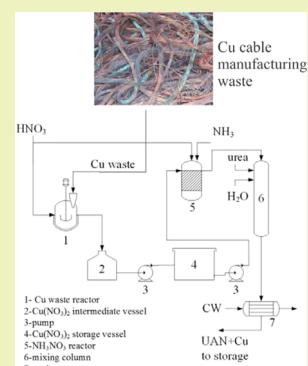


## Urea–Ammonium Nitrate Aqueous Solutions Containing Cu Micronutrient Obtained from Cable Manufacturing Solid Waste

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**ABSTRACT:** In this work, sustainable metal recovery from waste and conversion into Cu-micronutrient-containing N fertilizers was developed utilizing the HNO<sub>3</sub> extraction method. For this purpose, solubility diagrams, i.e., polytherms, were constructed of the ternary CO(NH<sub>2</sub>)<sub>2</sub>–Cu(NO<sub>3</sub>)<sub>2</sub>–H<sub>2</sub>O and NH<sub>4</sub>NO<sub>3</sub>–Cu(NO<sub>3</sub>)<sub>2</sub>–H<sub>2</sub>O systems to determine the corresponding phase equilibria and solid material chemical composition. Copper extraction in the form of water-soluble Cu(NO<sub>3</sub>)<sub>2</sub> was performed from the industrial Cu cable manufacturing waste, using HNO<sub>3</sub> concentrations relevant to the industrial conditions (56–58%) at a moderate temperature of 60 °C. Waste dissolution in aqueous NH<sub>4</sub>NO<sub>3</sub> solutions resulted in only partial dissolution of <60% after 30 min. Processes of Cu and Zn micronutrient extraction from solid waste and integration into the existing NH<sub>4</sub>NO<sub>3</sub> and nitrophosphate (NP and NPK) production technologies was proposed via an additional HNO<sub>3</sub> dissolution step, combined with the solid unreacted residue removal.

**KEYWORDS:** Urea, Ammonium Nitrate, Copper nitrate, Polytherm, Phase composition, Waste



## INTRODUCTION

The world is experiencing unprecedented economic growth together with an increase in human population that requires increasing use of air, land, water, and other Earth resources.<sup>1</sup> For this reason, sustainable material management via reuse and recycling or waste and byproducts is necessary in order to minimize environmental impacts.<sup>2</sup> Excessive use of materials can lead to serious ecological and societal problems as well as the accumulation of industrial and residential waste. This is apparent with the waste that requires large storage space such as coal combustion byproducts,<sup>3</sup> used tires,<sup>4</sup> phosphogypsum,<sup>5,6</sup> or metal-containing municipal wastewater sludge.<sup>7</sup> Extensive use of soluble fertilizers such as ammonium nitrate, urea, superphosphate, ammonium phosphate, and nitrophosphate can adversely affect human health,<sup>8</sup> whereas unbalanced major nutrient (N, P, K, Ca, Mg, and S) use as well as the absence of micronutrients (Zn, Cu, Fe, Mn, Mo, Co, and B)<sup>9</sup> can often preclude full utilization of the mineral fertilizers and as a result lead to the pollution of soil and groundwater.<sup>10</sup> It is important to balance the nutrient ratio during various growth stages<sup>11</sup> because nutrient excess that is not consumed is dispersed into the environment.<sup>12–14</sup>

Of particular interest in this work is the recovery of micronutrients from industrial waste and their reuse to facilitate the sustainable use of major nutrients. Main micronutrients (Zn, Cu, B, Mn, Mo, Co, and Fe) take a very active role in various plant biochemical processes.<sup>9</sup> Micronutrient deficiency leads not only to slowed growth and reduced yields but also to metabolic and developmental defects in plants.<sup>15</sup> Copper is an essential micronutrient required for the growth of plants. It is

especially important in seed production, disease resistance, and regulation of water.<sup>16</sup> Copper is added to fertilizers in the form of soluble or sparingly soluble inorganic salts, oxides, or chelated organometallic complexes. Chelated copper compounds currently used as a micronutrient source in fertilizers include derivatives of ethylenediaminetetraacetic acid (EDTA), including Na<sub>2</sub>CuEDTA (13–14% Cu) and NaCuEDTA (9% Cu).<sup>17</sup> Although chelated micronutrients may be more effective per unit of micronutrient, they are also more expensive. The price of these chelated fertilizers generally limits their use to higher value crops, such as horticultural crops,<sup>17</sup> and Cu-containing water-soluble waste can be regarded as an inexpensive alternative. The ability to obtain micronutrients from sustainable sources, e.g., industrial waste, would increase their affordability.

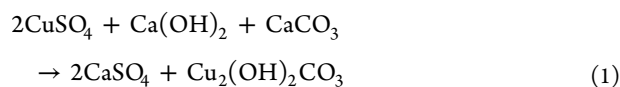
Copper is the third most-used metal in the world,<sup>16</sup> chiefly because of its thermal and electrical properties, inevitably present in the waste associated with but not limited to copper electrorefining units, textile, and copper-plating industries as well copper wire and cable manufacturing.<sup>18</sup> Only 30–40% of all metals used in the plating processes are effectively utilized, whereas the rest result in wastewater up to 500 mg/L.<sup>19</sup> The situation is complicated by the expensive technologies needed to extract metal ions, focused on adsorption (immobilization of Cu ions) on activated coal,<sup>20</sup> zeolites,<sup>21</sup> and chemical precipitation,<sup>22</sup> as well as electrochemical methods, such as

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cathodic reduction, electrowinning, electro dialysis, and electro-deionization.<sup>19</sup> In this work, we focus on the solid Cu-containing waste resulting from copper cable manufacturing because it represents an interesting case of immobilized copper waste. It is obtained after cleaning oxidized Cu cables with H<sub>2</sub>SO<sub>4</sub> followed by the adsorption (neutralization) of the resulting solution using calcium hydroxide and calcium carbonate to form very low solubility copper(II) hydroxycarbonate via the reaction



Although the resulting solid waste contains 9–14% Cu, it cannot be utilized efficiently, especially in agriculture as a micronutrient source because of the low solubility in aqueous solution; thus, it is stored in landfills. An immediate recognition of the fact that fertilizer manufacturing typically proceeds using strong HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> acids provides a lead in the possible route of Cu reuse.

