Phase Composition of Aqueous Urea–Ammonium Nitrate (UAN)–Zinc Nitrate Solutions for Sustainable Reuse of Zinc Containing Industrial Pigment Waste

J. Baltrusaitis*,[†] and A. M. Sviklas[‡]

[†]Department of Chemical and Biomolecular Engineering, Lehigh University, B336 Iacocca Hall, 111 Research Drive, Bethlehem, Pennsylvania 18015, United States

[‡]Department of Physical and Inorganic Chemistry, Kaunas University of Technology, Radvilenu street 19, LT-50254 Kaunas, Lithuania

ABSTRACT: Sustainable metal recovery from waste is of utmost importance. Zn is a micronutrient that is abundant in many industrial wastes. In this work, the process of converting industrial white pigment waste into a Zn micronutrient containing nitrogen fertilizers was developed utilizing an HNO_3 extraction method. For this purpose, solubility diagrams, polytherms, were constructed of the ternary $CO(NH_2)_2–Zn(NO_3)_2–H_2O$ and $NH_4NO_3–Zn(NO_3)_2–H_2O$ systems to determine the corresponding phase equilibria and solid material chemical composition. Complex salts containing Zn and two and four urea molecules were observed and the catalytic $Zn(NO_3)_2$ effect was observed at the decomposition temperature of $CO(NH_2)_2$ during thermal analysis. Two crystalline phases of NH_4NO_3, namely III and IV, were observed and the corresponding transition temperature decreased with increasing $Zn(NO_3)_2$ concentration in solution. Zn extraction in the form of soluble $Zn(NO_3)_2$ was performed from the white pigment industrial waste and optimal extraction parameters including HNO_3 concentration, stoichiometric amount and temperature were determined. These included a 60 °C solution temperature, 55% HNO_3 concentration and 140% of stoichiometric HNO_3 amount. This agreed well with the reactive conditions currently used in nitrophosphate fertilizer production potentially enabling direct production of micronutrient containing NP fertilizers without significant technology modification. Sensible compositions of UAN-28 and UAN-30 liquid fertilizers containing Zn micronutrient from industrial grade compounds and pigment waste extracted $Zn(NO_3)_2$ were obtained and their physicochemical properties were measured.

KEYWORDS: Urea, Ammonium nitrate, Zinc nitrate, Polytherm, Phase composition, Pigment waste
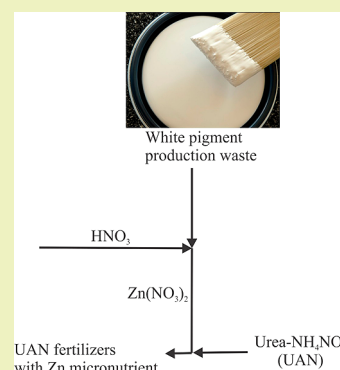
■ INTRODUCTION

Sustainable material management is a major societal challenge, as it is critical to minimize the environmental impact of materials currently used in both the residential and industrial sectors.[1] The world is experiencing an unprecedented growth in economic development and human population along an the ever increasing demand in the use of air, land, water and other Earth resources.[2] As economies grow, more materials are being consumed and transported large distances. This causes a shift in material sources from domestic to imported thus shifting, but not eliminating, the environmental burden.[3] Unless economic growth can be decoupled from resource use and waste generation, the environmental burden will significantly increase.[4] This is especially important for large economies such as the U.S., where highly complex and intertwined use and reuse of materials is necessary in the most productive and sustainable way across their entire life cycle. For example, serious ecological and societal problems may arise from the unbalanced use of traditional mineral fertilizers such as ammonium nitrate, urea, superphosphate, ammonium phosphate and nitrophosphate.[5] Use of unbalanced major nutrient

(N, P, K, Ca, Mg and S) amounts as well as the absence of micronutrients (Zn, Cu, Fe, Mn, Mo, Co and B)[6] can often preclude full utilization of the mineral fertilizers and as a result lead to the pollution of soil and groundwater.[7] This is due to the fact that every plant species has specific nutrient amounts as well as nutrient ratio requirements during various growth stages[8] and nutrient excess is not consumed but dispersed into the environment.[9−11]

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.[6] Microelement deficiency leads not only to slowed growth and reduced yields but also to metabolic and developmental defects in plants.[12] Effectively, the absence of these microelements in soil makes it impossible to improve the crop yields notwithstanding any excess of major

nutrients. Zn is of particular importance for plant growth. Zn is present in all plants and involved in many cellular processes including enzyme activation[13] as well as photo-[14] and protein[15] synthesis. Zinc also plays an important role in seed development, and zinc-deficient plants show delayed maturity.[15] Recent data indicates that large areas of Zn deficiency occur in Northern China, India, across the Middle East to the Eastern Mediterranean, South and Central Africa, Central America, Northeast Brazil and Southern Australia.[16] Zinc is added to fertilizers in the form of inorganic salts, oxides or chelated organometallic complexes. Currently used chelated zinc compounds as a micronutrient source in fertilizers include derivatives of ethylenediaminetetraacetic acid (EDTA) including $Na_2ZnEDTA$ (8−14% Zn), NaZnHEDTA (6−10% Zn), NaZnEDTA (9−13% Zn) and NaZnNTA (9−13% Zn). When zinc is included in solid fertilizers as a granular zinc chelate, it is likely to be more mobile and thus more effective than granular forms of inorganic sulfur sources such as zinc sulfate. However, when liquid fertilizers are used, zinc chelate does not outperform the inorganic sources of zinc. In general, zinc chelates are too expensive to be used at the rates needed to maintain necessary zinc levels in soil. This, in turn, leads to the increased NPK fertilizer price and consequently to high prices of crops.

