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**INTERACCIONES CON AGUA DE PRODUCTOS DE LA COMBUSTIÓN DEL CARBÓN (CCPs)
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WATER-REPELLENT COAL COMBUSTION PRODUCTS (CCPs): INTERACTIONS WITH WATER

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WATER-REPELLENT COAL COMBUSTION PRODUCTS (CCPs): INTERACTIONS WITH WATER

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Abstract: In many countries in the world it is common to use coal to generate electricity via power plants. Coal combustion generates products denominated CCPs, mainly ash, which is divided in three categories: fly-, bottom-, and gypsum/lignite-ash, usually in proportions of 70%, 25%, and 5%, respectively. In 2014, 880 million tons of CCPs where produced worldwide. The countries which produced the most were EEUU, China and India with an average of 120 million tons each. In South America, the problem is not the quantity of generated products because it is constantly decreasing. For instance, in Colombia 800 tons were produced in 2015. They were disposed in embankments, and in many cases the product was not compacted, generating possible environmental issues due to infiltrations and aeolian transport. Production in Colombia is not high compared to other countries given that coal-fired power plants generate just 5% of the total energy of the country and they usually work as backups to hydropower plants. In contrast, in the USA thermal energy generation takes approximately 40% of the total, and produces near 120 million tons of ash, of which 47.5% were reused in 2014. Usually, CCPs are disposed in impoundments regulated by EPA. This agency stated that reservoirs must be protected in its bottom by a layer that prevent the leached to go through the exterior. The minimal requirements for this layer are: (1) a layer of double membrane constituted by a layer of impermeable soils, which in many cases is hard to find in the reservoirs construction area and (2) a geomembrane and a drainage layer. However, CCPs can be reused with other materials in concrete, cement, pavements and fillers. Considering that the portion reused of CCPs continues being under half of the material annually produced, at the University of North Carolina in Charlotte (UNCC), this product is being reacted with organic chemicals called Organosilanes (OS), to measure the mixture properties and give it potential new uses. The OS has been used in the past in granular soils aiming to get hydrophobic soils. But in most recent researches at UNCC the O.S has been mixed with CCPs. Because of this, this experimental research is based in the sprayed addition of OS to CCPs samples. The CCPs samples used for this study were previously compacted to optimal water contents, according to Proctor curves developed for this material. The O.S amount was defined considering tests of penetration time of a water drop, contact angle and breakthrough pressures. In addition to that, OS profiles in CCPs samples and dried curves where developed to implement all the tests whit different water content. In the CCPs chemical and physical classification tests were done and used to compare to the same results in the literature. The results of this research were compared with those results found in literature to verify its reliability.

Keywords: Coal combustion products, Organosilane, Breakthrough Pressure, Contact Angle, CCPs Ponds, water drop penetration time.

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1. BACKGROUND

Organosilanes (OS) have been used as soil treatment to induce hydrophobicity for approximately 40 years (Jordan, 2014). The soils mostly treated to induce hydrophobicity correspond to granular soils, considering that they have high permeability coefficients.

Regarding the use of OS in coal combustion products (CCPs), at the University of North Carolina in Charlotte different experimental projects have been carried out where they measure mixture properties, varying the OS application method over CCPs. In 2009, an experimental research project (Daniels , et al., 2009) studied parameters such as infiltration rate, permeability, California Bearing Ratio (CBR) for an embankment section treated with CCPs. In this case, the compaction of CCPs was made with a combined solution of OS and water. The obtained results show a permeability decrease in more than one order of magnitude, from 1.40E-4 to 5.50E-5 m/s. In addition, the results of CBR were increased to almost the double and the swelling decreased to zero. These parameters were also estimated in laboratory following standardized tests. The most relevant results show that permeability decreased to almost zero.

In 2014 a research project carried out at UNCC (Jordan, 2014) studied the effects of temperature on parameters such as contact angle and breakthrough pressure in different treated soils, coarse sand, fine sand and CCP with OS. For all the treated soils, the measured contact angle was higher than 90 degrees. In the case of the estimated breakthrough pressure, it

can be observed that the results are between 0.3 to 300 meters of column of water, and this magnitude increases with the decrease of the material grain size.

In 1970, Fink measured the hydrophobicity of granular soils mixed with organic materials. Water drop penetration time (WDPT), contact angle, and breakthrough pressure tests were performed in soils with different treatments and quantities of organic matter. The results showed that with the increase of organic material, the hydrophobicity treatment increased as well. The first series of tests performed showed that the infiltration time of the water drop in the treated soil increased with the increase of the treatment. In all the cases it showed contact angles higher than 90 degrees and breakthrough pressures were also increased with the treatment (Fink, 1970).

2. CONCEPTUAL FRAMEWORK

2.1. Silanes and Organosilanes: The silanes (SIH_4), also known as silicon hydrides are the simplest hydrides and are compounds having a hydrogen-silicon link. The compounds are known as derivatives from the silane, having as prefix the substituents, for example, the triclorosilane HSiCl3. In this group are the organic silanes used in different industries such as the textile, leather and paper, given that when applied, they improve the waterproof and wastage properties. The most representative physical properties of this group are: initially soluble in water, do not form layers, the particles do not come together, the union mechanism is covalent, and form hydrophobic surfaces. (Debano, 2000)

2.2. CCP Impoundment: by products generated in factories, energy generators, and others, which can be very

damaging generating leachate that may contaminate water, the ground and the environment. For this reason, an engineered structure for the disposal of coal combustion products is created, including a multi-layer liner system (See figure 1).
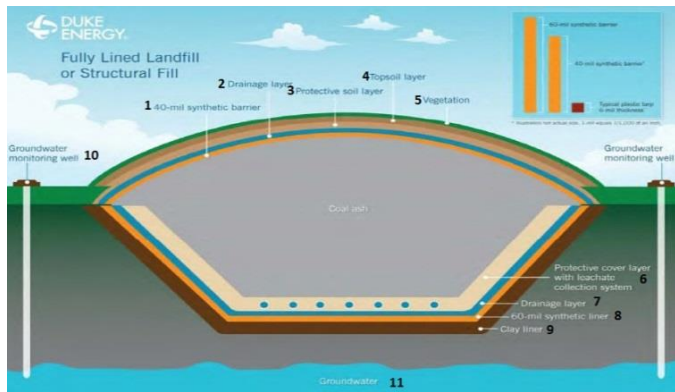

Figure 1 Disposal cell in a CCP reservoir (Duke Energy, 2014)

2.3.   Contact angle: normally when a drop of liquid gets in contact with a solid surface, there are three defined interfaces, and each one has a given surface tension. Aside from that, a cross section of the system shows that at the point where the three interfaces converge, three angles are formed summing 360°. The angle that is formed between the liquid and the solid surfaces is known as contact angle (Jaramillo J., 2004). The static contact angle is studied when examining ground-liquid properties like humidification, dehumidification, suction and permeability (Rillaerts & Joos , 1980) (see Figure 2).
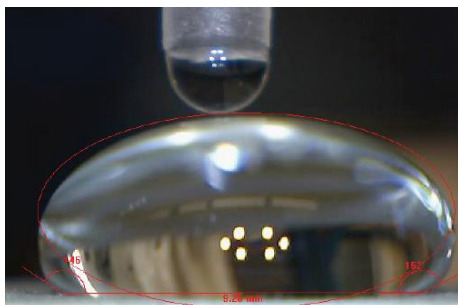

Figure 2 Contact Angle (Daniels J., 2015)

This angle is denoted Θ, and "in equilibrium, its magnitude depends on the thermodynamics and is governed by Young Law" (Rillaerts & Joos , 1980). [1] $\sigma sv = \sigma sL + \sigma Lv \cos \Theta$ where:

σsv is the surface energy, σsL is the surface energy of the interphase solid/liquid, and σLv is the surface tension of the liquid surface (Rillaerts & Joos , 1980).

2.4.   Breakthrough pressure: is the required pressure to allow the initial penetration of a fluid into the void space of a soil. Previous research in this topic started in 1921 when Washburn proposed that the pore size distribution could be measured with mercury penetration. Later on, the porosimeter was created using mercury. More recently, expressions have been found that the relationship between mercury with the soil corresponds to the space occupied for the mercury on the soil. The principal advantage of the conventional breakthrough pressure test is that, when performing it, the increase or decrease in the entry volume can be observed. (Mayer & Stowe , 1965).

3.   RESEARCH QUESTION

Are CCPs chemically modified with organosilanes feasible for use in ash-impoundment liner systems?

4.   HYPOTHESIS

It is possible to produce hydrophobic coal ashes, by treating ash with organosilanes, that can be used in ash-impoundment liner systems.

5. OBJECTIVES

5.1 General Objective

To determine the behavior of the interaction of water with the surface of a CCP chemically modified with organosilanes.

5.2 Specific objectives

- To determine the degree and stability of the hydrophobicity induced at the surface of a CCP chemically modified with organosilanes.

- To predict the implications of the behavior of CCPs chemically modified with organosilanes on lining systems that may implement this material.

6. MATERIALS

For this work it was decided to use a class-F CCP, that is defined by ASTM as puzzolanic ashes with CaO content lower than 10%. The CCP was collected from a coal-fired power plant from North Carolina and packed in sealed plastic bags of One-Ton each. This material was kept on a container stored outdoors.

The chemical manufacturer, Zydex (Shradhanand Marg, Delhi, India) produces an Organosilane called Terrasil which is a water soluble product, to be applied on surfaces via spray, that chemically converts water-absorbing silanol groups to water-resistant alkyl siloxane surfaces at ambient temperature. (Zydex). This chemical is produced by the reaction between silicon and hydrochloric acid that together will form trichlorosilane. The organosilanes were used as received, and

kept at room temperature between 19 and 22 ° C in tightly sealed plastic container of 5 gallons.

Distilled water was used in the experiments and also kept in plastic containers of 5 gallons at room temperature.

7. EXPERIMENTAL METHODS

The experimental methodology implemented for this study was divided in three major parts; the first one refers to all tests in the "untreated" fly ash form, as received from the power plant (U-CCP); the second one deals with methods to find the optimum dosage between CCP and organosilanes (Terrasil) using reconstituted compacted samples and the third phase discusses the tests performed on organosilane-treated coal combustion products (OS-CCP) sprayed with the dosage selected in phase two.

7.1 Index tests on U-CCPs

In the first phase of this research all the geotechnical characterization of CCPs was performed. This characterization included drying curves, particle size analysis (both dry and wet sieving and hydrometer analysis), specific gravity, standard Proctor compaction tests, chemical test using X-ray fluorescence (XRF), organic matter content (loss on ignition), minimum density, and ash-water characteristic curves (AWCC). In each case, test samples were prepared by sampling four different locations within the bag to reconstitute a specimen.

7.2 Drying Curves

The first test was non-standard, and had the purpose of selecting the correct temperature to use in drying ovens. The test consisted in drying the U-CCPs using two different

temperatures: 60 and 110 ° C, and three different ash weights: 50, 300 and 1500 grams. With these results, drying curves were prepared that show the evolution of sample weight through time.