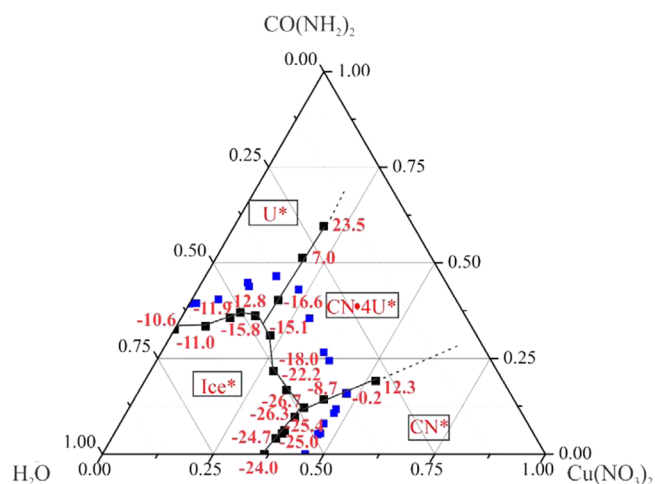
The work presented here focuses on utilization of the solid industrial Cu waste obtained during Cu cable processing for liquid fertilizer production using HNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> solutions. Liquid–solid equilibria of urea–ammonium nitrate (UAN) components as well as Cu(NO<sub>3</sub>)<sub>2</sub> were determined. Optimal extraction parameters of HNO<sub>3</sub> versus NH<sub>4</sub>NO<sub>3</sub> solution were also determined with the goal of integration into existing nitrogen fertilizer manufacturing processes such as those of ammonium nitrate synthesis and/or UAN solution. Finally, integration of industrial-waste-derived Cu into the existing industrial processes is proposed.

## EXPERIMENTAL DETAILS

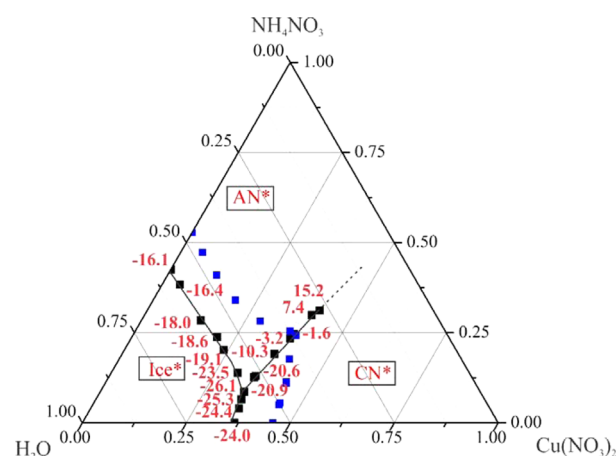
**Reagents.** CO(NH<sub>2</sub>)<sub>2</sub>, NH<sub>4</sub>NO<sub>3</sub>, and Cu(NO<sub>3</sub>)<sub>2</sub> were purchased from Sigma-Aldrich and were reagent-grade purity. These were used in constructing solutions for phase diagram measurements shown in Figures 1 and 2. Technical-grade CO(NH<sub>2</sub>)<sub>2</sub> (46.3% N), NH<sub>4</sub>NO<sub>3</sub> (34.4% N), and HNO<sub>3</sub> (57% aqueous solution) were obtained from SC Achema, Jonava, Lithuania and used as received for Cu extraction from industrial waste and for UAN-28, UAN-30, and UAN-32 manufacturing shown in Table 4. Double-distilled water was used to make solutions.

**Solubility Experiments.** The main goal of these experiments was the determination of the phase composition of CO(NH<sub>2</sub>)<sub>2</sub>-Cu(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O and NH<sub>4</sub>NO<sub>3</sub>-Cu(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O in a wide temperature range and of both UAN components, i.e., CO(NH<sub>2</sub>)<sub>2</sub> and NH<sub>4</sub>NO<sub>3</sub>, interactions with Cu(NO<sub>3</sub>)<sub>2</sub> that may have an effect on the phase equilibrium. Solubility measurements of ternary CO(NH<sub>2</sub>)<sub>2</sub>-Cu(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O and NH<sub>4</sub>NO<sub>3</sub>-Cu(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O mixtures were performed using the visual polythermal method. Six molecules of crystalline H<sub>2</sub>O were accounted for in ternary diagram composition. Two ternary phase diagrams were constructed because a single UAN (CO(NH<sub>2</sub>)<sub>2</sub> + NH<sub>4</sub>NO<sub>3</sub>)-Cu(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O phase diagram would need to be represented in a 4D space and would be too complex to interpret. This method has been successfully utilized before<sup>23</sup> and is based on the observation of the liquid surface. The liquidus temperature is the temperature at which the first crystals appear during cooling and the last crystal disappears during heating. The average value is then taken as the liquidus temperature. Typical cooling agents used were chosen depending on the crystallization temperature of the solids and were as follows: (i) ice + KCl (cooling down to -11.0 °C), (ii) ice + NH<sub>4</sub>NO<sub>3</sub> (down to -17.3 °C), (iii) ice + NaCl (down to -21.2 °C), and (iv) dry ice + ethanol (down to -72.0 °C).

For solubility measurements, 5 g of the solution was used, and temperature was measured using a Hg thermometer with the standard error of ±0.1 °C.



**Figure 1.** Measured phase diagram of the ternary CO(NH<sub>2</sub>)<sub>2</sub>-Cu(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O system. Four distinct crystalline phase regions can be distinguished by the black polytherm curve connecting the eutectic points measured: Ice\* (ice), U\* (urea), CN\* (copper nitrate), and CN·4U\* (copper nitrate-tetraurea). Crystallization temperatures are shown in red next to the corresponding points. Blue points represent 0 °C isotherm. Lines are for eye guidance only, dotted lines show phase boundaries where measurements were not performed because of the too high crystallization temperature. Concentrations are expressed in terms of fraction for brevity.



**Figure 2.** Measured phase diagram of the ternary NH<sub>4</sub>NO<sub>3</sub>-Cu(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O system. Three distinct crystalline phase regions can be distinguished by the black polytherm curve connecting the eutectic points measured: Ice\* (ice), AN\* (ammonium nitrate), and CN\* (copper nitrate). Crystallization temperatures are shown in red next to the corresponding points. Blue points represent 0 °C isotherm. Lines are for eye guidance only; dotted lines show phase boundaries where measurements were not performed because of the too high crystallization temperature. Concentrations are expressed in terms of fraction for brevity.

