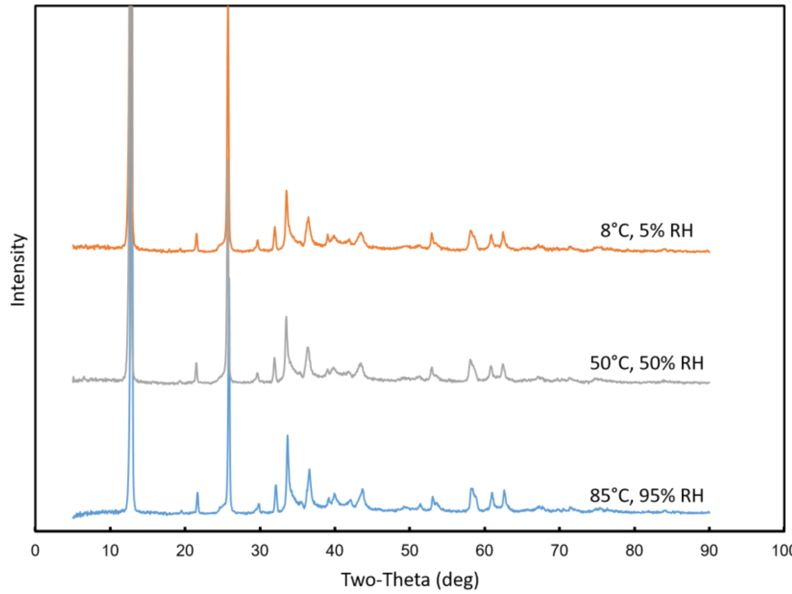


**Figure 3.** XRD data of BCN after 5 day exposure to the following conditions: 8 °C and 5% RH (top), 50 °C and 50% RH (middle), and 85 °C and 95% RH (bottom).

**Ageing of Related Materials**

To understand how the ageing of BCN compares to related materials, we studied the effect of temperature and humidity on ammonium nitrate ($NH_4NO_3$), copper nitrate crystals ($Cu(NO_3)_2.3H_2O$), and copper oxide (CuO). The solubilities of these materials vary greatly, with ammonium nitrate (297 g/100 mL at 40 °C) and copper nitrate crystals (381 g/100 mL at 40°C) showing the greatest water solubility, followed by BCN (0.015 g/100 mL at 50 °C) and copper oxide (insoluble). [4] It was anticipated that the materials with the greatest water solubility will be more susceptible to ageing. Similar to the BCN trials, samples of CuO, $Cu(NO_3)_2.3H_2O$ and $NH_4NO_3$ were stored in temperatures and relative humidities ranging from 8 °C to 85 °C and 5% to 95%, respectively. Since ammonium nitrate and copper nitrate crystals are water soluble and exhibit significant deliquescence at ambient conditions, the materials dissolved under moderate temperatures and humidities preventing the collection of surface area data for these materials under many conditions. However, CuO showed similar behavior to BCN. Specifically, a sample of CuO with a starting surface area 24 $m^2$/g decreased to 20.9, 17.8 and 16.9 $m^2$/g after storage at 25 °C and 25% RH, 65 °C and 75% RH, and 85 °C and 95% RH for 5 days, respectively (Table 8). Unlike BCN, SEM images of CuO do not show definitive evidence of particle size growth due to ostwald ripening (Figure 4). Additional studies are required with either more harsh conditions or longer storage periods to understand if the change in surface area correlates with visible changes in the particles.

**Table 8.** Copper oxide surface area as a function of temperature and relative humidity

Copper Oxide Surface Area

| Relative Humidity (%-RH) | 8 °C | 25 °C | 50 °C | 65 °C | 85 °C |
|---|---|---|---|---|---|
| 95%-RH | | | | | 16.87 |
| 75%-RH | | | | 17.80 | |
| 50%-RH | | | | | |
| 25%-RH | | 20.94 | | | |
| 5%-RH | 23.81 | | | | |
| 0 | | | | | |

Temperature (°C)

