WISCONSIN HIGHWAY RESEARCH PROGRAM # 0092-04-12

**EXPANDED STUDY ON THE EFFECTS OF AGGREGATE COATING
AND FILMS ON CONCRETE PERFORMANCE**

FINAL REPORT

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16. Abstract

The WisDOT sponsored study entitled: "Effects of Aggregate Coatings and Films on Concrete Performance", I.D: 0092-00-07, found that clay coatings showed a deleterious impact in concrete compared with other microfine mineralogy such as dust or carbonates. The principal aim of this research was to complement the previous project by identifying the primary variables that govern the effects of clay microfine coatings on concrete pavements and to use this knowledge to improve the present aggregate monitoring situation in Wisconsin. The materials selected for this research were a two naturally-coated igneous aggregates located near Eau Claire and an igneous clean coarse aggregate from Black River Falls which was lab-coated with four different clay suspensions (kaolin, illite, sodium montmorillonite and calcium montmorillonite). A total of ten batches: a control, two containing natural coatings and 4 containing each one of the select clays as coarse aggregate coatings at a 0.45 w/c ratio were prepared along with 3 additional batches with extra water to maintain workability. The major findings are that the effects of microfines in concrete are not only dependent on the amount of microfines but also on their nature. The methylene blue test together with P200 to calculate the modified methylene blue value is the best predictor of the influence of coatings on concrete performance, but the methylene blue test presents practical difficulties for WisDOT implementation and a new test is needed.

| 17. Key Words
Concrete, Coarse aggregate, microfines, coatings, P200, California Cleanness Test, Methylene Blue value, slump, compressive and tensile strength, drying shrinkage, freeze-thaw durability. | 18. Distribution Statement

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Executive Summary

Project Summary

During last few years, some problems have been reported by the Wisconsin Department of Transportation on concrete pavement construction. Some of the symptoms associated with these problems were stiffness in the mixture, cracking at aggregate-cement paste interface and low strength in concrete cores all in the presence of coarse aggregate coatings. State engineers and concrete pavers have speculated that one of the causes behind these problems could be the presence of coarse aggregate coatings with microfines contents under the P200 specification limit. Based on these problems, in October 2000, the WisDOT sponsored a study entitled: "Effects of Aggregate Coatings and Films on Concrete Performance", I.D: 0092-00-07. The main conclusions of this report were: first, the sample population used was not large enough to understand the extent of the aggregate coating across the entire state, so more sampling was recommended. Second, clay coatings showed a deleterious impact in concrete compared with other microfine mineralogy such as dust or carbonates. The development of this research was conceived to complement the previous project. This investigation was focused on clay coatings since they were identified as the most deleterious group. The main focus was to identify the primary variables that govern the effects of clay microfine coatings on concrete pavements and to use this knowledge to improve the present aggregate monitoring situation in Wisconsin.

Background

Microfine materials in concrete are defined as those able to pass through No. 200 sieve (75 µm). This fraction of material is normally found as a part of the aggregates used in concrete production. The mineralogy of these microfines has been studied for a long time (Goldbeck 1933). They could be classified into three major types: stone dust, clay minerals, or calcium carbonate. A recent study performed by Gullerud and Cramer, found that common mineralogy of microfines in Wisconsin falls under the previous classifications, and the clays are the fraction with higher deleterious potential (Gullerud 2002).

The characteristics of the clay fraction vary depending on the type of clay mineral. For example, some types of clay are held so tightly to the aggregate surface that they may not be displaced during washing, while other types of clay may be released into the water and are removed during aggregate washing or concrete mixing (Goldbeck 1933). Therefore, the effects of clays in concrete can be located in two different areas. First clay minerals, which weakly adhere to aggregates, will be dispersed in the mixing water and therefore will be integrated in the cement paste. Second, those types of clay minerals that are strongly bonded to the aggregate surface will remain mostly located at the aggregate surface after the mixing process and therefore may disrupt the aggregate-cement paste bond (Goldbeck 1933, Neville 1996, Schmitt 1990).

Research Plan

The overall project is divided into three main tasks. The first task involved strengthening the base understanding of the impacts of clay coatings on concrete performance and the second and third tasks were aimed at linking the theoretical results with actual field situations in Wisconsin.

