

Effect of calcium oxide dose on thermal reactions, lime speciation, and physical properties of alkaline stabilized biosolids

Karen A. Smith, Lori E. Goins, Terry J. Logan

ABSTRACT: Quicklime (CaO) was added to a single sample of dewatered biosolids at rates of 5, 15, 20, 25, 30, 40, and 50% by weight (based on wet weight of the dewatered biosolids) in the laboratory. Temperature rise and water loss were monitored to determine caloric energy expended in heating and evaporation, and these values were compared to heat generation. The limed biosolids were analyzed by x-ray diffraction and thermal gravimetric analysis to determine the lime species present, and the pH rise when added to selected soils. Effects of lime dose on biosolids physical properties were examined by measuring selected physical characteristics of the limed products. Addition of CaO to dewatered biosolids produces heat through the exothermic conversion of CaO to hydrated lime [Ca(OH)₂], with only small amounts of heat produced from the exothermic reaction of carbon dioxide (CO₂) with Ca(OH)₂ to form calcium carbonate (CaCO₃). All heat produced was dissipated during heating of the biosolids and evaporation of water. Because of the predominance of Ca(OH)₂ in the limed biosolids, care should be taken in using these materials as liming agents and soil amendments because of the very high initial soil pHs (greater than pH 12) that can persist for weeks or more. Increasing lime dose improved the density and water-holding capacity of biosolids and improved their physical consistency. *Water Environ. Res.*, **70**, 224 (1998).

KEYWORDS: soil, liming, pH, pasteurization, biosolids.

Introduction

The use of quicklime (CaO) or hydrated lime [Ca(OH)₂] for stabilizing municipal biosolids has been practiced at wastewater treatment plants since the 1890s (WEF, 1995). Extensive work has been done on lime stabilization of biosolids and especially on pH effects (Christensen, 1987; Eikum, 1983; and Paulsrud and Eikum, 1983). At low doses (less than 10% by weight on a dewatered cake solids basis), lime is primarily added to raise the pH to above 12 for the reduction of odor generation and for partial pathogen destruction (Burnham *et al.*, 1992a, and WEF, 1995). Under the U.S. Environmental Protection Agency (U.S. EPA) Part 503 biosolids regulations, this level of lime addition would qualify the process as Class B pathogen reduction (U.S. EPA, 1993). In recent years, however, several advanced alkaline technologies have emerged that use CaO or alkaline byproducts containing CaO to produce heat, as well as high pH for destruction of pathogens (Burnham *et al.*, 1992a and 1992b; U.S. EPA, 1993; and WEF, 1995). Heat is generated by the exothermic reaction of CaO with water to form Ca(OH)₂. Under the U.S. EPA Part 503 regulations, Alternative 1 provides a combination of temperature and time that will give complete pathogen destruction (Class A) (U.S. EPA, 1993). The lime-based technologies use lime doses between 20 and 50% on a cake solids basis to achieve the Alternative 1 criteria (70°C for

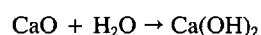
30 minutes); external heating is used to make up the heat needed to attain 70°C for 30 minutes where lower lime doses are used (Burnham *et al.*, 1992b).

Class A and Class B alkaline disinfection technologies are used increasingly in the U.S. and other countries because of their relatively low cost and ease of operation. The resultant products of these processes are being used, or are proposed to be used, as liming materials in agriculture, as topsoil additives in horticulture, as soil conditioners and soil substitutes in reclamation, and as soil replacements for landfill cover (Logan and Burnham, 1995). Though research has shown that most of the acid-neutralizing capacity of some alkaline stabilized biosolids is calcium carbonate (CaCO₃), and the liming reaction in soil is similar to that of agricultural limestone (Logan and Burnham, 1995), no work has been done to determine the chemical form of the residual lime in biosolids disinfection processes that use CaO exclusively. Likewise, little is known of the effects of lime dosage on the physical properties of the lime-stabilized biosolids and on their liming effects when added to soil. The agricultural industry has long used pulverized limestone as the primary liming agent (Barber, 1984) because of its relatively low cost and its slow reaction in soil. The latter property is important in maintaining target pHs after liming. More reactive liming materials like Ca(OH)₂ or alkaline byproducts have been used, but their use is restricted by high cost [in the case of Ca(OH)₂], a limited research database on their use, concerns for the high initial pHs of these materials, and their rapid rate of neutralization in the soil (which necessitates more frequent application than with limestone). Therefore, identification of the chemical form of the liming compounds in lime-stabilized biosolids is essential if these materials are to be used beneficially in agriculture, horticulture, and reclamation applications.

The objectives of this study were to determine the chemical form of the residual lime in the biosolids product, the heat and mass balances of reacting biosolids with varying rates of lime addition, and selected physical characteristics of the biosolids product.