Some industrial waste and byproducts contain microelements such as Zn and can potentially be used via microelement extraction or directly in fertilizer production because of their low cost.[16] Zinc is present in a variety of solid and liquid wastes originating from the dye and pigment industry, galvanization processes, electric arc furnaces, used tire ash, rubber, disposed batteries as well as metallurgical processes.[17] Zn is typically recovered from metallurgical processing waste using sulfuric acid, hydrochloric acid, ammoniacal solutions, sodium hydroxide as well as organic acids and further purified by cementation, solvent extraction, ion exchange or membrane recovery processes.[17,18] Zinc metal or its salt could further be produced from the purified solutions by electrowinning or crystallization and reused.[17,19] On the other hand, a much more direct, yet least explored method, of zinc waste utilization is its combination with the major nutrient containing fertilizers for their sustainable use. Nonpressure liquid nitrogen fertilizer, an aqueous mixture of urea and ammonium nitrate (UAN), is very widely used in the USA, Europe, India and other countries. It is safer to handle, store, transport and apply than its pressurized counterparts such as anhydrous or aqueous ammonia. In the U.S., 11.5 million tons of nonpressure liquid nitrogen fertilizers were consumed in 2011. UAN is produced in three concentrations containing 28, 30 and 32% nitrogen. Importantly, the crystallization temperature directly depends on the concentration of the nitrogen solution which are typically −18, −10 and −2 °C, respectively. However, when micronutrients are added, the crystallization temperature will be heavily affected. Thus, for Zn containing UAN to be obtained, ternary phase diagrams, including $CO(NH_2)_2$−$Zn(NO_3)_2$−H_2O and NH_4NO_3−$Zn(NO_3)_2$−H_2O, need to be constructed and the corresponding phase compositions need determined. The work presented here focuses on the liquid−solid equilibria of aqueous solutions involving UAN components as well as $Zn(NO_3)_2$. Although reagent grade chemicals were used to determine the corresponding phase diagrams, solid white pigment industrial waste in combination with industrial grade nitrogen fertilizers were used to obtain micronutrient enriched fertilizers. A sustainable source of zinc, $Zn(NO_3)_2$ obtained via

HNO_3 extraction was used and the resulting physicochemical parameters determined. Optimal extraction parameters of HNO_3 concentration, temperature and reactant stoichiometry were also determined with the goal of integration into existing nitrogen fertilizer manufacturing processes such as those of UAN solution or nitrophosphate production.

■ EXPERIMENTAL DETAILS

Reagents. $CO(NH_2)_2$, NH_4NO_3 and $Zn(NO_3)_2 \cdot 6H_2O$ 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 $CO(NH_2)_2$ (46.3% N),
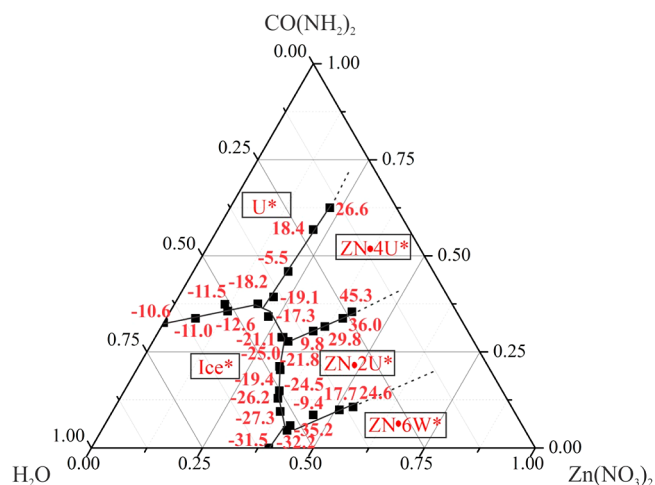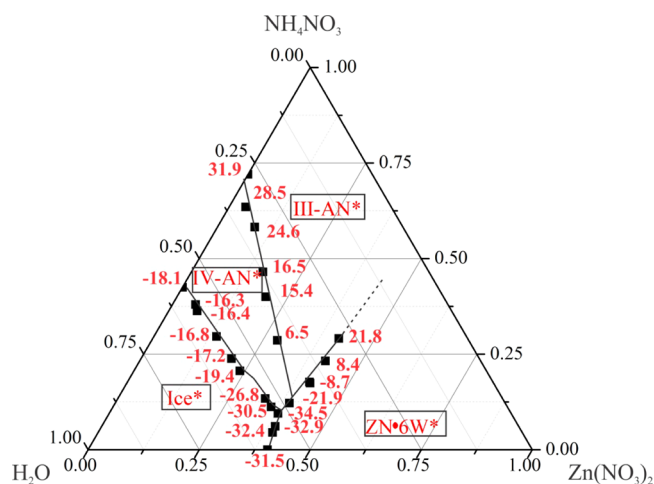

Figure 1. Measured phase diagram of the ternary $CO(NH_2)_2$−$Zn(NO_3)_2$−H_2O system. Five distinct crystalline phase regions, Ice* (ice), U* (urea), ZN·2U* (zinc nitrate−diurea), ZN·4U* (zinc nitrate−tetraurea) and ZN·6W* (zinc nitrate hexahydrate), can be distinguished by the black polytherm curve connecting the eutectic points measured. Crystallization temperatures are shown in red next to the corresponding points. Lines are for eye guidance only, dotted lines show phase boundaries where due to the too high crystallization temperature measurements were not performed. Concentrations are expressed in terms of fraction for brevity.

NH_4NO_3 (34.4% N) and HNO_3 (58% aqueous solution) were obtained from SC "Achema", Jonava, Lithuania and used as received for Zn extraction from industrial waste and UAN-28 and UAN-30 manufacturing shown in Table 1. Double-distilled water was used to make solutions.