1. Study the effects of clay coatings in concrete: a) characterization of detachment mechanism during the mixing process; b) effects in the interfacial transition zone (ITZ); and 3) determine the impact of these coatings on some of the most significant physical properties in concrete.
2. Evaluation of the current monitoring method employed to detect these coatings.
3. Characterization of properties from concrete made with real Wisconsin aggregates with and without clay coatings.

The materials used in part 1 were an igneous clean coarse aggregate from Black River Falls (Jackson County) and coated with four different clay suspension (kaolin, illite, sodium montmorillonite and calcium montmorillonite). These four clays present very different hydration properties. Kaolin and illite have a smaller and medium water absorption capacity, respectively. Both calcium montmorillonite (CaM) and sodium montmorillonite (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 has a crystalline swelling process where the water is able to enter principally in between the layers that form the structure of the particles. Finally, illite and kaolin are clays with very low water adsorption capacity and do not experience crystalline swelling

In part 3, two different coarse aggregates were identified as suitable for this research under the following premises: coarse aggregates commonly used in Wisconsin, and coarse aggregate with clay coatings. Finally, two coated igneous aggregate were selected both located near Eau Claire (Eau Claire). One was used in the construction of the Highway 53 where the microfine was a mix of dust and clay (Chlorite). The other one was used in the construction of the Highway 64 where the microfine was also a mix of dust and clay (Montmorillonite).

Research Process

The characterization of the detachment mechanism during the mixing process was modeled in part 1 by reproducing in a smaller scale the same mixing conditions of a 3 ft^3 concrete mixer in a Incubator Shaker Model G-27.

The effects of clay coatings in the interfacial transition zone (ITZ) were done by analyzing under scanning electron microscope (SEM) concrete samples sawed, polished and carbon coated. The samples studied were the two concretes containing natural coated aggregate and concrete containing manufactured clay coating (sodium montmorillonite and illite). Variables such as pore, unhydrated cement, and hydration products were analyzed in ITZ and bulk of each sample.

The impact of all coatings (natural and manufactured clays) on the most significant concrete properties was analyzed by preparing 6 batches with different microfines (Hw53, Hw64, Na

montmorillonite, Ca montmorillonite, illite, and kaolin) at 0.45 w/c ratio. The effect of addition of extra water to maintain workability was studied in 3 additional batches containing Ca montmorillonite, Na montmorillonite and kaolin, where 40, 20, and 4.4% of extra water was added, respectively. The target air content on all the batches was 6.0 ± 1 %. The proportions of all mixes were based on the WisDOT Grade A concrete mix design. The tests completed were slump (ASTM C143), unit weight (ASTM C138), fresh air content (ASTM C231), compressive (ASTM C39) and tensile (ASTM C496) strength, drying shrinkage (C490), freeze-thaw durability (C666).

Finally, the evaluation of the current monitoring method employed to detect these coatings was done 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.

Findings and Conclusions

Several conclusions are extracted from the current research project:

Part 1. Study the effects of clay coatings in concrete

a) When aggregates with clay coatings are used in the preparation of concrete, a fraction of the clay will enter the water phase before the dry cement is added. The degree of detachment depends on the nature of the clay. In addition, for a given clay detachment may depend on other variables, such as particle size, which was not explored in this research. The concentration of clay in the water phase before the dry cement is added will be a function of the nature of the clay and the original clay content of the aggregate. The presence of clays in the cement paste (equivalent to the cement bulk in concrete) influences the rate of the hydration reactions. The clay with macroscopic swelling (Na montmorillonite) is the most difficult to detach and decreases the rate of hydration. Clays with crystalline swelling (CaM) and no swelling (kaolin) are easier to detach and increase the rate of the hydration reactions.
b) The effect of clays in early hydration reactions depend on the nature of the clay. Pastes with NaM decrease the rate of hydration. CaM cement paste tends to increase the rate of hydration in concentrations equal or lower than 2.5% and decrease this rate when the concentration of clay is equal or larger than 5%. The presence of kaolin accelerates the hydration reaction in cement paste at any of the studied concentrations.
c) Clay coatings on coarse aggregates impact the properties of fresh and hard concrete samples even when they are present in amounts under the P200 limit of 1.5%. As in the other cases, the extent and nature of the impact depends on the nature and the quantity of the clay. Clays with higher Cation Exchange Capacity (CEC), such as Na and Ca montmorillonite, produce the higher impacts in fresh and hard concrete properties. Montmorillonite group clays, with a 0.76% P200 value, tend to adsorb high amounts of water and increase the stiffness of the plastic concrete mixtures. This stiffness in the mixture inhibits adhesion between cement paste and coarse aggregate. These effects lead to concretes with lower compressive and tensile strengths, and higher shrinkage and lower freeze-thaw durability. The addition of extra water in mixes containing this type of clay to maintain workability provoke an improvement in compressive and tensile strength but