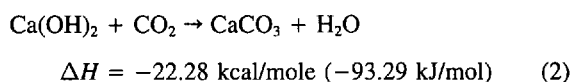
Methodology

Theory. Finely ground CaO reacts rapidly with the water in dewatered biosolids (typically 15 to 45% solids) to produce slaked or hydrated lime, Ca(OH)₂. This is an exothermic reaction with enough heat generated to increase the temperature of the biosolids, the extent of heat rise being dependent on the lime dose rate:



$$\Delta H = -15.58 \text{ kcal/mole } (-65.23 \text{ kJ/mol}) \quad (1)$$

where ΔH is the standard heat of formation (Weast and Astle [Eds.], 1981). A second reaction with $\text{Ca}(\text{OH})_2$ and carbon dioxide (CO_2) is possible if there is enough carbon dioxide available from the air or from decomposition of the biosolids:



The second reaction was demonstrated in the laboratory by pumping carbon dioxide into a limed biosolids sample (see below), but this reaction is likely to be kinetically inhibited by the diffusive flux of ambient carbon dioxide into the biosolids or by slow respiration in the limed material. It is likely that lime disinfection processes produce a mixture of $\text{Ca}(\text{OH})_2$ and CaCO_3 , but there may be other reaction products including calcium (Ca) salts of sulfate, chloride, and phosphate and calcium complexed with solid-phase and dissolved organic matter.

The form of the added calcium in the lime-treated biosolids will have significant effects on the chemical and physical properties of the resultant product. The two major inorganic calcium compounds, $\text{Ca}(\text{OH})_2$ and CaCO_3 , vary in important properties (National Lime Association, 1982): $\text{Ca}(\text{OH})_2$ has a water solubility of 1.2 g/L and CaCO_3 has a solubility of 0.018 g/L, so biosolids high in $\text{Ca}(\text{OH})_2$ will have higher soluble salts than biosolids higher in CaCO_3 ; $\text{Ca}(\text{OH})_2$ has a maximum pH in water of 12.5, and the pH of CaCO_3 in water in equilibrium with the atmosphere is 8.25. Equilibrium is not achieved rapidly, making it likely that the initial pH of a CaCO_3 -soil mixture will be different from 8.25. Biosolids with significant amounts of $\text{Ca}(\text{OH})_2$ will maintain pHs near 12 longer than will biosolids with less $\text{Ca}(\text{OH})_2$ and more CaCO_3 . Biosolids high in $\text{Ca}(\text{OH})_2$ will have higher theoretical acid-neutralizing capacities (expressed as CaCO_3 equivalency [CCE]) than CaCO_3 : the CCE of CaCO_3 is 100% by definition, while that of $\text{Ca}(\text{OH})_2$ is 135%. Because of the tendency of humic substances to disperse at alkaline pHs, biosolids high in $\text{Ca}(\text{OH})_2$ should have poorer structure and handling characteristics than those higher in CaCO_3 .

These potential effects of lime speciation in biosolids following lime stabilization prompted the present study. The general research approach was to add varying doses of CaO to a single dewatered biosolids in the laboratory. Temperature rise and water loss were monitored to determine caloric energy expended in heating and evaporation, and these values were compared to heat generation by Equations 1 and 2. The limed biosolids were then analyzed to determine the lime species present using x-ray diffraction and thermal gravimetric analysis and the pH rise when added to selected soils. Effects of lime dose on biosolids physical properties were examined by measuring selected physical characteristics of the limed products.

Materials

Dewatered (15% solids), anaerobically digested biosolids from the Department of Parks and Sewers in Columbus, Ohio, that had been lagoon settled for at least 15 years were used in the study. Finely pulverized lime was provided by the Dravo Lime Company (Black River Division, Butler, Kentucky). The lime was characterized as "lime fines," with 99% of the material less than 5 mm in size and 88% less than 3 mm. The material had a total CaO content of 90%, available CaO of 85%, and a magnesium oxide (MgO) content of 2.5%. The solids

content was 99.6% (analyses provided by Dravo Lime Company). Available lime was determined to be 83.5%.

Methods

Samples of the dewatered biosolids were mixed with the lime at rates of 5, 15, 20, 25, 30, 40, and 50% by weight (based on wet weight of the dewatered biosolids). The mixtures were immediately placed in 0.5-L Dewar flasks; enough of the mixture was added to fill the flask to the neck, and the top was left open to the atmosphere. Samples of the initial mixtures were weighed and oven dried at 105°C to determine solids content. Temperature was monitored over a 24-hour period with a Campbell Scientific 21X data logger (Campbell Scientific Inc., Logan, Utah), and three probes were inserted into the center of the mixture. The data logger recorded temperature in degrees Celsius every minute and averaged the readings for the three probes. The data were transferred to computer spreadsheet files and used to determine maximum temperatures and heating. After 24 hours, samples of the mixtures were oven dried to determine final solids content, and water evaporation was calculated as the weight difference between initial and final solids contents. Heat consumed by heating the lime-biosolids mixture and by evaporation was calculated from the maximum temperature rise and from the latent heat of evaporation of water (540 kcal/mole [2261 kJ/mol]). A mass-weighted specific heat was calculated using the mass ratios of lime, biosolids, and water. In the case of lime, the reference value for $\text{Ca}(\text{OH})_2$ was used because this was subsequently shown to be the dominant lime species in the mixes, and the differences between specific heats of CaO, $\text{Ca}(\text{OH})_2$, and CaCO_3 were small. Values used were 0.275, 0.18, and 1.0 kcal/kg · K (1.15, 0.75, and 4.2 kJ/kg · K) for biosolids, CaO, and water, respectively. The specific heat of the biosolids was estimated based on a range of 0.25 to 0.30 kcal/kg · K (1.05 to 1.26 kJ/kg · K) found in the literature (Burnham *et al.*, 1992b; Christie, 1990; and Haug, 1980). The heat consumed was compared to the exothermic heat of formation from Equations 1 and 2, with the molar ratios of the lime products, $\text{Ca}(\text{OH})_2$ and CaCO_3 , determined from the speciation analysis. It was assumed that all added CaO was consumed; this assumption was based on the fine-grain nature of the lime, lack of any difference between the hot and cold available-lime tests [the cold test identifies CaO and the hot test gives the sum of CaO and $\text{Ca}(\text{OH})_2$], and absence of CaO peaks in x-ray diffraction spectra of the biosolids mixes.

