Physicochemical characterization of cement kiln dust for potential reuse in acidic wastewater treatment

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ABSTRACT

Cement kiln dust (CKD) is a fine-grained material produced during the manufacture of cement. Current reuse options are limited and the bulk of CKD not reused in the cement manufacturing process is sent to landfills or stored on-site. Due to the calcium oxide (CaO) content of CKD, it has the potential to be used as a replacement for lime in treating acidic wastewaters such as acid rock drainage (ARD). This paper outlines the results of an examination of the physical and chemical properties of CKD samples collected from six cement plants. The CKD samples were analyzed for major oxides using X-ray diffraction (XRD), available lime, specific surface area, particle size, and morphology using scanning electron microscope (SEM) and compared with a commercial quicklime product. Conductivity, pH, and calcium concentrations of slaked CKD and quicklime solutions were used as indicators of reactivity of the CKD. Slaking of two of the CKD samples with the highest free lime contents (e.g., 34 and 37% free CaO) gave elevated pH values statistically comparable to those of the commercial quicklime sample that was characterized as having 87% available CaO. Acid neutralization trials indicate that even CKD samples with low free lime contents could be effective at neutralizing acidic wastewaters.

1. Introduction

Cement kiln dust (CKD) is a fine-grained, alkaline material that is generated as a by-product of the cement manufacturing process. In cement production, raw materials are fed into a kiln where they are heated to temperatures reaching between 1400 and 1550 °C. The main raw material used to produce cement is limestone ($CaCO_3$), with approximately 10% of the raw mix made up of a silica source (e.g., sand or clay), an alumina source and an iron source. Heating the raw materials to such high temperatures, a process called calcination, alters the chemical makeup of the materials to produce cement clinker [1].

Cement kilns can be defined in a number of ways. Wet process kilns are fed raw materials in a slurry form, and dry process kilns are fed raw materials in granular form. Kilns can also be long (length/diameter (L/D) $\cong$ 30) or short ($L/D \cong$ 10–15), and may include a preheater or precalciner [2]. Preheaters and precalciners are utilized in some cement plants to reduce power consumption since they use excess hot gases from the kiln to raise the temperature of the kiln feed (preheater) or start the calcination process (precalciner).

Large quantities of air used for combustion and to carry the fuel to the burning zone of a cement kiln results in an exhaust gas that is entrained with particles (i.e., CKD) of clinker, raw materials, and partially calcined raw materials [3]. CKD is separated from cement kiln exhaust gases in air pollution control devices such as baghouses or electrostatic precipitators. CKD generation has been estimated at approximately 15–20% of cement clinker production [4]. Most CKD currently generated in North America is returned to the head of the cement kiln for reprocessing. However, not all of the CKD generated can be reused in cement manufacturing due to chemical specifications, a potential reduction in the effectiveness of pollution control devices, and the possibility of damage to kilns [5]. One study found that of the 12.9 million tonnes of CKD generated in the United States in 1990, 8.3 million tonnes (64%) was recycled into the cement kiln, while approximately 0.4 million tonnes (3%) was reused off-site [5]. This leaves roughly 4.2 million tonnes (33%) of CKD to be landfilled or disposed off-site. Results of a more recent survey showed that for the 87 million tonnes of cement clinker produced in 2006, 1.2 million tonnes of CKD were reused on or off-site (not including recycling into kiln feed) while 1.4 million tonnes were landfilled. In addition, 0.3 million tonnes of CKD was reclaimed from landfills, mainly for use as kiln feed [6].

In the United States, CKD is currently classified as a special waste that is temporarily exempt from federal hazardous waste regulations (Subtitle C of the Resource Conservation and Recovery Act (RCRA)) [7]. In 1999, the USEPA proposed a rule for the management of CKD that includes standards for landfill placement and design to control the potential release of heavy metals to the environment through leaching and runoff, and to control airborne particle release

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through covers, and guidelines for continued monitoring [8]. Any CKD that is not managed following this rule would be classified as a hazardous waste and subject to regulation under Subtitle C of the RCRA [8]. CKD used for beneficial purposes (i.e., recycling) is exempt from this rule. In Canada, solid and hazardous waste disposal is regulated at the provincial level. There are no disposal regulations specific to CKD, however, landfill designs must be approved by the relevant agency.

Acidic waste streams like acid rock drainage (ARD) from base metal mines contain hazardous metals that, along with high acidity, damage ecosystems [9]. In practice, the neutralization of acidic wastewater streams often involves the addition of chemicals to raise pH levels and precipitate soluble metals. Elevating the pH of these waste streams causes the dissolved metals to precipitate in the form of hydroxides which can then be removed through settling or filtration processes. The most common material used in treatment of acid rock drainage from mines is quicklime in the form of lime slurries [9]. Quicklime is an alkaline product used in a variety of environmental and industrial applications. It is produced similarly to cement, by heating limestone in a kiln. The calcium carbonate $(CaCO_3)$ content present in a high-calcium limestone is converted into calcium oxide (CaO) during calcination to release carbon dioxide (CO_2) [10]. The production of magnesium oxide (MgO) can also occur if processing a dolomitic limestone that, by definition, contains 35–46% magnesium carbonate $(MgCO_3)$. The temperatures in lime kilns are generally lower than those in cement kilns, at approximately 1000 °C [10]. According to ASTM Standard C1529-06a, quicklime must contain a minimum of 90% CaO + MgO, and therefore the only raw material in quicklime manufacture is limestone. This is the specification for a high-calcium quicklime product for environmental uses and dictates that the limestone used as raw material must have a calcium content greater than 90%.

There are several current reuse options for CKD. These include soil stabilization, as an additive for blended cement products, solidification/stabilization of hazardous wastes, pasteurization of municipal biosolids, and as a fertilizer [11]. Several CKD characterization and reuse studies have demonstrated the presence of elevated concentrations of calcium oxide that highlights the potential for CKD to be used as a base material in the production of lime slurries for neutralization and precipitation processes. However, available information on the use of CKD for such applications is preliminary and isolated in that very few studies have been done on only selected types of wastewater and selected CKD samples. Zaki et al. [12] demonstrated that CKD leachate was effective at removing copper, nickel, and zinc ions from a synthetic wastewater by hydroxide precipitation. The CKD leachate in that study was prepared by washing varying amounts of CKD with water, then filtering out the remaining solids. Pigaga et al. [13] found that CKD was efficient in the removal of heavy metals from synthetic aqueous solutions.

