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WASTE MANAGEMENT

## Investigation of Copper Sorption by Sugar Beet Processing Lime Waste

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In the western United States, sugar beet processing for sugar recovery generates a lime-based waste product (~250,000 Mg yr<sup>-1</sup>) that has little liming value in the region's calcareous soils. This area has recently experienced an increase in dairy production, with dairies using copper (Cu)-based hoof baths to prevent hoof diseases. A concern exists regarding soil Cu accumulation because spent hoof baths may be disposed of in waste ponds, with pond waters being used for irrigation. The objective of this preliminary study was to evaluate the ability of lime waste to sorb Cu. Lime waste was mixed with increasing Cu-containing solutions (up to 100,000 mg Cu kg<sup>-1</sup> lime waste) at various buffered pH values (pH 6, 7, 8, and 9) and shaken over various time periods (up to 30 d). Copper sorption phenomenon was quantified using sorption maximum fitting, and the sorption mechanism was investigated using X-ray absorption spectroscopy. Results showed that sorption onto lime waste increased with decreasing pH and that the maximum Cu sorption of ~45,000 mg kg<sup>-1</sup> occurred at pH 6. X-ray absorption spectroscopy indicated that Cu(OH), was the probable species present, although the precipitate existed as small multinuclear precipitates on the surface of the lime waste. Such structures may be precursors for larger surface precipitates that develop over longer incubation times. Findings suggest that sugar beet processing lime waste can viably sorb Cu from liquid waste streams, and thus it may have the ability to remove Cu from spent hoof baths.

erates approximately 250,000 Mg of spent lime per year in southern Idaho and western Oregon due to sugar beet processing for sugar recovery. The process uses limestone to form calcium oxide and carbon dioxide, both of which are injected into thick beet juice to aid in impurity removal when calcium carbonate reforms (Ag Gold Standard, 2008). The calcium carbonate precipitate is eventually discarded and has little to no liming value in aridic, calcareous soils such as those found in the region. Thus, a challenge exists to find a beneficial use for the large quantity of lime waste generated each year. One such challenge may exist within the dairy industry.

THE AMALGAMATED SUGAR COMPANY LLC gen-

States, with approximately 550,000 head of dairy cows as of 2011 (USDA NASS, 2011). In south-central Idaho, there is an increasing concern over Cu accumulation in the environment because of the use of Cu hoof baths in the dairy industry. Dairies may use hoof baths containing between 5 and 10% Cu to control hoof infections, and in some instances the spent hoof baths are washed out of dairy barns and into liquid waste ponds. Within the waste pond, approximately 90 to 95% of the Cu is sorbed by organic phases (Stehouwer and Roth, 2009). However, 625 to 2500 mg Cu L<sup>-1</sup>, depending on initial hoof bath Cu content, remains soluble and is initially plant available when the effluent is used for irrigation. Thus, reducing the Cu quantities realized by soils when they receive Cu-laden dairy effluent may be as simple as preventing spent hoof bath waters from reaching waste ponds. Specifically, the lime waste may eventually be used to sequester excessive soluble Cu from the spent hoof bath.

The benefit of lime addition to Cu-containing waters for Cu removal has been proven successful in a number of settings (e.g., plumbing [Tam and Elefsiniotis, 2009], wastewaters [Baltpurvins et al., 1996], and waters [Shawabkeh et al., 2004]) and has been recognized for at least 100 yr. Bell and Taber (1907) studied the effect of adding various amounts of lime to Cu-containing solutions, suggesting that alkaline solutions cause precipitation of Cu in the hydroxide form. More recently, Aziz et al. (2008) used lime addition to remove metals (including Cu) from water.

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**Abbreviations**: EXAFS, extended X-ray absorption fine structure; FT, Fourier transform; FTIR, Fourier transform infrared spectroscopy; ICP–OES, inductively coupled plasma optical emission spectroscopy; XAFS, X-ray absorption fine structure; XANES, X-ray absorption near edge structure; XRD, X-ray diffraction.

The authors showed greater Cu removal at alkaline pH values and suggested that media surface roughness was beneficial for metal sorption. Thus, raising the solution pH using a rough surface–containing, lime-based product should force soluble Cu metal ions to precipitate or be sorbed as Cu(OH)<sub>2</sub>. Lime waste from sugar beet processing likely contains a high degree of surface roughness due to processing and thus would be an ideal candidate for use in sequestering Cu from liquid waste streams. Therefore, the objective of this preliminary proof-of-concept study was to identify, in a laboratory setting, the efficacy of spent lime waste to sorb Cu and determine the mechanisms behind sorption before potentially performing larger-scale studies.