Samples of the final mixtures were analyzed for pH. A 1:2 ratio of solids to deionized water (by weight) slurry was made, and the pH of the slurry was measured with a general-purpose combination electrode. The CCE was determined by the boiling acid method (AOAC, 1965), and CaO + $\text{Ca}(\text{OH})_2$ was determined by the sucrose-titration test for available lime (ASTM, 1993). Additional samples were analyzed by x-ray diffraction for presence and relative abundance of CaO, $\text{Ca}(\text{OH})_2$, and CaCO_3 using a Philips x-ray diffractometer (Phillips Electronic Instruments, Mahwah, New Jersey) with copper (Cu) $K\alpha$ radiation at 35 kV and 20 mA. Measurements were made with a step-scanning technique over a range of 0- to 70-deg 2θ using a counting time of 4 seconds with a step interval of 0.025-deg θ (θ is the angle between the surface of a solid and the incident x-ray radiation). Samples were analyzed on backfilled, randomly oriented mounts. A Seiko 1 TG/DTA 200 Thermogravimetric analyzer (Seiko Instruments, Inc., Torrance, California)

Table 1—Effects of lime addition to dewatered biosolids on lime speciation.

Lime added, % by wet weight	CaO added ^a	Speciation method I		Speciation method II		Speciation method III	
		Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃	Ca(OH) ₂	CaCO ₃
5	0.418	0.248	0.094	0.418 ^b	0	0.418 ^b	0
15	0.662	0.636	0.120	0.662 ^b	0	0.662 ^b	0
20	0.900	0.647	0.131	0.900 ^b	0	0.900 ^b	0
25	0.975	0.684	0.127	0.843	0	0.843	0.132
30	1.032	0.674	0.156	0.956	0	0.956	0.076
40	1.114	0.667	0.134	0.948	0	0.948	0.166
50	1.169	0.584	0.318	1.148	0	1.148	0.021

^a All values in mol/100 g dry weight, except as noted.

^b Measured values were 0.680, 1.451, and 0.914 mol/100 g for 5, 15, and 20% lime doses, respectively. Values were set equal to the moles of CaO added.

was used to quantify the content of Ca(OH)₂ by weight loss over the temperature range of 50 to 1 000°C.

Samples of the final samples were analyzed for bulk density; particle density; moisture retention at -5.9 and -33 kPa, and at -1.5 MPa matric potential; and liquid and plastic Atterberg limits using standard methods for soils (Klute [Ed.], 1986). Use of these procedures for lime-stabilized biosolids is described by Logan and Harrison (1994).

As a means of confirming the lime speciation based on direct analysis of the lime sludges, one of the materials (30% CaO dose rate) was reacted with two Ohio soils at rates equivalent to 10, 50, 100, 250, and 500 metric tons (t)/ha, and soil pH was measured over a period of 64 days. The pH response was compared to that of pure ground CaCO₃. The two soils used in the study were Miamian silt loam and Hazleton sand. The Miamian soil is typical of midwestern farm soils derived from glacial till and has a near-neutral normal pH. The Hazleton soil is derived from weathered sandstone and has a normal pH of less than 6. Characteristics of these soils are described by Logan *et al.* (1996). Soils were mixed in beakers with the requisite amount of the limed biosolids, wetted to soil-field capacity with deionized water, and incubated at ambient laboratory temperatures. Soil pH was measured approximately weekly in a 1:2 soil-to-water extract.

Results

Lime Speciation. The CCE of the limed biosolids increased with increasing lime dosage, reaching a maximum of 97.9% at the 50% lime rate (Table 1). If all of the acid-neutralizing capacity of the biosolids came from the added lime and all CaO were converted to Ca(OH)₂, the relationship between lime dosage and CCE would be linear and have a maximum theoretical CCE of 104% at the 50% lime rate. Conversely, if all of the lime were converted to CaCO₃, the relationship would still be linear and have a maximum theoretical CCE of 77% at the 50% lime dose rate. The available-lime test showed that there was no unreacted CaO and that Ca(OH)₂ formation peaked at 25% lime dosage and then declined (Table 1).

Speciation method I assumes that total CCE is the sum of the respective CCEs for CaO, Ca(OH)₂, and CaCO₃ and that the formation of CaCO₃ can be estimated by difference (Table 1). Because the available lime test indicated that all CaO was consumed, the amount of CaCO₃ present in the mixtures is

determined by subtracting Ca(OH)₂, as determined by the available lime test, from CaCO₃ + Ca(OH)₂, as determined by CCE. This estimate shows CaCO₃ generally increasing with lime dose rate (Table 1), particularly at the 50% rate, where there would be 60% as much CaCO₃ as Ca(OH)₂.