7.3 Particle size analysis

Particle size analyses were performed in duplicate using samples from different bags. Each test was performed with dry and wet techniques. The hydrometer technique (described in ASTM D-422-63-07) was adopted for particles smaller than 0.075 mm, while sieve analysis was used for particles larger than 0.075 mm, including the wet-sieved U-CCPs. In total, two curves were developed including fines and coarse particles.

7.4 Specific Gravity

Specific gravity was estimated as the average of two tests each one performed two times, following the procedure suggested in ASTM D854-14. One test was performed for each bag getting two results. The tests were performed using 250-ml and 500-ml pycnometers with a manual adjustable water level. 60 to 120 g of CCP were dried during 24 hours in the oven at 110 ° C. All test used distilled water.

7.5 Minimum density

The minimum density test is used to determine the loosest particle arrangement without any kind of compaction. Following the suggestions stated in the report "Geotechnical Properties of Fly Ash and Potential for Static Liquefaction" (Electric Power Research Institute , 2012) an acrylic cylinder was used for this tests. The cylinder had the following dimensions: 30 cm length, radius of 6.37 cm, and 150 +/-5 grams of dry CCPs were added. The cylinder was rotated once during 10 seconds, and then rotated until reaching the vertical position in 2 seconds; the

height was measured around the cylinder in four places. The final height corresponded to the average of these four measures (see Figure 3).

Figure 3 Illustration of the minimum density test.

7.6 Standard Proctor compaction

The standard Proctor test was used not only for determining the optimal water content and maximum dry density of CCPs, but also to reconstitute the CCP samples for further testing. In fact, each sample used was compacted in a Proctor mold and then extruded maintaining the compacted features. The Proctor tests were performed following ASTM D 698-12, one test per bag; in the first test, five data points were used at different water contents, and the second test was made with seven data points. In both cases the ash was mixed with varying water content amounts 24 hours prior testing and allowed to hydrate.

7.7 Mineralogy

Every CCP has different chemical components depending on the geological origin of the coal, the combustion conditions and efficiency at the power plant. Therefore, two U-CCPs were sent to American Assay Laboratories in Sparks, NV, where X-ray fluorescence analyses were performed. This test measured concentrations of Al, Ca, Ce, Cu, Fe, K, La, Mg, Mn, Mo, Na, Ni, P, Rb, Si, Sn, Sr, Ti, W, Zn, and Zr in the CCP in ppm. Additionally, in the UNCC Lab, the fly ash pH was measured.

7.8 Organic Matter Content (OMC; loss on ignition)

Following AASHTO T267-86-08 three loss-on-ignition tests were performed, each one using three samples on a tin and a muffle furnace able to supply and keep 450 ° C during 6 hours. In the first step the samples were dried at 110º C for 24 hours, and then they were placed in a muffle furnace at a temperature of 450º C during 6 continuous hours. The organic matter results were calculated as the difference between the weight of samples after the muffle furnace treatment and the dry weight of samples at 110º C. Later the organic matter content results were also used to estimate the Organosilanes content in the samples at different levels of sample profile.

7.9 Sample Preparation

All the ash samples used in this research were reconstituted by extrusion from a Proctor mold compacted at the optimal water content determined in the standard compaction test performed as described in the section 7. This method was selected because it is the closest to the constructions process of CCPs liners in ponds. For this purpose, a proctor extruding frame was used. After having the compacted CCP into the standard mold, this piston pushes the sample out because its diameter is equal to that of the internal mold diameter. In the upper frame there is a ring that blocks the mold and allows the ash sample extrusion (see Figure 4). The procedure consists in: (1) compacting the proctor mold at optimal water content, (2) placing the steel ring and a steel plate over the mold, (3) applying upward pressure using the piston until the steel plate touches the upper frame; at this moment, the ring is going to start entering to the mold, the pressure should be stopped when the Proctor mold touches the plate, (4) unloading the piston and the steel plate to remove the sample from the mold top, (5) again applying pressure using the piston until removing the fly ash layer with the steel ring inside, (6) trimming the layer and peel the ring border with a trimmer very carefully trying to avoid removing material inside of the ring, and, (7) taking a small piece for measuring water content.
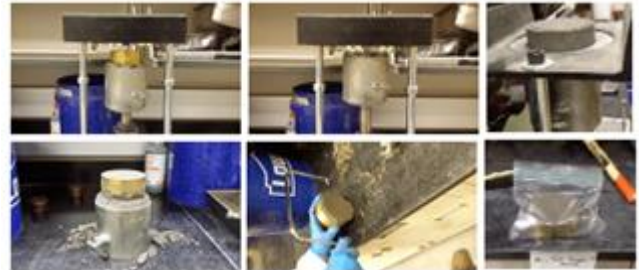
Figure 4 Sequence of photos showing the experimental protocol for recovering the ash samples.

7.10 Ash-water characteristic curves (AWCC) on U-CCPs

The AWCC were developed using a WP4c, as shown in Figure 5, which is a device that uses the chilled mirror dew point technique measure. It was manufactured by Decagon devices, Pullman, USA.

Figure 5 WP4c device

The procedure consisted in extruding an ash sample in a steel ring of 3.7 cm diameter, 1.0 cm height and 24 grams mass from a standard Proctor compacted mold at optimal water content, following the procedure described above. The density and water content of each sample was measured. The cylinder

corresponding for the WP4c rings has an open face where the sample was placed. By saturating the sample, this open face was covered with a porous stone that allows the flow of water across the sample but at the same time it doesn't allow changes in sample volume. The porous stone was locked to the ring using a clamp. All the setup inside the WP4c device was submerged into distilled water for at least 24 hours and the saturation was checked with weight differences to reach a Skempton "B" parameter of 98%. Before each reading, the WP4c device was verified using a vial of 0.5 mol/kg KCl. The KCl solution was emptied into a steel ring, placed in WP4c drawer and drawer knob turned to the reading position. The device initiated calibration readings that should be between -2.19 and -2.22 MPa depending on the temperature (at 20, 25 ° C the readings will be -2.19 and -2.22 MPa, respectively). When the device was calibrated and the sample saturated, the setup was ready for the first set of readings.

The device has tree operational modes, namely: (1) continuous mode from 0 to 2 MPa suction values, which should be used when the sample is saturated or near saturation, (2) precise mode for 2 to 40 MPa water potential values, in which case the device takes a large number of readings and calculates an average; this is the most accurate method, but it needs longer reading time than other modes (from 12 to 18 minutes), and, (3) fast mode, which is used in dry samples; here the device takes and saves each reading in approximately 3 minutes.

The WP4c device connected to computer was set on continuous mode, where the device will take consecutive readings. When the device is ready, the sample was placed into the drawer, the knob was turn to the *"read"* position, then every 3 +/-1 minutes the device sent a reading to a data logger installed on the computer (the total time depends of the number of readings taken). In this case, the process took 30 minutes where the device recorded 9 to 10 readings. The sample weight was taken twice, once prior to placing the sample into the drawer, and once when the 30 minutes passed. The weight used was the average between the weights before and after. When the sample was not being used to take readings, it was placed into a desiccator, thus protecting it from changes in temperature or cross-contamination.

When the water potential exceeded 2 MPa suction, the device was set in the precise mode. In this mode, only one reading was taken for each weight and each reading can take anywhere from 12 to 18 minutes. Once the reading was taken the sample went into the desiccator for 1 hour and the sample weight was taken using a high precision scale. This procedure was repeated with the WP4c until a reading of 40 MPa was achieved and measured.

The same procedure was used when the readings shown values greater than 40 MPa, changing the device mode of use once again. In this case, when the samples were almost dry or there were not significant mass changes, the manufacturer recommends using the fast mode setup. In this case, the readings were taken every hour, following the procedure described above.

7.11 Optimal Organosilane Dosage

The second phase of this project involved a determination of the optimal Organosilane dosage to be added on compacted CCP

samples thus rendering hydrophobicity. The Terrasil organosilane has a soluble principle; it was sprayed over compacted samples placed in steel rings of 7.30 cm diameter generating a surface effect.

This study did not adopt the amount of water and OS (W+OS) reported by previous studies at UNCC because these amounts were calculated per unit volume. Given that this new phase of the EREF project aimed at simulating construction conditions, a decision was made to compact ash samples at optimal water content, to subsequently apply OS treatment on the surface of the sample. For this reason, the quantities were calculated again on a surface-area basis.

The samples used to select the new measure correspond to fly ash compacted into a steel ring 7 cm diameter and 2.5 cm high. In this case, the mixing methodology was another important change because in previous works the W+OS solution was added by manually mixing dried ash into a steel pan. This study adopted a different methodology which consisted in spraying the W+OS solution onto compacted-and-extruded CCP samples, thereby simulating more realistic construction conditions.

A total of seven possible OS combinations were tested, beginning with the one the manufacturer suggested. It consisted in dissolving 1 part of OS in 300 parts of water (i.e., with three liters of this solution one square meter of soil could be treated). Therefore, the proportion of one square meter to a circular sample area of 0.072 cm diameter was calculated. The following calculations were performed:

- For one square meter:

$$3l_{solution} = 0.0033_{organosilanes}l + 0.9966_{water}l$$

- For a 0.072 cm diameter sample:

$$0.012l_{solution} = 0.00004_{organosilanes}l + 0.012_{water}l$$

The amount of solution in each sample was controlled for weight differences, converting the amount of solution from volume to weight units.

Having defined the first measure as 1:300 (as per the OS manufacturer's recommendation), that is equivalent to 0.33% of OS dissolved in water, the next level is to increase the amount of organosilanes keeping the same water amount as follows: 2:300 equivalents to 0.67%, 8:300 equivalents to 2.66%, and 16:300 equivalents to 5.33%. All the samples were sprayed with an OS amount that depended on the sample diameter. Previously the exact amount of water and OS were mixed using a magnetic stirrer set in medium speed during 5 minutes. The procedure was to place a 1000 ml beaker on the scale and the required OS and water in grams were added.

For this operation a regular spray hose was used, which extracted the solution from the beaker. The distance between spray and sample was 30 cm +/- 5cm, and the angle formed with the horizontal was 45º +/- 5 º (Figure 6). These conditions of angle and distance are normally found in standard irrigation trucks (NINOX, 2016).


Figure 6 Illustration of the spraying method

The samples where the water amount was 300 mL showed extreme soaking after being sprayed, which retarded the process of reaching hydrophobicity. For this reason, it was decided to increase the amount of OS and to decrease the amount of water. Therefore, the new measures were: 20:200 equivalent to 10%, 24:200 equivalent to 12% and 28:200 equivalent to 14%.

The solution with the lowest amount of OS was selected (see results section). To define the optimal dosage, the following criteria were considered: (1) the water drop penetration time (WDPT) on OS-CCPs should be greater than 5 minutes, (2) the contact angle measured on OS-CCPs samples should be greater than 90º degrees, and, (3) the breakthrough pressure measured on OS-CCPs should be as minimum 0.30 m H_2O.

Water drop penetration time (WDPT) on OS-CCPs samples

The first of these tests consisted in monitoring a water drop placed on the surface OS-CCP sample with respect to time. In this case the evaluating aspects they were the time required for an OS-CCP specimen to show water repellency, measured from the moment the sample was prepared and the time required for a water drop to infiltrate into the OS-CCP sample. The priority of these tests was to find the optimal dosage able to support a water drop. The procedure was to measure the time that a water drop could lie on the sample without infiltrating. By calculating the corresponding water content in each reading, the OS-CCP sample weight was measured. The evaporation was not expected to affect the results because the measuring time was short.