#### **Materials and Methods**

#### **Lime Waste Characterization**

Lime waste from sugar beet processing was collected from The Amalgamated Sugar Company LLC. The material was air dried, passed through a 2-mm sieve, and thoroughly mixed before use. Lime waste pH and electrical conductivity were determined on a 1:1 lime waste:deionized H<sub>2</sub>O suspension (Thomas, 1996). Organic matter content was determined via loss on ignition (Nelson and Sommers, 1996). Total N and C were determined by the dry combustion method outlined by Nelson and Sommers (1996) using a Flash EA1112 Elemental Analyzer (CE Elantec, Inc.). Inorganic C content was determined by a modified pressure-calcimeter method (Sherrod et al., 2002). Lime waste-extractable Cu, Zn, Fe, and Mn were determined using a diethylenetriaminepentaacetic acid extract (Reed and Martens, 1996) and analyzed using inductively coupled plasmaoptical emission spectroscopy (ICP-OES) (Soltanpour et al., 1996). Ammonium acetate-extractable Ca, Mg, Na, and K were determined according to the procedure outlined by Sumner and Miller (1996) and analyzed using ICP-OES. Extractable P was determined using the Olsen method (Kuo, 1996), and NO<sub>3</sub>-N was determined using a 2 mol L<sup>-1</sup> KCl extract (Mulvaney, 1996). Qualitative chemical characterization of the lime waste material was determined using X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The XRD scans of powder mount samples were analyzed on a Siemens D5000 diffractometer at 0.025° increments from 20 to 40°2  $\theta$  and 1.5-s count time. The data were analyzed using the Burker Diffracplus Eva evaluation program. The FTIR analyses were performed on a PerkinElmer system 2000 with diffuse reflectance accessory, using a mixture of 3% (wt.) mineral in optical-grade KBr. An average of 100 spectral scans were processed using the Kubelka-Munk algorithm provided in PerkinElmer Spectrum 2.0 software. Lime waste chemical characteristics are presented in Table 1 and Supplemental Fig. S1.

# Lime Waste Copper Sorption: Effect of Solution pH and Shaking Time

A range of buffered solution pH values was studied to identify the optimum pH for Cu sorption onto lime waste. The background solution pH was buffered by adjusting to pH 6 with 0.1 mol  $L^{-1}$  potassium hydrogen phthalate and 0.1 mol  $L^{-1}$  NaOH, or to pH 7, 8, or 9 with 0.1 mol  $L^{-1}$  tris(hydroxymethyl) aminomethane and 0.1 mol  $L^{-1}$  HCl (CRC, 1985). Phosphate-

based buffered solutions were not used to avoid interference issues during ICP–OES analysis. In triplicate, 1.00 g of lime waste and 50 mL of adjusted pH solutions containing 0, 50, 100, 250, and 500 mg L $^{-1}$  Cu (from CuCl $_2$ ·2H $_2$ O) were placed in 50-mL centrifuge tubes and shaken at 120 rpm for 24 h at 20°C. Solutions were then centrifuged at 1500 rpm ( $\sim\!500\times g$ ) for 10 min, decanted, filtered through a 0.45- $\mu$ m membrane filter, and analyzed for Cu using ICP–OES. Final solution pH values were not determined. The amount of Cu sorbed was calculated from the difference between the initial and final quantities of Cu in solution.

Lime waste was also shaken in Cu-containing solutions (pH 6) for 1 mo to determine the maximum Cu sorptive capacity. The background solution pH was adjusted with 0.1 mol L<sup>-1</sup> potassium hydrogen phthalate and 0.1 mol L<sup>-1</sup> NaOH (CRC, 1985). In triplicate, 1.00 g of lime waste was shaken with solutions containing 0, 50, 100, 250, or 500 mg L<sup>-1</sup> Cu (from CuCl<sub>2</sub>·2H<sub>2</sub>O), or 0.25 g of lime waste was shaken with solutions containing 375 or 500 mg L<sup>-1</sup> Cu. All materials were placed in 50-mL centrifuge tubes and shaken at 120 rpm and 20°C for 1 mo. After 1 mo, solutions were centrifuged, decanted, filtered through a 0.45-µm membrane filter, and analyzed for Cu using ICP–OES. The amount of Cu sorbed was calculated from the difference between the initial and final quantities of Cu in solution.

