Organo-silane chemistry: A water repellent technology for coal ash and soils

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ABSTRACT

This manuscript provides insight into a new approach to chemically-based ash improvement with organosilanes (OS). Specifically, OS serves as a coupling agent to create a hydrophobic surface on virtually any silica-based material. As an illustration, a laboratory and field testing program was conducted to evaluate the influence of OS modification on the compaction, strength, swell and hydraulic properties of several samples of Class F coal fly ash. OS modification resulted in notable changes to strength and swell potential and a dramatic reduction in infiltration capacity. Concatenating with previous results for reducing leachability, the data suggest that OS modification may have wide application in the management of coal combustion products.

INTRODUCTION

Coal combustion fly ash has long been used as an ingredient to improve the performance of materials such as concrete, flowable fill and stabilized soil. Likewise, a number of standard and proprietary additives have been used to improve the properties of fly ash in applications where it is the primary constituent, as in the case of a structural fill or an embankment. Mostly, this has involved mixing fly ash with relatively small proportions of lime[1-3], or cement[4], although flue gas desulfurization gypsum[5], sodium hydroxide[6], bentonite clay[7], enzymes[8], among other additives have also been used. The purpose of such modification has generally been to improve physical (e.g. strength, compaction, permeability) or chemical (e.g., leachability) performance.

More recently, a form of organic modification that uses organosilanes (OS) to irreversibly bond with fly ash or soil has been introduced as a water repellent technology. The concepts and chemistry of this approach is provided by the fields of applied clay science and catalysis. For example, the process of permanently grafting organic molecules to various substrates has been explored to develop polymer-clay nano composites[10-12] and to strengthen calcium silicate hydrates in cement paste

systems[13]. The purpose of this manuscript is to present example data related to ash stabilization using OS as an alternative to conventional methods such as lime or Portland Cement modification. OS modifies and reacts with individual particles without binding them together, in contrast to a cementitious/pozzolanic approach.
Data have been obtained in the laboratory through compaction, strength, swell, infiltration and hydraulic conductivity testing, as well as in the field through infiltration measurements.

MATERIALS AND METHODS

The work presented herein comprises two separate experimental components. First, the influence of OS on laboratory measurements of compaction, strength, swelling and hydraulic conductivity was evaluated for a Class F fly ash from a coal-fired power plant in the southeast U.S. Separately, a field trial was conducted to evaluate the potential for OS use stabilizing ash monofills. OS was obtained from Zydex Industries (Vadodora, India) through Hero Global Services (Fort Mill, SC, USA) and has the commercial names Zycosil and Zycosoil. Details regarding the source product have been presented in Daniels et al. (2009). Briefly, trialkoxy groups present in the OS solution form siloxane (=Si-O-Si=) bonds with soil surfaces. In addition, there is an organic group that contains a quaternary structure with a long alkyl chain ($C_{18}H_{37}$) which imparts molecular level hydrophobicity on the treated surface.

Laboratory Measurements

Treated ash was prepared by mixing dry ash with a solution composed of 100 parts water for every part of OS (100:1, by volume). This mixture was then allowed to fully air-dry prior to subsequent testing. Treated and untreated samples were tested for moisture-density relationships, California Bearing Ratio (CBR) and hydraulic conductivity. Current ASTM standards were used to guide laboratory protocol, as follows. Moisture-density relationships were evaluated in accordance with ASTM D698, Method A with standard Proctor effort[14]. The CBR test was conducted as per ASTM D1883[15]. Hydraulic conductivity was evaluated in accordance with ASTM 5084[16] using the constant head method, a back pressure of 345 kPa and a hydraulic gradient of 12.5. Samples used for CBR or hydraulic conductivity were prepared at or above 95% of the maximum dry density. In addition, approximately one month after treatment, infiltration properties of previously treated and untreated compacted ash samples were evaluated with a Mini Disk Infiltrometer from Decagon Devices. The device works by measuring the rate of seepage into partially saturated soils using a slightly negative (suction) pressure. Measurements were taken at a constant suction of -0.5 cm. Details on this device and its application may be found in the manual[17] with additional background discussion provided separately[18] as well as a comparison with other field techniques[5].

Field Measurements

Depending on the field objectives, OS can be incorporated into the molding moisture content during the construction of structural fills or it can be topically sprayed on the finished grade surface. For this work, the goal was to investigate the ability to create a thin barrier layer against infiltration. As such, OS was topically applied to two sections of an ash monofill, a relatively flat (< 5% slope) section and a slope (1.5H:2V) section, as shown in Figure 1. A Finn T60 Hydroseeder was used which incorporated a cannon sprayer, hose and built in agitator, with a 2271 liter tank. Water from the ash basin was used by way of a pump. A 30kg drum of OS concentrate solution was mixed with a full tank to produce a water:OS ratio of 75:1. The flat section was essentially square, with a total treatment area of approximately 900 m^2. The slope section was approximately 7 m in width and 12 m in length. Mini Disk Infiltrometer measurements were made approximately one month after treatment in both the slope and flat sections.