The main objective of this study was to perform a physicochemical characterization of six CKDs from cement plants across North America and compare these characteristics to those of a commercial quicklime product. The study focused on determining the impact of these properties on the viability of using CKD as a raw material for the production of calcium hydroxide $(Ca(OH)_2)$ slurries for use in wastewater treatment applications. The characterization of CKDs presented in this paper consists of (1) physical analysis including specific gravity, particle size distribution, and specific surface area, (2) chemical analysis including an analysis of major oxides and available lime, and (3) morphological analysis with scanning electron micrographs (SEMs) of unhydrated CKD samples. In addition, the chemical quality of the calcium hydroxide slurries generated using CKD samples characterized in this study were compared to those generated using a commercial quicklime product. The acid neutralization potential of the hydrated lime slurries generated from CKD samples was also evaluated and compared to that of quicklime.

2. Materials and methods

2.1. CKD sources

Six CKD samples were obtained from cement manufacturing plants from across North America for use in this study. Also, a commercially available quicklime product was obtained in order to compare the performance of the CKD samples with current industry standards. Table 1 summarizes the raw materials and manufacturing specifications of the six cement plants. All plants that supplied CKD samples used in this study have rotary kilns that operate in the temperature range of 1370–1480 °C. Plant C uses a wet feed process while all other plants use dry feed. Plant D has a 4-stage preheater, and Plant F has a precalciner. All of the plants except that which provided CKD-B use baghouses as their dust collection system. Plant B uses an electrostatic precipitator (ESP) to collect the CKD. Two separate samples of CKD were obtained from each plant at different times to evaluate the variability of the CKD properties within each plant. Sample 1 of each CKD was obtained in November 2007 and Sample 2 in July 2008.

2.2. Analytical methods

A manual stereopycnometer (Quantichrome) was used to measure specific gravity. A laser particle size analyzer (Model 2600, Malvern) was used to determine the particle size distribution of the different CKD samples. A major oxide analysis of each unhydrated CKD sample was done using ICP-OES (Vista-PRO Radial, Varian). Samples were first prepared using lithium metaborate/tetraborate fusion. Sulphur content was analyzed using a sulphur analyzer (LECO). The rapid sugar method was used to

Table 1
General cement plant information from CKD samples used in this study.

CKD ID	Raw materials used	Process	Kiln type	Kiln temperature (°C)	Fuels
CKD-A	Limestone (high CaO + high Al, Si, SO₃), fly ash, iron ore, sand	Dry	Long	1450	Coke/coal, plastic and broth[a] (up to 5%)
CKD-B	Cement stone,[b] mill scale	Dry	Long	1450	Coal, used oil, shingles (up to 10%)
CKD-C	Limestone, silica, shale, de-zinced lead slag	Wet	Long	1480	Coke/coal
CKD-D	Limestone, clay, coal boiler ash, mill scale	Dry, 4-stage preheater	Long	1475	Coke/coal
CKD-E	Limestone, sandstone, iron ore, silica, alumina	Dry	Long	1475	Coke/coal, tires (20%), other waste[c] (30%)
CKD-F	Limestone, clay, sand, mill scale	Dry, precalciner	Short	1370	Coke/coal, used tires (up to 5%)

[a] Broth is a waste product of the pesticide manufacturing industry that has a high carbon content.

[b] Cement stone is a naturally occurring limestone whose properties are ideal for making cement, therefore no clay or sand additives are necessary.

[c] Includes tire fluff, plastics, wood, and dried sewage sludge.

determine the available lime content as outlined in ASTM standard C 25-06. A Hitachi S-4700 FEG Scanning Electron Microscope (SEM) was used to obtain SEM images of the CKD samples. Specific surface area measurements were measured using a standard manual Blaine air permeability apparatus (Gilson) following the fineness by air permeability method as outlined in ASTM C110-06.

2.3. Bench-scale experiments

Bench-scale experiments to model the lime slaking process were conducted using a standard jar test apparatus (Phipps & Bird, Fisher Scientific). Several dosages of each CKD sample, normalized to its CaO content, were added to the jars with 750 ml of room temperature water (approximately 20 °C). Water was added at a slow and constant rate to avoid 'drowning' the CKD particles. Drowning occurs when water is added too quickly and creates an outer shell of hydrated lime ($Ca(OH)_{2(s)}$) that slows or prevents the interior of the particles from hydrating [10]. Each sample was then rapid mixed at 200 rpm for 30 min, with 250 ml of cold water (4 °C) added at the end and mixed for 1 min to ensure maximum dissolution of $Ca(OH)_2$. The temperature of the test solutions was monitored during the slaking process. The CKD dosages evaluated were 0.4, 0.6, 0.8, 1.0, 1.2, and 1.4 g CaO/L. After mixing, samples of the slurry were taken and analyzed for pH, conductivity, and calcium (Ca^{2+}) content. Separate samples were taken and passed through a 0.45 μm membrane filter (Whatman) and the same analyses were performed on the filtrate. Sulphate concentrations were also measured on the filtrate from the jar tests. The slaked solutions were filtered through a 1.5 μm Whatman filter in order to determine total suspended solids (TSS) concentrations of the samples. The filters were weighed before and after filtration and these measurements were compared to the mass of CKD that had been added at the beginning of the jar tests in order to estimate the percent dissolution of the CKD material.

The pH was measured using variable temperature electrodes (accuFlow, Fisher Scientific), and conductivity using four cell probes (accumet, Fisher Scientific), both using an XL50 meter from Fisher Scientific. Calcium ions were measured using an atomic absorption spectrometer (AAnalyst 200, PerkinElmer). Sulphate ion content was analyzed on the filtered samples using a compact ion chromatography system (Model 761, Metrohm) with autosampler (Model 788, Metrohm).

Acid neutralization potential of the CKD samples was evaluated following ASTM standard C 400-98. The pH of solutions containing 2.5 g of CKD and varying amounts of 1.5% sulphuric acid were measured for 30 min during these tests.

3. Results and discussion

3.1. Particle size and morphology

In the laser particle size distributions presented in Fig. 1, it is shown that CKD-A contained the finest particles while CKD-D contained the coarsest particles. Also shown in this figure, for comparison, is the particle size distribution of the commercial quicklime product, which was found to be coarser than all the CKD samples analyzed. CKD samples A and E were found to be notably finer than the quicklime sample and other CKD samples.