To predict maximum Cu sorption, the data were fitted to the exponential rise equation:

$$Q = a[1 - e^{(bx)}]$$
 [1]

where Q is the Cu (mg kg<sup>-1</sup>) sorbed by lime waste, a is the the maximum Cu sorption of lime waste (mg kg<sup>-1</sup>), b is the the rate constant for change in Cu sorbed by lime waste for a given change in Cu added, and x is the Cu added (mg kg<sup>-1</sup>).

### Lime Waste Copper Sorption: Synchrotron Speciation

Lime waste solids from the 24-h shaking period were air dried and analyzed using X-ray absorption fine structure (XAFS)

Table 1. Chemical characteristics of the sugar beet lime waste. All values presented on a dry-weight basis.

Property†	Lime waste
pH	9.0
EC, dS m <sup>-1</sup>	7.4
Organic matter, %	2.66
C, %	12.8
N, %	0.29
Inorganic C, %	8.90
DTPA-extractable Cu, mg kg <sup>-1</sup>	3.9
DTPA-extractable Zn, mg kg <sup>-1</sup>	1.7
DTPA-extractable Fe, mg kg <sup>-1</sup>	37
DTPA-extractable Mn, mg kg <sup>-1</sup>	2.7
NH <sub>4</sub> OAc-extractable Ca, mg kg <sup>-1</sup>	2400
NH <sub>4</sub> OAc-extractable Mg, mg kg <sup>-1</sup>	1430
NH <sub>4</sub> OAc-extractable Na, mg kg <sup>-1</sup>	69
NH <sub>4</sub> OAc-extractable K, mg kg <sup>-1</sup>	270
Olsen-extractable P, mg kg <sup>-1</sup>	43
NO <sub>3</sub> -N, mg kg <sup>-1</sup>	350

<sup>†</sup> DTPA, diethylenetriaminepentaacetic acid; EC, electrical conductivity.

spectroscopy to elucidate solid-phase Cu speciation. The XAFS experiments were conducted at the Materials Research Collaborative Access Team's beamline 10-ID, Sector 10, located at the Advanced Photon Source, Argonne National Laboratory. The electron storage ring operated at 7 GeV in top-up mode. A liquid N<sub>2</sub>-cooled double crystal Si(111) monochromator was used to select incident photon energies, and a platinum-coated mirror was used for harmonic rejection. The monochromator was calibrated by assigning the inflection point of the  $K\alpha$ -absorption edge of copper metal foil to 8979 eV. The samples were prepared as thin pellets with a handoperated IR pellet press. Samples were secured in sample holders with Kapton tape. Five XAS spectra were collected in fluorescence (Lytle detector) and transmission quick-scan mode (0.33 eV steps at 0.1 s integration) at room temperature from -200 to 1000 eV relative to the absorption edge position of Cu. Radiation damage was checked by evaluating successive scans; no damage was observed. Self-absorption was evaluated by comparing transmission and fluorescence spectra. This artifact was only observed in the highest loaded samples (pH 6 and 7; 500 mg L<sup>-1</sup>), and the difference in intensity was small enough that it did not affect data interpretation.

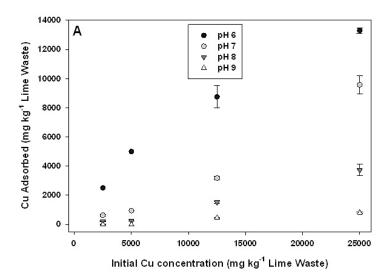
Data processing of X-ray absorption fine structure (XANES) spectra was done in the program Athena (Ravel and Newville, 2005). The extended X-ray absorption fine structure (EXAFS) spectra were processed by subtracting a cubic-spline fit between 0.5 and 12.5 Å<sup>-1</sup> from the background of the normalized spectra. The data were further processed by Fourier transforming using a square window between 1.4 to 10 Å<sup>-1</sup>. To determine the Cu speciation in the XANES sample, the following standards were compared: azurite  $[Cu_3(CO_3)_2(OH_2)]$ , malachite  $[Cu_2CO_3(OH)_2]$ , Cu(II) adsorbed on calcite  $(CaCO_3)$ , Cu(II) adsorbed on Elliot Humic acid (purchased from the International Humic Substances Society),  $Cu(NO_3)_2$  (aq), tenorite (CuO),  $Cu(OH)_2$  (details of these standard materials are presented in Strawn and Baker [2008]), and