Solubility Experiments. The main goal of these experiments was determination of the phase composition of $CO(NH_2)_2$−$Zn(NO_3)_2$−H_2O and NH_4NO_3−$Zn(NO_3)_2$−H_2O in a wide temperature range and both UAN component, $CO(NH_2)_2$ and NH_4NO_3, interactions with $Zn(NO_3)_2$ that may have an effect on the phase equilibrium. Solubility measurements of ternary $CO(NH_2)_2$−$Zn(NO_3)_2$−H_2O and NH_4NO_3−$Zn(NO_3)_2$−H_2O mixtures were performed using visual polythermal method. Six molecules of crystalline H_2O were accounted for in ternary diagram composition. Two ternary phase diagrams were constructed because a single UAN ($CO(NH_2)_2$ + NH_4NO_3)−$Zn(NO_3)_2$−H_2O phase diagram would need to be represented in a four dimensional space and would be too complex to interpret. This method has been successfully utilized before[20] 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:

- ice + KCl (cooling down to −11.0 °C)

Figure 2. Measured phase diagram of the ternary NH₄NO₃−Zn(NO₃)₂−H₂O system. Five distinct crystalline phase regions, Ice* (ice), IV-AN* (phase IV NH₄NO₃), III-AN* (phase III NH₄NO₃) and ZN·6W* (zinc nitrate hexahydrate), can be distinguished by the black polytherm curve connecting the eutectic points measured. Crystallization temperatures are shown in red next to the corresponding points. Lines are for eye guidance only, dotted lines show phase boundaries where, due to the too high crystallization, temperature measurements were not performed. Concentrations are expressed in terms of fraction for brevity.

- ice + NH₄NO₃ (down to −17.3 °C)
- ice + NaCl (down to −21.2 °C)
- 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.

Chemical Analysis. Total nitrogen in crystals obtained from both $CO(NH_2)_2$−$Zn(NO_3)_2$−H_2O and NH_4NO_3−$Zn(NO_3)_2$−H_2O systems were 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, the distillate being collected in an excess of standard sulfuric acid. The excess acid is titrated by means of a standard alkaline solution.[21] Zinc as well as other metal concentration in solutions was determined using an AAnalyst 400 (PerkinElmer, USA) atomic absorption spectrometer.

Instrumental Analysis. Differential thermal analysis was performed using a Du Pont Instruments 990 Thermal Analyzer operating at 10 mV/cm sensitivity and 10 °C/min temperature ramp time. Aluminum oxide was used as the inert material. The temperature interval used was 20−600 °C, accuracy reported of ±2 °C. Mass of the sample used was 500 mg.

RESULTS AND DISCUSSION

$CO(NH_2)_2$−$Zn(NO_3)_2$−H_2O System Phase Composition. The ternary phase composition was explored and a phase diagram was constructed based on the compositions, as shown in Table 2. In particular, a series of fixed $Zn(NO_3)_2$:H_2O ratio

Table 2. $CO(NH_2)_2$−$Zn(NO_3)_2$−H_2O and NH_3NO_3−$Zn(NO_3)_2$−H_2O Ternary Phase Composition Used in Analysis[a]

number	mass composition
$CO(NH_2)_2$−$Zn(NO_3)_2$−H_2O	
I	(5-x)[10% Zn(NO₃)₂+90% H₂O]+xCO(NH₂)₂
II	(5-x)[20% Zn(NO₃)₂+80% H₂O]+xCO(NH₂)₂
III	(5-x)[30% Zn(NO₃)₂+70% H₂O]+xCO(NH₂)₂
IV	(5-x)[40% Zn(NO₃)₂+60% H₂O]+xCO(NH₂)₂
V	(5-x)[50% Zn(NO₃)₂+50% H₂O]+xCO(NH₂)₂
VI	(5-x)[60% Zn(NO₃)₂+40% H₂O]+xCO(NH₂)₂
VII	(5-x)[10% CO(NH₂)₂+90% H₂O]+xZn(NO₃)₂
VIII	(5-x)[20% CO(NH₂)₂+80% H₂O]+xZn(NO₃)₂
IX	(5-x)[30% CO(NH₂)₂+70% H₂O]+xZn(NO₃)₂
X	(5-x)[40% CO(NH₂)₂+60% H₂O]+xZn(NO₃)₂
XI	(5-x)[50% CO(NH₂)₂+50% H₂O]+xZn(NO₃)₂
XII	(5-x)[60% CO(NH₂)₂+40% H₂O]+xZn(NO₃)₂
XIII	(5-x)[10% CO(NH₂)₂+90% Zn(NO₃)₂]+xH₂O
XIV	(5-x)[20% CO(NH₂)₂+80% Zn(NO₃)₂]+xH₂O
XV	(5-x)[30% CO(NH₂)₂+70% Zn(NO₃)₂]+xH₂O
XVI	(5-x)[40% CO(NH₂)₂+60% Zn(NO₃)₂]+xH₂O
XVII	(5-x)[50% CO(NH₂)₂+50% Zn(NO₃)₂]+xH₂O
XVIII	(5-x)[60% CO(NH₂)₂+40% Zn(NO₃)₂]+xH₂O
NH_3NO_3−$Zn(NO_3)_2$−H_2O	
I	(5-x)[10% NH₄NO₃+90% H₂O]+xZn(NO₃)₂
II	(5-x)[20%NH4NO₃+80% H₂O]+xZn(NO₃)₂
III	(5-x)[30% NH4NO₃+70% H₂O]+xZn(NO₃)₂
IV	(5-x)[40% NH4NO₃+60% H₂O]+xZn(NO₃)₂
V	(5-x)[50% NH4NO₃+50% H₂O]+xZn(NO₃)₂
VI	(5-x)[10% Zn(NO₃)₂+90% H₂O]+xNH₄NO₃
VII	(5-x)[20% Zn(NO₃)₂+80% H₂O]+xNH₄NO₃
VIII	(5-x)[30% Zn(NO₃)₂+70% H₂O]+xNH₄NO₃
IX	(5-x)[40% Zn(NO₃)₂+60% H₂O]+xNH₄NO₃
X	(5-x)[50% Zn(NO₃)₂+50%0 H₂O]+xNH₄NO₃
XI	(5-x)[20%NH₄NO₃+80% Zn(NO₃)₂]+xH₂O
XII	(5-x)[10%NH₄NO₃+90% Zn(NO₃)₂]+xH₂O

[a]Total of 5 g of material was used, and x varied from 0 to 5.

solutions from I through VI were prepared, and the amount of $CO(NH_2)_2$ added was varied. Further, a series of fixed

Table 1. UAN-28 and UAN-30 Liquid Fertilizers Containing Zn Micronutrient Obtained from White Pigment Production Solid Waste[a]