For each amount, all readings were performed at a different location on sample surface; the samples were marked clockwise, from 1 to 12, as shown in Figure 7.
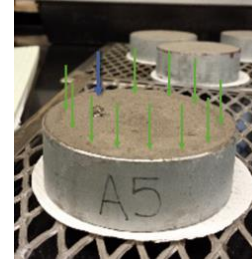
Figure 7 Water drop on the OS-CCP

Contact angle determination

After reaching a constant mass for all the samples, the next tests to be performed was the, contact angle test. It is a static test using the sessile drop technique that consisted in placing a water drop with fixed conditions of diameter and height on an ash sample surface. This technique calculated the angle *Theta* formed between the water surfaces and OS-CCP shown Figure 8. According to the contact angle theory, the material has hydrophobicity (water repellency) when the angle is greater than 90 º.
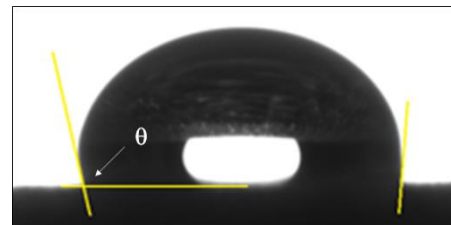
Figure 8 Contact angle measured on a sessile water drop

The contact angle readings were taken with a goniometer AVEN model #26700-200 connected to a computer where the Drop Image Advance software was installed and allowed the processing and collection of data. The procedure started where the previous test finished, so that the same samples were used. The steel rings with CCPs were placed on the lifting stage base

of the goniometer, perpendicular to a digital microscope and a lamp. In this method, the diameter drops were between 2.5 and 5.0 mm, controlled with a mechanical eyedropper.

Once the CCP samples were on the lifting stage goniometer perpendicular to the camera, a drop of water was placed on the sample surface, and the first photo was taken. This photo was used to place three rays; two vertical (left, right) and a horizontal. Their function in this test was to help with sample boundary visualization. When the rays were placed and the command was given to the computer, the device began to take readings (1 second each). The software calculated the angle and saved the data of left and right angles of the drops, as well as height and width. This is illustrated on Figure 9.

Figure 9 Illustration goniometer device and drop image software.

An advantage of the test is that it is non-destructive; therefore, the same samples were used in the next test corresponding to Breakthrough Pressure.

Breakthrough pressure determination

Traditional method

At UNCC, the breakthrough-pressure test was traditionally performed using an acrylic cell, normally used for permeability tests. For this EREF Project phase it was impossible to use the same method because it was hard to control the water flow between the ring and the acrylic wall Figure 10.

The breakthrough pressure has been traditionally measured using an acrylic chamber 8" diameter and 15" height, that was connected to a flow pump (FlowTrac-II manufactured by Geocomp®), that allows control of pressure and volume to the test cell, with pressure capacity of up to 200 psi (~1378 kPa). There was also a data logger connected to the computer software between the cell and the FlowTrac-II device. The maximum pressure range corresponds to 17.40 psi (~120 kPa). The software could save the reading each second, as well as the date and the pressure in milibar (mb). In these previous tests a porous stone was installed with the same chamber diameter, perpendicular to the acrylic walls. Any movement between the porous stone and the acrylic wall was blocked with Teflon or bentonite. The sample was a dry specimen placed over the porous stone without compaction, the chamber bottom was filled with water to the porous stone bottom, and the water pressure was raised at a specific rate of 0.5 kPa per second, until the breakthrough pressure was reached. At the beginning of this test, the described procedure was attempted, the only difference being the use of compacted samples. The OS-CCP sample was placed on the porous stone, the bottom chamber was full of water, the valve was opened and the pressure was turned on. Unfortunately, when following this procedure the breakthrough pressure could not be measured because the water flow showed wall effects whereby the water would easily flow between the acrylic wall and the steel ring.

New method

Due to the difficulties with the traditional procedure, it was decided to widen the Teflon amount by wrapping transversely the porous stone up to +/- 1 cm over the stone (Figure 10).
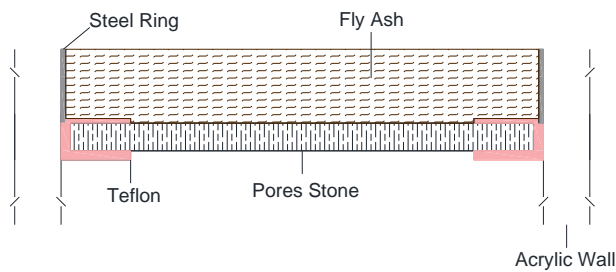

Figure 10 **Traditional Breakthrough pressure test**

This new arrangement in fact prohibited the water from flowing over the wall and forced the water flow across the sample. This method improvement allowed measurement of breakthrough pressure. However, it was just possible to use it once, because the two elements, steel ring and acrylic wall, were too fastened that it was not possible to actually recover the ring.

The suggested solution was to change the older cell by a triaxial-type cell. In this case the same principle of saturation in a triaxial test was used. Here the membrane was not allowing the water flow outside of the ring because the membrane outside was fastened with O-rings. They were placed over the membrane in three different places: the upper and bottom acrylic pedestal and the last one was plac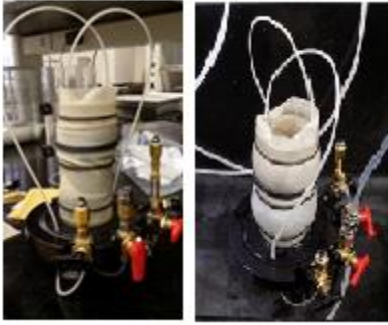ed on the same place where the ring was. The profile view from bottom to upper level consists on the following: (1) on the base there was an acrylic pedestal, (2) then an empty steel ring that was filled with water, (3) a porous stone, (4) *a* filter paper, (5) the OS-CCP into a steel ring, (6) a filter paper and porous stone, (7) an acrylic upper pedestal. This is illustrated on Figure 11.
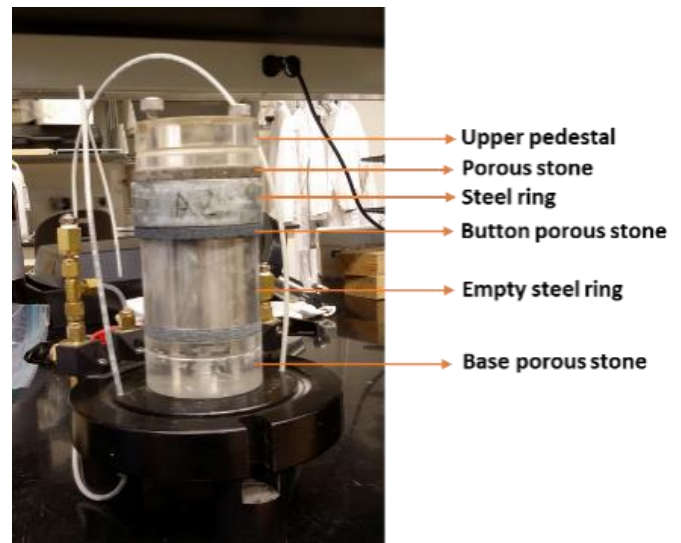
Figure 11 *Proposed breakthrough pressure test*

All the above elements were covered with a membrane and they all had the same diameter. When the assembling was ready, the pore valve was opened and the pressure rate from the flow pump started. The first test performed showed some problems; in this case the result was found at the same moment when the pressure was started, the water went out through small spaces and the bottom ring inflated the membrane (See Figure 12). In this case, the sample didn't have problem because the water could not seep through the sample and membrane but if the pressure had been higher than breakthrough pressure all the water would have flowed outside of the membrane. This problem was fixed by ensuring the lateral membrane movements with the tools used. The most precise mode was to confine the sample. In this case the cell pressure was not a key problem, because the external pressure could not modify the sample structure given that it was still in the ring, which is resisting all pressures. With these modification readings of pressure with respect to time could be taken. With this technique

seven breakthrough pressure tests on OS-CCPs samples were completed.

7.12 Organosilane Profile

In order to determine the OMC profile on OS-treated samples, the following procedure was adopted: *(1)* a CCP sample was compacted on a 10 cm height and 5 cm diameter steel ring *(2)* the OS solution was sprayed on the sample, waiting during 4 hours for the OS solution to freely infiltrate the sample. Then, the sample was split in similar pieces, approximately 1.5 cm each (pills), thus getting six soil layers at different heights in the sample; the height of each stratum is calculated as average between the upper and top layer of each sample *(3)* each ash pill was placed over a can previously marked to weight W_1 using a scale with minimum 3 significant decimal places (0.000), and then placed on an oven set to 110° C during at least 16 hours or until getting a constant mass. At this moment the weight sample must be taken W_2 *(4)* now, each sample should be placed on a Thermocouple set at 450° C during 6 hours, and the sample again must be weighted W_3.

Using W_1 and W_2, the sample water content could be calculated, 4 hours after mixing with OS, as $\frac{W_1-W_2}{W_2}$, and then being W_2 the sample dry weight the mix of Fly Ash and Organosilanes Organic Matter Content could be calculated as $\frac{W_2-W_3}{W_3} = OMC + O.S$. The difference between the latter value minus the average of OMC calculated in the first part of this section results in the Organosilanes content for each sample pill.

7.13 Tests on OS-CCP Samples

Having chosen the mixture amount and following the procedures described above, seven breakthrough pressure and contact angle tests were performed. In this case the amounts remained but the ash water content was varying from 0 (dry samples) to 28%.

A methodology was proposed to get specific OS-CCPs water contents. Three samples were dried differently. First, the samples were dried at laboratory room at 22 degrees Celsius. It took approximately 15 days to reach the dry state. The second methodology used a 150-watt incandescent bulb 40 cm above a cell where the samples were placed. The lamp was permanently active from 9 am to 6 pm. The third methodology also used a 150-watt incandescent bulb 40 cm above a cell where the samples were, but in this case the lamp was kept always on it means 24 hours.

Results showed that the second and third drying methods allowed getting specific water content sooner than the first one. A lamp with an infrared 175 WATS bulb was used to speed up the drying of the samples. The lamp was 30 cm above of the

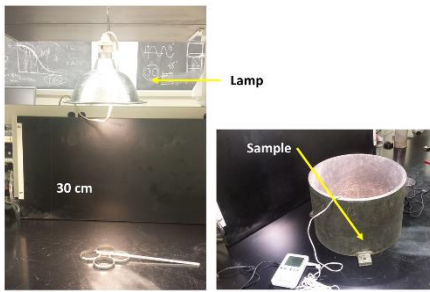samples that at the same time was into a big steel cylinder. (Figure 13).

Figure 13 Lamp assembly

The water content was calculated as a function of weight, therefore the OS-CCPs samples were constantly weighted to check the expected weight. Each time the weight was reached, the breakthrough pressure and contact angle tests were performed.