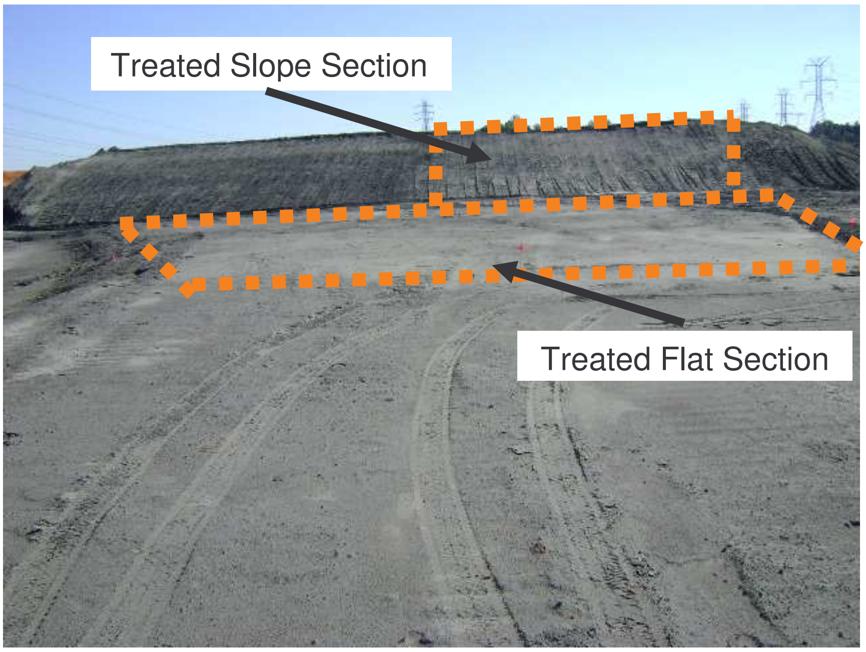

Figure 1. Treated and untreated sections of field test site (ash monofill).

RESULTS AND DISCUSSION

The results for the laboratory-derived moisture density relationships, hydraulic conductivity and CBR data are provided in Table 1, while Figure 2 provides a plot of the cumulative infiltration versus the square root of time[18] for both laboratory samples and field test sections.

Table 1. Laboratory data

Sample Description	Molded		Soaked		K_{20}*** (cm/s)	CBR**** %		Swell (%)
	w* %	MDD** kN/m3	w* %	MDD** kN/m3		2.5 mm	5.0 mm	4.5 kg
Ash *(Untreated)*	25.6	11.6	33.5	11.4	1.40 x 10^{-4}	3.3	4.3	2.7
Ash *(OS treated)*	24.8	12.4	24.4	12.4	5.50 x 10^{-5}	5.1	6.5	0.0

*Optimum Moisture Content, **Maximum Dry Density, ***Hydraulic Conductivity, corrected for 20℃, ****California Bearing Ratio, calculated at penetration shown