**Chemical Analysis.** Total N in crystals obtained from both CO(NH<sub>2</sub>)<sub>2</sub>-Cu(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O and NH<sub>4</sub>NO<sub>3</sub>-Cu(NO<sub>3</sub>)<sub>2</sub>-H<sub>2</sub>O systems was determined using Kjeldahl digestion. Briefly, urea is transformed quantitatively into ammonia by digesting it in the presence of sulfuric acid. Obtained ammonia is distilled from an alkaline medium, with the distillate being collected in an excess of standard sulfuric acid. The excess acid is titrated by means of a standard alkaline solution.<sup>24</sup> Copper in solution was determined using an AAAnalyst 400 (PerkinElmer, USA) atomic absorption spectrometer.

## RESULTS AND DISCUSSION

Liquid fertilizers are produced with a crystallization temperature of 0 °C, and every added salt compound, such as  $\text{Cu}(\text{NO}_3)_2$ , will affect that temperature. Furthermore, waste may contain several metal ions that may dissolve and further affect the crystallization temperature. For this purpose, we explored the conformational phase composition space of the two relevant ternary systems,  $\text{CO}(\text{NH}_2)_2$ - $\text{Cu}(\text{NO}_3)_2$ - $\text{H}_2\text{O}$  and  $\text{NH}_4\text{NO}_3$ - $\text{Cu}(\text{NO}_3)_2$ - $\text{H}_2\text{O}$ , as a first step in establishing relevant boundary conditions necessary to yield usable UAN liquid fertilizers.

### $\text{CO}(\text{NH}_2)_2$ - $\text{Cu}(\text{NO}_3)_2$ - $\text{H}_2\text{O}$ System Phase Composition.

The ternary phase composition was explored, and a phase diagram was constructed on the basis of the compositions shown in Table 1. In particular, a series of fixed  $\text{Cu}(\text{NO}_3)_2$ /

**Table 1.**  $\text{CO}(\text{NH}_2)_2$ - $\text{Cu}(\text{NO}_3)_2$ - $\text{H}_2\text{O}$  and  $\text{NH}_4\text{NO}_3$ - $\text{Cu}(\text{NO}_3)_2$ - $\text{H}_2\text{O}$  Ternary Phase Compositions Used in Analysis<sup>a</sup>

number	mass composition
$\text{CO}(\text{NH}_2)_2$ - $\text{Cu}(\text{NO}_3)_2$ - $\text{H}_2\text{O}$	
I	$(5-x)[10\% \text{Cu}(\text{NO}_3)_2 + 90\% \text{H}_2\text{O}] + x\text{CO}(\text{NH}_2)_2$
II	$(5-x)[20\% \text{Cu}(\text{NO}_3)_2 + 80\% \text{H}_2\text{O}] + x\text{CO}(\text{NH}_2)_2$
III	$(5-x)[30\% \text{Cu}(\text{NO}_3)_2 + 70\% \text{H}_2\text{O}] + x\text{CO}(\text{NH}_2)_2$
IV	$(5-x)[40\% \text{Cu}(\text{NO}_3)_2 + 60\% \text{H}_2\text{O}] + x\text{CO}(\text{NH}_2)_2$
V	$(5-x)[50\% \text{Cu}(\text{NO}_3)_2 + 50\% \text{H}_2\text{O}] + x\text{CO}(\text{NH}_2)_2$
VI	$(5-x)[10\% \text{CO}(\text{NH}_2)_2 + 90\% \text{H}_2\text{O}] + x\text{Cu}(\text{NO}_3)_2$
VII	$(5-x)[20\% \text{CO}(\text{NH}_2)_2 + 80\% \text{H}_2\text{O}] + x\text{Cu}(\text{NO}_3)_2$
VIII	$(5-x)[30\% \text{CO}(\text{NH}_2)_2 + 70\% \text{H}_2\text{O}] + x\text{Cu}(\text{NO}_3)_2$
IX	$(5-x)[40\% \text{CO}(\text{NH}_2)_2 + 60\% \text{H}_2\text{O}] + x\text{Cu}(\text{NO}_3)_2$
X	$(5-x)[50\% \text{CO}(\text{NH}_2)_2 + 50\% \text{H}_2\text{O}] + x\text{Cu}(\text{NO}_3)_2$
XI	$(5-x)[10\% \text{CO}(\text{NH}_2)_2 + 90\% \text{Cu}(\text{NO}_3)_2] + x\text{H}_2\text{O}$
XII	$(5-x)[20\% \text{CO}(\text{NH}_2)_2 + 80\% \text{Cu}(\text{NO}_3)_2] + x\text{H}_2\text{O}$
$\text{NH}_4\text{NO}_3$ - $\text{Cu}(\text{NO}_3)_2$ - $\text{H}_2\text{O}$	
I	$(5-x)[10\% \text{Cu}(\text{NO}_3)_2 + 90\% \text{H}_2\text{O}] + x\text{NH}_4\text{NO}_3$
II	$(5-x)[20\% \text{Cu}(\text{NO}_3)_2 + 80\% \text{H}_2\text{O}] + x\text{NH}_4\text{NO}_3$
III	$(5-x)[30\% \text{Cu}(\text{NO}_3)_2 + 70\% \text{H}_2\text{O}] + x\text{NH}_4\text{NO}_3$
IV	$(5-x)[40\% \text{Cu}(\text{NO}_3)_2 + 60\% \text{H}_2\text{O}] + x\text{NH}_4\text{NO}_3$
V	$(5-x)[50\% \text{Cu}(\text{NO}_3)_2 + 50\% \text{H}_2\text{O}] + x\text{NH}_4\text{NO}_3$
VI	$(5-x)[10\% \text{NH}_4\text{NO}_3 + 90\% \text{H}_2\text{O}] + x\text{Cu}(\text{NO}_3)_2$
VII	$(5-x)[20\% \text{NH}_4\text{NO}_3 + 80\% \text{H}_2\text{O}] + x\text{Cu}(\text{NO}_3)_2$
VIII	$(5-x)[30\% \text{NH}_4\text{NO}_3 + 70\% \text{H}_2\text{O}] + x\text{Cu}(\text{NO}_3)_2$
IX	$(5-x)[40\% \text{NH}_4\text{NO}_3 + 60\% \text{H}_2\text{O}] + x\text{Cu}(\text{NO}_3)_2$
X	$(5-x)[50\% \text{NH}_4\text{NO}_3 + 50\% \text{H}_2\text{O}] + x\text{Cu}(\text{NO}_3)_2$
XI	$(5-x)[60\% \text{NH}_4\text{NO}_3 + 40\% \text{H}_2\text{O}] + x\text{Cu}(\text{NO}_3)_2$
XII	$(5-x)[10\% \text{NH}_4\text{NO}_3 + 90\% \text{Cu}(\text{NO}_3)_2] + x\text{H}_2\text{O}$
XIII	$(5-x)[20\% \text{NH}_4\text{NO}_3 + 80\% \text{Cu}(\text{NO}_3)_2] + x\text{H}_2\text{O}$

<sup>a</sup>A total 5 g of material was used and  $x$  varied from 0 to 5.