In Speciation method II, all of the CaO was assumed to have been converted to Ca(OH)₂ (that is, no CaCO₃ was formed), and the amount of Ca(OH)₂ formed was estimated by thermogravimetric analysis (TGA). Method II assumes that there may have been products other than Ca(OH)₂, but they would not contribute to heating as exothermic reactions. The TGA indicated that Ca(OH)₂ formation could account for most of the added CaO (Table 1). In fact, TGA overestimated Ca(OH)₂ formation for the three lowest lime rates, and the values used in subsequent mass-balance calculations were adjusted so that Ca(OH)₂ formed was stoichiometrically equivalent to CaO added.

In Speciation method III, the amount of Ca(OH)₂ formed was estimated from TGA, and the difference between CaO added and Ca(OH)₂ formed was assumed to be CaCO₃ (Table 1). Method III predicts that no more than 15% of the added lime is converted to CaCO₃.

The x-ray diffraction was easily able to identify CaO and Ca(OH)₂ (as portlandite) in the limed biosolids. Diffraction patterns of the 30% limed biosolids confirmed the presence of primarily Ca(OH)₂; CaO was not detected, and there was only a trace of CaCO₃ (as calcite) (Figure 1). The same final limed biosolids were carbonated by pumping carbon dioxide under pressure into the sample for several hours. A rerun of the x-ray diffraction showed only the presence of calcite; thus, if significant amounts of CaCO₃ were being formed, as suggested by the available lime and CCE tests (speciation method I) (Table 1), they would have been detected by x-ray diffraction. X-ray diffraction can only be used to a limited extent to quantify the presence of crystalline solids, but relative magnitudes can easily be discerned. Both the CCE and available lime tests are indirect tests based on acid neutralization and are designed for relatively pure inorganic liming materials. Their use in limed biosolids assumes that the biosolids themselves do not undergo acid-base chemical reactions with the added CaO. This is highly unlikely. Depending on the nature and extent of stabilization, in this case anaerobic digestion, components of the biosolids could neutralize some of the added lime. This neutralization

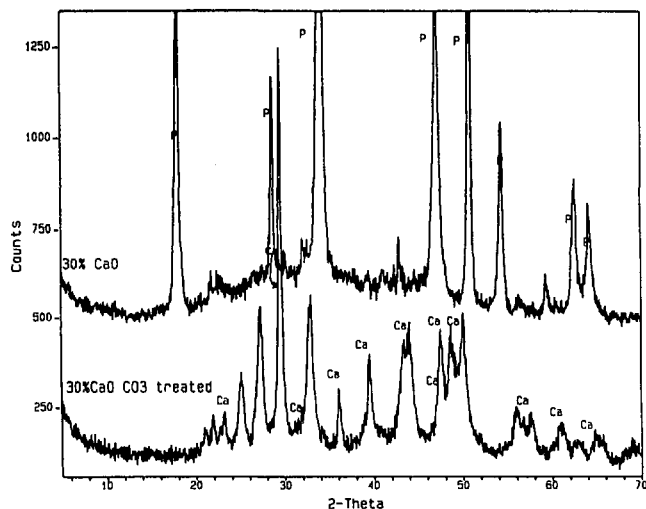


Figure 1—X-ray diffractogram of the 30% CaO dosed biosolids before and after carbonation [P = portlandite $[\text{Ca}(\text{OH})_2]$ and Ca = calcite $[\text{CaCO}_3]$].

could arise from reaction with organic acids (for example, acetic acid); oxidation of reduced iron (Fe), manganese (Mn), and sulfur (S) (in the case of anaerobically digested biosolids); and alkaline hydrolysis. Formation of neutral hydroxide and carbonate salts of metals in the biosolids could also contribute to acid neutralization. Though the CCE test is valid for determining the total acid-neutralizing capacity of the limed biosolids and for use in determining rates of application for liming acid soils, it and the available lime test are of limited value in determining the relative abundance of lime species in biosolids in the absence of other direct evidence, such as x-ray diffraction, or indirect evidence, such as liming reactions in soil. The x-ray diffraction data would support speciation method III.

Thermodynamic Mass Balance. Heating and water evaporation were used to calculate heat consumed from the exothermic reactions of the added lime. Maximum temperatures were reached within 1 hour and then declined exponentially (Figure 2). Maximum temperatures increased with increasing lime dose (Table 2) and reached a plateau near the boiling point of water for lime doses of 30% or higher. Lime doses less than 25% did not achieve 70°C for the 30 minutes required for Alternative 1 Class A disinfection, whereas doses of 30% or higher produced temperatures near that of boiling water, which would have killed most organisms in the biosolids. Burnham *et al.* (1992b) show that a lime dose of 16% on a wet-weight basis (for 15% solids as in this study) would be required to achieve the 70°C for 30 minutes required for Alternative 1 Class A disinfection, whereas doses of 30% or higher produced temperatures near that of boiling water, which would have killed most organisms in the biosolids. Burnham *et al.* (1992b) show that a lime dose of 16% on a wet-weight basis (for 15% solids as in this study) would be required to achieve the 70°C for 30 minutes required for Alternative 1 Class A disinfection, whereas doses of 30% or higher produced temperatures near that of boiling water, which would have killed most organisms in the biosolids. The geometry of the Dewar flask setup was such that evaporation only occurred from the open neck of the flask, and large-scale lime processing of biosolids may produce even greater passive evaporative drying and may also affect the maximum observed temperatures. The purpose of this study was to determine the chemical form of the residual lime; thus, replicating the heating and drying in large-scale liming operations was not a primary concern.