pseudomalachite [Cu<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)<sub>4</sub>·H<sub>2</sub>O]. The XAFS spectra of these standards were collected during the same beamtime as the Cu incubated lime waste samples. Evaluation of the Cu species in the Cu-sorbed lime waste samples was done by comparing peak position and intensity in the first derivative of the XANES spectra and the Fourier transforms of the EXAFS spectra. Fitting of the first shell in the EXAFS spectra was done in the program WinXAS (Ressler, 1998) using a theoretical Cu-O scattering shell model calculated using the program Feff 8.0 (Ankudinov et al., 1998). Scattering shells at longer distances could not be reliably fit because of their small intensity. Additional details on EXAFS fitting methods are as described in Strawn and Baker (2008).

#### **Results and Discussion**

# Lime Waste Copper Sorption at Different Solution pH Values

Lime waste sorbed greater Cu concentrations as the solution pH was decreased from 9 to 6 (Fig. 1A). This finding was similar



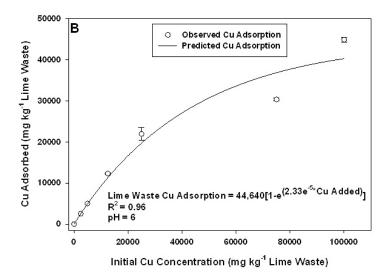


Fig. 1. Sugarbeet processing lime waste. (A) Effect of solution pH and Cu sorption over a 24-h shaking period. (B) Copper sorption maximum shaken over 30-d period at pH 6. Error bars represent 1 SEM.

to that found by Ippolito et al. (2012), who showed that Cu sorption increased on biochar as solution pH decreased from 9 to 6. The authors speculated that increased sorption was due to Cu preferentially bound to the carbonyl and hydroxyl functional surface groups present. Similarly, it was possible that Cu formed associations with organic phases present within the spent lime waste because the material contained 2.66% organic matter (Table 1). Although lower pH values would typically indicate a greater solution metal concentration, compiled data from over 70 different studies showed that only 29% of the variation in solution Cu content could be attributed to changes in pH; the prediction in solution Cu content improved when soil organic matter was also considered a factor (Sauvé et al., 2000).

In our study, greater Cu sorption at a solution pH of 6 could have been due to partial dissolution of the waste lime, leading to an increase in surface area for reaction. Similarly, Aziz et al. (2008) suggested that the rough surface of limestone can provide more contact, resulting in chemisorption of metal ions such as Cu. Based on XRD (Supplemental Fig. S1A), peaks were shifted from pure calcite, which may occur because of substitution of other ions for Ca in the structure. The FTIR analysis

(Supplemental Fig. S1B) shows typical calcite peaks at 1798, 878, and 714 cm $^{-1}$  and amorphous calcium carbonate, as seen in the width of the large peak at approximately 1400 cm $^{-1}$  and the large hydroxyl feature centered at 3600 cm $^{-1}$ . Thus, greater Cu sorption at pH 6 could also have been due to the presence of amorphous CaCO $_3$ .

Another possible explanation for the increased Cu sorption at pH 6 as compared with greater pH values was that the lime waste solid phase became partially dissolved, causing an increase in solution Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>, which led to increased Cu immobilization in the form of insoluble carbonate (Petrovic et al., 1999; Aziz et al., 2008). Hequet et al. (2001) suggested that Cu removal from waters using a high lime-containing fly ash was due to surface adsorption and precipitation and the formation of hydroxide species. The authors suggested that Cu precipitation reactions could occur at pH values above 5.6. Insoluble CuCO<sub>3</sub> species could also have precipitated at greater pH values, blocked pores, and made organic functional groups less available to participate in sorption reactions, leading to a decrease in overall Cu sorption (Ippolito et al., 2012).