When the samples reached their dry weight, breakthrough pressure tests were performed to measure the volume entrance in the sample. To measure this volume, the cell was connected to Geocomp software that read pressure values and also registers volume data. The ratio between diameter and height of the OS-CCPs samples tested ranged from 2 to 2.5

7.14 Index tests on OS-CCPs

A series of grain size analysis, specific gravity, pH, minimum density, organic matter content and chemical test were performed on compacted CCPs with OS samples. Most of the samples used in contact angle and breakthrough pressure tests were kept in a steel rectangular pan, ensuring the same OS and fly ash proportion. In this case, the grain size analysis (wet and dry method and hydrometer) was performed in the same way to CSRs without OS grain size. The test was changed because the material was not washed to pass through the sieve N.200. This

process was changed for more vibrating time in the automatic vibrator, of 3 to 6 minutes. The rest of tests were made following the same steps described at the beginning of this section.

8.   RESULTS

8.1. Drying curves

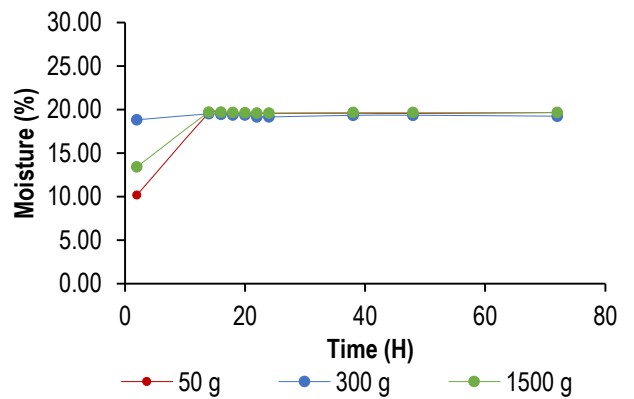The drying curves at 60 and 100 Degrees Celsius are shown below.

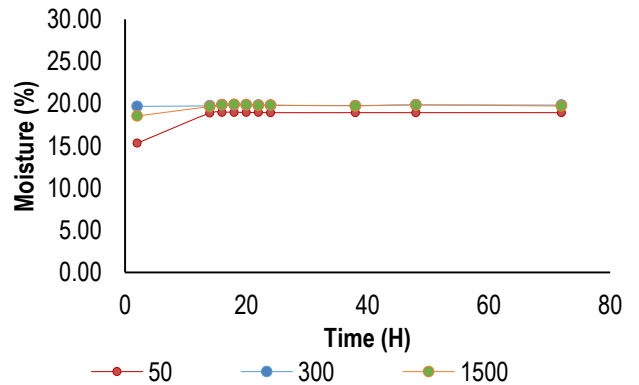*Figure 14 Drying curve at 60°*

Figure 15 Drying curve at 100°

For both cases, the X-axis represents the time since the sample was placed into the oven until the weight was read.

8.2. U-CCPs visual characterization

Using a Munsell Color Chart, the CCPs standardized color was determined. It corresponds to 5YR 6/1, where the result depends of three terms: the hue, the second and Chroma. The color of the sample gets darker when water is added.

This ash cannot be dried using the microwave method because the sample catches fire after three minutes in a 750-Watt microwave. The CCPs take more than 12 hours to reach the correct hydration. When the mixing time between CCP and water is earlier than this time a non-homogeneous mixture can be observed.

8.3. Index tests on U-CCPs

Atterberg limits determination presented some important challenges. The CCPs water content on the container corresponds to 0.00 %. With these conditions the liquid limit was calculated, but the results generated correspond to non-liquid, non-plastic cases (NL, NP). In this case, 6 samples were mixed with water contents between 10 and 20 %. These results were reported because it was impossible to find the necessary blows on Casagrande cup and/or it was nearly impossible to close the groove.

The CCP exhibited a sensitive behavior with respect to water content. In fact, with slight increases in water content, the ash would jump from near-shrinkage limit to plastic limit. Furthermore, with just 1-2% increase in water, the CCP would suddenly require less than 10 blows to close the groove.

Specific gravity

The Gs results ranged between 2.27 and 2.30.

Grain size analysis

The results are shown as percent passing a particle diameter in millimeters in the vertical axis, and in the horizontal axix in logarithmic scale, particle diameter, from the greatest value to smallest one.
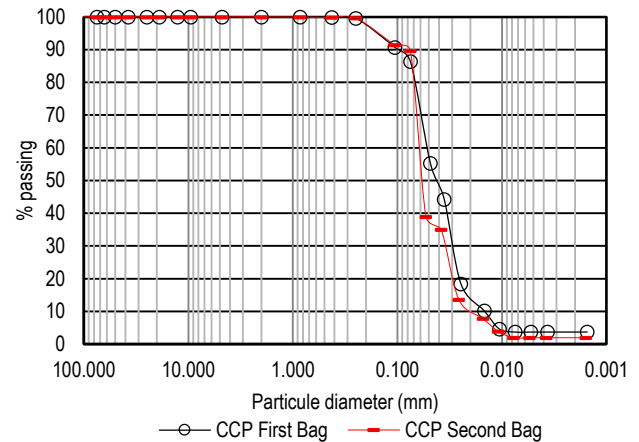

Figure 16 CCPs Grain size analysis

Table 1. Results of the grain size analysis for the selected materials.

Parameter	CCP First Bag	CCP Second Bag
% Gravel	0	0
% Sand	14	10
% Fines	86	90
D_{60}	0.055	0.06
D_{30}	0.03	0.035
D_{10}	0.016	0.02
C_u	3.44	3.00
C_c	1.02	1.02

Compaction

The maximum dry unit weight is defined on the basis of the standard compaction test. Results from the standard Proctor Test are shown on Figure 17. It can be observed that the maximum dry unit weight and optimal water content range from 13.38 to 13.80 kN/m³ when the samples are compacted with water contents values from 20 to 22 %. Using the specific gravities previously determined, the zero-air-voids curves (ZAVL) were superimposed.
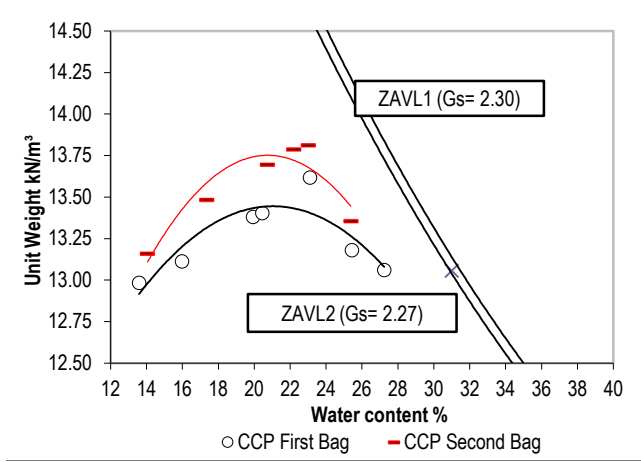
Figure 17 CCPs Compaction curve

Minimum unit weight

Minimum unit weight results calculated from 5 tests are 9.84, 9.48, 9.30, 9.70 and 9.82 kN/m³. Its statistic parameters as average, standard deviation and variation coefficient correspond to 9.628, 0.2326 and 2.41% respectively.

Organic matter content (OMC)

Results from the 6 OMC tests show an average of 0.7145%., with a standard deviation of 0.1327 and a coefficient of variance of 2.21%.

8.4 Ash-water characteristic curves (AWCC)

Results for two ash-water characteristic curves are shown on Figure 18. The first one corresponds to Bag 1, where the curve is divided in three parts; the first one corresponds to the average of several results (continuous mode), while the second and third parts show the points directly read from the device precise and fast mode in WP4c device. The results of the second curve (bag 2) corresponds to the point directly given from device (Figure 18).
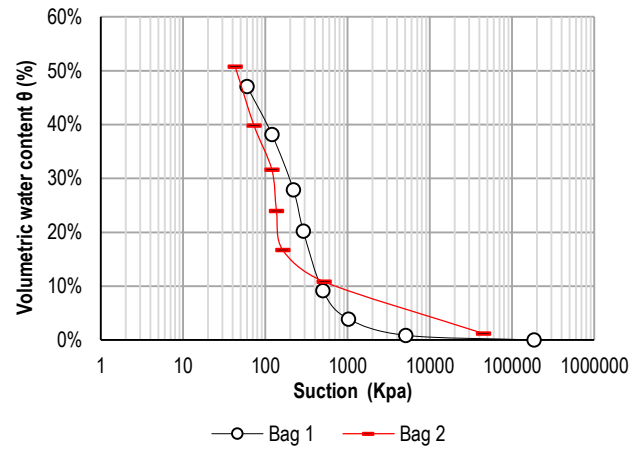
Figure 18 Ash-water characteristic curve

8.5 Chemical tests

The chemical test results from X-ray fluorescence are shown in Figure 19. The vertical axis represents the chemical concentration. These results are expressed in parts per million, while each chemical is shown on the horizontal axis.
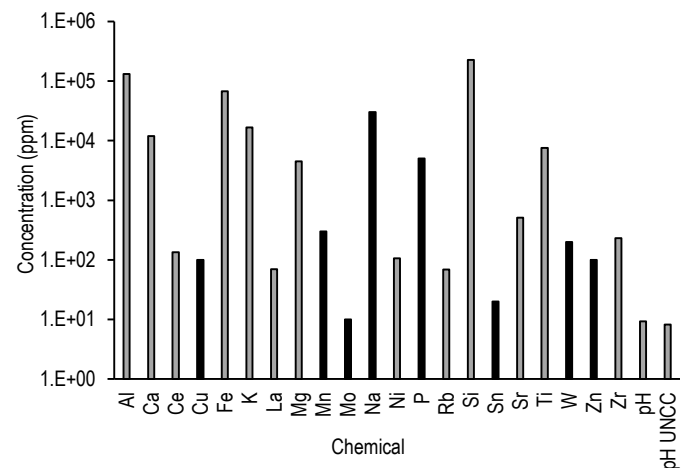

Figure 19 X-Ray Fluorescence results

The chemicals represented with darker colors means that its concentration value is greater than the value shown e.g. Mo > 10 ppm. All the tests were performed at external laboratories from UNCC, except the one marked "pH UNCC".

8.6. Sample preparation results

For this project, a total of 24 proctor test molds were compacted and 69 samples were extruded from the compacted molds. For all specimens the water content used ranged from 20 to 22 %, however the water content and maximum dry unit weight was measured each time. The results are shown on Figure 20. This figure superimposes both sample types: (1) samples from compacted molds (asterisks) and research samples obtained from the molds (hollow dots).
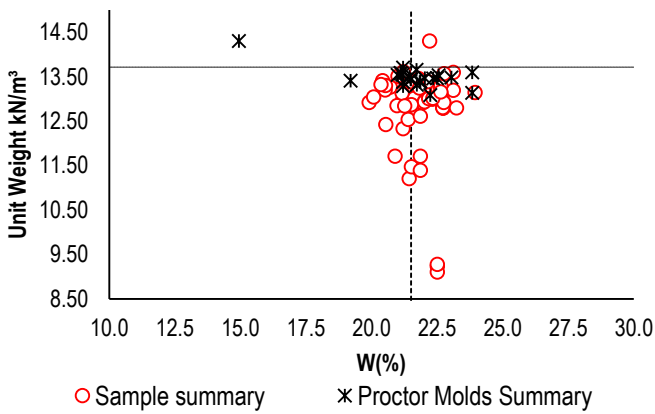

Figure 21 *OS content as organic matter*

Figure 20 **Unit weight and water content summary**

The dashed lines represent optimal water content and maximum dry unit weight as determined via mold compaction.