The heat consumed by heating and water evaporation were calculated and the results compared to the estimates of exothermic heat produced from $\text{Ca}(\text{OH})_2$ and CaCO_3 formation, based

on the three methods of lime speciation. Most of the heat produced was used in heating the mixture at the lower lime doses, whereas heat consumed in water evaporation increased relative to the temperature as it approached the boiling point of water (Table 2). The sum of heating and evaporation calories peaked at the 40% lime dose. Because x-ray diffraction showed that there was no unreacted CaO in the final mixes, the heat generated between the 40 and 50% lime doses must have been dissipated in other reactions, possibly endothermic chemical reactions. All three methods of calculating heat generation from exothermic lime reactions predicted less heat generation than was accounted for in heating and evaporation, with method III yielding the closest results, particularly at the highest lime doses (Table 2). Method III predicted no increase in heat production from the 40 to the 50% lime dose, as was observed from the sum of heating and evaporation. The heat balance, therefore, supports the speciation data, which suggest that almost all of the CaO is converted to $\text{Ca}(\text{OH})_2$, with only small amounts of CaCO_3 being formed. Kruzic and Petry (1994) examined alkalinity leaching of alkaline-stabilized biosolids and found that there were significant amounts of $\text{Ca}(\text{OH})_2$ in the biosolids that were not easily leached even at a 10% (wet-weight basis) lime dose rate.

Soil Liming Reactions. The speciation results were tested by incubating varying additions of one of the limed biosolids (30% dose rate) with two soils and by comparing the observed pH changes over time with those from addition of pure CaCO_3 . When $\text{Ca}(\text{OH})_2$ is added to soil, there is a rapid increase in pH, with maximum values approaching that of $\text{Ca}(\text{OH})_2$ itself (12.5); soil pH then falls as the lime is neutralized. Conversely, when CaCO_3 is added to soil, pH increases gradually to a maximum approaching that of CaCO_3 itself (8.2); this pH is maintained

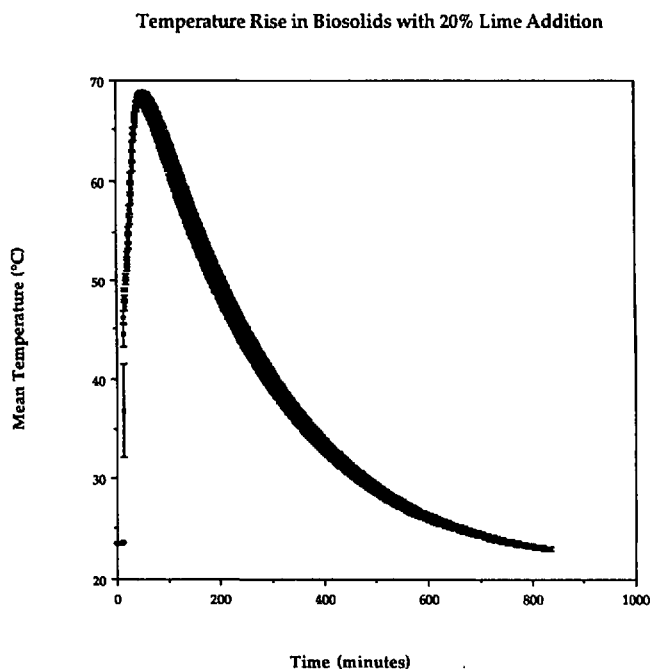


Figure 2—Temperature rise in biosolids with 20% lime addition. Means and standard deviations of readings from three temperature probes taken at 1-minute intervals are plotted.

Table 2—Effects of lime addition to dewatered biosolids on heating and water evaporation.

Lime added, % by wet weight	Maximum temperature, °C	Water evaporated, % by weight	Heat consumed, kcal/100 g dry weight			Heat produced by liming, kcal/100 g dry weight ^a		
			Heating	Evaporation	Total	Method I	Method II	Method III
5	36.91	2.49	6.13	1.34	7.47	5.95	6.51	6.51
15	60.39	2.98	11.40	1.61	13.01	12.58	10.31	10.31
20	67.75	3.02	11.64	1.62	13.26	13.00	14.02	14.02
25	82.09	7.78	13.46	4.19	17.65	13.49	13.13	16.07
30	95.05	6.99	14.78	3.77	18.55	13.98	14.89	16.58
40	91.55	12.67	13.18	6.83	20.01	13.38	14.77	18.49
50	93.94	16.11	11.54	8.69	20.23	16.19	17.89	18.36

^a Based on the relative formation of Ca(OH)₂ and CaCO₃ from CaO and the associated exothermic heat generation.

longer than that of Ca(OH)₂ because of the lower reactivity of CaCO₃ compared to Ca(OH)₂.