### **Lime Waste Copper Sorption Maximum**

Copper sorption data on lime waste, incubated for 30 d at a solution pH of 6, is presented in Fig. 1B. Data were fitted using Eq. [1], with the model predicting a maximum of 44,640 mg Cu sorbed kg<sup>-1</sup> lime waste ( $R^2 = 0.96$ ). A Cu sorption maximum of 50,840 mg kg<sup>-1</sup> was predicted by Illera et al. (2004) when using dolomitic residue as a sorbing agent. The predicted sorption maximum was also similar to that found by Ippolito et al. (2012), who, in a companion study, found that KOH-activated pecan shell biochar sorbed a maximum of 42,300 mg Cu kg<sup>-1</sup> at pH 6. Other research has found lower sorption capacities on different alkaline materials. Illera et al. (2004) studied Cu sorption onto phosphogypsum and red gypsum, noting sorption maximums between approximately 600 to 5700 mg kg<sup>-1</sup>. The sorption maximum of limed fly ash can range from 2900 to 4900 mg kg<sup>-1</sup> (Ricou-Hoeffer et al., 2001). Although sorption maximum was not determined, Hequet et al. (2001) showed that a limecontaining fly ash could sorb at least 6000 mg Cu kg<sup>-1</sup>. Findings in the current study suggest that sugar beet processing lime waste may be more advantageous than other materials for sorbing Cu.

# Lime Waste Copper Sorption Experiment: X-ray Absorption Fine Structure Speciation

Copper K-edge XANES is very sensitive to molecular coordination (Strawn and Baker, 2008), showing distinct transition energies and absorption intensities. Thus, the XANES can be used to infer molecular speciation by comparing differences in the energy and intensity of features. Evaluation of first-derivative spectra is particularly helpful for comparing features.

The 16 XANES spectra from the Cu adsorbed on the lime waste showed similar features despite pH or loading (Fig. 2A and 2B). Small differences in peak heights arise from noise in the lower loading levels that make consistent normalization difficult or from some self-absorption in the higher concentration samples that dampens amplitude. Self-absorption was greatest in the pH 6 and pH 7, 500 ppm equilibrated samples, which corresponded

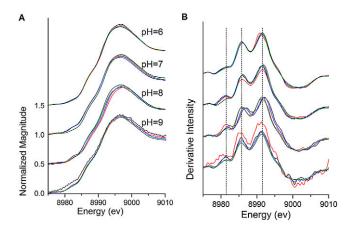


Fig. 2. X-ray absorption near edge structure (XANES) of Cu adsorbed on lime waste at four different pH and four different concentrations (50 ppm = red, 100 ppm = black, 250 ppm = blue, and 500 ppm = green). (A) Normalized XANES data. (B) Smoothed derivative of normalized intensity with vertical dashed lines aligned with major peaks in XANES.

to the highest loading level (Fig. 1A). Because the spectra were all very similar, it can be concluded that the molecular structure of Cu adsorbed on the lime waste under different equilibration conditions is similar. Similarities of chi spectra confirm this conclusion (data not shown).

Comparison of XANES spectra to standards showed that the peak positions in Cu(OH)<sub>2</sub> and azurite [Cu<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>] spectra were similar to the Cu-adsorbed lime waste spectrum (Fig. 3), with two main peaks in the second derivative spectra centered near 8985.3 and 8991.4 eV. Peak intensities of the Cu(OH)<sub>2</sub> XANES were much lower than azurite peaks. The peak intensity of the Cu(OH)<sub>2</sub> matched the peak intensity of the Cu adsorbed on the lime waste sample. Illera et al. (2004) modeled Cu sorption on liming materials, suggesting that Cu(OH)<sub>2</sub> formation was the main mechanism behind solution Cu removal. However, in the Cu(OH)<sub>2</sub> and azurite XANES, there is a shoulder or peak in the first derivative near 8996 eV that is not in the lime waste sample, suggesting that the molecular structure

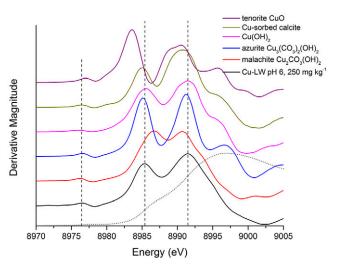


Fig. 3. First derivative of Cu standards and Cu adsorbed on lime waste (LW; sample 250 ppm pH 6). Vertical dashed lines are aligned on major peaks in X-ray absorption near edge structure (XANES) from Cu adsorbed on a lime waste sample. Overlay of nonderivative normalized XANES for the Cu adsorbed on lime waste sample is shown as dotted line.

of Cu in the lime waste samples is not identical to Cu(OH)<sub>2</sub> or azurite. Quantitative fitting of the Cu XANES spectra was done using linear combination fitting of the standards. The two main peaks at 8985.3 and 8991.4 eV in the lime waste XANES spectra could be reproduced with mostly Cu(OH)<sub>2</sub> and some azurite, with low residuals. However, there was a clear mismatch near 8996 eV. Based on the XANES results, the local molecular structure appears to be similar, but not identical, to Cu(OH)<sub>2</sub>. To make better conclusions about the molecular structure of Cu in the lime waste samples, analysis of the extended portion of the XAFS (EXAFS) is required.

