

Detection of Aggregate Clay Coatings and Impacts on Concrete

by Jose F. Muñoz, M. Isabel Tejedor, Marc A. Anderson, and Steven M. Cramer

Deleterious clay minerals often enter concrete as coatings on aggregates; the impacts of the certain clays introduced by this mechanism is the subject of this study. The effects of different clay properties, including cation exchange capacity (CEC) and the nature of the exchangeable cations on concrete, were measured. The material selected for this research was an igneous clean coarse aggregate which, for purposes of repeatability and experimental control, was lab-coated with four different clay suspensions (kaolin, illite, sodium montmorillonite, and calcium montmorillonite). The coated aggregate was then used to make concrete test specimens. The results clearly show that the impact of the clays is not only a function of the CEC of the clay but also of the nature of the exchangeable cation.

Keywords: cation exchange capacity; clays; coarse aggregate; coatings; crystalline swelling; methylene blue; microfines.

INTRODUCTION

The topic of the impact of microfines on concrete performance has been the subject of extensive study by several authors.¹⁻⁹ Based on these research efforts, it is generally accepted that the impact of these materials is not exclusively a matter of their quantity but also of their mineralogical nature. Furthermore, the presence of certain clay minerals in the microfines has the potential to impact final concrete performance. Clays with a high water absorption capacity will impact the overall water-cement ratio (w/c) of the concrete, provoking lower compressive strength and higher shrinkages.^{1,3,5} This water demand of clays has been related to their surface area¹⁰ and their ability to absorb water molecules between their layered structure.⁸

An analysis of the available bibliography in this subject area of microfines prompts two main observations concerning the state of the art. First, most of the existing research examines the impact of clay materials as additives to the bulk paste but, to the authors' knowledge, no studies have been performed using these materials as coatings of aggregates, which is the common vector by which many deleterious microfines enter into the concrete structure. Because of surface charges, these clay particles may not always detach from the aggregate during mixing. Secondly, the abundant knowledge related to the impact of these clay mineral fines on macroscopic concrete performance contrasts with the uncertain information with respect to their mechanism of action both physical and chemical on the microstructure of the concrete. In fact, only a couple of hypotheses have been proposed¹¹⁻¹³ to account for the deleterious mechanism by which these fines operate.

RESEARCH SIGNIFICANCE

The introduction of clay minerals (that adhere to aggregate as coatings) to the concrete is shown to be detrimental. This paper clarifies the role of the unique clay hydration

processes such as crystalline and macroscopic swelling on key concrete properties. Results from these studies are used to evaluate the effect of current microfine monitoring methods, including ASTM C117 (P200), California Test 227 (CCT), ASHTO TP57 (MBV), and the modified methylene blue value index (MMBV), which relates results from the P200 and MBV tests. This information could be valuable for the development of an effective treatment strategy for preventing the detrimental effects of clay minerals.

BACKGROUND

The water absorption capability of a clay mineral is the main characteristic appearing to have the greatest effect on concrete performance. To fully understand these mechanisms, a brief review of clay mineral structure is presented herein.

Clay minerals are phyllosilicates of small particle size ($<2 \mu\text{m}$).¹⁴ They are formed by combining two basic sheet structures. One is a continuous two-dimensional (2D) tetrahedral sheet of composition T_2O_5 ($\text{T} = \text{Si}$ or $\text{Si}_{4+}/\text{Al}_{3+}$) with individual tetrahedra linked by sharing three corners of each, and with the fourth corner pointing in any direction. The second is an octahedral sheet built of YO_6 octahedrons sharing edges ($\text{Y} = \text{Al}_{3+}$ or Mg^{2+} or Fe^{3+}). The different combinations of octahedral and tetrahedral sheets that form the unit layer of the clay, in turn, generate different types of clays: when the unit layer is comprised of one tetrahedral sheet superimposed on one octahedral sheet, the clay is classified as a 1:1 layer silicate; if the unit layer of the clay consists of two outer tetrahedral sheets and an inner octahedral sheet, the clay is classified as 2:1 layer silicate.

Negative charge development on silicate clays is mainly due to isomorphous substitution in either sheet. When the intra-layer charge balance of the 2:1 type silicates is incomplete, the net charge deficit is balanced by alkaline and alkaline earth cations situated between the layers. These cations can be replaced easily by a different cation if the clay is immersed in a solution of an appropriate salt. The most common exchange cations are calcium, sodium, and magnesium.

In the case of smectites and vermiculites, the interlayer region contains water molecules. The amount of inter-lamellar water is a function of the exchangeable cation and the relative humidity of the ambient atmosphere. For instance, the water absorption will increase following this sequence: $\text{K}^+ < \text{Na}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$.¹⁵ The interlayer water increases the separation of layers so that the repeat unit of the structure normal to the sheets is larger than that in the dehydrated minerals ($\approx 1 \text{ nm}$).

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Table 1—Characteristics of clays and dip-coating conditions

Clay	CEC, meq/100 g	Hydration properties	Clay suspension, g/L	No. of dip cycles
NaM	74 to 79	Macroscopic swelling	80	4
CaM	74 to 79	High crystalline swelling	140	4
Illite	15	No crystalline swelling	160	4
Kaolin	1.7 to 2.4	No crystalline swelling	30	4

Note: CEC is cation exchange capacity.