always with values lower than the control. In contrast, one of the clays with low CEC (kaolin) and with a 0.70% P200 value only affects workability by decreasing the slump. The other clay, Illite, with a smaller P200 does not affect workability. However, the analysis of compressive strength in mixes with both clays shows weak evidence that their results are equal to the control, meaning that higher P200 values of these two clays could lead to a decrease in compressive strength. The addition of extra water in the batch containing kaolin coatings produced a deterioration of both strengths of the concrete.

d) The study of the drying shrinkage reveals two main facts: 1) the clays with crystalline swelling cause higher values of drying shrinkage in concrete and 2) the addition of extra water did not cause significant increases in the final shrinkage. The shrinkage values at 0.45 w/c ratio and with extra water for NaM and kaolin coated aggregates were equal. In the case of CaM, the batch with extra water displayed a final shrinkage value at 120 day less than the batch at 0.45 w/c ratio. It was noticed also, that the addition of extra water delays the kinetics of drying shrinkage in all tested sample.

e) An increase in the AEA demand was observed when clay coatings were present in the mixture, with the exception of the illite coating. The most dramatic cases were for clays with high CEC. The properties of the AEA appear to be inhibited by the presence of these clays since the addition of amounts of AEA were unable to produce mixtures with sufficient air contents. This was ameliorated by the addition of extra water. Two mechanisms are proposed to explain this phenomenon: 1) the high water adsorption capacity of these clays lead to an insufficient amount of water for the AEA to produce optimal results and 2) an interaction appears to be occurring between AEA molecules and clay particles.

Part 2. Evaluation of the current monitoring method to detect microfine coatings.

a) The P200 index is an index that does not reflect the detrimental or innocuous nature of the coatings. The extent and impact of microfines in concrete not only depends on quantity but also in the nature of the microfines.

b) It is demonstrated that both the California Cleanness Value (CV) and the Methylene Blue Value (MBV) are better indicators of concrete performance than P200 index.

c) The CV is unable to predict shrinkage in concrete containing those coatings with clays having crystalline swelling.

d) The test producing the Modified Methylene Blue Value (MMBV) best predicts the quality of concrete but presents practical difficulties for WisDOT implementation.

Part 3. Characterization of properties from concrete made with real Wisconsin Aggregates

Two different coarse aggregates containing microfines were analyzed. Both microfines were a mix of dust and clays. The primary clays detected were chlorite for one microfine and montmorillonite for the other sample. No impacts were detected in the fresh and hard concrete properties analyzed under the curing conditions of the tests. The sample containing montmorillonite had an observable decrease in workability and the slump of the concrete.

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1. Problem Statement

Concrete pavement construction is generally a robust process which can be successfully accomplished under a variety of conditions. As new materials are introduced in concrete mixtures, on occasion, problems have been encountered that seem to be counter to this historical construction robustness and with resulting performance disappointments. In Wisconsin some of the symptoms associated with these problems were stiffness in the mixture, cracking at aggregate-cement paste interface and low strength in concrete cores all in the presence of coarse aggregate coatings. State engineers and concrete pavers have speculated that one of the causes behind these problems could be the presence of coarse aggregate coatings with microfines contents under the P200 specification limit. Based on these problems, in October 2000, the WisDOT sponsored a study entitled: "Effects of Aggregate Coatings and Films on Concrete Performance", I.D: 0092-00-07. A small set of samples, selected as the most representative coatings in Wisconsin, were used to determine the impact of microfine coatings under P200 regulation on concrete properties. Additionally, the efficiency of current Wisconsin P200 specification was compared with alternative methods such as California Cleanness Test (CCT), Methylene Blue Value (MBV), and Modified Methylene Blue Value (MMBV). The main conclusions of this report were: first, the sample population used was not large enough to understand the extent of the aggregate coating across the entire state, so more sampling was recommended. Second, clay coatings showed a deleterious impact in concrete compared with other microfine mineralogy such as dust or carbonates. And finally, the P200 test is not a suitable tool to distinguish between deleterious coatings and non deleterious coatings. The current WisDOT solution to this problem is to remove all coatings through a washing process. However, the benefit of removing coatings may be exceeded by the cost of washing and stockpiling of the fines that are removed and a small amount of some coatings adhere so tightly to the aggregate that they are not removed during washing process. Consequently, a better understanding of the aggregate coatings could have a significant impact on the robustness of concrete pavement manufacturing and economics of aggregate processing.