Shown in Fig. 2 are the SEMs that were taken of the dry, unhydrated CKD samples. The SEMs qualitatively show the relative particle sizes of the CKDs, with CKD-F appearing to have the largest particle size and CKD-A having the finest and most uniform particle size. It can be seen from the SEMs that CKD samples A and E demonstrated the highest amounts of fine particles, which corresponds with the laser particle size data. The SEMs also show the
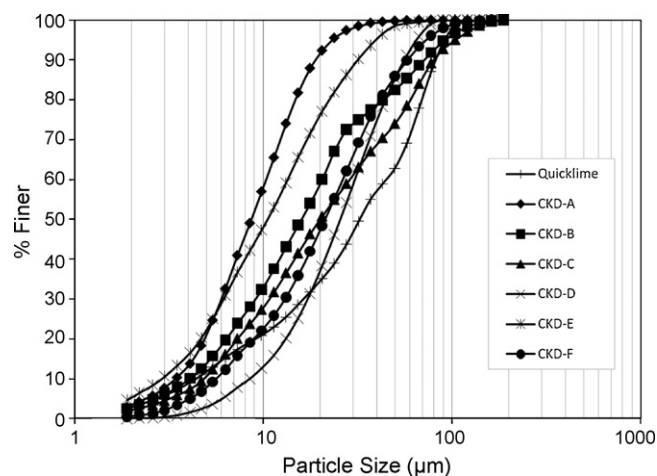

Fig. 1. Laser particle size distributions of CKD and quicklime samples.

large variability in composition and particle shape of the different CKD samples.

Using results from a study performed for the Portland Cement Association (PCA) by Todres et al. [14], the USEPA [5] found that dry kilns with precalciners produced the largest sized CKD particles, followed by wet kilns, with long-dry kilns producing the smallest CKD particles. Similar results were found using another study conducted on four CKD samples that concluded that CKD generated in long, dry kilns had the smallest particles size while CKD generated in dry kilns with a precalciner had the largest particle sizes [15]. The results of both previous studies correspond to results found in this study (at the 50% finer particle size), in that the analysis of CKD samples taken from long-dry kilns (CKD-A, CKD-B, and CKD-E) demonstrated that 50% of the particles were smaller than 8–16 μm. Samples taken from the wet, long kiln (CKD-C) and dry, short kiln with precalciner (CKD-F) were found to have a slightly larger particle size distribution, with 50% of the particles smaller than approximately 20 μm. The CKD samples taken from the dry, long kiln with preheater was found to have the largest particle size distribution of all of the CKD samples analyzed in this study, with 50% of the particles smaller than 25 μm.

3.2. Specific surface area

The Blaine air permeability test was used to determine the specific surface area of the CKD samples. The specific gravity measurements of the CKD samples were used to convert the laser particle size distributions into specific surface area values. As can be seen from the results in Table 2, the calculated surface areas from the laser particle size distributions were found to be consistently lower than those from the Blaine method. This can be attributed to the assumption used when estimating surface area from particle size distributions that all particles are spherical in shape, which, in

Table 2
Specific gravity and specific surface area measurements. (Error represents one standard deviation.).

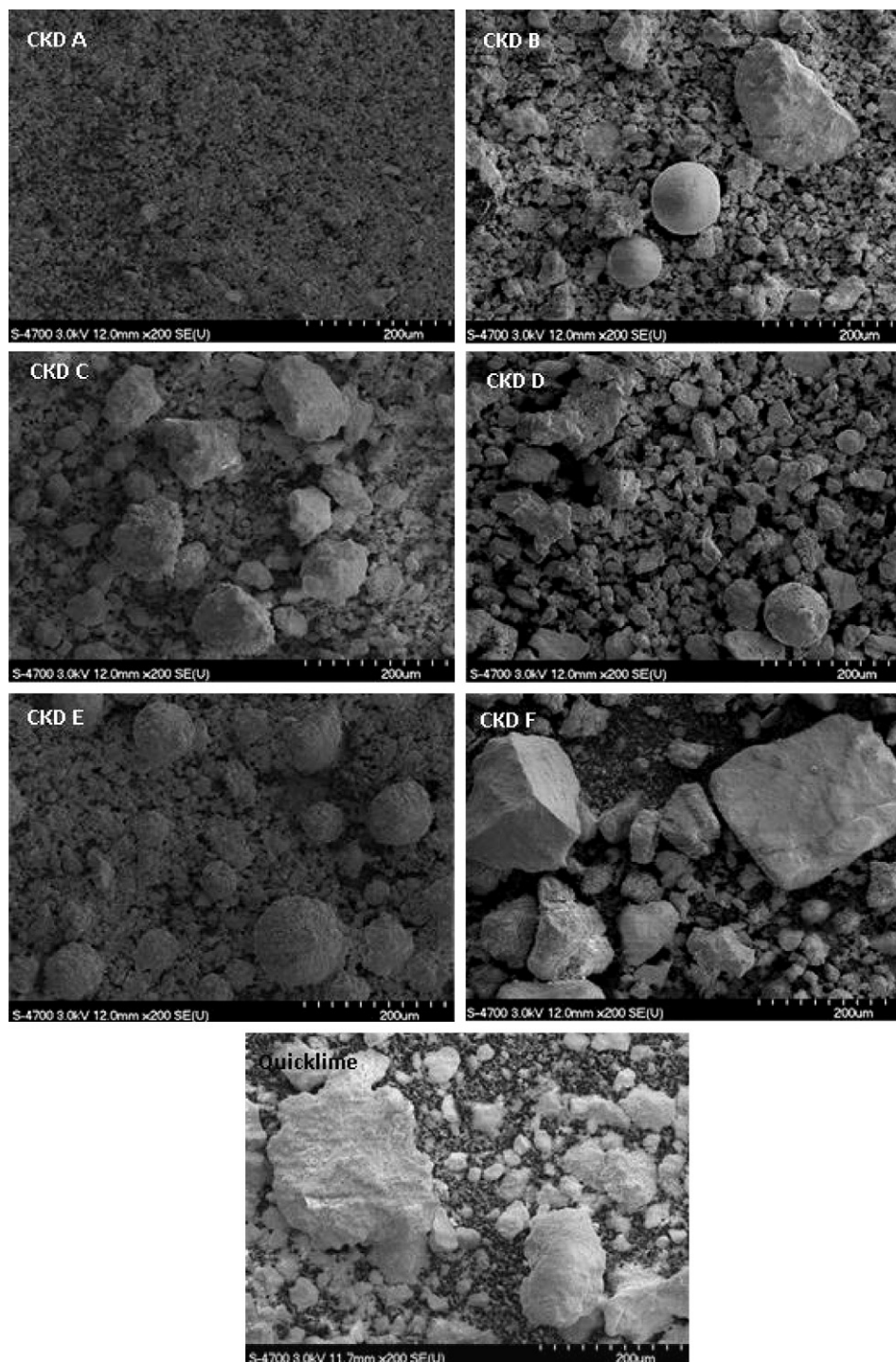| CKD ID	Specific gravity	Specific surface area ($m^2 g^{-1}$)	
		Blaine method	Particle size method
CKD-A	2.84 ± 0.05	0.502 ± 0.008	0.10 ± 0.03
CKD-B	2.87 ± 0.06	0.350 ± 0.008	0.06 ± 0.07
CKD-C	2.83 ± 0.02	0.5 ± 0.2	0.025 ± 0.007
CKD-D	2.98 ± 0.02	0.194 ± 0.006	0.03 ± 0.02
CKD-E	2.76 ± 0.05	0.65 ± 0.06	0.061 ± 0.004
CKD-F	2.94 ± 0.05	0.4 ± 0.2	0.03 ± 0.02
Quicklime	3.28	0.164	0.021