UAN-28					UAN-30				
micronutrient amount, %		measured properties			micronutrient amount, %		measured properties		
Zn	Cu	density, kg/m³	pH	T_{cryst}, °C	Zn	Cu	density, kg/m³	pH	T_{cryst}, °C
0.025	0.004	1281	6.2	−16.0	0.025	0.004	1312	6.1	−5.4
0.05	0.009	1283	6.1	−11.6	0.05	0.009	1316	6.0	−4.7
0.125	0.02	1289	5.9	−8.9	0.125	0.02	1321	5.8	−3.2
0.25	0.04	1294	5.7	−7.2	0.25	0.04	1326	5.6	−2.1
0.5	0.08	1301	5.5	−5.6	0.5	0.08	1331	5.4	−0.5

[a]UAN-28: NH₄NO₃ = 40.1%, urea = 30.0% and H₂O = 29.9%. UAN-30: NH₄NO₃ = 42.2%, urea = 32.7% and H₂O = 25.1%. Technical grade $CO(NH_2)_2$ (46.3% N), NH₄NO₃ (34.4% N) and HNO₃ (58% aqueous solution) were obtained from SC "Achema", Jonava, Lithuania and used as received while Zn(NO₃)₂ was obtained via extraction from industrial waste using industrial grade 58% HNO₃.

Table 3. CO(NH₂)₂−Zn(NO₃)₂−H₂O Phase Diagram Critical Points with the Corresponding Solution Composition and Solid Phase Detected

sample	solution composition, wt %			crystallization temperature, °C	solid phase detected
	Zn(NO₃)₂	CO(NH₂)₂	H₂O		
−	0.0	32.6	67.4	−10.6	Ice*+U*
I	6.6	33.7	59.7	−11.0	Ice*+U*
II	12.9	35.6	51.5	−12.6	Ice*+U*
III	18.8	37.5	43.7	−18.2	Ice*+U*
IV	21.3	45.7	32.6	−5.5	U*+ZN·4U*
IV	28.5	28.8	42.7	−21.1	ZN·4U*+Ice*
V	21.6	56.8	21.6	18.4	U*+ZN·4U*
	34.8	30.4	34.8	9.8	ZN·4U*+ZN·2U*
	45.7	8.6	45.7	−9.4	ZN·2U*+ZN·6W*
VI	22.5	62.5	15.0	26.6	U*+ZN·4U*
	39.8	33.7	26.5	36.0	ZN·4U*+ZN·2U*
	53.6	10.7	35.7	24.6	ZN·2U*+ZN·6W*
	40.6	0.0	59.4	−31.5	ZN·6W*+Ice*
VII	41.9	5.8	52.3	−35.2	ZN·6W*+Ice*+ZN·2U*
VIII	35.6	12.9	51.5	−26.2	ZN·2U*+Ice*
	51.0	9.8	39.2	17.7	ZN·2U*+ZN·6W*
IX	32.4	20.3	47.3	−19.4	ZN·2U*+Ice*
X	30.5	27.7	41.8	−25.0	ZN·2U*+Ice*+ZN·4U*
	11.4	37.4	51.2	−11.5	U*+Ice*
XI	36.8	31.6	31.6	29.2	ZN·2U*+ZN·4U*
	21.4	39.3	39.3	−19.1	U*+Ice*+ZN·4U*
XII	41.0	35.4	23.6	45.3	ZN·2U*+ZN·4U*
	22.0	46.8	31.2	0.8	ZN·4U*+U*
XIII	41.8	4.6	53.6	−32.2	ZN·6W*+Ice*
XIV	37.8	9.5	52.7	−27.3	ZN·2U*+Ice*
XV	34.9	14.9	50.2	−24.5	ZN·2U*+Ice*
XVI	31.8	21.2	47.0	−20.8	ZN·2U*+Ice*
XVII	28.8	28.8	42.4	−21.3	ZN·4U*+Ice*
XVIII	22.8	34.2	43.0	−17.3	ZN·4U*+Ice*

CO(NH₂)₂:H₂O ratio solutions from VII through XII were prepared and the amount of Zn(NO₃)₂ added was varied. Finally, a series of fixed CO(NH₂)₂:Zn(NO₃)₂ ratio solutions from XIII through XVIII 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 3, whereas 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 +49.0 to −35.2 °C. In general, high crystallization temperature solutions had high either Zn(NO₃)₂ or CO(NH₂)₂ concentrations and crystallized in complex compositions of Zn complexed with urea. On the other hand, medium and low crystallization temperature solutions were diluted and when crystallized, separate phases of ice, urea and Zn−urea complexes were obtained. In total, five distinct chemical composition compounds were isolated, including ice (labeled in Figure 1 as Ice* phase), CO(NH₂)₂ (U*), Zn(NO₃)₂·2CO(NH₂)₂ (ZN·2U*), Zn(NO₃)₂·4CO(NH₂)₂ (ZN·4U*) and Zn(NO₃)₂·6H₂O (ZN·6W*), as shown according to their corresponding concentration regions in Figure 1. Not surprisingly, Ice* phase crystallized in H₂O rich conditions. Somewhat unexpectedly, complex ZN·2U* and ZN·4U* phases were obtained when high concentrations of urea and Zn(NO₃)₂ were used rather than the isolated corresponding crystalline phases. However, the presence of complex salts has been observed in earlier literature while exploring the isotherms of CO(NH₂)₂−

Zn(NO₃)₂−H₂O systems at 0, 15 and 25 °C.[22−25] Urea is a known supramolecular chemistry building block, and several recent publications utilized it as a complexing metal for the ligand via nitrogen atoms.[26,27] While stoichiometrically Zn-(NO₃)₂·2CO(NH₂)₂ and Zn(NO₃)₂·4CO(NH₂)₂ compositions were determined using chemical analysis in the present work, a complex crystalline structure with urea atoms being in proximity of Zn metal has been shown to result when the corresponding solid compounds are dissolved and recrystallized from aqueous ethanol solutions.[27] Thermogravimetric analysis of the complex Zn(NO₃)₂·2CO(NH₂)₂ and Zn(NO₃)₂·4CO-(NH₂)₂ salts was performed and results presented in the following section to better understand the nature of these complex salts.