2. Objectives and Scope of Research

The development of this research was conceived to complement the previous project in which the impact of aggregate coatings in concrete performance was studied. In this project, the investigation was focused on clay coatings since they were identified as the most deleterious group. The main focus was to identify the primary variables that govern the effects of clay microfine coatings on concrete pavements and to use this knowledge to improve the present aggregate monitoring situation in Wisconsin.

The aggregate monitoring aspect of the project could not be completed due to staffing problems and backlogs within WisDOT that prevented timely aggregate monitoring and data transfer to the research team. As a result, in 2005, the project objectives were reorganized into two parts. The first part involved strengthening the base understanding of the impacts of clay coatings on concrete performance and the second part was aimed at linking the theoretical results with actual field situations in Wisconsin. This work then focused on the following three tasks:

1. – Study of the effects of clay coatings in concrete. In order to minimize the variables of this study a coarse aggregate was coated with four different clays of controlled mineralogy. The investigation was divided into three levels: a) characterization of detachment mechanism during the mixing process; b) effects in the interfacial transition zone (ITZ); and 3) determine the impact of these coatings on some of the most significant physical properties in concrete.

2. – Evaluation of the current monitoring methods employed to detect coatings. The results obtained in the first task provided a basis for recommending improvements to the WisDOT method of detecting deleterious aggregate coatings.

3. – Measurement and analysis of properties from concrete made with Wisconsin aggregates with and without clay coatings. The sample selected for this objective was evaluated using the tests described in the previous task.

3. Background

Microfine materials in concrete are defined as those able to pass through No. 200 sieve (75 µm). This fraction of material is normally found as a part of the aggregates used in concrete production. The mineralogy of these microfines has been studied for a long time (Goldbeck 1933). A review of existing literature shows that aggregate coatings could be classified into three major types: stone dust, clay minerals, or calcium carbonate (Dolar-Mantuani 1983, Lang 1931, Schmitt 1990). Distinguishing between these coating types is important because the mineralogy of the coating will likely have an impact on the properties of many fresh and hardened concretes and therefore on the ultimate quality of resulting pavements (Hanna 2003). A recent study performed by Gullerud and Cramer, found that common mineralogy of microfines in Wisconsin falls under the previous classifications, and the clays are the fraction with higher deleterious potential (Gullerud 2002).

The characteristics of the clay fraction vary depending on the type of clay mineral. For example, some types of clay are held so tightly to the aggregate surface that they may not be displaced during washing, while other types of clay may be released into the water and are removed during aggregate washing or concrete mixing (Goldbeck 1933). Therefore, the effects of clays in concrete can be located in two different areas. First clay minerals that weakly adhere to aggregates, will be dispersed in the mixing water and therefore will be integrated in the cement paste. Second, those types of clay minerals that are strongly bonded to the aggregate surface will remain mostly located at the aggregate surface after the mixing process and therefore may disrupt the aggregate-cement paste bond (Goldbeck 1933, Neville 1996, Schmitt 1990).

Several studies were done to investigate the effects of clay microfines in the cement paste, particularly where the microfines were presented in sand (between 10-20% of p200). Where the clay contents were assessed by the modified methylene blue methods (Ahn, Phelan, Fowler and Hudson 2001, Unikowski 1982) the results showed, not surprisingly, that clays increase the demand of water in mortar samples. The necessity of satisfying this water demand provokes lower compressive strength and higher shrinkages. In these studies, the water demand of clay minerals was related to their specific surface. The highest water demand was observed in clays having the largest surface areas (He, Osbaeck and Makovicky 1995).