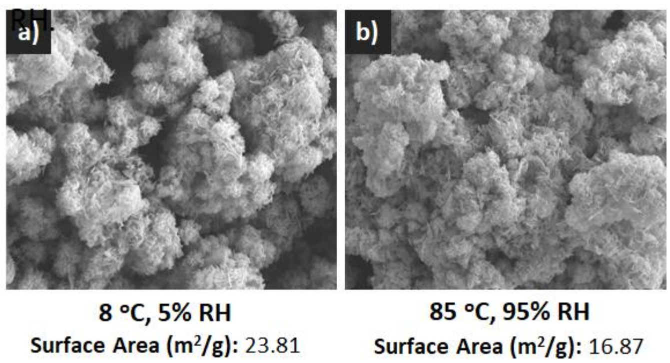


**Figure 4.** SEM images of CuO at a) 8 °C and 5% RH, and b) 85 °C and 95% RH.

## Protecting BCN Materials Through Improved Packaging

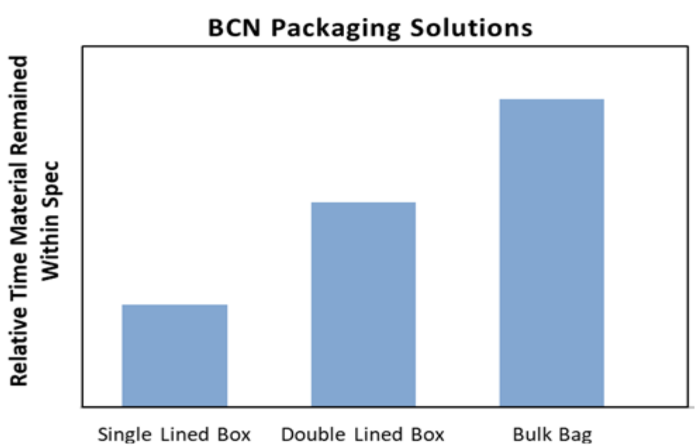


**Figure 5.** Dependence of BCN Stability on Packaging

Based on the above information, one of the best techniques for suppressing BCN ageing is to limit its exposure to moisture. In comparison to the open jar experiments discussed above, effective packaging is a very practical method for improving the surface area stability of these types of material. To illustrate this point, we evaluated the impact of 3 different packaging options (single lined box, double lined box, and bulk bag) on the relative time that manufactured BCN would still meet our product's surface area specification when stored under in a warehouse without climate control in Cincinnati, OH. As expected, batches of BCN boxed with a double polyethylene liner continued to meet specifications for approximately twice as long as batches packaged in a box with a single polyethylene liner. Bulk bags with moisture resistant polymer liner exhibits significantly more protection from the outside humidity. This observation is almost certainly due to slower diffusion of moisture through the bulk product since these packages contain significantly more material than the smaller boxes. These results illustrate that choices in packaging can play a critical role in the shelf-life of BCN.

**Advancing BCN Materials to Resist Ageing**

Additionally, we are evaluating new proprietary synthetic techniques to reduce BCN's susceptibility to moisture accelerated ageing. Initial results suggest that modifications to the preparation process can have a drastic impact on how BCN ages in the presence of elevated temperatures and moisture (Table 2). For instance, 5 samples of BCN prepared under our new proprietary method showed no significant change in surface area after exposure to 95% relative humidity and 50 °C for 5 days. However, our standard BCN exhibited an approximate 30% drop in surface area over the same period of time.

**Table 9.** Surface area measurements before and after exposure to 50 ºC and 95% RH for samples of BCN prepared with the standard synthesis vs. proprietary BCN synthesis

| | Surface Area Measurement Before Exposure ($m^2/g$) | Surface Area Measurement After Exposure ($m^2/g$) |
|---|---|---|
| **Standard BCN** | 4.77 | 3.43 |
| **Proprietary BCN Synthesis** | 4.72 ± 0.22 | 4.54 ± 0.10 |

**Conclusions**

As seen with BCN, CuO, $Cu(NO_3)_2.3H_2O$ and $NH_4NO_3$, most inorganic materials will age over time as they are exposed to different environmental conditions. The aim of this study was to characterize the ageing process for BCN and related materials, and use this information to design new particles, processes or packaging to help protect these chemicals from environmental ageing. From this study we have shown that BCN undergoes environmental ageing through an ostwald ripening-like process. However, the limited solubility of BCN makes the ripening process more like that of CuO as opposed to $Cu(NO_3)_2.3H_2O$ and $NH_4NO_3$ which dissolve under conditions above 50 °C and 50% RH. SEM data provides further verification that the ageing process involves increasing the size of the primary particles and sintering of the aggregated particles through an ostwald ripening-like process which results in the decrease of surface area. Despite the changes in particle morphology, the crystalline morphology remains unchanged under the conditions evaluated in this study, therefore BCN remains as BCN. Other physical properties like particle size, density, moisture and pH did show some variability, but not consistent with changes in temperature or relative humidity. We also explored how to minimize the effects of BCN ageing using two approaches. First, we evaluated how changes in packaging can help minimize BCN's exposure to humidity. In the packaging reported here, bulk bags show the most significant improvement in BCN shelf life. Additionally, we developed an advanced BCN material that is resistant to ageing at 50 °C and 95% RH for 5 days. Additional studies are necessary to verify that this new product will exhibit improved shelf-life under longer storage conditions.

## References


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