In the next graphs the profiles of organosilane (OS) content with depth for two 100-mm samples are shown as determined via loss-on-ignition. These profiles reflect the downward OS flow behavior through the samples.

Two graphs are presented, where each one shows the results for two samples. The first graph, Figure 21, represents the OS content as organic matter at each sample elevation. The second plot, Figure 22, shows the distribution of OS relative to the total OS in each sample, at different sample heights.
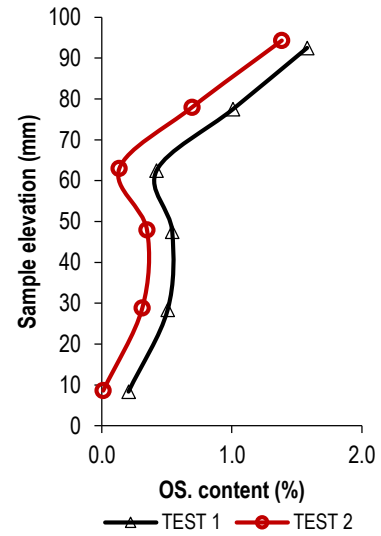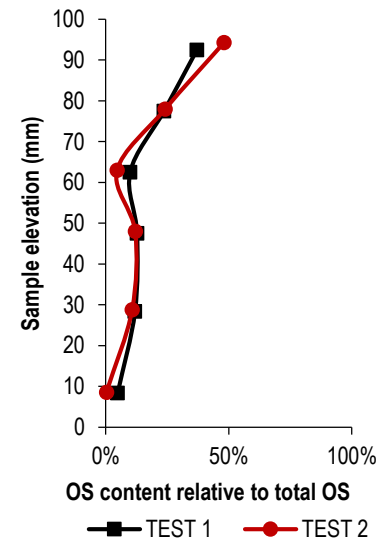

Figure 22 *OS distribution*

8.7. Optimal Organosilane Dosage Results

Three results, namely *(1)* water drop penetration time, WDPT, over a sample, *(2)* contact angle, and *(3)* breakthrough pressure were used to define the optimal OS amount.

Water drop penetration time, WDPT

In the first test, water drop penetration time (WDPT), the y-axis represents the time in seconds that the water drop stayed without infiltrating over a compacted CCP sample. The x-axis represents the time since the samples were treated. Figure 23

shows the results for 7 different mixtures, from 1:300 to 28:200 where the first term corresponds to the OS amount and second one to the dilution water amount.

This figure also shows a reference time to compare the results of each sample, as a horizontal line at 300 seconds (5 minutes). This time was selected for contact angle tests because the water drop requires at least 30 seconds stabilizing, and the rest of the time is the required to visualize the drop behavior.
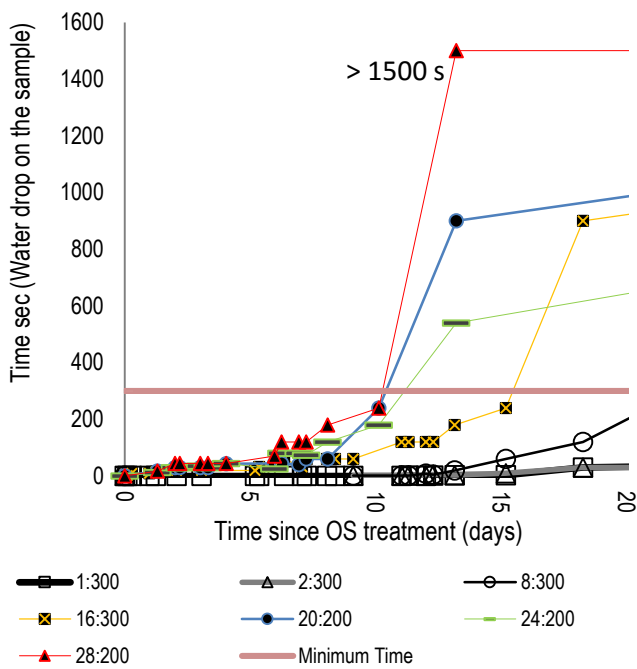

Figure 24 *Contact angle average*

Figure 23 *Water drop penetration time*

Contact angle

For the contact angle tests, the y-axis shows the angle obtained for each different sample. The results for six samples are shown in degrees. For almost all the tests, the contact angle was measured within ten minutes. Figure 24 shows the average between left and right angle and Figure 25 and Figure 26 containing the drop height and width, respectively.
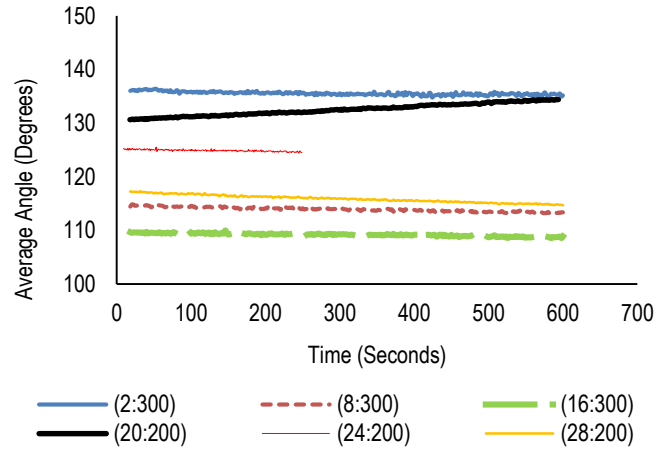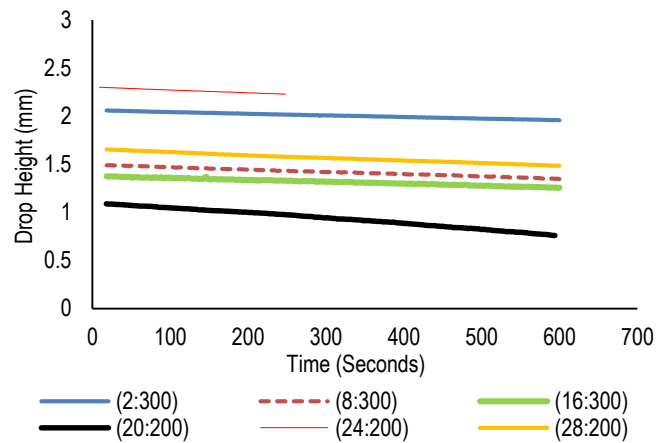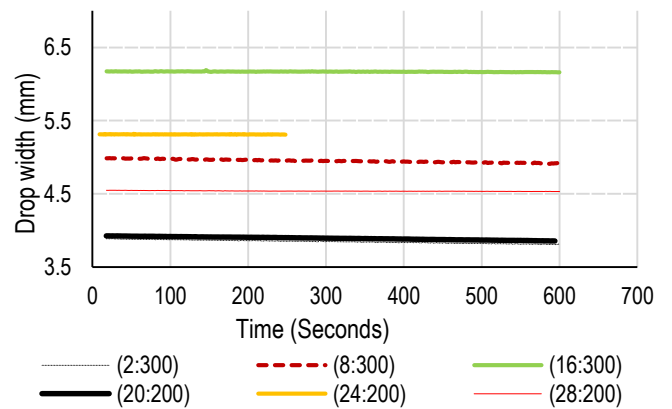

Figure 25 *Height Drop*

Figure 26 *Width drop*

All the graphs show six results corresponding to six amounts, though in the last graph only five dosages can be seen because one is superimposed over others.

In addition to graphs, some statistics for each dosage follow.

Values as number of data, average, standard deviation and variation coefficient are shown on Table 2.

Table 2. Contact angle information

| Sample	(2:300)	(8:300)	(16:300)	(20:200)	(24:200)	(28:200)
Data	292	292	292	289	241	292
Initial Value	136,02	114,44	109,64	130,64	125,24	117,25
Average	135,53	113,93	109,18	133	125	116
Standard Deviation	0,31	0,40	0,27	1,09	0,18	0,69
Variation Coefficient	0,23	0,35	0,25	0,82	0,14	0,60

Breakthrough pressure

Breakthrough pressure results are shown as the maximum value obtained from the software. All the results are shown in Figure 27 where the y-axis shows the pressure behavior through time. The test rate was defined as 0.5 kPa per 1 second.
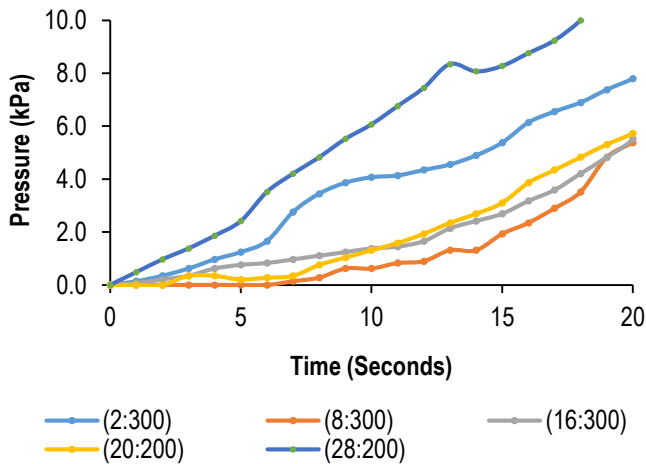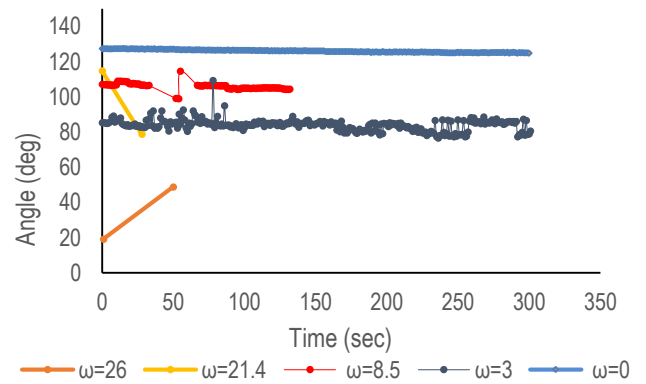

Figure 27 Different dosages Breakthrough pressure

8.8. Behavior of OS-CCPs (Treated CCPs)

The previous tests were used to select an optimal dosage (15:200). Once selected, contact angle and breakthrough pressure tests were performed with the optimal dosage. The results are shown below.
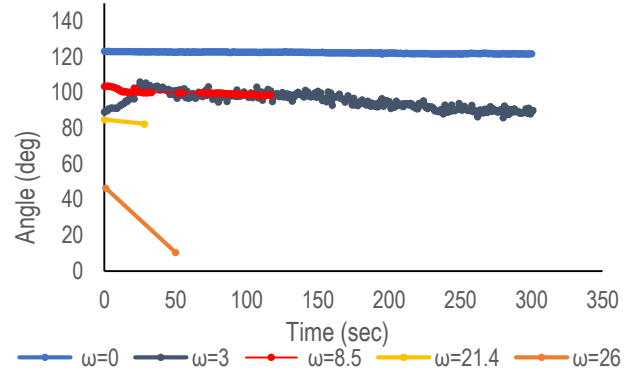
Figure 28 Right contact angle