The reactions that clays instigate in contact with cement have been hypothesized by different authors (Fam and Santamarina 1996, Noble 1967). Based on stabilized soils studies,

Noble describes the reactions between clay and cement in the following order: 1) Hydration of cement compounds with the production of $Ca(OH)_2$, 2) introduction Ca^{2+} in the clay structure by cation exchange mechanisms, 3) adsorption of $Ca(OH)_2$ on the clay surface, 4) encapsulation of $Ca(OH)_2$ crystallites by fine clay particles and hydration products, 5) possible encapsulation of cement grains by clays and hydration products, and finally, 6) chemical combination of $Ca(OH)_2$ with SiO_2 and Al_2O_3. The mechanism proposed by Fam and Santamarina also suggested a transformation of clays into calcium clays through ion exchange. The high pH of the cement hydration drastically increases the solubility of SiO_2 and Al_2O_3 that can combine with CaO. Finally, the clay particles tend to disappear with the evolution of the hydration reaction. Noting these reactions, Pike theorized that the loss of strength in mortars containing clay fines is caused by clays adsorbing part of the water in the mix and forming "impermeable envelopes" around the cement grains. Ultimately, these effects slow hydration and disrupt the adhesion of the fines to the cement (Pike 1992).

As it was mentioned some of the clay coatings can remain attached to surface of the aggregate after washing or mixing, and therefore they can modify the bond between aggregates and cement paste. Especially if clays have high water adsorption capacity, significant amounts of water can be retained in the surface of the aggregates and increase the porosity of the interface between aggregates and cement paste. The porosity of this particular area has an influence on the durability of concrete. As an example, in severe marine environments, a porosity and weak zone between the aggregate and cement paste will improve the access of water and the intrusion of harmful ions into the concrete matrix (Caliskan, Karihaloo and Barr 2002).

4. Materials and Methodology

4.1. Materials

Coarse Aggregates

The two principal characteristics for selecting suitable coarse aggregates for the study were: 1) coarse aggregates commonly used in Wisconsin, and 2) coarse aggregate with clay coatings. The aggregate coatings in Wisconsin can be classified in three groups: dust, clay and carbonate coatings, as it is shown in Figure 1. Aggregate from the Northern part of the state have predominantly a combination of dust and clay materials and are typically associated with igneous aggregates. Carbonate coatings are the most typical coatings in the Southern areas of the state, and are mostly associated with limestone aggregates (Gullerud 2002).
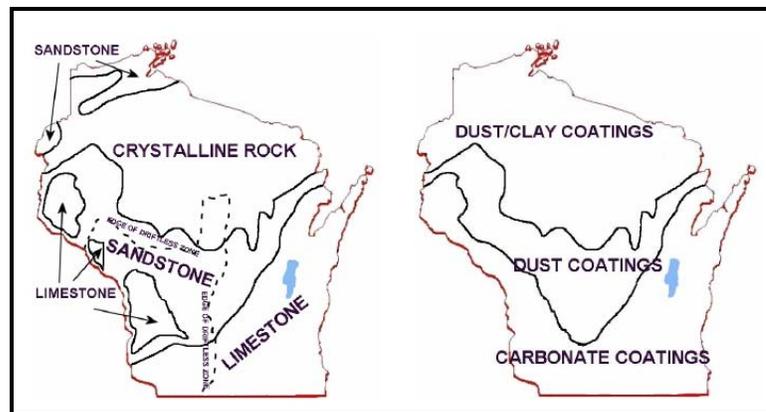
Figure 1 - Aggregate and Coating Types in Wisconsin (Gullerud 2002)

Based on this mineralogy classification, the targeted aggregates to be studied were igneous aggregates which are susceptible to adherent clay coatings. Three different aggregates from the Northern area of the states were selected to be used in phase 1 and 3 of the study.

Phase 1. A coated igneous coarse aggregate from Black River Falls (Jackson County) was selected to be used in the preparation of manufactured coated coarse aggregates. These materials were selected because the coarse aggregate was representative of igneous aggregate used in Wisconsin and its coating was easily removed through a washing process (Denny Brush, P.E., personal communication).