$\text{H}_2\text{O}$  ratio solutions, I–V, were prepared, and the amount of  $\text{CO}(\text{NH}_2)_2$  added was varied. Further, a series of fixed  $\text{CO}(\text{NH}_2)_2$ / $\text{H}_2\text{O}$  ratio solutions, VI–X, were prepared, and the amount of  $\text{Cu}(\text{NO}_3)_2$  added was varied. Finally, a series of fixed  $\text{CO}(\text{NH}_2)_2$ / $\text{Cu}(\text{NO}_3)_2$  ratio solutions, XI–XII, were prepared, and the amount of water added was varied. The crystallization temperatures along with the corresponding solution-phase and crystallized solid-phase compositions are summarized in Table 2, and the corresponding data are plotted in a ternary diagram shown in Figure 1. Crystallization temperatures for the solution compositions explored in this work ranged from 47.3 to –26.7 °C. In general, high-crystallization-temperature solutions had high concentrations

of either  $\text{Cu}(\text{NO}_3)_2$  or  $\text{CO}(\text{NH}_2)_2$  and crystallized as urea and copper nitrate and a complex salt. Medium- and low-crystallization-temperature solutions were diluted with  $\text{H}_2\text{O}$  and crystallized as a combination of ice, urea, and copper nitrate–urea complex. Four distinct chemical composition compounds were obtained, including ice (labeled in Figure 1 as Ice\* phase),  $\text{CO}(\text{NH}_2)_2$  (U\*),  $\text{Cu}(\text{NO}_3)_2 \cdot 4\text{CO}(\text{NH}_2)_2$  (CN·4U\*), and  $\text{Cu}(\text{NO}_3)_2$  (CN), shown according to their corresponding concentration regions in Figure 1. One complex CN·4U\* phase was obtained at intermediate concentrations of both urea and  $\text{Cu}(\text{NO}_3)_2$ . This is due to the urea acting as a supramolecular chemistry building block via nitrogen–metal coordination.<sup>25,26</sup>  $\text{Cu} \cdot 4\text{CO}(\text{NH}_2)_2 \cdot \text{Cl}_2$  has previously been reported to be stable up to 428 K.<sup>27</sup> Although of possible interest as a N fertilizer containing micronutrient Cu, CN·4U\* contains a rather large metal concentration. From the polytherm shown in Figure 1 and Table 2, it can be seen that up to ~47% of  $\text{Cu}(\text{NO}_3)_2$  can be present in aqueous solutions at 0 °C. However, only 10–16% of  $\text{Cu}(\text{NO}_3)_2$  in aqueous urea solutions can be present at 0 °C, urea concentrations typical to those in UAN. More importantly, it implies that possibly other, less soluble metal salts can be present in urea solutions still providing solubility necessary to yield 0 °C liquid fertilizers. This is especially true for metal salt mixtures obtained from complex manufacturing waste containing several metals that may result in sudden crystallization temperature increase as opposed to pure, single-metal salt solutions.<sup>28</sup> Next, we will explore solubility parameters in the  $\text{NH}_4\text{NO}_3$ - $\text{Cu}(\text{NO}_3)_2$ - $\text{H}_2\text{O}$  system.

### $\text{NH}_4\text{NO}_3$ - $\text{Cu}(\text{NO}_3)_2$ - $\text{H}_2\text{O}$ System Phase Composition.

The ternary phase composition was explored, and a polytherm was constructed on the basis of compositions shown in Table 1. In particular, a series of fixed  $\text{Cu}(\text{NO}_3)_2$ / $\text{H}_2\text{O}$  ratio solutions, I–V, were prepared, and the amount of  $\text{NH}_4\text{NO}_3$  added was varied. Further, a series of fixed  $\text{NH}_4\text{NO}_3$ / $\text{H}_2\text{O}$  ratio solutions, VI–X, were prepared, and the amount of  $\text{Cu}(\text{NO}_3)_2$  added was varied. Finally, a series of fixed  $\text{NH}_4\text{NO}_3$ / $\text{Cu}(\text{NO}_3)_2$  ratio solutions, XI and XII, were prepared and the amount of  $\text{H}_2\text{O}$  added was varied. The crystallization temperatures measured, along with the corresponding solution-phase and crystallized solid-phase compositions, are summarized in Table 3, and the corresponding data are plotted in a ternary diagram shown in Figure 2. Crystallization temperatures for the solution compositions explored in this work ranged from 36.5 to –26.1 °C. In general, high  $\text{H}_2\text{O}$  content samples resulted in ice crystallization, whereas only  $\text{Cu}(\text{NO}_3)_2$  was observed with no complex salts formed. This is similar to the previous work because<sup>28</sup> the N atom is protonated in  $\text{NH}_4\text{NO}_3$  and cannot be directly involved in binding the metal atoms. Solubility data in the literature provides only for a 25 °C isotherm for the  $\text{NH}_4\text{NO}_3$ - $\text{Cu}(\text{NO}_3)_2$ - $\text{H}_2\text{O}$  ternary system<sup>29</sup> and also reports no complex crystalline solid compounds crystallized. The data in Table 3 suggest that up to 40.0–44.8%  $\text{Cu}(\text{NO}_3)_2$  can be dissolved in aqueous  $\text{NH}_4\text{NO}_3$  solutions at 0 °C. However, 5–11%  $\text{Cu}(\text{NO}_3)_2$  can be dissolved at 0 °C at  $\text{NH}_4\text{NO}_3$  concentrations typical to those in UAN (41–47%).