Figure 29 Left contact angle

A sequence of pictures of a dry sample taken at different times are shown below. Figure 30 shows the pictures were taken at 0, 50, 100 and 200 and Figure 31 shows the picture taken at 300 seconds.
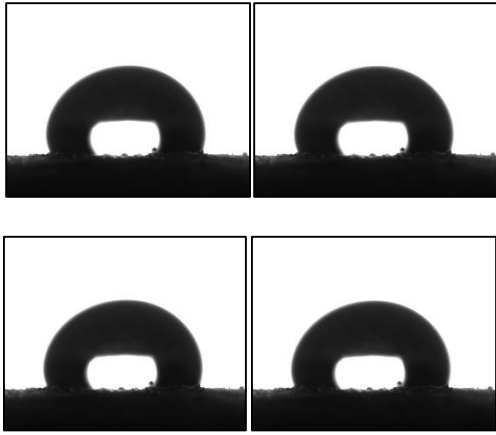
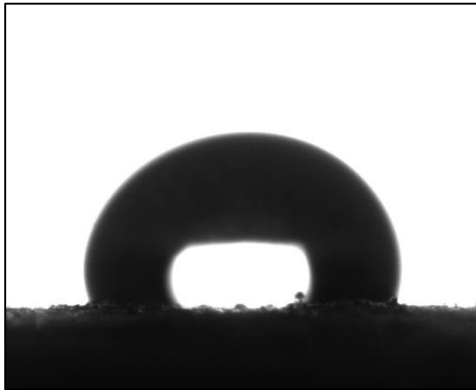*Figure 30 Photos taken at 0, 50, 100 and 200 seconds*

Figure 31 Photo taken 300 seconds

Immediately after measuring the contact angles, samples were recovered and reused in breakthrough pressure tests. In this case, the samples had the same water content as in the previous tests, namely 0, 3, 8.5, 21.4 and 26%. The breakthrough pressure (water-entry values) results are shown below. It is shown that the vertical axis represents the measured breakthrough pressure and the horizontal axis represents the time of test. Additionally, a curve is added for a breakthrough pressure test in a sample without any treatment of OS. This is shown in Figure 32.
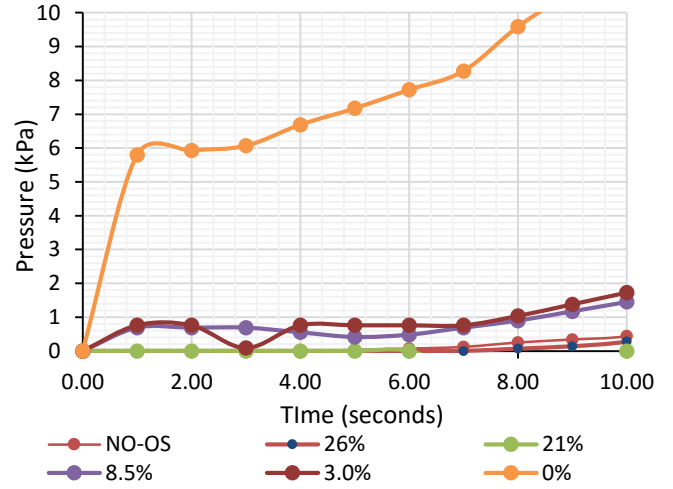

Figure 32 Different breakthrough pressure variating the water content to treated samples with (15:200)

Finally, the breakthrough pressure test results are presented in the more conventional chart of volume passed vs. pressure. The results shown correspond to samples at 0% of water content. A total of 10 curves were developed at varying confinement stress (total stress provided by the triaxial chamber). This is shown in Figure 33, 34 and 35. The breakthrough pressure can be identified with the initial entry of water, i.e., when the water volume starts to increase.

Table 3. Breakthrough Pressure Test Results Summary

Breakthrough Pressure Test Summary			
Figure	$\vartheta_{3}*$	**BP (Psi)**	**BP (kPa)**
33	2.5	0.15	1.034
33	5	0.35	2.413
33	5	0.7	4.826
34	10	0.4	2.758
34	10	0.9	6.205
35	15	0.3	2.068
35	15	0.7	4.826

* Confining stress

Figure 33 *Breakthrough pressure with volume measuring at 2.5 and 5 Psi*

Figure 34 *Breakthrough pressure with volume measuring at 10 Psi*

Figure 35 *Breakthrough pressure with volume measuring at 15 Psi*

9. DISCUSSION

The first step to ensure that the results found in this research project are reasonable and within the ranges reported in the literature, is to compare them with the results obtained in scientific articles.
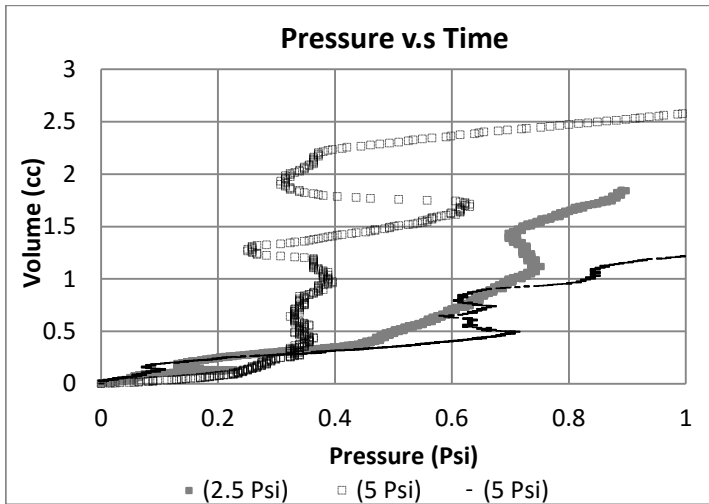
In most cases, the next step was to compare the results obtained from both OS-treated and untreated samples; in other cases the comparison was not made because there are not expected changes when the OS treatment is applied. As a final step, all results were analyzed taking into consideration the objectives of this project.
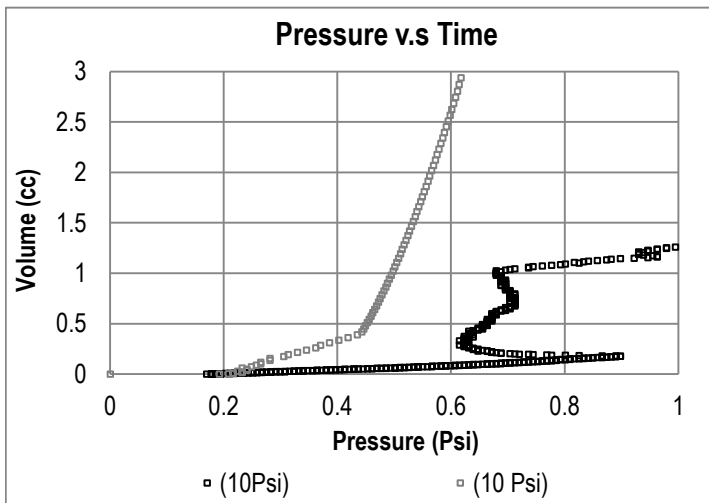
Index properties

In general, the specific gravity of CCPs differs depending on the geology of the region from which the samples were recovered, the properties of coal used in furnaces, the type of CCP produced (fly ash, bottom ash, lignite, among others), and combustion temperature. Bearing this in mind, Prakash & Sridharan presented a compilation of affecting factors and found that specific gravity ranges from 1.47 to 2.90 overall, as shown in Table 4 (Prakash & Sridharan, 2009).

Table 4. *Specific gravity of Coal Ashes from Different Countries Modificated of (Prakash & Sridharan, 2009)*
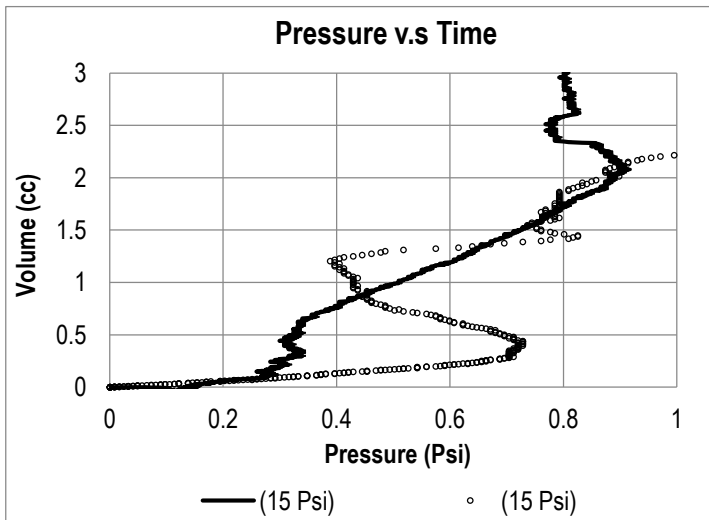
Type of coal ash	Country	Specific gravity
Fly ash	India	1,66-2,55
	U.S.A.	2,03-2,49
	U.K.	1,90-2,37
	Canada	1,90-2,90
	Thailand	2,27-2,45
Pond Ash	India	1,64-2,66
	U.K.	2,10-2,24
	Poland	1,90-2,31
Bottom Ash	India	1,47-2,19
	U.S.A.	2,28-2,78

If only results for fly ash obtained from the USA are taken into consideration, the range decreases from 2.03 to 2.49. It can be observed that the experimental results obtained from this study show all data points are within this range; 2.32, 2.31, 2.28, 2.30, 2.27 and 2.06. In other articles in which CCP properties are evaluated, specifically on samples recovered from the State of Indiana, the data ranges from 2.30, 2.61 and 2.81, for different sites, as stated by Bumjoo & Monica.

The graphs that summarize grain size distribution curves developed in this study show poorly graded curves with high content of fine particles, mostly corresponding to volatilized material in blast furnace silos that is transported via slurry to CCP disposal impoundments.

Santamarina (2012) presents a set of grain size distribution curves for CCPs, specifically upper- and lower-boundary limits. It can be observed that the CCPs results obtained for this research project falls into Santamarina (2012) zone. Results were also compared to those found by Bumjoo and Monica (2008), as shown in Figure 36.
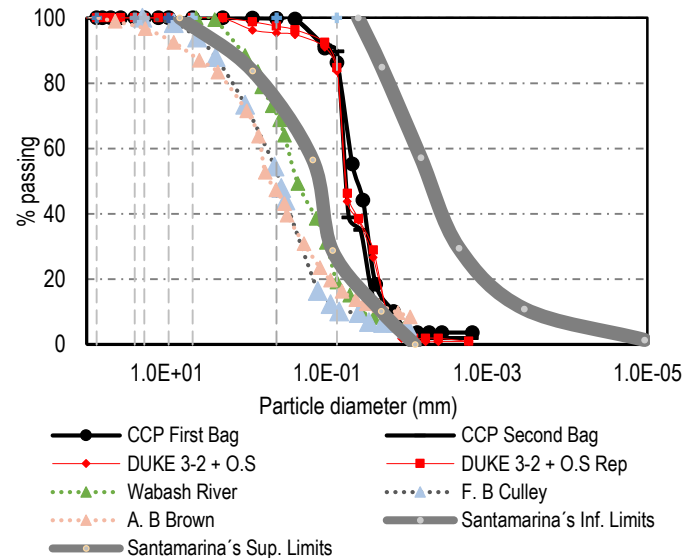
Figure 36 Coal ash Grain size analysis range

Adapted from Prakash & Sridharan, 2009, Bumjoo & Monica, 2008 and Santamarina 2012.