Fig. 2. SEMs of CKD and quicklime samples.

the case of CKD, they are not. The laser particle size method cannot penetrate the particles to measure the internal surface area as well as external, which the Blaine method does. Collectively, the results demonstrate that the CKD particles have a higher specific surface area than quicklime; the specific surface area of the CKD samples was between 213 and 398% greater than that of the quicklime product evaluated. The specific surface area measurements also agree with particle size distributions and SEMs in that CKD-A and CKD-E have the finest particle sizes as well as the highest surface areas. Due to the fineness of the CKD particles, there is a larger surface area available for the reaction of CaO with water to produce

$Ca(OH)_2$. This indicates that the oxide particles present in CKD may demonstrate greater reactivity due to the increased surface area. Increased surface area also allows more space for metal adsorption, since CKD has been demonstrated to act as both a neutralizing agent and sorbent [13].

3.3. Major oxides and available lime

The results of the major oxides analysis are presented in Table 3. Also included in Table 3 is the available lime, or free CaO, content of each sample. The major oxide measurement of the calcium oxide

Table 3
Major oxides analysis of CKD samples as weight percentage. (Error represents one standard deviation.).

Chemical composition (XRD)	CKD-A	CKD-B	CKD-C	CKD-D	CKD-E	CKD-F	Quicklime
Al_2O_3	4.8 ± 0.7	3.9 ± 0.3	2.6 ± 0.2	3.7 ± 0.3	5.0 ± 0.8	4.7 ± 0.3	0.36
CaO	44 ± 3	47.8 ± 0.0	40 ± 3	57 ± 3	35 ± 3	57 ± 3	90.1
Free CaO[a]	15 ± 5	$8.8 \pm .6$	5.0 ± 0.3	34 ± 3	3.5 ± 0.1	37 ± 5	87.2
Fe_2O_3	1.80 ± 0.09	1.39 ± 0.07	1.5 ± 0.3	2.19 ± 0.05	1.6 ± 0.2	3.1 ± 0.5	0.19
K_2O	5.7 ± 0.7	2.0 ± 0.5	8 ± 2	5 ± 2	11 ± 4	2.6 ± 0.2	0.08
MgO	1.3 ± 0.04	1.0 ± 0.2	1.9 ± 0.2	4.1 ± 0.3	1.1 ± 0.2	1.2 ± 0.01	0.29
Na_2O	1.0 ± 0.3	0.25 ± 0.08	0.4 ± 0.1	0.6 ± 0.2	1.0 ± 0.4	0.2 ± 0.03	0.12
P_2O_5	0.11 ± 0.03	0.01 ± 0.02	0.04 ± 0.02	0.10 ± 0.01	0.08 ± 0.03	0.3 ± 0.2	0.01
SiO_2	13 ± 2	15 ± 2	13 ± 2	12.9 ± 0.4	9 ± 2	20 ± 5	4
TiO_2	0.23 ± 0.04	0.20 ± 0.03	0.13 ± 0.02	0.12 ± 0.00	0.15 ± 0.02	0.21 ± 0.03	0.021
SO_3[b]	14.2 ± 0.5	20 ± 20	9.3 ± 0.2	9 ± 3	11 ± 5	4 ± 3	N/A
LOI[c]	13 ± 3	10 ± 20	23 ± 3	5 ± 2	22 ± 5	5.6 ± 0.6	4

[a] Analysis done by the rapid sugar method.

[b] Analysis done by the LECO total sulphur method.

[c] Loss on ignition at 1000 °C.

(CaO) content assumes that all calcium in the sample is in the form of CaO, however, this is not the case. Some of the calcium content may be in the form of calcium carbonate, $CaCO_3$ (i.e., the unreacted limestone), or calcium sulphate ($CaSO_4$). Available lime is a measure of the CaO content that is readily available for reactions [10], and was of interest in this study to evaluate the amount of CaO in each CKD that would react with water to form calcium hydroxide ($Ca(OH)_2$). Previous studies have found that CKD can contain from 8.1 to 61.3% by weight of total CaO [11–14,16–18]. CKD samples D and F were found to contain both the highest total CaO (57% for both) and free CaO (34 and 37%, respectively) content, after quicklime (90% total and 87% free). In contrast, CKD-C and CKD-E demonstrated the lowest CaO content at 40% and 35% for total, respectively and 5% and 3.5% for free. High loss on ignition (LOI) indicates that the CKD is high in slow-reacting calcium carbonate and low in reactive free lime [19]. The LOI values for the CKD samples further support the total and free lime analysis results, in that CKD-D, CDK-F and quicklime were found to have LOI values less than 6.0, indicating lower $CaCO_3$ and higher free lime content in comparison to the other CKD samples analyzed. Table 3 also demonstrates the low variability within each plant. Error values are due to the variation between the two samples taken at each plant and represent one standard deviation.