**Cu-Micronutrient-Enriched Liquid Nitrogen Fertilizers Using Industrial-Grade  $\text{CO}(\text{NH}_2)_2$ ,  $\text{NH}_4\text{NO}_3$  as Well as  $\text{Cu}(\text{NO}_3)_2$  Obtained from the Solid Waste.** Cu-containing waste was taken from the copper cable manufacturing plant in Panevezys, Lithuania, after the cable-cleaning step. Water-insoluble byproduct of Cu cable processing contains 9–14% Cu, but to become bioavailable,  $\text{Cu}_2(\text{OH})_2\text{CO}_3$  needs to be

**Table 2.**  $\text{CO}(\text{NH}_2)_2\text{-Cu}(\text{NO}_3)_2\text{-H}_2\text{O}$  Phase Diagram Critical Points with the Corresponding Solution Composition and Solid Phase Detected

sample	solution composition (wt %)			crystallization temperature (°C)	solid phase detected
	$\text{Cu}(\text{NO}_3)_2$	$\text{CO}(\text{NH}_2)_2$	$\text{H}_2\text{O}$		
I	0.0	32.6	67.4	-10.6	Ice* + U*
	6.6	33.4	60.0	-11.0	Ice* + U*
	12.6	37.0	50.4	-12.8	Ice* + U*
III	18.1	39.7	52.2	-15.8	Ice* + U*
IV	37.9	5.3	56.8	-25.0	Ice* + CN*
	33.2	16.8	50.0	-22.2	CN·4U* + Ice*
	19.5	51.3	29.2	7.0	U + CN·4U
V	42.9	14.2	42.9	-8.7	CN* + CN·4U*
	20.2	59.6	20.2	23.5	U* + CN·4U*
VI	38.0	6.2	55.8	-25.4	Ice* + CN*
VII	39.4	12.1	48.5	-26.7	CN* + Ice* + CN·4U*
VIII	27.8	21.7	50.5	-18.0	CN·4U* + Ice*
	47.2	15.8	37.0	-0.2	CN·4U* + CN*
IX	11.0	35.6	53.4	-11.9	U* + Ice*
	22.4	31.0	46.6	-15.1	CN·4U* + Ice*
	52.2	19.1	28.7	12.3	CN·4U* + CN*
X	19.6	40.2	40.2	-16.6	U* + Ice* + CN·4U*
XI	37.1	4.1	58.8	-24.7	Ice* + CN*
XII	38.6	9.6	51.8	-26.3	Ice* + CN*
	36.6	0.0	63.4	-24.0	CN* + Ice*

**Table 3.**  $\text{NH}_4\text{NO}_3\text{-Cu}(\text{NO}_3)_2\text{-H}_2\text{O}$  Phase Diagram Critical Points with the Corresponding Solution Composition and Solid Phase Detected

sample	solution composition (wt %)			crystallization temperature (°C)	solid phase detected
	$\text{Cu}(\text{NO}_3)_2$	$\text{NH}_4\text{NO}_3$	$\text{H}_2\text{O}$		
I	0.0	42.5	57.5	-16.1	Ice* + AN*
	6.4	35.8	57.8	-16.8	Ice* + AN*
	14.3	28.4	57.3	-18.0	Ice* + AN*
III	23.9	20.2	55.9	-19.1	Ice* + AN*
IV	35.0	12.6	52.4	-20.9	AN* + CN*
	38.3	23.4	38.3	-3.2	AN* + CN*
VI	35.0	6.5	58.5	-25.3	Ice* + CN*
VII	30.4	13.9	55.7	-23.5	Ice* + AN*
	35.2	13.0	51.8	-20.6	AN* + CN*
VIII	20.5	23.8	55.7	-18.6	Ice* + AN*
	36.7	19.0	44.3	-10.3	AN* + CN*
IX	4.3	38.3	57.4	-16.4	Ice* + AN*
	38.6	24.6	36.8	-1.6	AN* + CN*
X	40.2	29.9	29.9	7.4	AN* + CN*
XI	41.5	31.1	27.4	15.2	AN* + CN*
XII	35.7	4.0	60.3	-24.4	Ice* + CN*
XIII	34.6	8.6	56.8	-26.1	Ice* + AN* + CN*
	36.6	0.0	63.4	-24.0	CN* + Ice*

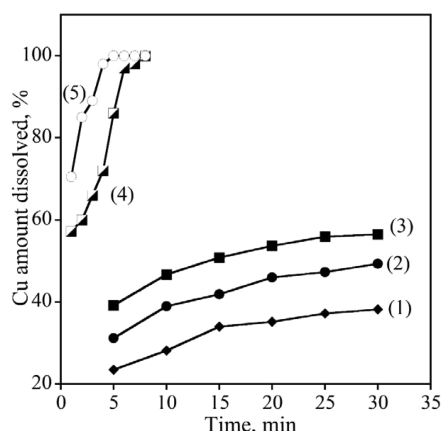
converted into water-soluble species. We utilized aqueous solutions of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , as well as urea and  $\text{NH}_4\text{NO}_3$ , all readily available in fertilizer manufacturing processes, to perform Cu-ion extraction. We explored a range of  $\text{H}_2\text{SO}_4$  concentrations from 30 to 98% and reaction temperatures from 20 to 60 °C but did not obtain satisfactory dissolution of  $\text{Cu}_2(\text{OH})_2\text{CO}_3$ . Addition of  $\text{H}_2\text{SO}_4$  always resulted in increased mass viscosity with no Cu released into the solution. This is possibly due to the presence of calcium in the reacting medium and the resulting insoluble gypsum formation.

Next, we investigated the solubility of Cu solid waste in urea. Urea, as well as  $\text{NH}_4\text{NO}_3$ , are components of UAN, a widely used aqueous fertilizer. Direct solubility of Cu waste in either

UAN component would provide economically feasible integration into the existing UAN manufacturing process. Our data indicated that in the temperature interval between 20 and 60 °C using 60% aqueous urea solution, Cu waste dissolution was very slow: after 30 min of reaction only about 0.1–0.5% Cu became solubilized even at a high waste:urea mass ratio of 1:200.

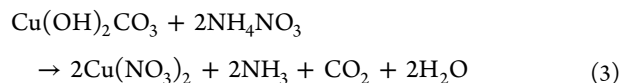
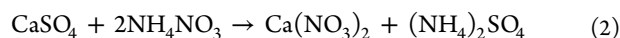
Finally, we attempted Cu waste dissolution using 57%  $\text{HNO}_3$  as well as 60%  $\text{NH}_4\text{NO}_3$  solutions with a fivefold excess of  $\text{HNO}_3$  or  $\text{NH}_4\text{NO}_3$ , which yielded the highest extent of Cu solid waste dissolution. These data are shown in Figure 3. In particular, 57%  $\text{HNO}_3$  resulted in nearly 100% dissolution of the total Cu waste after 5 min at 60 °C with a very weak





**Figure 3.** Cu amount measured in solution obtained from dissolved Cu-containing solid waste in 60% aqueous  $\text{NH}_4\text{NO}_3$  solution (1–3) and 57%  $\text{HNO}_3$  (4 and 5). Dissolution temperature used was 40 °C (1 and 5), 60 °C (2 and 4), and 80 °C (3). Points shown are the average of three independent measurements. Typical standard deviation measured did not exceed 3%.

temperature dependence: At 40 °C, full solubilization of Cu waste took place in 8 min. However, 60%  $\text{NH}_4\text{NO}_3$  solution dissolved Cu waste much slower and not to completion. Further, temperature dependence was observed with the maximum amount of 38.2% dissolved at 40 °C and 56.5% at 80 °C, as shown in Figure 3. The extent was limited because of reactions 2 and 3, between the two salts.