For practical applications, these complex salts can act as solid fertilizers containing both nitrogen and micronutrient Zn. However, rather low Zn concentrations (<1%) are needed for crops and thus appropriate aqueous solutions were determined using polytherms derived in this work and shown in Figure 1. The 0 °C isotherm data from composition XVII in Table 2 indicated that typical CO(NH₂)₂ concentrations in UAN of 30.0 to 32.7%, up to 31% Zn(NO₃)₂ can be dissolved. This, in principle, defines the maximum concentration of Zn(NO₃)₂ that can be present in aqueous UAN solutions. Because NH₄NO₃ is also present in the solution and will affect solubility, we will later explore similar solubility parameters in the NH₄NO₃−Zn(NO₃)₂−H₂O system.

Thermogravimetric Analysis. $CO(NH_2)_2–Zn(NO_3)_2–H_2O$ system phase equilibrium compositions indicated the formation of complex salts that have been observed previously.[22−25] Our chemical analysis indicated the presence of both $Zn(NO_3)_2·2CO(NH_2)_2$ and $Zn(NO_3)_2·4CO(NH_2)_2$. In principle, these compounds can be proposed for use in Zn containing solid nitrogen fertilizers. This is important because complex salts containing urea and strong acid groups could be used to potentially address a major problem of nitrogen sustainability due to its loss from urea fertilizers.[28] Urea promptly hydrolyzes in wet soil in the presence of bacteria urease to yield NH_3 and CO_2[29,30] and the presence of strong acid groups in one crystalline cell can inhibit NH_3 release. To assess the thermal stability of these compounds, thermal measurements were performed by recording the extrema observed during the differential temperature analysis and thermogravimetric analysis. The observed values are shown in Table 4. In addition to the complex salts, the thermal properties

Table 4. Thermal Characterisitics Measured of the Solid Compounds Detected and Crystallized out of the Ternary $CO(NH_2)_2–Zn(NO_3)_2–H_2O$ System[a]

compound	$T_{melting}$, °C	$T_{decomposition}$, °C	$T_{decomposition-final}$, °C
$Zn(NO_3)_2·6H_2O$	37	332	420
$CO(NH_2)_2$	132	180, 245, 400	540
$Zn(NO_3)_2·2CO(NH_2)_2$	50	140, 370	470
$Zn(NO_3)_2·4CO(NH_2)_2$	70	140, 350−370	520

[a]$Zn(NO_3)_2·6H_2O$ and $CO(NH_2)_2$ were standard compounds, whereas $Zn(NO_3)_2·2CO(NH_2)_2$ and $Zn(NO_3)_2·4CO(NH_2)_2$ were isolated from the ternary system via crystallization.

of their parent compounds, $CO(NH_2)_2$ and $Zn(NO_3)_2·6H_2O$, were measured and also shown in Table 4. $Zn(NO_3)_2·2CO(NH_2)_2$ exhibited two endothermal effects with the onsets at 50 and 100 °C. They were assigned to the melting and decomposition temperatures of the complex salts. Decomposition proceeds fastest at 140 °C and 23% of material decomposes. The measured decomposition rate at 140 °C was 30 mg/min. A third endothermal effect was observed at 370 °C with a very rapid decomposition rate of 600 mg/min and the final decomposition temperature of 470 °C resulting in ZnO. This assignment is supported from the mass consideration where 23% of the initial mass was remaining. $Zn(NO_3)_2·4CO(NH_2)_2$ starts melting at 70 °C. This compound also decomposes in distinct stages with the first onset at 120 °C. A maximum decomposition rate of 19 mg/min is achieved at 140 °C and 9% mass is lost during this decomposition step. The second and most intensive decomposition step is observed at 350−370 °C with a rate of 800 mg/min. The compound fully decomposes at 520 °C to form ZnO as inferred from the decrease in the initial mass of 82%.

The thermal data obtained for the complex salts shown in Table 4 significantly differ from those of the corresponding pure compounds. For example, $Zn(NO_3)_2$ starts melting at 37 °C whereas $CO(NH_2)_2$ at 132 °C. In addition, the decomposition rate of complex salts is much greater than $CO(NH_2)_2$ implying catalytic $Zn(NO_3)_2$ effect. Importantly, the data presented in Table 4 imply that temperature limitations exist during the synthesis process. Temperature cannot be kept higher than 100−120 °C due to the ensuing decomposition and the corresponding loss of material.

$NH_4NO_3–Zn(NO_3)_2–H_2O$ System Phase Composition. The ternary phase composition was explored and a phase diagram was constructed based on compositions, as shown in Table 2. In particular, a series of fixed NH_4NO_3:H_2O ratio solutions from I through V were prepared and the amount of $Zn(NO_3)_2$ added was varied. Further, a series of fixed $Zn(NO_3)_2$:H_2O ratio solutions from VI to X and the amount of NH_4NO_3 added was varied. Finally, a series of fixed NH_4NO_3:$Zn(NO_3)_2$ ratio solutions XI and XII were prepared and the amount of H_2O added was varied. The crystallization temperatures measured, along with the corresponding solution phase and crystallized solid phase compositions, are summarized in Table 5, whereas 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 +46.0 to −32.9 °C. In general, high H_2O content samples resulted in ice crystallization whereas $Zn(NO_3)_2·6H_2O$ crystallized from samples with high $Zn(NO_3)_2$ content. No complex salts were observed, which is different from the $CO(NH_2)_2–Zn(NO_3)_2–H_2O$ system because the nitrogen atom is protonated in NH_4NO_3 and cannot be directly involved in binding the metal atoms. Isotherms in $NH_4NO_3–Zn(NO_3)_2–H_2O$ and $NH_4NO_3–Zn(NO_3)_2·6H_2O–H_2O$ ternary systems were explored and constructed at −25, −20, +20, +25 °C[31,32] and 0, +15, +20 °C,[33,34] respectively. The polytherm determined in this work and shown in Figure 2 explores a full compositional space and provides for the proposed Zn micronutrient containing UAN compositions that occur in the narrow range of crystallization temperatures of ∼0 °C. The data corresponding to 0 °C isotherm in the case of H_4NO_3 obtained from the composition VII in Table 2 suggested that, at typical NH_4NO_3 concentrations in UAN 40.1 to 42.2%, NH_4NO_3 does not crystallize up to the $Zn(NO_3)_2$ concentrations of 12%. This is smaller than the value obtained in the $CO(NH_2)_2–Zn(NO_3)_2–H_2O$ system and can be considered the upper solubility limit for UAN solutions which will further be lowered when both $CO(NH_2)_2$ and NH_4NO_3 are present in solution.