Phase 2. For this part of the project the research group, with the help of the WCPA, sought igneous coarse aggregates during the construction seasons of 2004 and 2005 that showed anomalies during the construction process. Two coarse aggregates were obtained that met these requirements:

- Aggregate 1 was a coated igneous aggregate used in the construction of the Highway 53 in Eau Claire (Eau Claire County). The concrete made with this aggregate exhibited several problems: significant loss in air content (about 3%) and in slump (about 2 inches) in a five minute haul to the paver, and development of cracks in the concrete pavement sections after the first 24 hours of curing. Cracks appeared close to slab joints shortly after construction suggesting an interaction with saw cutting and potential shrinkage problems.

- Aggregate 2 was a coated igneous aggregate used in the construction of the Highway 64 near Eau Claire (Eau Claire County). In this case the pavement problem reported was a high water demand to maintain desirable workability. This water demand was subsequently reduced by a washing process of both coarse and fine aggregates. The original concrete produced with unwashed sand and aggregate presented high shrinkage and low strength.

Clays

The mineralogy of natural coating is complex. Based on experience in the previous project on this topic, isolating the cause and effect of a multicomponent natural coating cannot be achieved without first isolating the effect of single components (Gullerud 2002). As a result, four laboratory clays of known and pure composition were selected for use in phase 1 of the project. These clays were used to coat coarse aggregate from Black River Falls. The selected clays were: kaolin, illite, sodium montmorillonite (NaM), and calcium montmorillonite (CaM). The first three clays were obtained from The Source Clays Repository from the Clay Mineral Society (CMS). CaM was created by exchange from the NaM. The sodium cations were exchanged by immersion of the clay in 1 N solution of $CaCl_2$ with 6 hours of agitation followed by a dialysis process of 24 hours for removing the excess of Ca^{2+} and Cl^-. Therefore, CaM would have the same characteristics as the NaM with the only difference in the nature of the cation exchange. The chemical composition of the clays is presented in Table 1.

Table 1 - Chemical Composition in Percentage of the Clays

Clay	SiO$_2$	Al$_2$O$_3$	TiO$_2$	Fe$_2$O$_3$	FeO	MnO	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$	S	F
Kaolin	43.9	38.5	2.08	0.98	0.15	--	0.03	--	<0.005	0.065	0.045	0.02	--
Illite	49.3	24.25	0.55	7.32	0.55	0.03	2.56	0.43	0	7.83	0.08	--	--
Na-M	62.9	19.6	0.09	3.35	0.32	0.006	3.05	1.68	1.53	0.53	0.049	0.05	0.11
Ca-M	62.9	19.6	0.09	3.35	0.32	0.006	3.05	1.68	1.53	0.53	0.049	0.05	0.11

These four clays present very different hydration properties and cation exchange capacities (CEC), as seen in Table 2 (Jaynes and Bigham 1986). Kaolin and illite have a smaller and medium water absorption capacity, respectively. 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 has a crystalline swelling process where the water is able to enter principally in between the layers that formed the structure of the particles. Finally, illite and kaolin are clays with very low water adsorption capacity and do not suffered crystalline swelling.

Table 2 - Characteristics of the Clays

Clay	CEC (meq/100 g)	Hydration Properties
NaM	74-79	Macroscopic Swelling
CaM	74-79	High Crystalline Swelling
Illite	15	No Crystalline Swelling
Kaolin	1.7-2.4	No Crystalline Swelling

Fine Aggregate

The fine aggregate used in this study was a natural river sand from South Central Wisconsin supplied by Wingra Corp., Madison. This material was not known to contain clay and presented a control situation.

Cement

The cement used was a Type II Cement manufactured by Lafarge. The chemical composition of the cement is presented in Table 3. The results were obtained according to ASTM C114 by the company.

Table 3 - Chemical Composition of the Cement in Percentage.

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	SO_3	Loss on Ignition	Insoluble Residue	Free Lime	C_3S	C_3A	Total Alkaline
20.7	4.7	2.6	2.2	65.7	2.5	1.5	0.37	1.42	68	8	0.52

Air Entraining Agent (AEA)

The air content of the batches were achieved through use of a Vinsol resin air-entraining agent (SikaLatex).