Reaction 3 was confirmed by the presence of gaseous  $\text{NH}_3$ . The resulting products were soluble in aqueous solutions and suitable for incorporation into UAN. These data show that  $\text{NH}_4\text{NO}_3$  alone, although possessing strong acid anion, is not capable of dissolving significant amounts of Cu waste, implying constraints on feed location for integration into the existing technological UAN process.

We synthesized Cu-enriched UAN solutions from industrial-grade  $\text{CO}(\text{NH}_2)_2$  and  $\text{NH}_4\text{NO}_3$  by adding aqueous solution of  $\text{Cu}(\text{NO}_3)_2$  obtained from the Cu waste using  $\text{HNO}_3$  digestion. UAN-28 solution was prepared by dissolving 40.1% of  $\text{NH}_4\text{NO}_3$  and 30.0% urea in 29.9% of  $\text{H}_2\text{O}$ . UAN-30 was obtained using 42.2%  $\text{NH}_4\text{NO}_3$ , 32.7% urea, and 25.1%  $\text{H}_2\text{O}$ . UAN-32 was obtained using 44.3%  $\text{NH}_4\text{NO}_3$ , 35.4% urea, and 20.3%  $\text{H}_2\text{O}$ . Technical-grade  $\text{CO}(\text{NH}_2)_2$  (46.3% N),  $\text{NH}_4\text{NO}_3$  (34.4% N), and  $\text{HNO}_3$  (58% aqueous solution) were obtained

from SC Achema, Jonava, Lithuania, and used as received.  $\text{Cu}(\text{NO}_3)_2$  was added to obtain a Cu concentration of 0.1%, a value typical for micronutrient concentrations in industrial fertilizers, and the physicochemical properties of the resulting aqueous solutions including their density, pH, and  $T_{\text{crist}}$  measured. Density and pH changes were almost negligible, whereas  $T_{\text{crist}}$  increased slightly from the values of pure UAN solutions, as shown in Table 4. UAN-32 crystallization onset proceeded at  $-0.8$  °C, well within the limits necessary to transport and dispense it.

### Integrating Solid Cu Waste Dissolution into Nitrogen Fertilizer Manufacturing Processes.

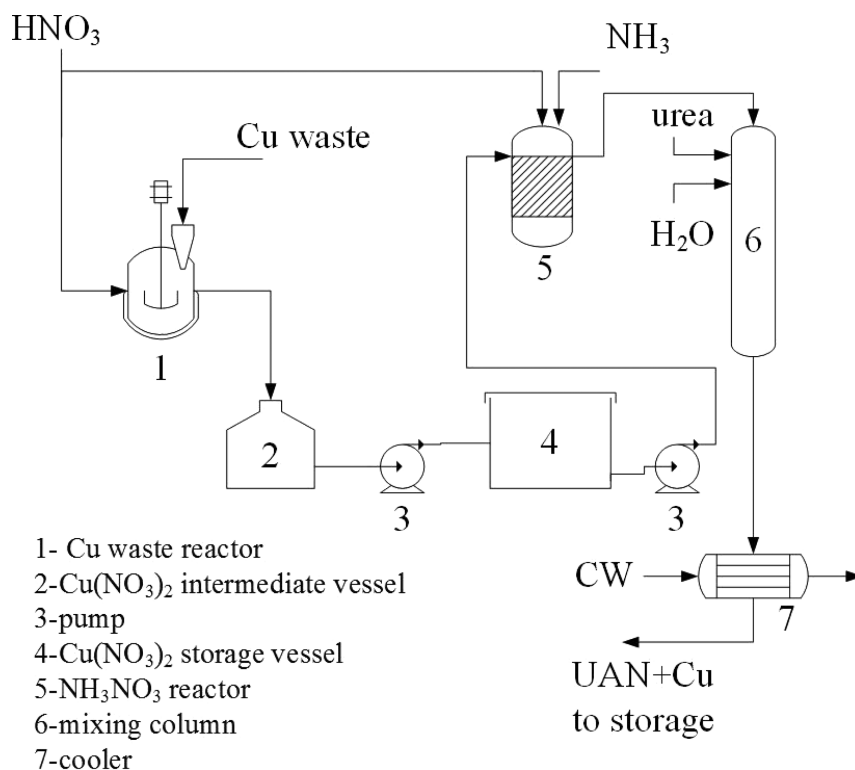
Data presented in this work suggest integration of Cu waste compound processing into fertilizers via existing processes utilizing  $\text{HNO}_3$ , rather than via  $\text{H}_2\text{SO}_4$ . This is facilitated by the remarkable solubility of Cu- as well as Zn-containing<sup>28</sup> waste in nitric acid. Additionally, copper sulfate salts have rather low solubility in some aqueous fertilizers with 10–34–0 (N:P<sub>2</sub>O<sub>5</sub>:K<sub>2</sub>O) polyphosphate fertilizers, dissolving 2.0% of  $\text{CuSO}_4$ , whereas in 8–24–0 orthophosphate-based fertilizers, this amount is only 0.5%.<sup>30</sup> To a certain extent, even aqueous  $\text{NH}_4\text{NO}_3$  solutions can be used for Cu and Zn micronutrient waste dissolution because the pH is adjusted to be slightly acidic to avoid  $\text{NH}_3$  loss during the synthesis process, although the data presented in Figure 3 show only partial Cu waste dissolution and imply the need for solid material separation. This can present engineering challenges during the prilling of  $\text{NH}_4\text{NO}_3$  product. Because of these limitations, an apparent advantage needs to be taken of the metal waste dissolution stage before fertilizer synthesis, with the separation of the insoluble remainder via separation by flotation and/or filtration.