Addition of the limed biosolids raised initial pHs from an unlimed value of 6.8 to between 8.5 and 12.1 in the Miamian soil (Figure 3). Initial pH declined at all application rates, the decline occurring later as application rate increased. In the case of CaCO₃, pH increased from initial values, reaching a maxi-

imum near pH 8 and declining more slowly than the limed biosolids (Figure 3). A similar response was observed in the more acidic (unlimed pH of 5.8) Hazleton soil (Figure 4). The highest rates of CaCO₃ yielded pHs higher than the equilibrium pH of CaCO₃ in the poorly buffered Hazleton soil. This may have been the result of the mixture not reaching equilibrium after 64 days. The differences in the liming curves for limed

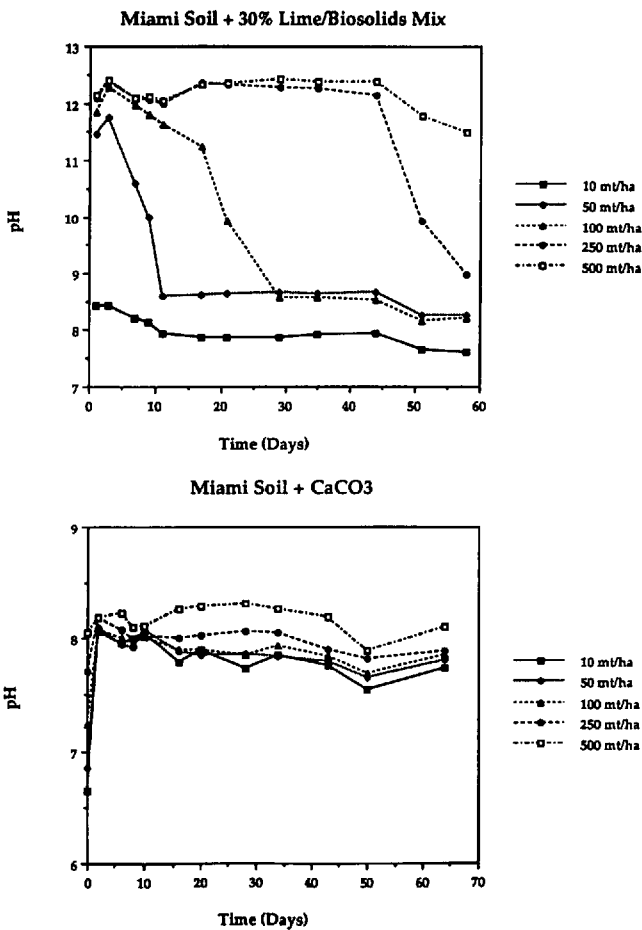


Figure 3—Change in pH of Miamian soil amended with 30% lime-treated biosolids at rates ranging from 10 to 500 mt/ha (dry solids) equivalent; mean of duplicate treatments.

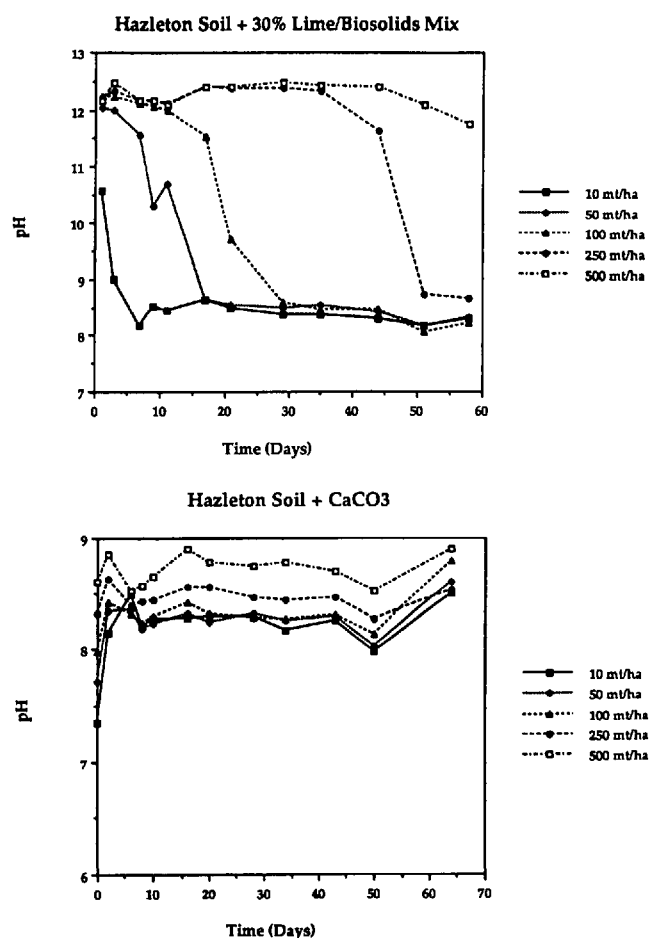


Figure 4—Change in pH of Hazleton soil amended with 30% lime-treated biosolids at rates ranging from 10 to 500 mt/ha (dry solids) equivalent; mean of duplicate treatments.

Table 3—Effects of lime addition to dewatered biosolids on soil physical properties.