For example, a fully hydrated vermiculate, containing two layers of inter-lamellar water and its basal spacing, can increase up to 1.5 nm through hydration. In smectites, basal spacing could increase from 0.95 to 1.00 nm in the dehydrated state up to 1.25 to 1.9 nm in the hydrated form. The swelling behavior changes for certain clays in aqueous solution depending on the nature of the cation located in the interlayer region. As an example, while vermiculites—as well as K^+ and NH_4^+ smectites—do not normally expand beyond 1.5 nm, most Na^+ and Li^+ smectites in water or dilute solutions swell macroscopically into a gel-like state in which the average layer separation is greater than 4.0 nm and increases in proportion to $1/\sqrt{c}$, where c is the electrolyte concentration in the liquid phase.¹⁶ This is known as macroscopic or double-layer swelling and is associated with the formation of a diffuse electrical double layer on each surface of the structural layer of the silicate. In this case, the clay particles are said to be destacked or exfoliated. The water molecules absorb in between layers, increasing the basal spacing to a limit where the unit layers separate from each other. This process is known as macroscopic swelling. In contrast, those clays only able to swell between 1.0 and 2.2 nm are known to have crystalline swelling. It is expected that these two behaviors in water solutions may have a different but possibly profound impact on concrete properties.

EXPERIMENTAL INVESTIGATION

Materials

Clays—Four clays of known and pure composition were selected to coat coarse aggregate. The selected clays were kaolin, illite, sodium montmorillonite (NaM), and calcium montmorillonite (CaM). Pure composition clays were selected to allow isolation of the impact of particular clay types, whereas field aggregate coatings typically contain a complex blend of clay and mineral types. The first three

clays were obtained from The Source Clays Repository from the Clay Mineral Society (CMS). CaM was created by exchanging sodium (Na) for Calcium (Ca) from the NaM. The sodium cations were exchanged by immersing the clay in a 1 N solution of $CaCl_2$ for 6 hours with agitation. This procedure was followed by a dialysis process (placing the suspension in dialysis tubing in distilled deionized water) of 24 hours to remove the excess Ca^{2+} and Cl^- ions. Therefore, the CaM obtained should have the same characteristics as the precursor NaM with the only difference being the nature of the exchangeable cation. The chemical composition of the clays was provided by the CMS.

As seen in Table 1, these four clays show very different hydration properties and cation exchange capacities (CECs).¹⁷ Both CaM and NaM have a large capacity to absorb water and swell. The NaM, when immersed in water, suffers a destacking process; in other words, individual silicate layers separate from each other. The CaM only shows a crystalline swelling process where the water is able to enter principally between the layers that formed the structure of the particles and separate them to a finite distance. Finally, illite and kaolin are clays with very low water adsorption and do not suffer swelling.¹⁶ Thus, these four clays represent the range of water absorption from nonswelling to crystalline swelling to larger degrees of swelling.

Aggregates and cement—An igneous coarse aggregate from Jackson County, WI, with easily removed natural coatings, was selected to be used in the preparation of manufactured clay-coated coarse aggregates. The fine aggregate used in this study was glacially-derived quartz-rich sand from South Central Wisconsin.¹⁸ This material did not contain appreciable amounts of clay minerals. The cement used was a Type II Cement.

Methods

Coating of coarse aggregate with clays—The clay coatings on coarse aggregates were prepared by the method known as dip coating. A stable suspension of the clay was prepared by adding the clay to deionized water (18.2 MΩ.cm resistivity at 77°F [25°C]) and stirred until all the clay became a part of a stable suspension. Suspensions with different concentrations of solids were used to coat the aggregates to study the influence of this variable on coating thickness.

The percentage of clay covering the surface of the aggregate was varied and adjustable by a combination of suspension withdrawal speed, the concentration of clay in the suspension, and the number of times that the aggregate was subjected to this coating procedure. Trials were done to ensure that the process was controlled and repeatable. The final concentration of the clay suspension used and the numbers of dip cycles (held constant) are reported in Table 1. While the overall intent was to achieve relatively equal amounts of each aggregate coating, this objective was confounded by the significantly different adhesion characteristics of each clay.

Despite the introduction of the clays as aggregate coatings, it is expected that due to the mixing sequence followed in the experiments (first aggregates and water, and then cement powder), part of the coating will be detached. In previous work done with same clay coatings, it was established that a fraction of the clay will enter the water phase before the dry cement is added.¹⁹ The fraction of detached clay depends on its nature: NaM mostly remains on the aggregate upon mixing (10 and 20% detached, at a pH of ~7 and 12, respectively), CaM and kaolin detached very readily and entered the water phase (CaM: 69 and 77% and kaolin: 50 and 79%

Table 2—Batch description, clay coating characterization, and tests' fresh concrete properties

Batch ID	w/c	P200, %	CCT	MBV	MMBV	AEA	Slump, in. (mm)	Unit weight, lb/ft ³ (kg/m ³)	Air content, %
Control	0.45	0	100	0	0.000	200.0	3 (76.2)	143.7 (2301.8)	5.8
NaMI	0.45	1.45	66	15.8	0.229	459.5	0	140.7 (2253.8)	4
NaMII	0.54	1.42	66	15.8	0.224	486.5	1/2 (12.7)	164.8 (2639.8)	5.5
CaMI	0.45	0.79	94	106.6	0.843	540.5	3/4 (19.0)	142.8 (2287.4)	2.5
CaMII	0.63	0.75	94	106.6	0.800	189.2	7 (117.8)	155.2 (2486.1)	7
Illite	0.45	0.4	95	6.6	0.027	351.4	2 3/4 (69.8)	164.8 (2639.8)	5.5
KI	0.45	0.68	94	6.7	0.046	243.2	2 (50.8)	165.7 (2654.2)	5.6
KII	0.47	0.7	94	6.7	0.047	189.2	4 (101.6)	157.2 (2518.1)	6.5

for a pH of ~7 and 12, respectively). Therefore, depending on the nature of the clay, its influence will not be only circumspect to the interfacial transition zone (ITZ) but also to the bulk area of the concrete.