A rather unexpected observation was inflection points in the solubility curves IV through VIII that indicated two different phases in the solid material crystallizing. Chemical composition (equal total nitrogen content and absence of Zn) indicated formation of two different NH_4NO_3 phases. Literature data indicate that phase IV to phase III transformation proceeds in the 43 to 51 °C range in solid sample,[35] although 32 °C is the typically observed value.[36] This is in accordance with the values observed in this work at 6.5, 15.4, 16.5, 24.6, 28.5 and 31.9 °C for decreasing concentrations of $Zn(NO_3)_2$, as shown in Figure 2. A closely related observation can be inferred that increasing $Zn(NO_3)_2$ in solution lowers IV→III transition temperature for NH_4NO_3, in agreement with some recent work on solid phase transitions of $NH_4NO_3–KNO_3$ mixture,[37] which have profound implications for NH_4NO_3 fertilizers. Because 32 °C occurs in warm climates, day−night cycles can result in many crystalline phase transformations occurring which involve granule volume change and thus degradation of the granule integrity. Our data indicate that adding small amounts of micronutrient salts such as $Zn(NO_3)_2$ can lower the NH_4NO_3 IV→III crystalline phase transition temperature where it is not dependent on the day−night cycles and significantly improve the structural integrity of the granules while delivering micronutrients necessary for crops.

Zn Extraction from the Solid White Pigment Waste. Metal oxides including ZnO, FeO(OH) and $CoAl_2O_4$ are

Table 5. NH$_4$NO$_3$−Zn(NO$_3$)$_2$−H$_2$O Phase Diagram Critical Points with the Corresponding Solution Composition and Solid Phase Detected

| sample	solution composition, wt %			crystallization temperature, °C	solid phase detected
	NH$_4$NO$_3$	Zn(NO$_3$)$_2$	H$_2$O		
−	0.0	40.4	59.6	−31.5	Ice*+ZN·6W*
I	6.1	39.1	54.8	−32.9	Ice*+ZN·6W*
II	13.4	33.2	53.4	−26.8	Ice*+IV-AN*
II	12.2	39.2	48.6	−21.9	IV-AN*+ZN·6W*
III	23.8	20.4	55.8	−17.2	IV-AN*+Ice*
	17.7	41.0	41.3	−8.7	IV-AN*+III-AN*+ZN·6W*
IV	38.0	5.2	56.8	−16.3	Ice*+IV-AN*
	28.6	28.3	43.1	6.5	IV-AN*+III-AN*
	23.2	41.8	35.0	8.4	IV-AN*+ZN·6W*
V	29.1	41.9	29.0	21.8	IV-AN*+ZN·6W*
	40.0	20.0	40.0	15.4	IV-AN*+III-AN*
	42.5	0.0	57.5	−16.1	Ice*+IV-AN*
VI	36.3	6.4	57.3	−16.4	Ice*+IV-AN*
	63.5	3.7	32.8	28.5	IV-AN*+III-AN*
VII	29.6	14.1	56.3	−16.8	Ice*+IV-AN*
	58.2	8.4	33.4	24.6	IV-AN*+III-AN*
VIII	20.6	23.9	55.5	−19.4	Ice*+IV-AN*
	46.5	16.1	37.4	16.5	IV-AN*+III-AN*
	72.0	0.0	28.0	31.9	IV-AN*+III-AN*
IX	11.2	35.6	53.2	−30.5	Ice*+IV-AN*
X	17.4	41.3	41.3	−8.7	IV-AN*+III-AN*+ZN·6W*
XI	9.5	38.0	52.5	−34.5	Ice*+IV-AN*+ZN·6W*
XII	4.5	39.3	56.2	−32.4	Ice*+ZN·6W*

routinely used in transparent pigment production,[38] and any resulting waste can potentially be utilized as a sustainable corresponding micronutrient source. Although ZnO is no longer a major white pigment component and has been superseded by TiO$_2$, it improves film formation, durability, and resistance to mildew (having a synergistic effect with other fungicides) because it reacts with acidic products of oxidation and can absorb UV radiation.[39] All ZnO production methods result in 93−99.5% purity ZnO with other micronutrients such as Cu present in trace amounts. Additionally, other metal oxides can be present, depending on the pigment manufacturing process. The particular solid white pigment waste collected at SC "Jiesia", Kaunas, Lithuania, was analyzed and contained 70.5% ZnO and 11.6% CuO, whereas the remainder (17.9%) was composed of very low solubility Fe, Al, Mg and Mn oxides. A major obstacle in using these metal oxides as micronutrients was their very low solubility in H$_2$O. Several strong acids were employed to dissolve metals from the pigment waste. Use of concentrated H$_2$SO$_4$ did not result in appreciable amounts of metals released into the solution as the pigment waste matrix reacted with H$_2$SO$_4$ and solidified. HNO$_3$, on the other hand, dissolved Zn and Cu into solution resulting in soluble nitrate salts suitable for liquid fertilizer production. This agrees well with previous work where various HNO$_3$ (often diluted to 0.01 M) concentrations were used to extract Zn from tire waste.[40] Industrially, HNO$_3$ is produced from 58 to 63% concentration via the Ostwald process and is available in large amounts necessary for large scale Zn extraction. Insoluble Zn and Cu salts are released into solution, solubilized, via reactions 1 and 2