Lime added, % by wet weight	Bulk density, Mg/m ³	Particle density, Mg/m ³	Total porosity, % by volume	Water retention, % by volume				Final solids, % solids	Liquid limit, % solids	Plastic limit, % solids
				–5.9 kPa	–33 kPa	–1.5 MPa	Available water			
5	0.185 5	2.05	90.95	0.52	0.48	— ^a	—	—	—	—
15	0.283 3	2.10	86.51	0.46	0.44	0.37	0.09	36.2	51.0	59.2
20	0.257 4	2.11	87.80	0.35	0.31	0.31	0.04	43.4	51.0	60.4
25	0.349 9	2.19	84.02	0.42	0.38	0.32	0.10	49.4	46.5	61.3
30	0.335 5	2.19	84.68	0.36	0.33	0.26	0.10	50.1	49.8	61.2
40	0.368 7	2.20	83.24	0.34	0.31	0.16	0.18	65.0	52.4	59.0
50	0.365 7	2.14	82.91	0.33	0.26	0.13	0.20	76.7	56.3	57.7

^a Not measured.

biosolids and CaCO₃ in the two soils confirm that the limed biosolids have lime that is more reactive than CaCO₃, and the liming reaction is similar to that of Ca(OH)₂. Application of limed biosolids at rates as low as 10 t/ha poses few potential problems for soil conditions, but rates of 50 t/ha and higher would result in soil pHs as high as 12 for periods of up to several weeks. These higher rates might be used when biosolids are applied at a nitrogen supply rate for field crops or when biosolids are used as soil amendments, for land reclamation, or as a topsoil blend. These pHs are high enough to inhibit microbial processes, damage plant roots and standing vegetation (when applied to pasture or turf), interfere with the nutrient supply to the plant, and damage soil structure by dispersing soil organic matter. Research in Sweden indicated that biosolids treated with high doses of lime produced a material that was harmful to soil unless application rates were kept very low (Morling, 1995). The use of these materials at moderate to high application rates should, therefore, be implemented with caution, and their use should be based on soil incubation tests, as performed in this study, as well as on CCE and soil lime requirement tests.

Physical Properties of Limed Biosolids. Lime addition increased the bulk density (BD) of the limed biosolids, as would be expected from the mixing of a relatively light organic material with a nonporous inorganic solid (Table 3), but BD peaked at 30% lime addition. Particle density (PD) (the density of the material in the absence of void space) also increased, as expected, but not markedly. The calculated total porosity (1 – BD/PD) decreased, primarily because of the increase in BD. Density and porosity respond nonlinearly to lime addition because of the complex physicochemical interactions of lime with biosolids. Part of the density increase can be explained by the addition of denser, less porous lime to the biosolids, but the addition of polyvalent Ca²⁺ and high pHs have counteracting effects. Polyvalent cations are effective in flocculating biosolids, whereas high pHs are known to dissolve organic matter. The net effect is a complex physicochemical mixture of organic and inorganic solids.

Water retention by limed biosolids at –5.9 kPa, –33 kPa, and –1.5 MPa matric potentials generally decreased with lime dose (Table 3), particularly at the highest tension (–1.5 MPa). Biosolids have a high water retention capacity at –1.5 MPa (Logan and Harrison, 1994, and Logan *et al.*, 1996), apparently much more so than Ca(OH)₂. Water available to plants (calcu-

lated as the difference between –5.9 kPa and –1.5 MPa matric potentials) increased with lime addition. This suggests that capillary pores in the limed biosolids capable of holding water against gravity drainage increased with lime addition through the formation of structural aggregates.

Lime application had no consistent effect on the liquid and plastic Atterberg limits of the limed biosolids (Table 3). The liquid limit is the maximum solids content at which the material will flow under an applied shear force, while the plastic limit is the maximum solids content at which the material can be deformed without crumbling. If the normal solids content of a material is less than its liquid and plastic limits, then the material is considered to exhibit liquid and plastic properties. If the normal solids content of a material is less than its plastic limit but greater than its liquid limit, then the material is considered to exhibit plastic properties. Those materials that have normal solids contents greater than their plastic limits are considered to exhibit neither liquid nor plastic properties. Materials to be used as agricultural amendments (applied through a spreader), as soil amendments, for reclamation, or as topsoil blends should exhibit neither liquid nor plastic properties. Thus, their normal solids contents should be greater than their liquid or plastic limits.

The 5, 15, and 20% lime doses yielded products with liquid and plastic properties; the 25 and 30% lime-dose products exhibited only plastic properties; and the 40 and 50% lime doses gave products that were neither liquid nor plastic (Table 3). The 40 and 50% lime-dosed products would be most acceptable for use as agricultural amendments.

Conclusions

The results of this study showed that the addition of CaO to dewatered biosolids produces heat through the exothermic conversion of CaO to Ca(OH)₂, with only small amounts of heat produced from the exothermic reaction of CO₂ with Ca(OH)₂ to form CaCO₃. Heat balances showed that all heat produced was dissipated in heating the biosolids and in evaporating water. Because of the predominance of Ca(OH)₂ in the limed biosolids, care should be taken in using these materials as liming agents and soil amendments because of the very high initial soil pHs (more than 12) that can persist for weeks or more. Limed biosolids applied at agronomic rates would probably not cause elevated soil pHs; however, limed biosolids applied at reclamation rates could result in very high soil pH values. Increasing lime

dose improved the density and water-holding capacity of biosolids and improved their physical handling characteristics, although lime doses of 40% and higher were required to produce nonplastic products.