Microfine coating monitoring tests—The coatings of the coarse aggregate samples were characterized with established monitoring tests including P200, CCT, and MBV. Finally, the MMBV results were evaluated.

P200 is the most common method for quantifying the amount of microfines ($\leq 75 \mu\text{m}$) in mineral aggregates and refers to material passing the No. 200 sieve. The maximum amount of P200 material recommended by ASTM C33 in coarse aggregates is 1.5% of mass when the material is free from deleterious substance, such as certain types of clays or shale.

CCT establishes the relative amount of clay-sized particles clinging to the aggregate by measuring the sedimentation of microfines in a solution of glycerin and calcium chloride. The amount of fines that sediments in a determined time is used to calculate a cleanliness value, which is indicative of the particle size, and mineralogy of specific type of clay minerals.²⁰ The height of the sediment in a tube is measured and given a cleanliness grade from 0 (dirty) to 100 (clean). Lower cleanliness values (longer time to settle) are given to aggregates with smaller particles and/or clay minerals with macroscopic swelling. A minimum cleanliness of value of 75 on the coarse aggregates is specified by the California Department of Transportation to avoid problems in concrete associated with microfines.

MBV is a tool to estimate the exchange capacity of a clay. The method is based on the unique properties of certain clay minerals to absorb the methylene blue. A water suspension of the P200 material is titrated with this dye. The method is susceptible to operator interpretation. A limit of 10 mg/g was established by the French concrete specifications, as the maximum MBV allowed for microfines extracted from fine aggregate to be used in concrete production.¹³ In recent studies, Quiroga et al.⁶ proposed a lower MBV limit; they have shown that microfine coatings with an MBV index above 3 mg/g for dry sieving and 5 mg/g for wet sieving will likely provoke high water demand in concrete mixtures.

Mixture design—The proportions of all of the mixtures prepared in the study were based on the WisDOT Grade A concrete mixture design. For each batch, the cement content was 20.9 lb/ft³ (334.8 kg/m³) with a coarse aggregate; fine aggregate; and net w/c of 3.5, 2, and 0.45, respectively. The target air content was 6.0 ± 1%. Increased air content in the mixture was aided through the use of a Vinsol resin air-entraining agent (AEA). To ensure a constant w/c, the amount of water added to each concrete batch was adjusted to reflect the absorption of the coarse and fine aggregates according to

ASTM C127 and ASTM C128, respectively. The absorptions of water on the aggregate microfine coatings were neglected when the workability of each mixture was not altered by the presence of these coatings. Only on those batches where the presence of the coatings induced obvious changes in workability was an extra batch prepared with additional water to increase workability. This was the case of batches prepared with aggregates coated with kaolin, NaM, and CaM, where 4, 20, and 40% extra water was necessary to increase the concrete's workability to an acceptable level (refer to Table 2). These extra amounts of water were estimated based on water absorption capacities of the clays in high relative humidity atmosphere.

Concrete batches were mixed in a 3 ft³ (0.085 m³) drum mixer using the ASTM C192 procedure. Following mixing, air content and slump were determined under ASTM C231 Type B and ASTM C143, respectively. A sufficient amount of concrete per batch was prepared to cast: 1) eight 4 x 8 in. (102 x 203 mm) cylinders for compressive and tensile strength tests; 2) three 4 x 4 x 11 in. (102 x 102 x 280 mm) prisms for shrinkage tests; and 3) three 3 x 4 x 15 in. (76 x 102 x 381 mm) prisms for freeze-thaw durability tests.

All of the specimens were consolidated, covered with wet burlap and a plastic sheet for 24 hours, removed from molds, and stored at 74°F (23°C) and a relative humidity of 100% until testing.

Hardened concrete tests—All batches were tested for compressive strength (ASTM C39), tensile strength (ASTM C496), drying shrinkage (ASTM C490), and freeze-thaw durability (ASTM C666). To better compare the compressive strength of batches having different air content, the compressive strength of each specimen was adjusted to a nominal air content of 6.0% using the compressive strength versus air content relationship recommended by ACI.²¹

The air void content and the spacing factor of hardened concrete of the most representative batches were analyzed using a microscope at low magnification. Specimens were sawed from the original concrete sample and analyzed under the microscope. Several images of 800 x 600 pixels were taken from each sample and merged to create profiles.