4.2.Methodology

4.2.1   Characterization of Natural Coatings

The analysis of the mineralogy of the coatings was accomplished using X-ray diffraction. A small quantity of the microfines was analyzed using a High Star 2-D X-ray diffractometer. The diffractograms were registered in a single run and in step mode. The program Power X was used to normalize the background of the diffractograms. Unknown crystalline phases present in the sample were identified by matching the diffraction pattern to the patterns stored in the Powder Diffraction Files (PDF).

4.2.2   Cleaning Coarse Aggregates

The preparation of cleaned coarse aggregate was required for different tasks in the research project. In all the cases the coarse aggregate cleaned was the aggregate from Black River Falls but the cleaning methodology varied depending on the use of the material as outlined below:

I.   Phase 1. Task: the study of the clay detachment of clays during mixing process. The washing was carried out by immersing the aggregates in water (200 g of aggregates/ 200 ml water), and sonicating the mixture for 24 hours. Next, the aggregate was

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separated from the suspension of fines by percolation. This operation was repeated until no fines appeared in the water.

II. Phase 1 and 2. Task: the study of the effects of clay manufactured and natural coatings in the most significant physical properties in concrete. The clean aggregate was used as a control batch and also as a base material to prepare the manufactured clay coatings. In this case, the necessity of significant amounts of clean aggregate (170 lb/batch) rendered impractical the sonication method outline above. So the necessary amount of coarse aggregate was washed by spraying them with water.

4.2.3 *Coating of Clean Aggregate with Clays*

The manufactured clay coating coarse aggregates where prepared by the method known as "dip-coating". A stable suspension of the clay was prepared by adding the clay to a MQ water and stirred until all the clay become a part of the stable suspension. In order to determine the desired coating thickness, the research group experimented suspensions with different concentrations of solids.

The coating device used for aggregate preparation is outlined in Figure 2. The aggregate was held in a cylindrical wire mesh basket, concentrically placed, inside of a bigger cylindrical container. The base of the large container was connected to a peristaltic pump. The clay suspension was pumped into the cylinder until all of the gravel was covered and then subsequently drained at a constant chosen velocity to achieve the desired thickness. The percentage of clay on the aggregate was attained 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. The pump was operated at a 0.5 gpm of withdrawal velocity. Under this condition, the level of the suspension drops at a velocity of 0.6 inch/min in the large cylindrical container.
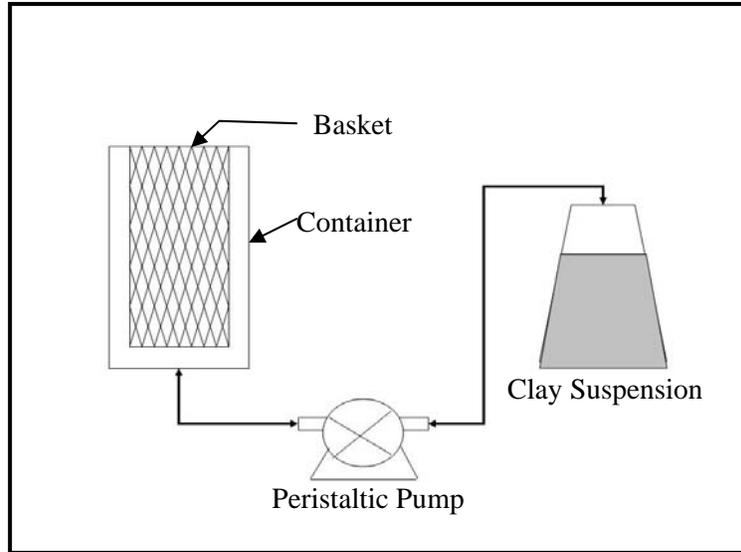
Figure 2 - Schematic Representation of Dip-Coating Device

Two different values of concentration were used for all the clays with the exception of the illite where only one clay concentration was tried. The values for these concentrations are reported in Table 4. Also, aliquots of the aggregates were subjected to different numbers of coating cycles (1, 2, 4, and 6).

Table 4 - Clay Suspension Concentration Used for Coating Aggregates.