As was the case for the XANES spectra, the EXAFS spectra from all of the lime waste samples were very similar. The sample that showed the best signal to noise and no self-absorption was the 250 mg L<sup>-1</sup> loaded sample, which was used for EXAFS fitting. The chi spectrum of the pH 6 lime waste sample incubated at 250 mg L<sup>-1</sup> was dominated by a monotonic signal indicative of Cu-O backscattering (Fig. 4). This backscatterer corresponded to the largest peak in the Fourier transform (FT), located at 1.51 Å (Fig. 5). Compared with the EXAFS of the standards, the lime waste chi spectrum is most similar to Cu adsorbed on the calcite standard. The lack of distinct beat patterns, or shoulders, in the chi spectrum and the correspondingly small peaks beyond the first Cu-O peaks in the FT indicates that the Cu is sorbing on the lime waste surface as opposed to forming a secondary precipitate, such as Cu(OH), or CuCO<sub>3</sub>.

Fitting of the EXAFS provides absolute bond distances for the Cu-O pair and potentially second shells. The Cu-O fit distance for the pH 6 lime waste sample incubated in 250 mg L<sup>-1</sup> Cu was 1.94 Å. This is shorter than the bond distance expected for Cu incorporated in a calcite structure (Elzinga et al., 2006) and is indicative of Jahn Teller distorted Cu octahedral coordination. Elzinga and Reeder (2002) observed that Cu adsorbed on calcite surfaces via inner-sphere bonding had Cu-O bond distances of 1.95 Å, which is in agreement with the Cu-O sorbed on calcite standard used in this study ( $R_{\rm fir}=1.95$  Å).

The lime waste sample has second shell features as indicated by the backscatter peaks in the FT between 2 and 4 Å. Despite their presence, fitting of the second- and third-shell features in the lime waste sample spectrum was not done because the peaks are small and likely resulted from backscattering off of Cu-C, a second Cu-O, and Cu-Ca, which are difficult to differentiate in EXAFS fitting when the data range is limited or when their contribution to the overall spectrum is small. However, qualitative comparison of the peaks in the lime waste FT spectrum and the peaks in the Cu adsorbed on the calcite standard show similarities in the peak positions at 2.13, 3.11, and 3.46 Å (Fig. 5), suggesting the Cu on the lime waste sample is in a similar structural environment. The FT peak at 2.55 Å is more prominent in the lime waste sample than the Cu adsorbed on the calcite standard. Elzinga and Reeder (2002) reported that Cu adsorbed on calcite as mononuclear inner-sphere complexes, which has second shell Cu-C, Cu-O, and Cu-Ca backscatterers with no Cu-Cu scattering. We confirmed the fitting for the Cu adsorbed on the calcite standard in this study, verifying that the Cu speciation in the standard is accurate. The position of the peak at 2.55 Å in the FT was similar to the position of the Cu-Cu peak in the FT of the Cu(OH), spectrum (Strawn et al., 2004). Thus, the second

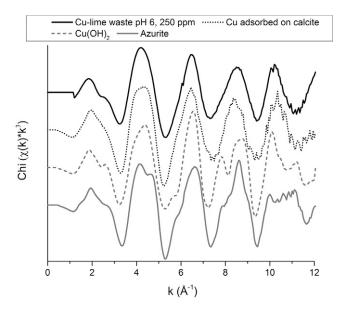


Fig. 4. Extended X-ray absorption fine structure (EXAFS) Chi spectra of Cu incubated with lime waste at pH 6 and 250 ppm Cu (which is very similar to EXAFS from other samples) and selected standards.

shell peak at 2.55 Å in the lime waste sample spectrum suggests a possible Cu-Cu backscatterer that is not present in the Cu adsorbed on calcite standard. Based on this qualitative analysis (specifically, the presence of a likely Cu-Cu backscatterer yet no extensive long-range precipitation as evidenced by lack of strong backscatterers in the chi structure), the molecular structure of Cu sorbed on the lime waste sample is either a small multinuclear complex sorbed on the surface of the lime waste minerals or there exists a mixture of innersphere mononuclear complexes and a small amount of Cu(OH), precipitate. Elzinga et al. (2006) incubated calcite with various concentrations of Cu for up to 2.5 yr and did not observe ripening or transformations of small crystals redepositing onto larger crystals. Their XAFS data did not show the presence of Cu-Cu, as in this study, so a Cu precipitate precursor was not present. However, Aziz et al. (2008) studied Cu sorption onto limestone and proposed that monolayer surface precipitation occurs. Given that our lime waste sample XANES spectra look similar to the Cu(OH), XANES spectrum, it is likely