The air void content was measured by a 2D analysis of a 0.22 in.² (3570 mm²) profile and image analysis software. The spacing factor was determined using profiles of approximately 1.2 in. (30 mm) long by measuring the transverse length through the paste divided by four times the total number of air voids intersected. The spacing factors were determined in compliance with ASTM C457 with the exception that the linear traverse distance of 1.2 in. (30 mm) was significantly less than that required in the standard protocol. This deviation was partly compensated by examining three different specimens from the same concrete prism. Based on

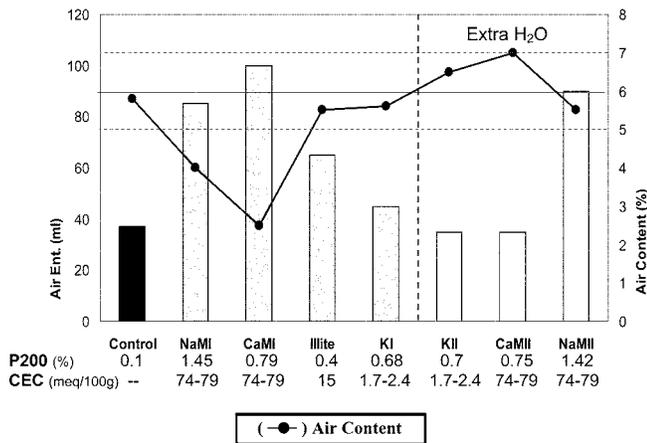


Fig. 1—Effects (bars) in air entrainment and air content of clay-coated batches.

the lack of variability of results for the three specimens, it was determined that further specimens were not needed to reasonably determine the spacing factor or air void for the purposes of this research.

To compare the characteristics of each batch against the control, that is, obtaining a numerical indicator of performance and due to the size of the sample population, Wilcoxon (Mann-Whitney) tests were performed by comparing the median mechanical properties of the control against the batches of interest.²²

RESULTS AND DISCUSSION

Clay coating characterization tests

The manufactured clay coatings were characterized with traditional monitoring tests (CCT and MBV) before entry to the mixer. The results are shown in Table 2. As expected, the NaM fines failed the CCT criterion (< 75) with a low cleanness value of 66. This can be explained due to the tendency of this clay to exhibit a destacking process in water, thereby forming a gel structure that does not sediment. Also, this clay did not pass the MBV test because the measured index was above 10 mg/g. The same montmorillonite, but with calcium instead of sodium as the exchangeable cation, was able to pass the CCT with an index of 94. This clay only suffers a crystalline swelling when it is suspended in water and it is able to sediment. When the clay was subjected to the methylene blue test, the results were not as satisfactory. In this case, the CaM fails with a MBV value of 106.7 mg/g. Finally, the illite and kaolin had similar results for both monitoring tests. They both met the requirements of CCT with an acceptable cleanness values—95 and 94, respectively—and also met the requirements of MBV with slightly higher values of 6.6 and 6.7 mg/g, respectively. Neither of these clays displayed obvious swelling properties in water. Based on the recent limits proposed by Quiroga et al.⁶ and these results, all of the clays could impact slump and workability during concrete placement. It is not known if the scales of the CCT and MBV are linear with respect to their impact on concrete.

It is well known that methylene blue cations can be used to determine the CEC of the clays;³⁻²⁵ however, the obtained MBV, with the exception of the kaolin, corresponded with smaller CEC than those reported in the literature. These discrepancies can be attributed to the imprecise methodology to detect the end point of the titration because it depends on the operator subjectivity and therefore can lead to the detection

of false end points. The inaccuracy is exacerbated with both montmorillonites. Because CaM was prepared from the NaM, both clays had the same CEC (74 to 79 meq/100g). It was logical to expect more similar results of the MBV, and even a higher value for the NaM because the sodium is more easily exchanged by the methylene blue molecule than the calcium.²³ The MBVs were 106.7 for CaM and 15.8 for NaM, which corresponds with 33 and 5 meq/100 g of CEC, respectively. These large differences are again related with the end point determination. The protocol establishes that a drop containing a suspension of the material is deposited in a filter paper. The maximum quantity of compound absorbed is determined when a blue halo corresponding to the presence of methylene blue cations on the water phase appears on the area surrounding the deposited drop. As was mentioned previously, the macroscopic swelling, suffered by the NaM, significantly increases the exposed area of small clay unit layers and, thus, the superficial adsorption of methylene cations.²⁶ The diffusion of these tiny particles into the water phase surrounding the deposited drop can induce an earlier end point determination with the NaM than with the CaM.

Effect on fresh concrete properties

Once the concrete mixtures were prepared, parameters such as air entrainment, slump, unit weight, and air content were measured to understand and quantify the impacts of clay coatings on fresh concrete properties. Values for these parameters are reported in Table 2.

All manufactured clay coatings decreased the slump with the exception of the illite. The most dramatic decreases were registered for the NaMI and CaMI coatings, the former producing a stiff mixture with no slump and the latter a 0.75 in. (19.0 mm) slump. The 0.70% of kaolin coating produced a decrease in slump of 1 in. (25.4 mm) with respect to the control. The addition of extra water in the mixtures containing these three clays rendered better workability. The most dramatic change was observed in the CaMII batch, where a 40% increase in water content produced an excessive slump of 7 in. (177.8 mm). Finally, the coating of illite with a P200 of 0.40% did not change the slump of the mixture with respect to the control. This behavior can be attributed to the type of clay and to the low amount of coating present in the aggregate, reflected by a P200 of less than 0.5%. In view of the aforementioned results, one can conclude that the influence of the clay coatings on concrete slump depends on the nature of the clays and the amount of the coating. The influence of the nature of the clay is clearly illustrated when the KI and CaMI samples are compared. In this case, both batches have a similar value of P200—approximately 0.70%—but a different CEC and therefore a different water absorption capacity. The results show that the decrease in slump is higher in clays with high CEC and therefore high water adsorption capacity.