Also, it can be observed that the principal difference between the CCPs studied by Bumjoo and Monica (2008), with the results found in this research project, is the grain size for each material. Not only is the volatized CCP, but also that obtained from the bottom of the silo, which in most of the cases are coarser than the regular fly ash. The three graphs proposed in that article, show a more even distribution, and when comparing parameters such as D_{60}, D_{30} and D_{10} an increase of up to one order of magnitude can be observed.

The results obtained from the grain size analysis for samples prepared with and without the addition of OS show no visible changes in the results. Therefore, based on hydrometer test results, the OS treatment fails to change the velocity at which the particles fall through the apparatus.

The Atterberg limits results corresponding to this study show that the CCP shows no liquid and plastic limit. Although from point to point, the increase of water content was minimal; for low

water content a high number of blows was required (blows > 30) to reach a distance of 13 mm. While for another increment of +/- 1% water, less than 8 blows were needed to reach the objective, closing almost suddenly. This behavior suggests high sensitivity to water interaction that is shown by the sample. The plasticity of the OS+CCP was not measured because after adding the chemical to the water samples, these required high volumes of water would form a "sludge".

Compaction

Compaction properties of the CCPs were also evaluated in the article previously mentioned. These results were used to compare those obtained in this study. With compaction tests, following the Standard Proctor procedure, Bumjoo and Monica (2008) measured the dry unit weight and optimum water content of three samples. Figure 37 shows these results.
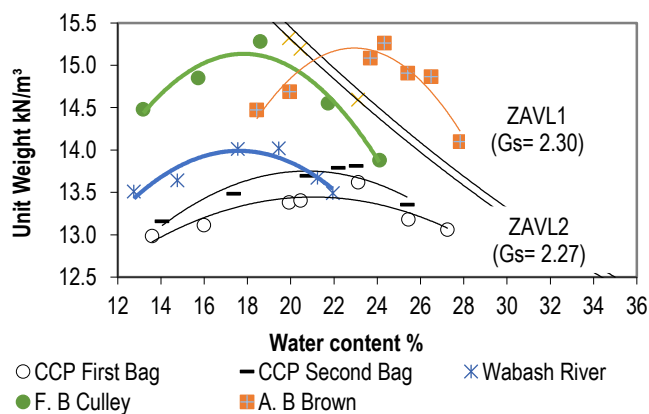

Figure 37 Compaction Curve Adapted of (Bumjoo & Monica, 2008)

The figure shows that water content and unit weight results obtained for all the tests are within the same range. Mixing the materials at different levels of water content for at least twelve hours before compacting was required in order to achieve these results. This time allows the water to lubricate the particles in

CCP. In the cases where lubrication was not possible, the dispersion of water content of each simple was increased, which was calculated with three different water contents.

Although not recommended, the compaction curve of some soils can be done with just three points; that was unverifiable for this study because increasing the water content to achieve a lower unit weight than the previous, would on the contrary, yield a lower unit weight although one could visibly see that the maximum density had been surpassed and was in the wet side of the test. In most cases getting to the wet side required just a minimum increase of water content, which produced a sudden drop apropos the unit weight.

Minimum density

The minimum density tests yielded results consistent with those found with the Proctor Standard tests, as they are much lower and allow to clearly see the range in which the material will be in Figure 38 reflects the comparison of the results obtained by Santamarina (2012). Where the values are related with the specific gravity values obtained of different CCPs The minimum densities are found in Santamarina experiments. It can be observed that between the maximum and minimum founded densities it can be defined a range in which are all the densities of this work. (Santamarina , 2012)
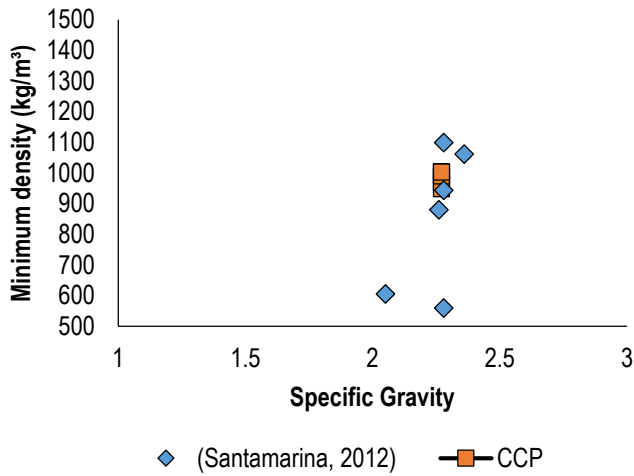
Figure 38 minimum density (adapted from Santamarina (2012))

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Figure 39 Ash water characteristic curve

Ash-Water Characteristic Curve (AWCC)

Figure 36 shows the ash water characteristic curve results, where it is easy to identify the main curve parts. For example, the air-entry value has essentially the same slope as other fly ash curves found in the literature; however, the curve of this work is shifted to the left around one order of magnitude in suction. Figure 39 that shows six CCPs from New Mexico, USA. This study's AWCC were fit to the Van Genuchten equation $\theta = \theta r + \frac{\theta_s + \theta_r}{\left(\ln\left(e + \left(\frac{¥}{a}\right)^n\right)\right)^m}$. It can be seen that the curves found in this research have several properties in common with those labeled BA E curve that correspond to bottom ash from New Mexico. The parameter (n) of the curves on this work had to be adjusted from 1.51 to 2. This parameter determines the slope for the desaturation zone of the curve (Maček, Smolar , & Petkovšek, 2013).
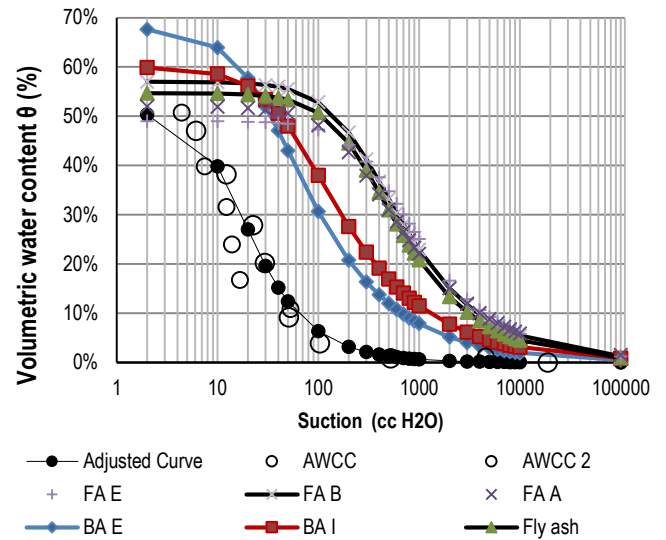
The final Van Genuchten fitting parameters for the CCPs in this study are: 0.08 for the Inverse of Air Entry α and 2 for the Curve Fitting Parameter n, 0 residual water content, saturated water content 0.51 (Webb, Stormont, Stone, & Thomson, 2014).

Chemical analysis

The results of XRF tests for U-CCPs and OS-CCPs show no significant changes for inorganic elements, specifically metals please refer to Figure 40. The OS are composed of organic compounds R-Si, where R corresponds to Alkyl or Organic Functional group and Si to silica (Daniels , et al., 2009).
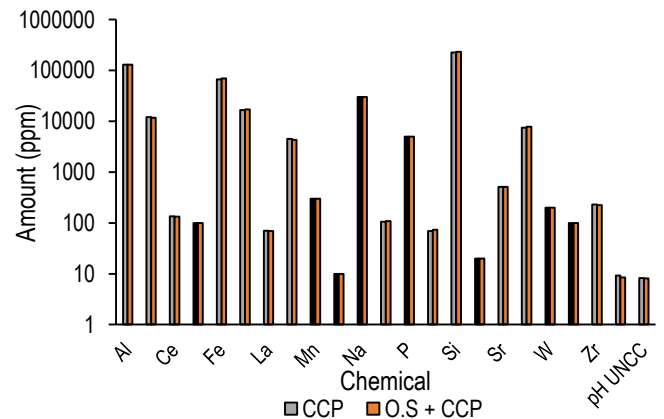

Figure 40 Chemical analysis

OS Spatial Distribution in CCP Samples

The percolation of the H$_2$O+OS solution across compacted samples upon spraying is relevant to estimate the possible depth of influence of OS upon treatment. Results on Figure 21 show that, for 10-cm-high compacted samples, approximately 72% of OS accumulates in the top 4 cm of the CCP samples. In this study, upon treatment an OS-layer is observed at the sample top after extraction of the compacted and treated samples. Such layer of OS-CCP is approximately 2-mm thick.

Although the profile that relates the sample height and amount of OS in the sample shows that approximately 72% of the chemical stays within the top 4 cm, the "crust" recovered from treating and extracting the sample from the sampler ring suggests that a large part of the 72% doesn't distribute evenly through the first 4 cm; on the contrary, it stays on the surface of the sample.
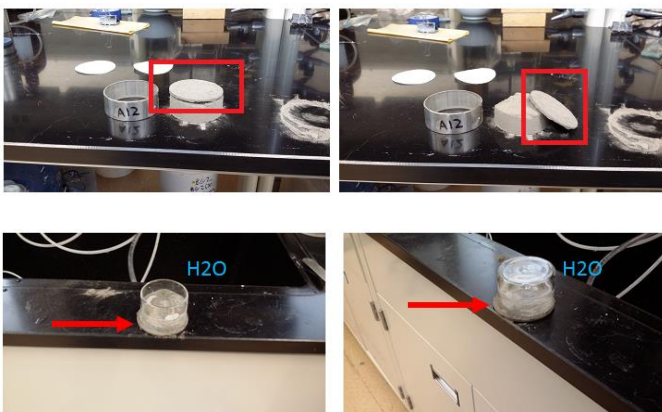
Figure 41 CCP + OS surface

Degree of Water-Repellency: Contact Angle

Figure 23 above shows the results of water drop penetration time (WDPT) as a function of CCP-OS reaction time. In general, the initial rate of CCP-OS reaction was low; meaning that the time required to achieve 60-second WDPT was at least 5 days within all the samples tested. In fact, in order to reach the 5-min WDPT criterion, at least 10 days were required. However, once the 5-min WDPT was reached, reaction rates were significantly higher.

It can be seen that, with the exception of the 20:200 and 24:200 mixes, WDPT increases steadily with the net amount of OS in the CCP, reflecting progressively stronger water-repellent behavior. In addition, the higher the OS amount, the shorter the time required to attain the 5-min WDPT criterion.