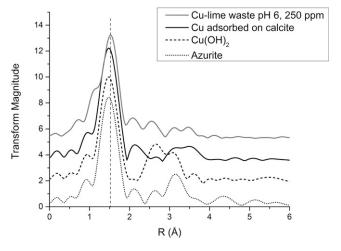


Fig. 5. Fourier transform of Cu extended X-ray absorption fine structure spectra of Cu incubated with lime waste at pH 6 and 250 ppm Cu.

that the Cu is sorbed on the lime waste as small  $\text{Cu(OH)}_2$ -like multinuclear surface precipitates, which supports our wet chemistry Cu sorption observation.

#### **Conclusions**

Copper sorption onto sugar beet processing lime waste was maximized at approximately 45,000 mg kg<sup>-1</sup> in a buffered solution (pH 6). The reaction product, Cu(OH)<sub>2</sub>, likely occurred as small multinuclear precipitates on the lime waste surface. Understanding the Cu form present on lime waste should be important for subsequent Cu recovery and reuse. Our findings suggest that sugar beet processing lime waste can viably sorb Cu from liquid waste streams; thus, it may have the ability to remove Cu from spent hoof baths. We plan to focus future research on the use of lime waste for Cu sorption from spent hoof baths.

### **Supplemental Information**

Supplemental Fig. S1. Lime waste (A) X-ray diffraction and (B) Fourier transform infrared spectroscopy profiles.

#### References

- Ag Gold Standard. 2008. The value and benefits of lime. http://www.crystalsugar.com/agronomy/gold/fact/lime.pdf (accessed 16 Nov. 2012).
- Ankudinov, A.L., B. Ravel, J.J. Rehr, and S.D. Conradson. 1998. Real space multiple scattering calculation of XANES. Phys. Rev. B 58:7565–7576. doi:10.1103/PhysRevB.58.7565
- Aziz, H.A., M.N. Adlan, and K.S. Ariffin. 2008. Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: Post treatment by high quality limestone. Bioresour. Technol. 99:1578–1583. doi:10.1016/j.biortech.2007.04.007
- Baltpurvins, K.A., R.C. Burns, and G.A. Lawrence. 1996. Heavy metals in wastewaters: Modeling the hydroxide precipitation of copper(II) from wastewater using lime as the precipitant. Waste Manag. 16:717–725. doi:10.1016/S0956-053X(97)00014-7
- Bell, J.M., and W.C. Taber. 1907. The action of lime in excess on copper sulphate solutions. J. Phys. Chem. 11:632–636. doi:10.1021/j150089a005
- CRC. 1985. CRC handbook of chemistry and physics. 65th ed. CRC Press, Inc., Boca Raton. FL.
- Elzinga, E., and R. Reeder. 2002. X-ray absorption spectroscopy study of Cu2+ and Zn2+ adsorption complexes at the calcite surface: Implications for site-specific metal incorporation preferences during calcite crystal growth. Geochim. Cosmochim. Acta 66:3943–3954. doi:10.1016/S0016-7037(02)00971-7
- Elzinga, E.J., A.A. Rouff, and R.J. Reeder. 2006. The long-term fate of Zn2+, Cu2+ and Pb2+ adsorption complexes at the calcite surface: An X-ray absorption spectroscopy study. Geochim. Cosmochim. Acta 70:2715–2725. doi:10.1016/j.gca.2006.02.026
- Hequet, V., P. Ricou, I. Lecuyer, and P. LeCloirec. 2001. Removal of Cu2+ and Zn2+ in aqueous solutions by sorption onto mixed fly ash. Fuel 80:851–856. doi:10.1016/S0016-2361(00)00153-8
- Illera, V., F. Garrido, S. Serrano, and M.T. Garcia-Gonzalez. 2004. Immobilization of the heavy metals Cd, Cu and Pb in an acid soil amended with gypsum-and lime-rich industrial by-products. Eur. J. Soil Sci. 55:135–145. doi:10.1046/j.1365-2389.2003.00583.x
- Ippolito, J.A., D.G. Strawn, K.G. Scheckel, J.M. Novak, M. Ahmedna, and M.A.S. Niandou. 2012. Macroscopic and molecular investigations of copper sorption by a steam-activated biochar. J. Environ. Qual. 41:1150– 1156. doi:10.2134/jeq2011.0113