Use of  $\text{HNO}_3$  implies two end-product fertilizers of interest. First, nitro(ammo)phosphate fertilizers have recently been of particular interest because they can compete with more common diammonium phosphate (DAP)-based fertilizers in efficient phosphorus delivery to various crop species.<sup>31</sup> Previous work already pointed out that conditions of  $\text{HNO}_3$  concentration and temperature for Zn extraction from industrial pigment waste are very similar to those used industrially in phosphate rock reaction to produce compound NP (nitrophosphate) fertilizers.<sup>32</sup> Second, UAN solutions utilize  $\text{NH}_4\text{NO}_3$  obtained using 56–58%  $\text{HNO}_3$ . Both processes utilize relatively low temperature 60 °C  $\text{HNO}_3$ , nitrophosphate for phosphate rock dissolution, whereas ammonium nitrate solution synthesis typically further preheats  $\text{HNO}_3$  before synthesis, utilizing steam or feed-effluent heat exchangers. Because the concentration of the micronutrients needed for plants is typically <1%, the presence of Cu and Zn is not expected to significantly affect the phase equilibria of the resulting solutions, as supported by our phase equilibrium data.

**Table 4.** UAN-28, UAN-30, and UAN-32 Liquid Fertilizers Containing Cu Micronutrient Obtained from Industrial Solid Waste<sup>a</sup>

UAN grade	measured properties							
	Cu (%)	density (kg/m <sup>3</sup> )	pH	$T_{\text{crist}}$ (°C)	Cu (%)	density (kg/m <sup>3</sup> )	pH	$T_{\text{crist}}$ (°C)
UAN-28	0.0	1.28	6.25	-18.2	0.1	1.29	6.15	-17.8
UAN-30	0.0	1.30	6.30	-10.2	0.1	1.31	6.25	-9.7
UAN-32	0.0	1.32	6.35	-2.3	0.1	1.33	6.30	-0.8

<sup>a</sup>UAN-28:  $\text{NH}_4\text{NO}_3$  = 40.1%, urea = 30.0%, and  $\text{H}_2\text{O}$  = 29.9%. UAN-30:  $\text{NH}_4\text{NO}_3$  = 42.2%, urea = 32.7%, and  $\text{H}_2\text{O}$  = 25.1%. UAN-32:  $\text{NH}_4\text{NO}_3$  = 44.3%, urea = 35.4%, and  $\text{H}_2\text{O}$  = 20.3%. Technical-grade  $\text{CO}(\text{NH}_2)_2$  (46.3% N) and  $\text{NH}_4\text{NO}_3$  (34.4% N) were obtained from SC Achema, Jonava, Lithuania and used as received, whereas  $\text{Cu}(\text{NO}_3)_2$  was obtained via extraction from industrial waste using industrial-grade 57%  $\text{HNO}_3$ .



**Figure 4.** Proposed process flow diagram for UAN synthesis using Cu solid waste as micronutrient source.

Thus, the experimental conditions of Cu as well as  $\text{Zn}^{28}$  removal from solid waste can be applied directly in existing industrial processes without modifications resulting in micronutrient-enriched N, NP, and NPK fertilizers.

Our proposed conceptual flow diagram of the solid Cu incorporation process into UAN is shown in Figure 4. Solid Cu waste is dissolved in the reactor (1) with 56–58%  $\text{HNO}_3$ , the main stream of which is directed to  $\text{NH}_4\text{NO}_3$  synthesis. Dissolution product overflows into the intermediate vessel (2) where any suspended solid product is separated and removed. Aqueous  $\text{Cu}(\text{NO}_3)_2$  solution is pumped into the storage vessel (4), from which it is supplied into the  $\text{NH}_4\text{NO}_3$  synthesis reactor. Resulting Cu-enriched  $\text{NH}_4\text{NO}_3$  solution is mixed with aqueous urea solution in vessel 6 and diluted with  $\text{H}_2\text{O}$  to the concentration necessary. The resulting UAN+Cu solution is cooled in the heat exchanger (7) and pumped into storage. Similarly, Cu can be directly digested during the nitrophosphate synthesis process during the apatite dissolution with  $\text{HNO}_3$ .

## CONCLUSIONS

Solubility relationships were determined for the ternary  $\text{CO}(\text{NH}_2)_2\text{-Cu}(\text{NO}_3)_2\text{-H}_2\text{O}$  and  $\text{NH}_4\text{NO}_3\text{-Cu}(\text{NO}_3)_2\text{-H}_2\text{O}$  systems to determine achievable crystallization temperatures of liquid nitrogen fertilizers in the presence of  $\text{Cu}(\text{NO}_3)_2$ . Cu extraction in a form of soluble  $\text{Cu}(\text{NO}_3)_2$  was performed from industrial cable manufacturing waste using  $\text{HNO}_3$  concentrations relevant to the industrial conditions (56–58%) at a moderate temperature of 60 °C. Aqueous  $\text{NH}_4\text{NO}_3$  solutions resulted in a partial dissolution of Cu-containing waste. Cu and Zn micronutrient extraction and integration into the existing  $\text{NH}_4\text{NO}_3$  and nitrophosphate (N, NP, and NPK) technological processes was proposed with an additional  $\text{HNO}_3$  dissolution step, combined with the solid unreacted residue removal step.