As illustrated in Fig. 1, some of the natural clay coatings have an impact on the required air entrainment dosage and the final amount of air entrained. The higher impact was produced by the coatings with higher water absorption capacity such as NaMI and CaMI. The air content achieved in batch NaMI was 4% and 2.5% in batch CaMI with both being well under the target air content, despite additions of higher amounts of AEA. These two batches were only able to meet the air content requirements when extra water was added to maintain workability. When 20% extra water was added to NaMII batches, 3.06 fl oz. (90 mL) of AEA was

Table 3—Hardened mechanical concrete properties

Batch ID	Compression strength at 28 days		Tensile strength at 28 days		Shrinkage, days (microstrain)				ASTM C666 DF, %	
	psi (MPa)	COV	psi (MPa)	COV	57	COV	120	COV	16 cycles	420 cycles
Control	4735 (32.6)	5.0	397 (2.7)	15.6	50.0	9.2	61.3	6.8	97.6	98.5
NaMI	563 (3.9)	13.1	82 (0.7)	35.4	84.3	0.7	94.3	1.2	4.0	0.0
NaMII	2194 (15.1)	4.0	255 (1.7)	14.9	78.7	3.7	92.7	3.3	—	—
CaMI	1189 (8.2)	11.2	138 (0.9)	21.7	152.6	44.3	159.3	43.4	—	—
CaMII	2495 (17.2)	3.4	236 (1.6)	3.0	83	1.1	100.3	17.3	—	—
Illite	3960 (27.3)	2.6	333 (2.3)	4.5	54.7	1.1	62.3	7.7	—	—
KI	4108 (28.3)	3.0	379 (2.6)	8.4	61.3	5.0	74.3	5.1	96.8	98.7
KII	2846 (19.6)	4.9	260 (1.8)	18.5	60.0	3.3	71.0	2.4	—	—

Note: COV is coefficient of variation.

enough to produce an air content of 5.5%. In the case of the CaMII samples, 40% extra water resulted in an air content of 7% with only 1.19 fl oz. (35 mL) of AEA added. The 4.4% extra water added in batch KII, made it possible to achieve a higher air content than for KI, 6.5% versus 5.6%, respectively, despite having less AEA, 1.19 versus 1.53 fl oz. (35 versus 45 mL).

Effect on compressive strength

The compressive strength of the all of the batches was measured after 28 days of curing. The results are presented in Table 3. Clay coatings can be separated into two large groups in relation to their effect on the compressive strength of concrete—the ones with strong impact and the ones with virtually no impact. NaM and CaM clays belong to the first group; concrete batches containing these clays showed a large decrease in compressive strength of approximately 88% for NaM and 75% for CaM, with respect to the control. This could be explained by the fact that both types of clays have a high water absorption capacity and during the mixing process, they captured a large portion of the mixing water, resulting in the formation of a thick coating of mortar around the coarse aggregate particles. This resulted in low slump concrete that could not be readily consolidated. This behavior confounds the usual understandings about w/c and strength. While the water is captured and inhibits the workability and cohesiveness of the mixture, it is less clear to what degree the water is available for cement hydration. It is likely that these clay coatings further increase the w/c in the interfacial transition zone, creating a weaker interface that is not offset by a decrease in the w/c of the surrounding paste. The addition of 20% extra water for batches with NaM improved workability and actually increased the compressive strength from 563 to 2194 psi (3.9 to 15.1 MPa) (refer to NaMI versus NaMII). A similar behavior was observed for batches containing CaM; 40% of extra water increased the compression strength from 1189 psi (8.2 MPa) (CaMI) to 2495 psi (17.2 MPa) (CaMII). This unusual behavior could be explained by the fact that the addition of extra water yielded a mixture that could be consolidated; this improved consolidation led to an increase in the overall compressive strength.^{27,28} The final result is a stronger specimen with respect to the batch with no extra water, but weaker with respect to the control.

Kaolin and illite coatings belong to the group of clay coatings with virtually no impact on compressive strength. The statistical analysis suggests that results from coated batches and control are essentially equal. Aggregate coatings consisting of clays with low water absorption capacities had, at most, a small impact on compressive strength even at P200 values

approaching specification limits. In contrast with the previous group of clays, the addition of extra water in these mixtures was detrimental to compressive strength. In batches of KII, with 4% more water than KI batches, a decrease of 30% in the overall compressive strength at 28 days of curing was observed.

Effect on tensile strength

The 28-day tensile strength values for all batches are presented in Table 3. The tensile strength of clay-coated samples showed a similar behavior as observed for compressive strength. The two clay coatings with high impact on compressive strength also dramatically decreased the tensile strength. Batches NaMI and CaMI suffered a loss in tensile strength of 80% and 65%, respectively, with respect to the control for reasons similar to those expressed with regard to compressive strength. The negative effects of both coatings were partially ameliorated by the addition of extra water. The tensile strength rose from 82 psi (0.7 MPa) in the NaMI batch to 255 psi (1.7 MPa) in the NaMII batch, and from 138 to 236 psi (0.9 to 1.6 MPa) in Batches CaMI and CaMII, respectively. Kaolin and illite coatings did not appear to impact the tensile strength of the concrete. The Wilcoxon test result indicated that there were no differences between the kaolin containing specimens and the control, although the same comparison between illite and the control did not show such strong evidence. As shown in Table 3, the addition of 4% water in KII significantly decreased the tensile strength with respect to the control.