$$ZnO + 2HNO_3 \rightarrow Zn(NO_3)_2 + H_2O \tag{1}$$

,

$$CuO + 2HNO_3 \rightarrow Cu(NO_3)_2 + H_2O \tag{2}$$
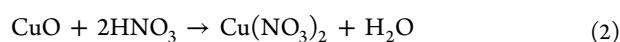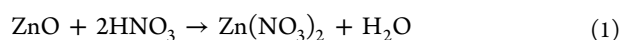
e.g., nitrate salts compatible with major nutrient−nitrogen fertilizers. We used 58% technical grade HNO$_3$ to determine dissolution dynamics of Zn from white pigment waste. In particular, we determined the dissolved Zn amount in HNO$_3$ solution from white pigment waste as a function of (a) HNO$_3$ concentration, (b) temperature and (c) excess from the calculated stoichiometric amount (where stoichiometric is 100%). These data are presented in Figure 3. In our calculations, we estimated that 80% of HNO$_3$ reacts with the Zn and Cu compounds according to reactions 1 and 2 present in the pigment waste, whereas the rest is used to dissolve the remaining compounds. In all cases, the nondigested amount of white pigment waste was separated using filtration and composed 10−15% of the initial sample mass. Points shown in Figure 3 are the average of five independent measurements. Typical standard deviation measured did not exceed 3%.

First, we investigated the HNO$_3$ concentration effect on the dissolved Zn amount. Specifically, 20%, 35%, 45% and 55% HNO$_3$ were used at 60 °C with 140% of the stoichiometric amount. Data in Figure 3a indicate that in all cases the Zn amount increases with time achieving a near steady state after 60 min of reaction. Utilizing 20% HNO$_3$, 54.9% Zn can be extracted from waste while using 55% HNO$_3$, 84.9% Zn was extracted after 60 min. Initial dissolution kinetics were slower for 45% HNO$_3$; but after 60 min, the amount of Zn was only slightly smaller than in the 55% HNO$_3$ case. We propose this is due to the slower diffusion of HNO$_3$ molecules through the particle matrix. For further experiments, 55% HNO$_3$ was used because it provided the fastest Zn dissolution and was closest to commercially available HNO$_3$ analogues.

We next determined the Zn dissolution dynamics using 55% HNO$_3$ at 60 °C as a function of HNO$_3$ stoichiometric amount. In particular, 80%, 100%, 120% and 140% of the stoichiometric amount for the reaction 1 were used and the dissolved Zn
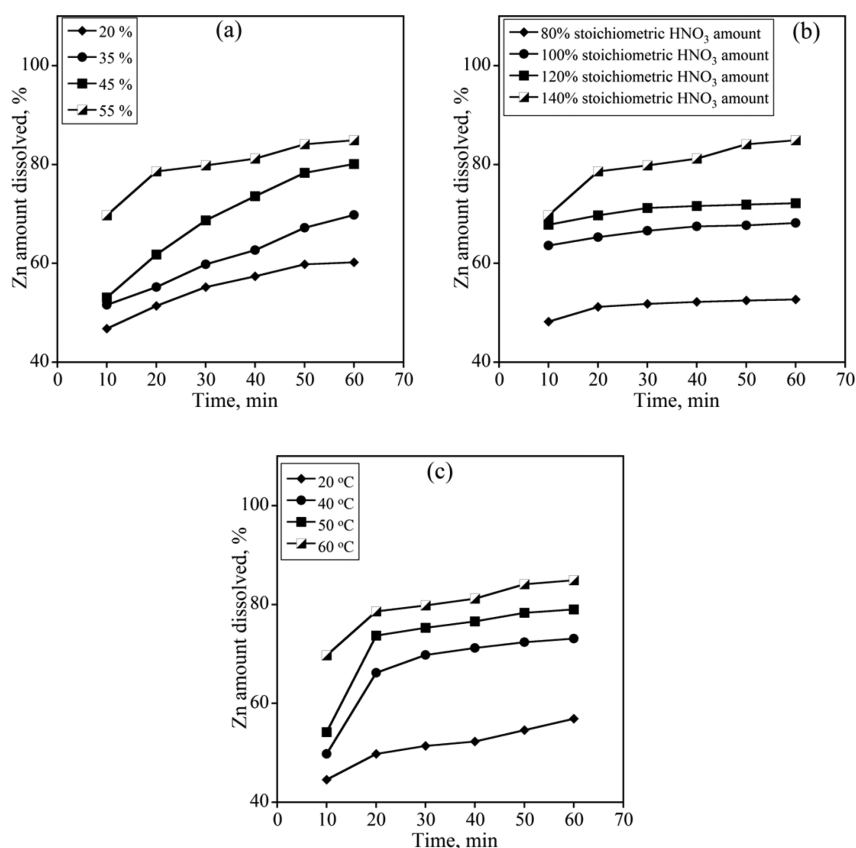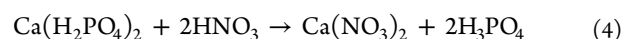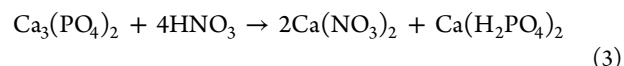
Figure 3. Zn amount measured in solution obtained from dissolved white pigment solid waste using HNO_3 as a function of (a) HNO_3 concentration, (b) HNO_3 amount used and (c) temperature of the dissolution.

amounts obtained are shown in Figure 3b. It can be seen that using an exactly stoichiometric HNO_3 amount (100%) after 60 min, 68.2% Zn is dissolved, whereas when 140% was used, 84.9% of Zn is dissolved.
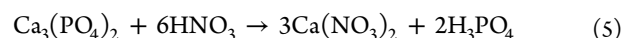
Finally, dissolved Zn amount as a function of temperature was explored using 55% HNO_3 and 140% stoichiometric amount, as shown in Figure 3c. Dissolution experiments were performed at 20, 40, 50 and 60 °C, and a monotonical increase in dissolved Zn amounts was observed in all cases increased with temperature. At 60 °C, the highest amount of Zn dissolved was 84.9%.