- Kuo, S. 1996. Phosphorus. In: D.L. Sparks, editor, Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI. p. 869–919.
- Mulvaney, R.L. 1996. Nitrogen- inorganic forms. In: D.L. Sparks, editor, Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI. p. 1123–1184.
- Nelson, D.W., and L.E. Sommers. 1996. Total carbon, organic carbon, and organic matter. In: D.L. Sparks, editor, Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI. p. 975–977.
- Petrovic, M., M. Kastelan-Macan, and A.J.M. Horvat. 1999. Interactive sorption of metal ions and humic acids onto mineral particles. Water Air Soil Pollut. 111:41–56. doi:10.1023/A:1005084802830
- Ravel, B., and M. Newville. 2005. ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 12:537–541. doi:10.1107/S0909049505012719
- Reed, S.T., and D.C. Martens. 1996. Copper and zinc. In: D.L. Sparks, editor, Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI. p. 703–722.
- Ressler, T. 1998. WinXAS: A program for X-ray absorption spectroscopy data analysis under MS-Windows. J. Synchrotron Radiat. 5:118–122. doi:10.1107/S0909049597019298
- Ricou-Hoeffer, P., I. Lecuyer, and P. LeCloirec. 2001. Experimental design methodology applied to adsorption of metallic ions onto fly ash. Water Res. 35:965–976. doi:10.1016/S0043-1354(00)00341-9
- Sauvé, S., W. Hendershot, and H.E. Allen. 2000. Solid-solution partitioning of metals in contaminated soils: Dependence of pH, total metal burden, and organic matter. Environ. Sci. Technol. 34:1125–1131. doi:10.1021/es9907764
- Shawabkeh, R., A. Al-Harahsheh, and A. Al-Otoom. 2004. Copper and zinc sorptioin by treatedoil shale ash. Separ. Purif. Tech. 40:251–257. doi:10.1016/j.seppur.2004.03.006
- Sherrod, L.A., G. Dunn, G.A. Peterson, and R.L. Kolberg. 2002. Inorganic carbon analysis by modified pressure-calcimeter method. Soil Sci. Soc. Am. J. 66:299–305. doi:10.2136/sssaj2002.0299
- Soltanpour, P.N., G.W. Johnson, S.M. Workman, J.B. Jones, Jr., and R.O. Miller. 1996. Inductively coupled plasma emission spectrometry and inductively coupled plasma-mass spectrometry. In: D.L. Sparks, editor, Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI. p. 91–139.
- Strawn, D.G., and L.L. Baker. 2008. Speciation of Cu in a contaminated agricultural soil measured by XAFS, μ-XAFS and μ-XRF. Environ. Sci. Technol. 42:37–42. doi:10.1021/es071605z
- Strawn, D.G., N.E. Palmer, L.J. Furnare, C. Goodell, J.E. Amonette, and R.K. Kukkadapu. 2004. Copper sorption mechanisms on smectites. Clays Clay Miner. 52:321–333. doi:10.1346/CCMN.2004.0520307
- Stehouwer, R., and G. Roth. 2009. Copper sulfate hoof baths and copper toxicity in soil. http://animalscience.psu.edu/news/2004/dd200403-03 (accessed 16 Nov. 2012).
- Sumner, M.E., and W.P. Miller. 1996. Cation exchange capacity and exchange coefficients. In: D.L. Sparks, editor, Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI. p. 1201–1229.
- Tam, Y.S., and P. Elefsiniotis. 2009. Corrosion control in water supply systems: Effect of pH, alkalinity, and orthophosphate on lead and copper leaching from brass plumbing. J. Environ. Sci. Health A Tox. Hazard. Subst. Environ Eng. 44:1251–1260. doi:10.1080/10934520903140009
- Thomas, G.W. 1996. Soil pH and soil acidity. In: D.L. Sparks, editor, Methods of soil analysis. Part 3. Chemical methods. SSSA, Madison, WI. p. 475–490.
- USDA National Agricultural Statistics Service. 2011. 2011 Agricultural statistics annual. Chapter 8. Dairy and poultry statistics. http://www.nass.usda.gov/Publications/Ag\_Statistics/2011/Chapter08.pdf (accessed 22 Feb. 2013).