Effect on drying shrinkage

The drying shrinkage of all the batches was monitored over a period of 3 months. Table 3 shows the shrinkage measured for the concrete samples at 57 and 120 days. The shrinkage with the four types of clay coating samples fell within a wide range, between 60 microstrain units for the innocuous clay, and up to 160 microstrain units for the most harmful clays. The illite coating batch with a 0.4% value for the P200 test did not suffer a significant change in shrinkage with respect to the control; however, the batch containing kaolin, with a P200 of 0.7%, underwent a increase in shrinkage—15%—at 120 days with respect to the control ($p = 0.1$). Nevertheless, NaMI and CaMI were the batches that experienced the greatest increase in shrinkage, from 66 microstrain units in the control up to 94 microstrain units for NaMI and 160 microstrain units for CaMI. The effect of CaM on shrinkage was even greater with respect to that of NaM when taking into account the value of P200 in these batches: 0.79% in the case of CaMI versus 1.49% in the

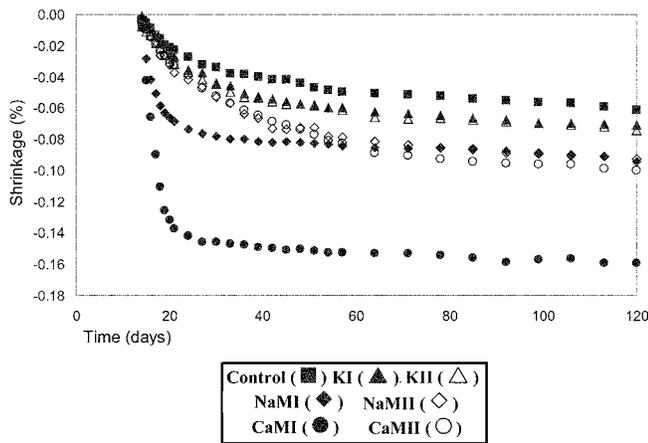


Fig. 2—Drying shrinkage evolution.

NaMI batch. Both clays have a similar structure and CEC capacity. The only difference exists in the nature of the exchangeable cation. The difference in the nature of the exchange cation produces a very different hydration behavior of these clays in water media. NaM will suffer a destacking or defoliation process known as macroscopic swelling. CaM will tend to increase the size of its particles in one direction due to the incorporation of water molecules between the layers of its structure, this process is called crystalline swelling. The values of shrinkage at 120 days suggest that the crystalline swelling process, as shown with sample CaMI, has a larger impact than the macroscopic swelling.

The effect of extra mixture water on the observed shrinkage is shown in Table 3. In contrast to what would be expected, the addition of extra water did not increase the amount of shrinkage. The addition of 4% and 20% extra water in Batches KII and NaMII, respectively, did not change the value of drying shrinkage at 120 days (compared with values for Batches KI and NaMI); however, the addition of 40% extra water in the case of CaM containing batches decreased the shrinkage by 37% at 120 days. An analysis of the shrinkage of the concrete batches as a function of time, presented in Fig. 2, yields additional information about the drying shrinkage mechanism produced by adding extra water. The batches fabricated with montmorillonite coatings and extra water had a slower shrinkage development. For example, 85% of the total shrinkage recorded for Batch NaMI was achieved in the first 33 days, whereas in Batch NaMII, made with 20% more water, the same amount of shrinkage was achieved after 57 days of testing. A similar effect was observed in the case of Batch CaMI for which 92% of the total shrinkage was reached at 27 days, whereas for Batch CaMII, with 40% extra water, 92% of the shrinkage was attained only after 78 days. As mentioned previously, the addition of extra water in the batches containing montmorillonite increases the plasticity of cement paste and reduces the large voids between coarse aggregates. In other words, the specimens consolidated with less void content than the batches with no extra water. The evaporation of the water trapped inside of the clays, which is the major contributor to the overall shrinkage in these denser samples, is significantly slower and, thus, the lower rate of shrinkage.

Effect on freeze-thaw durability

The study of freeze-thaw durability was performed on specimens from only two batches: KMI and NaMI. These two clay coating specimen types were selected due to their largely different effects on the properties of concrete. Kaolin represents those clays with low water adsorption, no significant impact on compression and tensile strengths, and low air dry shrinkage. NaM represents those clays with high water absorption and high impact on the mechanical properties of concrete. The durability factor (ASTM C666), as measured via the relative modulus of the samples, were monitored during 420 freezing-and-thawing cycles. Results of this study are presented in Table 3.

No statistical differences were found between the kaolin sample and the control with regard to freeze-thaw durability measurements. The presence of this coating had no effect on stiffness and weight durability under these experimental conditions. A much different result was obtained when the sample contained the NaM clay. After 16 cycles, the stiffness durability dropped to under 60% of the initial stiffness, and the test was aborted at this time, consistent with ASTM C666. Thus, one could say that coatings with high water absorption capacities produced a concrete with very low durability characteristics.