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Authors. Karen Smith is employed by Chemical Abstracts Service and is a postdoctoral continuing education student at The Ohio State University, Columbus. Lori Goins is a research assistant in the School of Natural Resources and an M.S. student in the Environmental Science Graduate Program at The Ohio State University. Terry Logan is a professor of soil chemistry in the School of Natural Resources, The Ohio State University. Correspondence should be addressed to Terry J. Logan, The Ohio State University, School of Natural Resources, 2021 Coffey Road, Columbus, OH 43210-1085.

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References

- Association of Official Agricultural Chemists (1965) *Agricultural Liming Materials*. Official Methods of Analysis of the Association of Official Agricultural Chemists, Washington, D.C., 1.
- ASTM (1993) *Annual Book of ASTM Standards. Cement, Lime, Gypsum*. P. Fazio *et al.* (Eds.), Philadelphia, Pa., 4.01, 24.
- Barber, S.A. (1984) Liming Materials and Practices. In *Soil Acidity and Liming*. F. Adams (Ed.), 2nd Ed., Am. Soc. Agron., Madison, Wis., 171.
- Burnham, J.C.; Hatfield, N.; Bennett, G.F.; and Logan, T.J. (1992a) Use of Kiln Dust and Quicklime for Effective Municipal Sludge Pasteurization and Stabilization with the N-Viro Soil Process. In *Innovations and Uses for Lime*. D.D. Walker, T.B. Hardy, D.C. Hoffman, and D.D. Stanley (Eds.), ASTM STP 1135, Philadelphia, Pa., 128.
- Burnham, J.C.; Donovan, J.F.; Forste, J.; Gschwind, J.; Logan, T.J.; and Zenz, D. (1992b) Production and Distribution of Municipal Sewage Sludge Products. In *Municipal Sewage Sludge Management*. C. Lue-Hing *et al.* (Eds.), Technomic Publications., Lancaster, Pa., 479.
- Christensen, G.L. (1987) Lime Stabilization of Wastewater Sludges. In *Lime for Environmental Uses*. K.A. Gutschick (Ed.), ASTM STP 931, ASTM, Philadelphia, Pa., 78.
- Christie, P.G. (1990) Process Equipment Considerations for Lime Stabilization Systems Producing PSRP and PFRP Quality Sludge. *Proc. Status Munic. Sludge Manage. 1990s. Water Pollut. Control Fed.*, Alexandria, Va.
- Eikum, A.S. (1983) Lime Stabilization of Sewage Sludges. In *Sludge Characteristics and Behavior*. NATO ASI Ser., Ser. E, **66**, 359.
- Haug, R.T. (1980) *Compost Engineering Principles and Practice*. Ann Arbor Science Publishers, Inc., Ann Arbor, Mich.
- Klute, A. (Ed.) (1986) *Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods*. Soil Sci. Soc. Am., Madison, Wis., 1187.
- Kruzic, A.P., and Petry, T.M. (1994) A Study of Alkalinity Leaching and Residual Strength of Alkaline Stabilized Sludge. In *Proceedings of National Environmental Engineering. Critical Issues in Water and Wastewater Treatment*. J.N. Ryan and M. Edwards (Eds.), Am. Soc. Civ. Eng., New York, N.Y., 129.
- Logan, T.J., and Burnham, J.C. (1995) The Alkaline Stabilization with Accelerated Drying Process (N-Viro): An Advanced Technology to Convert Sewage Sludge into a Soil Product. In *Agricultural Utilization of Urban and Industrial By-Products*. D.L. Karlen (Ed.), Am. Soc. Agron. Spec. Pub. No. 58., 209.
- Logan, T.J., and Harrison, B.J. (1994) Physical Characteristics of Alkaline Stabilized Sewage Sludge (N-Viro Soil) and Their Effects on Soil Physical Properties. *J. Environ. Qual.*, **24**, 153.
- Logan, T.J.; Harrison, B.J.; McAvoy, D.C.; and Greff, J.A. (1996) Effects of Olestra in Sewage Sludge on Soil Physical Properties. *J. Environ. Qual.*, **25**, 153.
- Morling, S. (1995) The Use of Lime in Waste Water Treatment for Sludge Stabilization, a Case History in Sweden. Technical Report, N-Viro International Inc., Toledo, Ohio.
- National Lime Association (1982) *Lime: Handling Application and Storage in Treatment Processes*. Bulletin 213, Natl. Lime Assoc., Arlington, Va., 74.
- Paulsrud, B., and Eikum, A.S. (1983) Experiences with Lime Stabilisation and Composting of Sewage Sludge. In *Proceedings of Water Resources Center Conference. Sewage Sludge Stabilization and Disinfection*. A.M. Bruce (Ed.), Horwood, Chichester, U.K., 261.
- U.S. Environmental Protection Agency (1993) Standards for the Use or Disposal of Sewage Sludge. 40 CFR Part 503, *Fed. Regist.*, **58**, 9387.
- Water Environment Federation (1995) *Wastewater Residuals Stabilization*. Manual of Practice No. FD-9, Alexandria, Va., 244
- Weast, R.C., and Astle, M.J. (Eds.) (1981) *Handbook of Chemistry and Physics*. CRC Press Inc., Boca Raton, Fla., 73.