Outstanding questions remaining in sustainable waste material reuse because micronutrients in N, NP, and NPK fertilizers via  $\text{HNO}_3$  route rely on the complex and diverse nature of the waste materials that might be used. Specific waste sources need to be investigated to assess their effect on the phase composition and crystallization temperature of the resulting solutions. This is especially true if less soluble metal salts are obtained, as opposed to those of Cu and Zn. By the same token, some metals present in the waste, while soluble, might be actually toxic to the plants even at trace concentrations. For this reason, agrochemical experiments need to be performed to determine the suitability for the specific waste to improve plant viability. Outside the need for agrochemical response to these micronutrient-enriched fertilizers, proposed research will focus on the selective extraction of the specific metals from waste, rather than complete dissolution of waste material. Finally, the presence of any organic compounds in waste materials could result in secondary reactions with  $\text{HNO}_3$ , a powerful oxidant, and the reactive organic intermediates, and their toxicity would need to be explored.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Fiksel, J. A framework for sustainable materials management. *JOM* **2006**, *58*, 15–22.
- (2) Allen, F. W.; Halloran, P. A.; Leith, A. H.; Lindsay, M. C. Using material flow analysis for sustainable materials management. *J. Ind. Ecol.* **2009**, *13*, 662–665.
- (3) Siddique, R. Utilization of coal combustion by-products in sustainable construction materials. *Resour., Conserv. Recycl.* **2010**, *54*, 1060–1066.
- (4) Calkins, M. *A Complete Guide to the Evaluation, Selection, and Use of Sustainable Construction Materials*; John Wiley & Sons Ltd: Hoboken, NJ, 2008.
- (5) Smadi, M. M.; Haddad, R. H.; Akour, A. M. Potential use of phosphogypsum in concrete. *Cem. Concr. Res.* **1999**, *29*, 1419–1425.
- (6) Hunter, A. H. *Use of phosphogypsum fortified with other selected essential elements as soil amendment on low cation exchange soils*; Publication 01-034-081 prepared for Florida Institute of Phosphate Research: Bartow, FL, 1989.
- (7) Fytali, D.; Zabanitoutou, A. Utilization of sewage sludge in EU application of old and new methods—A review. *Renewable Sustainable Energy Rev.* **2008**, *12*, 116–140.
- (8) Townsend, A. R.; Howarth, R. W.; Bazzaz, F. A.; Booth, M. S.; Cleveland, C. C.; Collinge, S. K.; Dobson, A. P.; Epstein, P. R.; Holland, E. A.; Keeney, D. R.; et al. Human health effects of a changing global nitrogen cycle. *Front. Ecol. Environ.* **2003**, *1*, 240–246.
- (9) He, Z. L.; Yang, X. E.; Stoffella, P. J. Trace elements in agroecosystems and impacts on the environment. *J. Trace Elem. Med. Biol.* **2005**, *19*, 125–140.
- (10) Fields, S. Global nitrogen: cycling out of control. *Environ. Health Perspect.* **2004**, *112*, A556–A563.
- (11) Ågren, G. I. Stoichiometry and Nutrition of Plant Growth in Natural Communities. *Annu. Rev. Ecol., Evol., Syst.* **2008**, *39*, 153–170.
- (12) Kochian, L. V. Plant nutrition: Rooting for more phosphorus. *Nature* **2012**, *488*, 466–467.
- (13) Elser, J.; Bennett, E. Phosphorus cycle: A broken biogeochemical cycle. *Nature* **2011**, *478*, 29–31.
- (14) Conley, D. J.; Paerl, H. W.; Howarth, R. W.; Boesch, D. F.; Seitzinger, S. P.; Havens, K. E.; Lancelot, C.; Likens, G. E. Controlling Eutrophication: Nitrogen and Phosphorus. *Science* **2009**, *323*, 1014–1015.
- (15) Mohr, H.; Schopfer, P. *Plant Physiology*; Springer: New York, 1995.
- (16) Wuana, R. A.; Okieimen, F. E. Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. *ISRN Ecol.* **2011**, 402647.
- (17) Bell, R. W.; Dell, R. *Micronutrients for Sustainable Food, Feed, Fibre and Bioenergy Production*; International Fertilizer Industry Association: Paris, France, 2008.
- (18) Agrawal, A.; Kumari, S.; Sahu, K. K. Iron and copper recovery/removal from industrial wastes: A Review. *Ind. Eng. Chem. Res.* **2009**, *48*, 6145–6161.
- (19) Dermentzis, K.; Davidis, A.; Papadopoulou, D.; Christoforidis, A.; Ouzounis, K. Copper removal from industrial wastewaters by means of electrostatic shielding driven electrodeionization. *J. Eng. Sci. Technol. Rev.* **2009**, *2*, 131–136.
- (20) Monser, L.; Adhoum, N. Modified activated carbon for the removal of copper, zinc, chromium and cyanide from wastewater. *Sep. Purif. Technol.* **2002**, *26*, 137–146.
- (21) Panayotova, M. I. Kinetics and thermodynamics of copper ions removal from wastewater by use of zeolite. *Waste Manage. (Oxford, U.K.)* **2001**, *21*, 671–676.
- (22) Matlock, M. M.; Howerton, B. S.; Atwood, D. A. Chemical precipitation of heavy metals from acid mine drainage. *Water Res.* **2002**, *36*, 4757–4764.
- (23) Baltrusaitis, J.; Sviklas, A. M.; Galeckiene, J. Liquid and Solid Compound Granulated Diurea Sulfate-Based Fertilizers for Sustainable Sulfur Source. *ACS Sustainable Chem. Eng.* **2014**, *2*, 2477–2487.
- (24) European Parliament, Council of the European Union. Regulation (EC) No. 2003/2003 of the European Parliament and of the Council of 13 October 2003 relating to fertilisers. *Off. J. Eur. Union, L* **2003**, *304*, 1–194.
- (25) Prior, T.; Kift, R. Pseudosymmetry in  $\text{Cr}(\text{urea})_4(\text{H}_2\text{O})_2 \cdot 3\text{NO}_3 \cdot \text{J. Chem. Crystallogr.}$  **2011**, *41*, 1616–1623.
- (26) Prior, T.; Kift, R. Synthesis and crystal structures of two metal urea nitrates. *J. Chem. Crystallogr.* **2009**, *39*, 558–563.
- (27) Stojceva Radovanovic, B. C.; Premovic, P. I. Thermal behaviour of  $\text{Cu}(\text{II})$ -urea complex. *J. Therm. Anal.* **1992**, *38*, 715–719.
- (28) Baltrusaitis, J.; Sviklas, A. M. Phase composition of aqueous urea-ammonium nitrate (UAN)-zinc nitrate solutions for sustainable reuse of Zn containing industrial pigment waste. *ACS Sustainable Chem. Eng.* **2015**, *3*, 950–958.
- (29) Ibnlfassi, A.; El Kacemi, K.; Kaddami, M. Study at 25° C of the liquid-solid equilibria of three ternary systems  $\text{H}_2\text{O} - \text{Zn}(\text{NO}_3)_2 - \text{NH}_4\text{NO}_3$ ;  $\text{H}_2\text{O} - \text{Cu}(\text{NO}_3)_2 - \text{NH}_4\text{NO}_3$ ;  $\text{H}_2\text{O} - \text{Zn}(\text{NO}_3)_2 - \text{Cu}(\text{NO}_3)_2$ . *Phys. Chem. News* **2003**, *14*, 92–98.
- (30) UN Industrial Development Organization, International Fertilizer Development Center, Eds. *Fertilizer Manual*, 3rd ed.; Springer: New York, 1998.
- (31) Khurana, H. S.; Saroa, G. S.; Vig, A. C. Nitrophosphates and DAP are equally effective as P fertilizers for various crop species grown in rotation on a Typic Haplustept. *Nutr. Cycling Agroecosyst.* **2004**, *68*, 273–281.
- (32) Sullivan, J.; Grinstead, J., Jr.; Kohler, J. Nitric acid acidulation of phosphate rock and pyrolysis of acidulate to produce phosphatic and nitrogen fertilizers. *Fertil. Res.* **1992**, *32*, 239–248.