Air void system results

The determination of air content in hardened concrete was conducted for five samples using micrographs processed with image analysis software and following the general procedures of the ASTM C457 linear traverse method but with shorter traverse distances. These samples were divided in three groups: 1) one batch prepared with cleaned coarse aggregate, control; 2) two batches using manufactured clay-coated aggregates, NaM and kaolin with a w/c of 0.45; and 3) batches prepared using the clay-coated aggregates of Group 2 but with extra mixture water. As in the freeze-thaw durability study, NaM and kaolin clay coatings were selected because of their large differences in water absorption properties and effects on concrete. The comparison between the fresh and hardened air content measurements is shown in Table 4.

The most striking result is the high value—28.2%—for the air content measured in the NaMI hard concrete batch ($w/c = 0.45$). This was due to the high quantity of large air voids between coarse aggregates and the overall lack of consolidation. This high level of entrapped air was attributed to the high water absorption of the NaM coating, resulting in an unusual accumulation of mortar around the coarse aggregate particles. This problem was subsequently mitigated by the addition of extra water. The addition of 20% of extra water improved the workability of the concrete, and reduced the entrapped air in the hardened concrete (decreased from 28.2 to 4.9%). As expected, the effectiveness of the AEA increased as the viscosity of the fresh mixture decreased, as the air content in fresh concrete was slightly higher for the NaMII batch (5.5% versus 4.0%). It was not clear that the decreased effectiveness of the AEA could be completely contributed to the decreased viscosity of the mixture or whether a chemical effect from the clay coatings was also present. Finally, the air voids contained in hardened concrete for both kaolin-coated batches, one at 0.45 w/c and the other with 4% of extra water, were in accordance with the results obtained for the air content in fresh concrete. As expected, this clay had only a slight effect on the effectiveness of the AEA; the mixture demanded more AEA than the control mixture to achieve the

same level of air content in the fresh concrete. Also, the addition of extra water improved the effectiveness of the AEA and higher air contents resulted.

Based on results shown in Table 4, the presence of either clay coating tended to increase the spacing factor with respect to the control concrete. The statistical analysis of the results using the nonparametric test attributed a low probability to the assumption of clays and control batches being equal. A statistical increase in the spacing factor was registered for the NaM coatings, from 0.10 to 0.32 ($p = 0.1$), indicative of a concrete with a poorer freeze-thaw durability resistance. A similar phenomenon was observed for the concrete containing the kaolin coating; but in this case, the increase in the spacing factor was lower—0.10 to 0.22 ($p = 0.1$)—and the value was close to that recommended for a durable concrete. The NaM sample displayed a poor freeze-thaw resistance while kaolin maintained a similar resistance as control. This increase in the spacing factor due to the presence of these types of clay coatings could be explained by the tendency of these materials to decrease the effectiveness of AEA. These clays tend to absorb mixing water, so the ability of AEA to create bubbles was potentially reduced.

Finally, the effect of the addition of extra water on the spacing factor was determined by studying Batches NaMII and KII. In both cases, the extra amount of water significantly improved the spacing factor. In particular, the spacing factor decreased more than half in both coated samples, from 0.32 for NaMI to 0.17 for NaMII, and from 0.22 for KI to 0.07 for KII.

Evaluation of monitoring aggregate cleanness tests

The abilities of the most common tests used to predict the deleterious effects of microfine coatings were examined to foresee the influence of the aggregate coatings of this study in the quality of concrete. The evaluation was performed by correlating the value of each test for the different coated aggregates with the measured values of physical properties of both hardened and fresh concrete prepared with these aggregates. The population of samples was limited to those prepared with the same w/c (0.45) to eliminate the effect of extra water addition. The tests under evaluation were

ASTM C117, California Test 227, ASHTO TP57, and the modified methylene blue value index (MMBV) with related results from ASTM C117 and ASHTO TP57. Results from these analyses are reported in Table 5.

The values of the correlation coefficients reveal that the P200 value of the ASTM C117 test was the poorest predictor of all of the concrete properties analyzed, except for slump. The correlation coefficient value ranged between 0.15 and 0.52 for AEA demand, fresh air content, and concrete strength, and durability while for slump the correlation coefficient increased in magnitude to -0.72 . The California Test 227 anticipated the properties of the concrete better than the P200, except for shrinkage. This test showed the highest correlation coefficient with values for slump ($R = 0.74$) and concrete durability ($R = 0.94$) compared to the rest of the tests evaluated in this study. The correlation was not as strong with values for AEA demand and fresh air content, -0.38 and 0.32 , respectively. The lack of correlation between the values for this test and the values for shrinkage ($R = -0.09$) is worth mentioning. A further analysis of the correlation between these two data sets shows that by removing from the study the CaM containing system, the correlation between the CV test and shrinkage values improves up to 0.93. Indeed, the concrete batch prepared with CaM-coated aggregate (CaMI), that passed the California Test 227 with a CV of 94 (refer to Table 2), suffered a very large drying shrinkage (refer to Table 3). Thus, it can be said that the California test was not a good predictor of the deleterious character of CaM microfines. The particles of CaM were large enough to easily sediment in aqueous media, resulting in high CV values. The fact that these clay particles were able to absorb mixing water between their layers and expand in one direction and latter contract over the hydration process of the cement is the likely explanation for the large drying shrinkage. After concrete sets, the environment of the clay particle becomes drier; thus, the clay particles desorb water and contract. The contraction of the particle is manifested as a high shrinkage in the overall concrete structure. Based on these facts, it can be said that the California Test 227 was unable to detect the impact of clay coatings with crystalline swelling on shrinkage.