In their 1993 report to Congress, the USEPA [5] found that there was no apparent trend in CKD chemical composition (i.e., major oxide distribution) relating to process type, based on a limited sample for analysis. However, other studies have demonstrated that as an industrial by-product, the composition of CKD may be linked as a function of process variables. A study by Bhatty and Todres [19] on the use of CKD as a soil stabilizer determined that CKD can be segregated into two categories, precalciner kiln dust and long-wet or long-dry kiln dusts. The results of that study concluded that precalciner kiln dust particles were coarser and higher in free lime, while CKD particles generated in long kilns contained more $CaCO_3$ with reduced amounts of free lime. Those results are in agreement with the results of the current study with regards to CKD-F (e.g., precalciner process) which demonstrated a larger particle size distribution and higher free lime content in contrast to the other long kiln CKD samples analyzed. Results of the analysis of CKD-D also demonstrates that kiln dust particles generated in plants with preheaters are similar to those generated in precalciner kiln processes (e.g., coarser particle sizes and elevated free lime content).

The presence of particles other than calcium oxide can affect the solubility of CaO into $Ca(OH)_2$. Specifically, interfering oxides such as magnesium oxide (MgO), silica (SiO_2), aluminum oxide (Al_2O_3), and unreacted $CaCO_3$ particles may slow the rate of dissolution of $Ca(OH)_2$ [10]. However, both magnesium oxide and potassium oxide (K_2O) will react with water to form magnesium hydroxide ($Mg(OH)_2$) and potassium hydroxide (KOH), which are known for their acid neutralizing capabilities in environmental applications. In wastewater treatment, $Mg(OH)_2$, or milk of magnesia, has a higher basicity per unit added than either lime or caustic soda (NaOH) for equivalent neutralization [20]. However, its slower reaction rate in precipitating high concentrations of metals (e.g., >2000 ppm) or neutralizing weak organic acids and associated longer required reactor residence times is known to be a primary disadvantage of magnesium hydroxide treatment.

The collective results of the major oxide analysis presented in Table 2 show that all of the CKDs analyzed demonstrated significantly higher levels of MgO, K_2O, SiO_2 and Al_2O_3 compared to the commercial quicklime product analyzed in this study. These results are in agreement with the results of other studies [12,13,16–18]. While silica and alumina would present potentially interfering materials in the dissolution reactions of $Ca(OH)_2$, the presence of elevated magnesium and potassium oxide levels in CKD and reactions with water to produce $Mg(OH)_2$ and KOH would potentially enhance the neutralizing capabilities of CKD slurries for acidic wastewater treatment applications.

3.4. Hydrated CKD slurry quality

The parameters used to characterize the reactivity of the CKDs when slaked in water were pH, conductivity, and calcium ion (Ca^{2+}) content. Both filtered and unfiltered samples were analyzed for all three water quality parameters. pH was chosen as the major indicator of CKD reactivity for this experiment because of the importance of this parameter in neutralizing acidic wastewater streams. Conductivity is generally a measure of the ionic strength of a solution, or how many free ions are in solution. Robinson and Burnham [21] found in their study of dissolution rates of hydrated limes that conductivity increased close to linearly with lime dosage. Conductivity has also been directly related to the concentration of $Ca(OH)_2$ in a pure solution, though it also varies with temperature [10].

Shown in Fig. 3 are the pH results for the filtered samples and in Fig. 4 the conductivity results for the filtered samples. The data in Figs. 3 and 4 represent the average outcome of three trials, with error bars representing one standard deviation. The unfiltered samples (data not presented) had slightly higher pH and conductivity values, but followed the same trend as the filtered samples. As can be seen from these graphs, all of the CKD samples and the quicklime sample show the same general trend of increasing pH and conductivity with increasing dosage. In terms of achieving increased pH with product addition, CKD-D and CKD-F performed the best, and did not show statistically significant ($p > 0.05$) differences from quicklime in this regard. This was concluded from an ANOVA test conducted on the results of the filtered sample pH and conductiv-
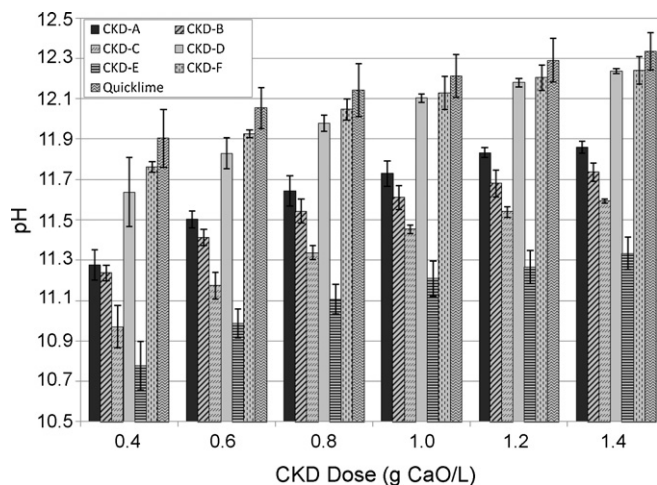
Fig. 3. Filtered pH results from slaking trials. (Error bars represent one standard deviation.)

Fig. 5. Filtered vs. unfiltered calcium results from slaking trials at a dose of 1.2 g equivalent CaO/L. Percentage in brackets next to CKD labels is the percentage of total CaO that is available CaO. (Error bars represent one standard deviation.)

ity measurements of CKD-D and CKD-F and quicklime. Zaki et al. [12] found pH values of CKD slurries fell between 12 and 13 for solutions containing between 10 and 40 g/L CKD, increasing with concentration.