Figure 23 also shows that the minimum OS amount required to attain the 5-min WDPT criterion in less 15 days is 16:300. Also, it was noticed that 300 mL of solution water would take long time to dry out completely. Therefore, an amount of 15:200 was finally adopted as the optimal amount/quantity for the subsequent CCP contact angle and breakthrough pressure measurements. Still, after the 15:200 amount/mix/quantity was adopted, additional WDPTs were measured 19 days later (see Figure 23, thus confirming enhanced water repellency with time. Remarkably, the 2:300 amounts did surpass the 5-min WDPT criterion after a total of about 42 days.

Results obtained from contact angle measurements, shown in Figure 24, reveals that the contact angle is above 90 degrees and in most cases it decreases slowly over time. However, in one particular case, the sample with concentration of 20:200, the average between the left and right drop angle indicates the angle is increasing, even though the photos automatically taken by the device show otherwise. Upon analyzing the photos, it was observed that the left angle was influenced by some microscopic features of irregular excess CCP, as observed in Figure 42, which likely were an altering factor in further readings

for this device. Additionally, for this particular sample the results of drop height and width were also monitored, which as expected slowly decreased over time.
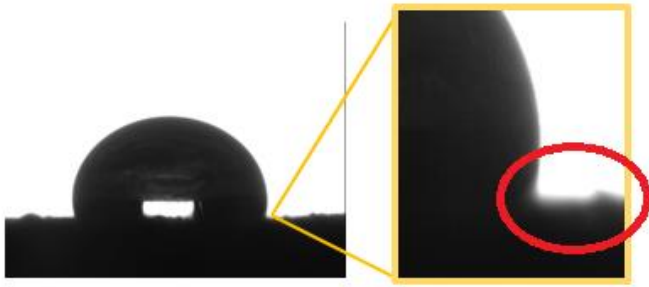
Figure 42 microscopic features of irregular excess

Even though the surface of all samples used to run the contact angle tests were carefully trimmed and refined to spray the OS on them, it was noticed that some steps in the procedure impact the reliability of the results. For example,the process of spraying the ash samples with OS solution from a defined distance and angle produces a jet of water and air out of the sprayer that occasionally open new pores which could hardly be seen by the naked eye, smaller than about 1 mm in size. This problem was perceived while taking measurements with the microscopic camera, which caused some erroneous readings of the angle. Also,the horizontality of the samples. In some cases, the rings with which the samples were taken were not 100% horizontal, as they formed a small angle at the base of the goniometer. Both problems could hardly be seen with the naked eye, as they were only perceived with the use of the microscopic camera.

Table 2 shows statistics calculated from the results obtained with the contact angle tests, approximately 300 results, which show very low dispersion, with standard deviation values below 1% from the mean. These results can be compared to those

found by Jordan (2014). The same chemical was used, TERRASIL, in both Jordan's 2014 thesis and this study. However, there are two major differences between these studies: (1) the way the chemical is mixed with the CCPs samples, since Jordan (2014) fully mixed the entire sample mass with OS, while in this study only the surface of the samples was sprayed and (2) Jordan (2014) considered different temperatures while taking the measurements and all measurements in this study were made at room temperature. In addition, Jordan's (2014) average contact angle throughout different temperatures is 143° while the one obtained in this study at different OS concentrations of OS is 121°.

In another research project carried out in the University of North Carolina-Charlotte, Keatts (2014) worked with granular soil and a CCP, for which geotechnical and chemical properties were measured. Both the CCP studied by Keatts (2014) and that used in this project correspond to F-type, bear similar specific gravities of 2.2 and 2.3, and in both cases the predominant material is fine-grained. The difference between the experimental studies, similar to the comparisson with Jordan (2014), is the mixture method applied to the CCP. Nevertheless, the results of contact angle and breakthrough pressure are comparable to those found here.

Keatts (2014) prepared dried samples at different contents of OS by CCP and granular material that: (1) the contact angle increases with greater contents of OS, something that could not be verified in this experimental work, taking into account the reliability of the obtained data given the small sample irregularities mentioned above due to the pressure of the hose

used to spray the OS solution; (2) in all cases, as well as in this research, the OS dosage generated measured angles that exceeded 90° (Keatts, 2014).

Stability of Water-Repellent CCPs: Water-Entry Value

The breaking pressures measured by Keatts (2014) are directly proportional to the OS quantity, and the values range from 10 to 600 cm of water (about 1 to 60 kPa) depending on the material density. In addition, it shows that the maximum values found by Keatts (2014) exceed in up to five times those found in this research. Nevertheless, it is not possible to define an overall behavior because the OS quantities used in both researches are not comparable.

The results corresponding to breakthrough pressure made with different doses of OS can be observed in Figure 27. It is difficult to identify the first pressure of water-entry into the treated samples. The breakthrough pressure was defined in each of the tests by analyzing all the data for changes in slope of the graphs, data dispersion, etc. However, it was still challenging to determine the exact points when the water began to enter the samples; in such case, the breakthrough pressure was found by defining the changes in slope and different graph behaviors and physically noting the instant when the data-acquisition device registered a change of volume.

The results obtained by Jordan (2014) were used again to make a comparison with the data obtained in this study. For different temperatures, the breakthrough pressures were measured on samples treated with TERRASIL, where it could be noted that the graphs obtained had similar behaviors, however, the breakthrough pressure was also hard to obtain.

With the three tests previously mentioned (water drop penetration time, contact angle and breakthrough pressure) it was determined that all doses except for the first one (1:300) show some degree of hydrophobicity. Nevertheless, the 16:300 dose started to show this behavior after 15 days, the readings of the measured angles were more stable, and had a breakthrough pressure of approximately 0.2 psi (1.38 kPa), which is why a similar dose was chosen to continue the investigation.

Figure 28 and 29 show the behavior of the average contact angle for the same dose (optimal) at different water contents and it can be seen that for high water contents, higher than 20%, the contact angle is very unstable. In fact, no measurements can be done after the drop has been on the sample for more than one minute. An angle greater than 90° can be obtained after two minutes as the water content of the sample decreases but is impossible to continue taking readings. For the latter two cases, both 0% and 3% water content on the samples show stable contact angle readings and can be measured after 5 minutes.

The breakthrough pressure tests were performed using the same samples and water contents as for the contact angle tests. The first test, i.e., the red curve in Figure 32 represents a sample that was not treated with OS which was tested at compaction water content (22.5%); the curves at 21% and 26% water content show the water pressure did not have to suddenly increase to break the OS-rich barrier, while for the samples with 3% and 8% water content there is an approximately 1 psi increase in the water pressure. Finally, the sample with no water

content has a substantial increase in the water-entry value reaching about 0.85 psi (5.8 kPa).

In order to obtain a clearer picture of the breakthrough pressure (water-entry value) results, the volume of infiltrated water upon break was considered and monitored for dry OS-treated samples (see Figures 33, 34 and 35). These results allow for a clearer and more reliable method of measuring breakthrough pressure, since the volumes are low to zero until breakthrough occurs, when the volume suddenly starts to increase.

Although there are many authors who have prepared hydrophobic soils by mixing them with organic chemicals, insecticide, etc., it is not straightforward to compare their results with those from this study, due to the difference in the variables used in all the experiments. For example, Fink (1970), aimed at measuring the hydrophobicity with tests similar to those used in this investigation (contact angle and break pressure); nevertheless, there are difference between the material treated and the treatment itself. Fink (1970) added different dosages of organic substances that worked as coating to granular soils and granular soils mixed with fines. The results allowed to conclude that as the quantity of organic material increase, the results of break pressure and contact angle are higher. Among the results found, it can be observed that the contact angles vary between 90 and 160 degrees for samples with the highest treatment concentration. The highest break up pressures for treatments with high dosages are close to 55 cm of water (5.3 kPa).

Fink's (1970) experimental study was used for comparison because of the type of treatment which is also by the square meter; nevertheless, the quantities of water-repellent agent are much higher, in the order of 1×10^5 g/m² while those used in this study correspond to 1×10^2 g/m².

10. PRACTICAL IMPLICATIONS

The results obtained for the breakthrough pressure in this study range from 2.74 kPa to 5.39 kPa. This affirmation is restricted to the reservoirs to be in normal conditions, i.e. when the drain systems are in proper operation and handle up to 30 cms (2.94 kPa) of leachate above the lining layer.

Having into account that the proposed spray methodology simulates the construction process that will be applied in field, a likely limitation will be the possible brittle crust that is formed in the samples surfaces (see Figure 41) when the samples are compacted and sprayed. That fragile layer can get fissures when vertical forces are applied or shear forces when the slurry is disposed over the existing liners. However, these breakthrough pressure tests with volume measuring did not present any problem given that there were not found any fissures when cell pressures were applied. This can be concluded because in none of the breakthrough pressure tests an immediate entrance of water was perceived.

Another important factor that must be considered when applying the method in field is that the material needs to be dry, or at least having a very small content of water. Having into account that usually the CCPs disposal ponds are vast (thousands of square meters), for the practical field case, the drying lamp method used in this experiment cannot be replicated. However, a jet drying truck or similar may be used instead. It should start the drying process once the material is compacted and sprayed. Or

also a solution that keeps the OS quantity and decreases the water quantity could be applied.

Having into account the observed behaviors in the Proctor and Liquid Limit results, it is necessary to be strict with the water used to compact the CCP, given that excess in water content can generate sudden behaviors when compacting the material. This condition could change the properties of compacted CCP, and with this could affect the OS-CCP performance.

11. CONCLUSIONS

- The results suggest that, for a liner system built with compacted OS-CCPs (assuming no geomembrane), even in the low-likelihood event of a drainage system clogging and failing, the OS-CCP liner may be able to withstand about 28.11 to 55.8 cm of leachate before allowing seepage. Normally, drainage systems are designed to prevent the liner from bearing more than 30 cm of leachate.

- The hydrophobic behavior of the CCPs is optimal when there is very low to zero content of water in the OS-CCP.

- Considering the results obtained in this research, a higher amount of OS does not necessarily imply higher hydrophobicity. This is an unusual behavior when compared to previous research. This behavior can be explained because the OS amount is relatively small and so are the changes between dosages.

- Following the proposed method, compaction and OS spray, a thin and fragile layer is formed on top of the OS-CCP.

- The sensitivity of the CCPs appears to be high, given that with a small increase of water content, its consistency behavior changes drastically (both in compaction and liquidity index).

- The results of the laboratory tests show that OS-treated samples at low to zero water content exhibit higher degree of hydrophobicity than those at high water content.

- The test proposed in this research allows to identify the exact moment when the volume starts to increase. This allows identifying the precise value of breakthrough pressure.

- The proposed spraying method guarantees a homogeneous and exact distribution of the OS on the compacted CCP sample. Also this method is an easy and quick way to treat the CCPs.

12. FUTURE WORK

A number of new research ideas stem from this study, including:

- To identify what is the behavior of OS-CCP after the breakthrough pressure is exceeded and subjected to wetting-drying processes.

- To determine the stability and durability of the OS-CCP when subjected to short and long periods of water.

- To implement a method for the OS test that define the OS profile through OS-CCP, in which the height of the samples can be decreased, and the number of the samples can be increased.

- To further investigate the correlation between confinement stress and breakthrough pressure; more repetitions and higher-resolution testing devices with more precision are needed.

13. ACKNOWLEDGMENTS

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