Importantly, the data presented in Figure 3 show that Zn (and possibly other micronutrients, such as Cu) can be extracted from pigment waste at the conditions of HNO_3 concentration and temperature very similar to those used industrially in phosphate rock reaction to produce compound NP (nitrophosphate) fertilizers.[41] Nitrophosphate fertilizers have recently been of particular interest since they can compete with more common diammonium phosphate (DAP) based fertilizers in efficient phosphorus delivery to various crop species.[42] One of the advantages of nitrophosphates over the DAP production using phosphoric- and sulfuric acid-based routes is their low cost of manufacturing. Energy requirements of nitrophosphate production are 20% lower than sulfur-based P fertilizer processing routes.[43] Additionally, from an environmental point of view, nitrophosphate manufacturing does not lead to the generation of sulfur dioxide and wastewater. Optimal Zn containing pigment waste dissolution conditions within the spectrum explored were HNO_3 concentration of 55%, reaction time of 60 min, 140% stoichiometric amount and 60 °C temperature. For comparison, the commercially used

Odda process utilizes 60% HNO_3 and 60 °C for phosphate rock dissolution with HNO_3[44] via simplified reactions 3 and 4

$$Ca_3(PO_4)_2 + 4HNO_3 \rightarrow 2Ca(NO_3)_2 + Ca(H_2PO_4)_2 \tag{3}$$

$$Ca(H_2PO_4)_2 + 2HNO_3 \rightarrow Ca(NO_3)_2 + 2H_3PO_4 \tag{4}$$

with an overall reaction 5

$$Ca_3(PO_4)_2 + 6HNO_3 \rightarrow 3Ca(NO_3)_2 + 2H_3PO_4 \tag{5}$$

.Thus, the experimental conditions of Zn removal from solid pigment waste can be applied directly during the rock dissolution stage in existing industrial processes without modifications, resulting in micronutrient enriched NP fertilizers.

Zn Micronutrient Enriched Liquid Nitrogen Fertilizers Using Industrial Grade $CO(NH_2)_2$, NH_4NO_3 as well as $Zn(NO_3)_2$ Obtained from White Pigment Waste. Finally, we synthesized UAN solutions from industrial grade $CO(NH_2)_2$ and NH_4NO_3 by dissolving them in aqueous solution of $Zn(NO_3)_2$ obtained from the pigment waste using HNO_3 digestion methods described in the previous section. UAN-28 solution was prepared by dissolving 40.1% of NH_4NO_3 and 30.0% urea in 29.9% of H_2O. UAN-30 was obtained using 42.2% NH_4NO_3, 32.7% urea and 25.1% H_2O. Technical grade $CO(NH_2)_2$ (46.3% N), NH_4NO_3 (34.4% N) and HNO_3 (58% aqueous solution) were obtained from SC "Achema", Jonava, Lithuania and used as received while $Zn(NO_3)_2$ was obtained via extraction from industrial waste using industrial grade 58% HNO_3. $Zn(NO_3)_2$ was altered from 0.025 to 0.5% of Zn, values typical for micronutrient concentrations in industrial fertilizers,

and the physicochemical properties of the resulting aqueous solutions including their density, pH and T_{cryst}, measured. Notably, because the pigment waste contained 11.6% CuO, all of the solutions obtained had trace amounts (0.004 to 0.08%) of soluble Cu micronutrient present. Zn micronutrient containing UAN fertilizer crystallization temperature was sensitive to Zn concentration. Its increase from 0.025 to 0.5% resulted in a 10 °C increase in the T_{cryst} of UAN-28. We assign this to the presence of multiple components ($CO(NH_2)_2$, NH_4NO_3, $Zn(NO_3)_2$, H_2O and minor phases of the metal nitrates in the waste) in the aqueous system. The corresponding solution pH decreased from 6.2 to 5.4. This is due to the strong acid-weak base properties of $Zn(NO_3)_2$. For this reason, higher pH soils can be fertilized using the urea–Zn fertilizers described here.

CONCLUSIONS

The process of converting industrial pigment derived waste into a micronutrient containing nitrogen fertilizers was developed. For this purpose, solubility relationships were determined for the ternary $CO(NH_2)_2$–$Zn(NO_3)_2$–H_2O and NH_4NO_3–$Zn(NO_3)_2$–H_2O systems to determine the achievable crystallization temperatures of liquid nitrogen fertilizers in the presence of $Zn(NO_3)_2$. Resulting solid phase composition was measured, and complex salts containing $Zn(NO_3)_2$ and two and four urea molecules were detected. The catalytic $Zn(NO_3)_2$ effect was observed on the decomposition temperature of $CO(NH_2)_2$ during thermal analysis. Two crystalline phases of NH_4NO_3, IV and III, were observed and the corresponding transition temperature decreased with the increasing $Zn(NO_3)_2$ concentration in solution. Zn extraction in a form of soluble $Zn(NO_3)_2$ was performed from white pigment industrial waste and optimal extraction parameters, including HNO_3 concentration, stoichiometric amount and temperature, were determined. Those were 60 °C solution temperature, 55% HNO_3 concentration and 140% stoichiometric HNO_3 amount. This agreed very well with the reactive conditions currently used in nitrophosphate fertilizer production, thus enabling direct production of a micronutrient containing NP or NPK fertilizers without significant technology modification. Finally, sensible compositions of UAN-28 and UAN-30 liquid fertilizers containing Zn micronutrient from industrial grade compounds and pigment waste extracted $Zn(NO_3)_2$ were obtained and their physicochemical properties measured.

On a broader note, the method described in this work can also be applied to extract Zn from other waste types. For example, the discovery of the first organic accelerators for vulcanization in 1906 added to the importance of ZnO, which acts as an activator in these materials.[45] Ever since, ZnO has been used in rubber to reduce the time needed for vulcanization. For this reason, there is 0.04 to 1.55 wt % Zn in tires.[40,46] Every year, about 270 million used tires are disposed of according to the Environmental Protection Agency (EPA) in the U.S. alone, thus presenting a sustainable source of Zn. The work performed here will be extended to Zn recovery from used tires and Zn rich tire fly ash obtained via combustion of used tires, the most common way of their utilization.[47]

AUTHOR INFORMATION

Corresponding Author

*J. Baltrusaitis. E-mail: job314@lehigh.edu. Phone: +1-610-758-6836.

Notes

The authors declare no competing financial interest.

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