Fig. 5 presents the measured calcium concentrations in each of the CKD and quicklime slurry samples. Calcium concentrations measured in filtered samples from CKD-D and CKD-F (1030 and 940 mg/L, respectively) were not found to be statistically significantly ($p > 0.05$) different from those measured in the filtered quicklime slurry sample (1200 mg/L), demonstrating that the CaO content of both of these CKD samples reacted with water to form $Ca(OH)_2$ to a similar level as quicklime. Analysis of the unfiltered samples consistently showed higher calcium concentrations than measured in the filtered samples for both the CKD and quicklime slurries, demonstrating the presence of unreacted calcium in the solids after the slaking period. For the samples generated with CKD-A, CKD-B, CKD-C and CKD-E, the majority of the calcium remained in the particulate form after they had been slaked with water. For these CKD samples, these results are most likely due to the high-calcium content but relatively low free lime (i.e., CaO available for reactions) content of the samples, as presented in Table 3. The percentages in brackets beneath the CKD labels in Fig. 5 represent the percentage of total CaO content that is as free lime. As shown in Fig. 5, there are smaller differences between the calcium concen-
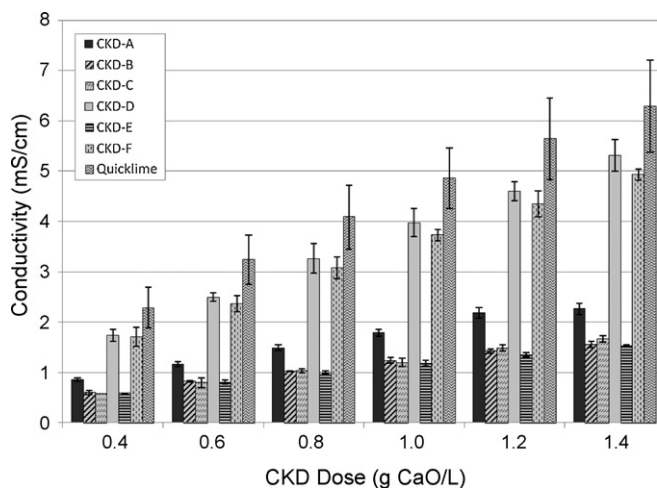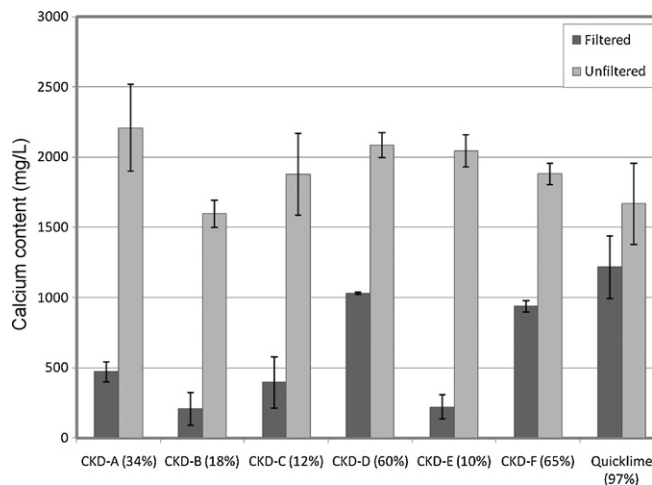
tration in the filtered and unfiltered samples from CKD-D, CKD-F, and quicklime, which have high free lime contents, compared to those of the other CKD samples used in the study which have large differences between total and free CaO content.

The amount of solids dissolved in each of the slaking trials was calculated by measuring the total suspended solids of the slaked CKD and quicklime slurries and subtracting this from the initial amount of sample added. Analysis of the quicklime samples showed that 65% of the solids dissolved during slaking. Overall, the percent of solids dissolved during the slaking trials for each of the CKDs was less than that of quicklime. For CKD-D and CKD-F, which contain a higher free lime content than the other CKDs studied, 52 and 47% of the solids were found to dissolve during slaking, respectively. For the remaining CKD samples, dissolution of the solids decreased to less than 30%.

In order to further evaluate the specific oxides reacting with water during slaking, a sample of the solids remaining after filtering the slurry produced from slaking CKD-F were analyzed for major oxides content. Results showed that total CaO content decreased by 37%, demonstrating the dissolution of this oxide during slaking of this CKD sample. Other major oxide weight percentages that decreased were K_2O by 12%, Na_2O by 13%, and SO_3 by 25%. These results demonstrate that other oxide particles present in the CKD are also prone to reaction with water. In particular, the dissolution of the potassium oxide after slaking offers an explanation for the elevated pH and conductivity values measured in the CKD-F slurries (due to the generation of KOH) which were close in value to those obtained in the quicklime slurry samples. For the other CKD samples that had comparable (CKD-D) or lower free lime contents, the generation of KOH and/or $Mg(OH)_2$ during slaking would explain the elevated pH and conductivity results obtained in this study.

3.5. Sulphate

Calcium sulphate ($CaSO_4$) interferes with the solubility of calcium hydroxide ($Ca(OH)_2$) in solution, even at very low levels [10]. For this reason, sulphate (SO_4^{2-}) levels were measured in the slaked slurries to determine if this could lower the effectiveness of the generated CKD slurries evaluated in this study. Sulphate measurements were only performed on test slurries made with the second set of CKD samples used in this study. The results in Fig. 6 show that sulphate ions measured in the filtrate of the CKD slurries were consistently 1.8–16 times higher than those measured in the filtrate of the quicklime slurry sample. Overall, the sulphate concentrations
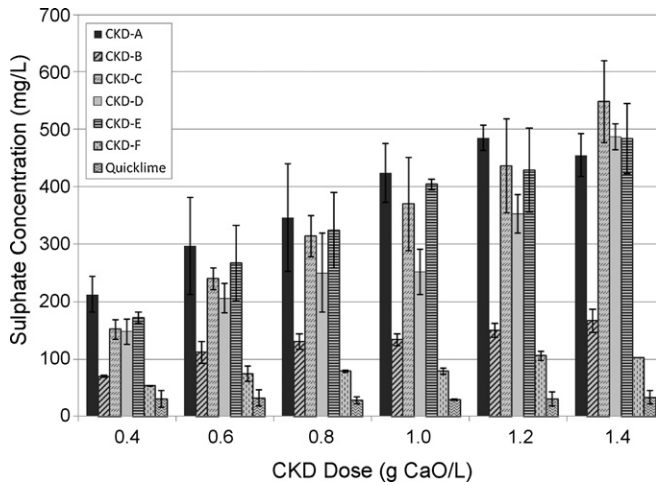

Fig. 4. Filtered conductivity results from slaking trials. (Error bars represent one standard deviation.)

Fig. 6. Sulphate results from slaking trials. (Error bars represent one standard deviation.)

in the filtrate from the slaked CKD samples were found to be less than 500 mg/L, and it is important to note that most countries in the world recommend a drinking water standard for sulphate between 250 and 500 mg/L. Sulphate ions have the potential to negatively affect the performance of CKD by reacting with the calcium that it contains. Sulphate ions could also indicate the potential for scaling

of infrastructure due to gypsum ($CaSO_4 \cdot 2H_2O$) precipitation. However, in some environmental applications such as neutralization of acid rock drainage, reactions between calcium hydroxide and sulphate are known to occur and result in feed streams that can have SO_4^{2-} concentrations in excess of 5000 mg/L. The added sulphate from the CKD would be minimal in comparison.

3.6. Regression analysis

Regression analyses were performed in order to compare the pH achieved at a CaO dose of 1.2 g/L for each of the CKDs to several physical and chemical characteristics. The characteristics compared were CaO content, free CaO content, specific surface area by the Blaine Method, and the 50% finer particle size. Results of these analyses are presented in Fig. 7. The correlation coefficients indicate a clear relationship between reactivity as pH achieved and free lime content ($R^2 = 0.95$), a weak relationship between reactivity and total CaO content ($R^2 = 0.79$), a weak inverse relationship between pH achieved and surface area ($R^2 = 0.79$), and almost no correlation between pH and particle size ($R^2 = 0.38$).