In comparison with California Test 227, the MBV was an excellent indicator of shrinkage and air content, with 0.98 and -0.91 values of R , respectively, and also a good indicator of AEA demand with a 0.77. Finally, the combination of P200 and MBV values represented in the MMBV indicated that, in general, this index was the best indicator when it can be conducted in a repeatable manner. The MMBV showed strong correlations with fresh air content, shrinkage, concrete durability, AEA demand, and both compression and tensile strengths.

Table 4—Fresh, hardened air content and spacing factor

Batch	P200, %	Fresh air content, %	Hardened air content, %	Spacing factor, in. (mm)	Standard deviation
Control	0.1	5.8	6.9	4.00×10^{-3} (0.10)	0.02
NaMI	1.45	4.0	28.2	12.6×10^{-3} (0.32)	0.04
NaMII	1.42	5.5	4.9	6.69×10^{-3} (0.17)	0.04
KI	0.68	5.6	4.9	8.66×10^{-3} (0.22)	0.05
KII	0.7	6.5	7.0	2.27×10^{-3} (0.07)	0.02

Table 5—Correlation coefficients (R) for batches with 0.45 w/c

Test	Slump	AEA	Fresh air cont	Strength		Shrinkage, 120 days	Stiffness, 300 cycles	Weight, 300 cycles
				Compressive	Tensile			
P200	-0.72	0.23	-0.41	-0.49	-0.43	0.15	-0.52	-0.52
CV	0.74	-0.38	0.32	0.70	0.69	-0.09	0.94	0.94
MBV	-0.54	0.77	-0.91	-0.65	-0.63	0.98	-0.86	-0.84
MMBV	-0.65	0.81	-0.96	-0.73	-0.72	0.99	-0.91	-0.90

CONCLUSIONS

Effects of clay coatings in concrete performance

Clay coatings on coarse aggregates impact the properties of fresh and hardened concrete samples even when they are present in amounts under the P200 limit for coarse aggregate of 1.5%. The extent and nature of the impact depends on the nature and the quantity of the clay present. Clays with a higher CEC (Na and Ca montmorillonite) will typically produce higher impacts on fresh and hardened concrete properties. Montmorillonite group clays, with a 0.76% P200 value, tended to absorb high amounts of water and increase the stiffness of the plastic concrete mixtures. This stiffness increase led to unworkable concrete and samples with visible voids. This effect led to concretes having lower compressive and tensile strengths, and a lower freeze-thaw durability. While the higher shrinkage was provoked by the water absorption of the clay particles and the release of moisture after the hardening stage of concrete was achieved. The addition of extra water in mixtures containing this type of clay to maintain workability provided an improvement in compressive and tensile strength but always with values lower than the control. In contrast, one of the clays with a low CEC (kaolin) and with a 0.7% P200 value only affected workability by decreasing the slump. Illite, under the conditions of this study, with a small P200 value, did not affect workability. However, the statistical analysis of compressive strength in mixtures with both clays shows weak evidence that their results were generally equal to the control, meaning that higher P200 values of these two clays could lead to a decrease in compressive strength in field conditions, particularly those that may not be as ideal as laboratory curing. The addition of extra water in the batch containing kaolin coatings produced a deterioration of both compressive and tensile strengths of the concrete.

The study of the drying shrinkage revealed two main observations: 1) the clays with crystalline swelling caused highest values of drying shrinkage in concrete; and 2) the addition of additional water did not cause significant increases in the final shrinkage. The shrinkage values for 0.45 w/c and with additional water for NaM and kaolin-coated aggregates were equal. In the case of CaM, the batch with additional water displayed a final shrinkage value at 120 days less than the batch at 0.45 w/c. It was also noticed that the addition of extra water delays the kinetics of drying shrinkage in all tested samples.

Finally, an increase in the air entraining agent demand was observed when clay coatings were present in the mixtures, with the exception of the illite coating. The most dramatic cases were for clays with high CEC. The properties of the AEA additive were inhibited by the presence of these clays because the addition of greater amounts of AEA were unable to produce mixtures with sufficient air contents. This was eventually ameliorated by the addition of extra water. Two mechanisms are proposed to explain this phenomenon: 1) the high water absorption capacity of these clays leads to insufficient mixing flow for the AEA to stabilize air bubbles; and 2) a specific interaction between AEA molecules and clay particles inhibits the AEA molecules from stabilizing air bubbles.

Evaluation of current monitoring methods to detect microfines coatings

Four main conclusions can be drawn from the evaluation of the current methods for detecting or limiting microfines.

1. The P200 index does not and cannot reflect the detrimental or innocuous nature of the coatings. We have shown that the extent and impact of microfines in concrete not only depends on quantity but also in the nature of the microfines.

2. It has been demonstrated that both CV and MBV are better predictors of the effect of microfines in concrete than the P200 index.

3. The CV index is unable to foretell shrinkage in concrete made with aggregates coated with clays having crystalline swelling.

4. The MMBV is the method that best predicted the quality measures of the concrete in this study. While the P200 test combined with the MBV test provides the best available prediction of concrete properties, the methylene blue test is susceptible to variations resulting from operator technique and interpretation. Given this situation, the combination of both tests cannot be strongly recommended for implementation in monitoring operations. The complimentary rapid and practical test needed for use by contractors and transportation officials does not exist and requires development.

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