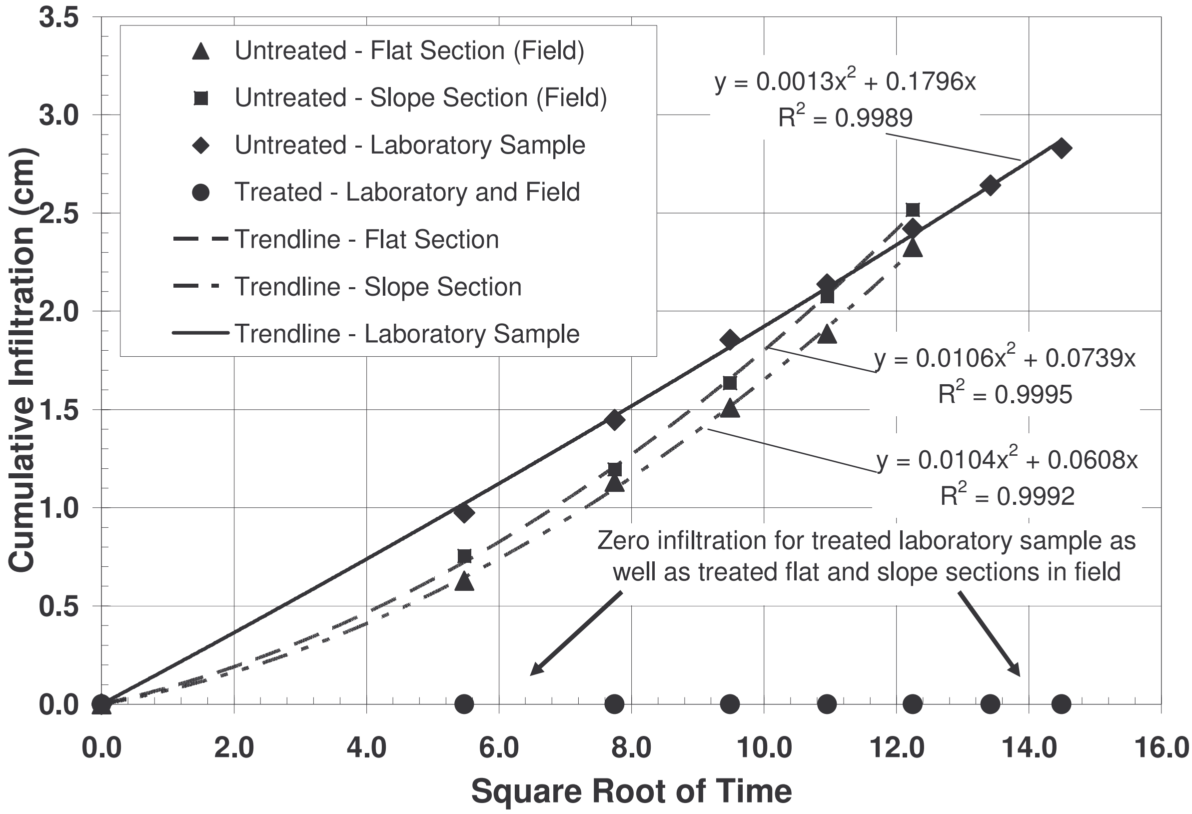

Figure 2. Infiltrometer results for laboratory and field samples

As indicated by Table 1, the influence of OS treatment was to reduce the optimum moisture content and increase maximum dry density. A similar trend was also reported[9] whereby a modest but consistent trend of increasing OS dosage correlated with increasing dry density and decreasing optimum moisture content for another Class F coal combustion fly ash. In terms of CBR results, the strength of the treated ash increases, with a dramatic difference observed in terms of the change in water content after soaking. Specifically, the water content of the untreated ash sample increased from 25.6% to 33.5% while the water content of the treated sample actually decreased slightly, from 24.8% to 24.4%. These differences also manifest as a commensurate reduction in swell, i.e., from 2.7% to 0%. As such, OS-treatment appears to mitigate volume changes in ash that could otherwise be susceptible to swelling. Naturally, this has implications according to ash mineralogy, e.g., neomineral formation and ettringite control.

Moisture content changes in untreated ash have practical implications relative to on site workability and slope stability, both of which can be exacerbated with increases in moisture. Figure 3 illustrates the typical hydrophobicity that developed on the OS-treated flat section of the field site. While untreated ash would immediately imbibe moisture, OS-treated surfaces serve to pond water according to the grade. Likewise, Figure 4 shows a picture of the slope section of the field site after treatment and subsequent precipitation events. The left side of the slope shown in Figure 4 is untreated while the right side is OS-treated. The untreated section is a visibly darker hue, owing to previous saturation as was confirmed on-site.

Figure 3. Development of hydrophobicity on OS-treated flat section of field site (typical)

As noted[17] and similarly presented[19], the polynomial used to fit the infiltration data collected for the untreated sections is of the form:

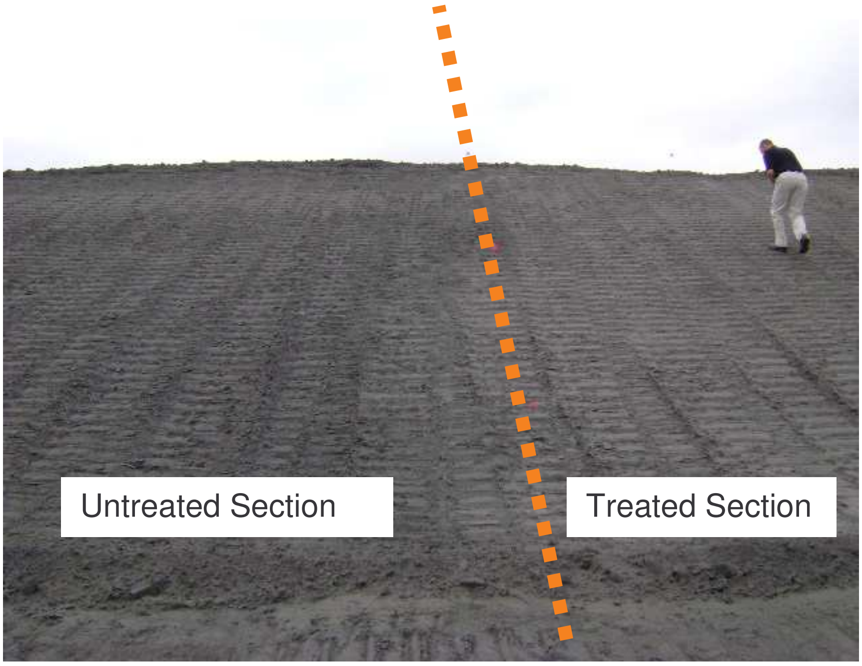

Figure 4. Example of slope after precipitation event – right side remained dry, as evidenced in part by a lighter color (from top to bottom) and verified on-site.

$$I = C_1 t + C_2 \sqrt{t} \qquad (1)$$

In Eq. 1, I is the cumulative infiltration, C_1 is related to the hydraulic conductivity, C_2 is related to the soil sorptivity at t is the elapsed time. Hydraulic conductivity, k, is then given by:

$$k = \frac{C_1}{A} \qquad (2)$$

In Eq. 2, A is computed for a given level of suction pressure and soil properties[17]. In particular, it is related to van Genuchten parameters, as tabulated separately[20]. Accordingly, a value of A equal to 8.1 was selected, which approximates a fly ash (analogous to a silt loam) at the -0.5 cm suction applied by the infiltrometer to measure hydraulic conductivity. Note that the value computed by Eq. (2) is the corresponding in situ hydraulic conductivity at the prevailing moisture content and level of suction. No infiltration was recorded for the treated material, which translates to a hydraulic conductivity of zero at this level of suction. Table 2 provides the values of C_1, C_2 (from trendlines plotted in Fig. 2), A and the computed value for hydraulic conductivity, k, for the laboratory samples and field test sections.

Table 2. Infiltrometer data and computed values of unsaturated hydraulic conductivity

Description	C_1	C_2	A	k (cm/s)
Lab Sample (Untreated)	0.0013	0.1796	8.1	1.60×10^{-4}
Lab Sample (OS-treated)	0	0	8.1	0
Flat Section-Field (Untreated)	0.0104	0.0608	8.1	1.28×10^{-3}
Flat Section-Field (Treated)	0	0	8.1	0
Slope Section-Field (Untreated)	0.0106	0.0739	8.1	1.31×10^{-3}
Slope Section-Field (Treated)	0	0	8.1	0

Note that the observed values of saturated and unsaturated hydraulic conductivity are about the same (1.40×10^{-4} cm/s vs. 1.60×10^{-4} cm/s) for the untreated ash. As such, it's worth ruminating as to why OS treatment resulted in slight reductions in terms of saturated hydraulic conductivity (1.40×10^{-4} cm/s to 5.50×10^{-5} cm/s) while the influence was far more dramatic in the case of infiltration-derived values of unsaturated hydraulic conductivity (1.60×10^{-4} cm/s to 0 cm/s). These results illustrate a vital point as it relates to determining the value of hydraulic conductivity in the laboratory, versus what may realistically develop in the field. In particular, laboratory tests commonly ensure saturation through back pressurization, as was likewise reported herein (345 kPa). Indeed the hydraulic conductivity of a soil is at a maximum in the saturated condition, which with time, can develop in natural field conditions (e.g., near or below the groundwater table, landfill liners with sufficient head, etc.). However, it does not appear that ash treated with OS can be saturated in the absence of a considerable amount of artificial pressure, as similarly suggested[19] and reiterated herein. Soil-water or ash-water interaction is more often characterized by a contact angle of approximately zero, implying near perfect wetting[21]. However, the contact angle is likely greater than 90° after OS-modification[9]. As such, it may be instructive to compare water/OS-modified ash matrix with a Mercury/unmodified ash matrix. The latter scenario occurs when using the mercury intrusion method to force mercury into porous media[22]. The pressure required for a given level of penetration varies according to pore size and so one can determine the prevailing pore size distribution. By analogy, water only penetrates OS-treated ash provided sufficient pressure is available. This characteristic emphasizes the need to carefully match laboratory testing against anticipated field conditions.

CONCLUSIONS

OS modification represents another approach to ash improvement, with possible increases in strength and reductions in swell potential and hydraulic conductivity. More dramatic results were observed for in situ measurements of infiltration. In particular, the hydraulic conductivity, as measured with a negative pressure of -0.5 cm, was reduced from the range of 10^{-4} to 10^{-3} cm/s, for a laboratory sample and field sections to 0 cm/s, upon treatment with OS. Concatenating with previous results for reducing leachability, the data suggests that OS modification may have wide application in the management of coal combustion products, along with geotechnical applications for soils.

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