Moropoulou et al. [22] found in their study on limestone and quicklime properties that the specific surface area can be an indicator of quicklime reactivity. That study found that the greater the specific surface area, the more reactive the quicklime, based on temperature increase when mixed with water. It can be assumed that these properties would translate to CKD particles as well. However, the results presented in this paper indicate otherwise. It seems
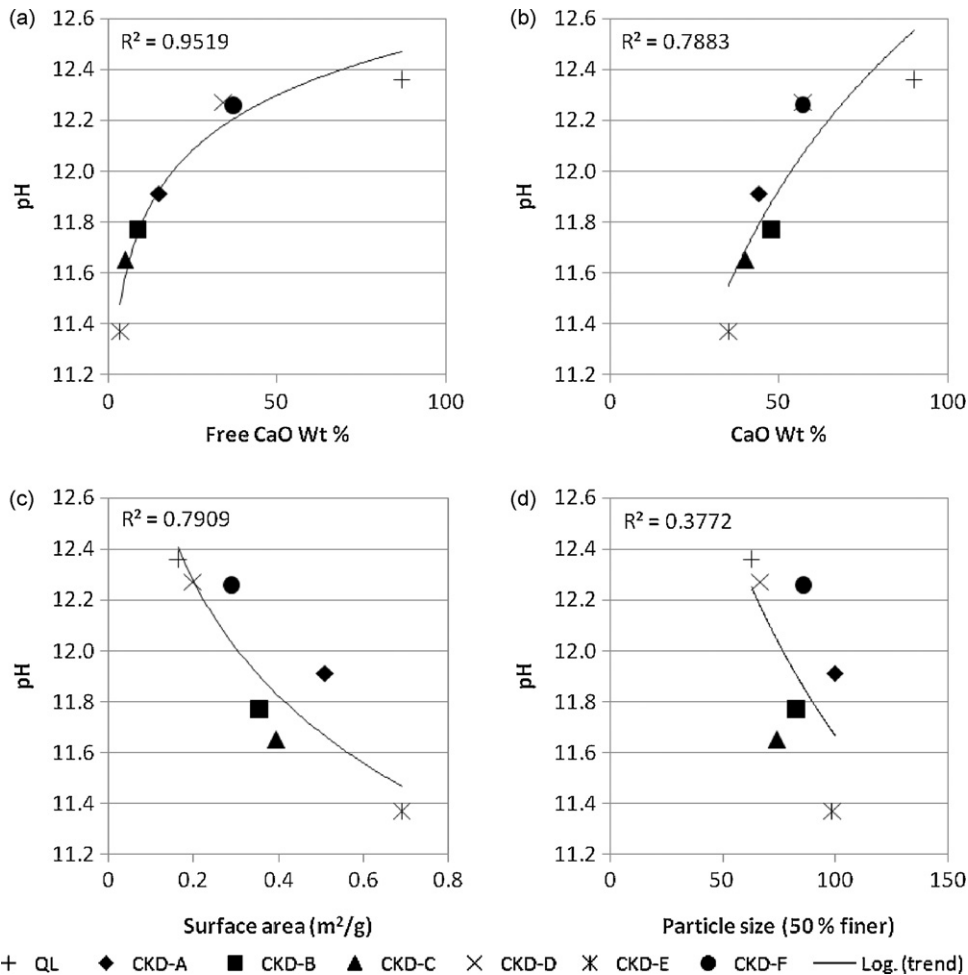

Fig. 7. Logarithmic regression graphs of pH achieved at a CaO dose of 1.2 g/L for: (a) free CaO content, (b) total CaO content, (c) surface area by the Blaine method, and (d) particle size at the 50% finer level.
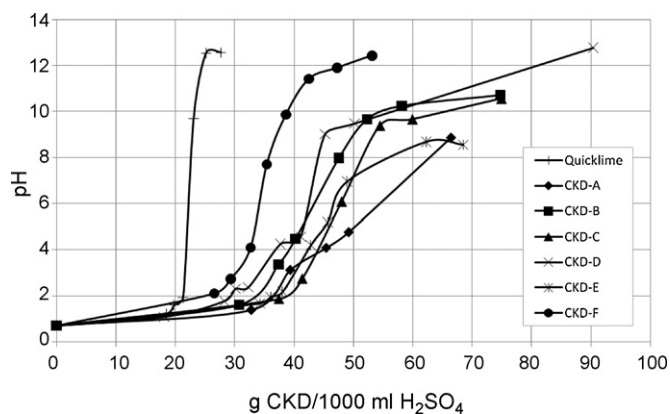
Fig. 8. Acid neutralization test results.

counterintuitive that CKD samples that have particles with larger surface areas would give lower pH values. However, it is important to note that all of the slaked CKD samples demonstrated pH levels greater than 11.0, and that particle size distribution and specific surface size analysis were conducted on bulk CKD samples that were not specific to the type of particles present in the CKD samples (e.g., CaO particles versus SiO_2 particles). This, in combination with the strong relationship found between the free lime content of CKD on pH achieved, would potentially influence any impact surface area may have on CaO dissolution during the CKD experiments.

3.7. Acid neutralization

Acid neutralization tests were performed as part of this study using each of the CKD samples to determine the viability of using CKDs with different properties to treat acidic wastewater. Fig. 8 shows the results of the acid neutralization trials, in grams of CKD per 1000 ml of sulphuric acid versus pH achieved after 30 min. The results show that CKD-D and CKD-F, the two CKD samples with the highest free CaO content and those that responded best in the slaking trials, achieved the highest pH at the lowest CKD dosage, and were closest to the results from the quicklime sample. Specifically, CKD-D required 56.6 g to achieve a pH of 10, while CKD-F required 39.0 g, and quicklime, 23.3 g. However, all CKD samples achieved pH values greater than 10, at varying doses of CKD for each. CKD E, which has the lowest free lime content, required 287 g to achieve a pH of 10. These results show potential application for even CKD samples with low free lime contents to be effective at neutralizing acidic wastewater.

4. Conclusions

Physico-chemical characteristics of the six CKD samples analyzed in this study were comparable to other previously published studies on CKD. What is unique about this study is that variability within each plant was looked at and additional characterization was completed in comparison with other studies. The focus of this study was on the hydrated calcium oxide ($Ca(OH)_2$) slurries and the impact of CKD characteristics on the use of these slurries in wastewater treatment applications. Previous studies have mainly focused on the potential reuse of CKD in a solid form.

It was found that the CKD samples tested have smaller particle sizes and higher specific surface areas than a commercial quicklime sample. The kiln with a precalciner (Plant F), and that with a preheater (Plant D), produced CKD samples with larger particle sizes than those from the long-dry kilns (Plants A, B, and E), confirming earlier studies [5,14,15]. The one wet kiln (Plant C) gave a

median CKD particle size between that of the long-dry kilns and the kilns with a preheater or precalciner, validating the USEPA's [5] conclusions.

CKD samples were found to have low variability within each plant. This was determined by comparing the physico-chemical characteristics of two separate samples taken from each plant, one in November of 2007 and one in July 2008. The low variability can be seen from the low deviation in particle size and specific gravity (Table 2) and major oxides distribution (Table 3).

Samples of CKD-D and CKD-F, which were found to have the highest free lime contents, showed statistically comparable results to the commercial quicklime sample when slaked, in terms of pH achieved, conductivity, and calcium ion (Ca^{2+}) content. The main factor affecting the reactivity of CKD was found to be free lime content, and this could be used as an indicator of the potential for CKD material to be used in neutralizing acidic wastewaters.

In comparison to the commercial quicklime product evaluated in the acid neutralization experiments, the slurry made from CKD-F samples performed equally well, with only slightly more raw material required. Collectively, the results of the acid neutralization experiments show that even the CKD samples with low free lime contents achieved a pH greater than 10, demonstrating the viability of the reuse of CKD in acidic wastewater neutralization applications.

Acknowledgements

References

[1] S.H. Kosmatka, B. Kerkhoff, W.C. Panarese, N.F. MacLeod, R.J. McGrath, Design and Control of Concrete Mixtures, seventh ed., Cement Association of Canada, Ottawa, 2002.

[2] G.C. Bye, Portland Cement, second ed., Thomas Telford, London, 1999.

[3] D.H. Albeln, R.J. Hastings, R.J. Schreiber, C. Yonley, Detailed Illustration of Contingent Management Practices for Cement Kiln Dust, SP115T, Portland Cement Association, Skokie, 1993.

[4] USEPA, Study on Increasing the Usage of Recovered Mineral Components in Federally Funded Projects Involving Procurement of Cement or Concrete to Address the Safe, Accountable, Flexible, Efficient Transportation Equity Act: A Legacy for Users, April 2008, Retrieved February 7, 2009 from USEPA Wastes: http://www.epa.gov/waste/conserve/tools/cpg/products/cement2.htm.

[5] USEPA, Report to Congress on Cement Kiln Dust, 1993, Retrieved January 15, 2009 from USEPA Wastes: http://www.epa.gov/epawaste/nonhaz/industrial/special/ckd/cement2.htm.

[6] W.S. Adaska, D.H. Taubert, Beneficial Uses of Cement Kiln Dust IEEE-IAS Cement Industry Committee, Portland Cement Association, Skokie, 2008.

[7] USEPA, Cement Kiln Dust Wastes, Last updated September 10, 2008, Retrieved August 5, 2009 from USEPA Wastes: http://www.epa.gov/epawaste/nonhaz/industrial/special/ckd/index.htm.

[8] USEPA, Standards for the Management of Cement Kiln Dust; Proposed Rule, August 20, 1999 (64 FR 45632), Retrieved August 5, 2009 from USEPA Wastes: http://www.epa.gov/epawaste/nonhaz/industrial/special/ckd/ckd/ckd-fr.pdf.

[9] P.L. Younger, S.A. Banwart, R.S. Hedin, Mine Water: Hydrology, Pollution, Remediation, Kluwer Academic, Dordrecht, 2002.

[10] R.S. Boynton, Chemistry and Technology of Lime and Limestone, second ed., John Wiley and Sons, Inc, New York, 1980.

[11] J.I. Bhatty, Alternative Uses of Cement Kiln Dust, Portland Cement Association, Skokie, 1996.

[12] N.G. Zaki, I.A. Khattab, N.M. Abd El-Monem, Removal of some heavy metals by CKD leachate, J. Hazard. Mater. 147 (2007) 21–27.

[13] A. Pigaga, R. Juskenas, D. Virbalyte, M.G. Klimantaviciute, V. Pakstas, The use of cement kiln dust for the removal of heavy metal ions from aqueous solutions, Trans. Inst. Met. Finish. 83 (2005) 210–214.

[14] H. Todres, A. Mishulovich, J. Ahmad, Cement Kiln Management: Permeability, Portland Cement Association, Skokie, 1992.

[15] S. Peethamparan, Fundamental Study of Clay-Cement Kiln Dust (CKD) Interaction to Determine the Effectiveness of CKD as a Potential Clay Soil Stabilizer, PhD Thesis, Purdue University, West Lafayette, 2006.

[16] S. Peethamparan, J. Olek, J. Lovell, Influence of chemical and physical characteristics of cement kiln dusts (CKDs) on their hydration behavior and potential

suitability for soil stabilization, Cem. Concr. Res. 38 (2008) 803–815.

[17] A. Sreekrishnavilasam, S. King, M. Santagata, Characterization of fresh and land-filled cement kiln dust for reuse in construction applications, Eng. Geol. 85 (2006) 165–173.

[18] M.H. El-Awady, T.M. Sami, Removal of heavy metals by cement kiln dust, Bull. Environ. Contam. Toxicol. 59 (1997) 603–610.

[19] J.I. Bhatty, H.A. Todres, Use of Cement Kiln Dust in Stabilizing Clay Soils, Portland Cement Association, Skokie, 1996.

[20] J.E. Kogel, N.C. Trivedi, J.M. Barker, S.T. Krukowski, Industrial Minerals & Rocks: Commodities, Markets, and Uses, seventh ed., Society for Mining, Metallurgy and Exploration (SME), Littleton, 2006.

[21] R.B. Robinson, J. Burnham, Relative dissolution rates of several hydrated limes, J. Environ. Eng. (Reston, VA, U.S.) 127 (2001) 565–568.

[22] A. Moropoulou, A. Bakolas, E. Aggelakopoulou, The effects of limestone characteristics and calcination temperature to the reactivity of the quicklime, Cem. Concr. Res. 31 (2001) 633–639.