Clay sample	Clay Suspension Concentration (g/L)
Na-Montmorillonite	40
	80
Ca-Montmorillonite	80
	140
Kaolin	80
	160
Illite	30

4.2.4   Quantification of Coating Detachment during Mixing Process

The study of the detachment of clays during the mixing process was performed in a concrete mixer of 3 ft^3 for one of the clays. In this experiment 11 lbs (5 kg) of clay-coated aggregate was placed in the mixer with 0.5 lbs (1 L) of water and mixed for 2 minutes. Data on the quantity of detached clay were used to establish the conditions to be used in a shaker in order to yield the same level of agitation that can be expected during concrete mixing with a laboratory

drum mixer. The idea behind this procedure was to be able to use samples of smaller size that could be placed into smaller bottles and placed into a laboratory shaker. In this fashion, several samples could be studied simultaneously. For the experiments in the shaker, the size of the samples was of 250 g of coated aggregate, far smaller than the 5 kg used for the ones performed in the concrete mixer. The detachment of clays were studied at two different pH values (~7, which is approximately the natural pH of clay suspensions, and ~12, which is similar to the pH of calcium hydroxide). Every experiment was repeated four times to achieve repeatability. In this fashion, the conditions of time and shaking strength were established for the Incubator Shaker Model G-27 that would yield the same clay detachment as that in the concrete mixer. This translated into an enormous savings of time and materials. The concentration of detached clay was measured gravimetrically, following the same, previously mentioned, procedure used in evaluating the amount of clay in the coatings.

4.2.5   *Microfine Coating Monitoring Tests*

The coatings of the coarse aggregate samples were characterized with current most popular monitoring tests such as, P200, CCT, and MBV. Finally a combination of results from P200 and MBV known as MMBV were evaluated (Gullerud 2002).

The P200 is the most common test in the USA for controlling microfines in coarse aggregates. In 46 of the 50 states, the quantity of microfine allowed is controlled by specifying a maximum percentage of material passing the No. 200 sieve (P200) per mass of aggregate. The P200 percentage was obtained using ASTM C117.

The CCT is mostly used in California. The test in this research was conducted in general compliance with the standard procedure in California Test 227. In this test the aggregate is mechanically washed to remove adhering fines. The wash water is then passed through a No. 200 sieve, placed in a graduated cylinder and mixed with a solution of glycerin and calcium chloride. After 20 minutes the height of the sediment is measured and given a cleanliness grade from 0 (dirty) to 100 (clean).

The MBV describe in the AASHTO TP 57 was the third method evaluated. It is a measurement of the exchange capacity of the aggregate coating. The method is based on the unique properties of certain clay minerals to absorb the methylene blue. A water suspension of P200 material is titrated with this dye.

4.2.6   *Mix Design*

The proportions of all the mixes prepared in the study were based on the WisDOT Grade A concrete mix design (WisDOT 1996) and are shown in Table 5.

Table 5 - Batch Quantities, lb/ft^3 (Kg/m^3).

Material	Batch Weights	Batch Proportions
Cement	20. 9 (334.8)	1
Coarse Aggregate	69.4 (1111.7)	3.5
Fine Aggregate	46.3 (741.6)	2
Water (Net)	9.4 (150.6)	0.45

For each batch, the net water-cement ratio was 0.45 and the target air content of 6.0 ± 1%. To ensure a constant water-cement ratio, the amount of water added in each concrete was adjusted as a function of the absorption of the coarse and fine aggregates according to ASTM C127 and C128, respectively. The absorption of the aggregate coatings was neglected when the workability of the mixes was not altered by their presence. Only on those batches where the presence of the coatings induced obvious changes in workability, an extra batch was prepared with additional water to maintain workability. This was the case of batches prepared with aggregates coated with kaolin, NaM, and CaM, where 4.4%, 20% and 40% of extra water was necessary to keep workability. For the batch made with aggregate from Hw64 a decrease of slump was detected, unfortunately there was not enough material available to prepare an extra batch with extra water.

Concrete batches were mixed in a 3-ft^3 drum mixer using the ASTM C192 procedure. Following mixing, air content and slump were determined under ASTM C231 Type B and C143, respectively. A sufficient amount of concrete per batch was prepared to cast:

1. Eight 4-in. by 8-in. cylinders for compressive and tensile strength tests.
2. Three 4-in. by 4-in. by 11-in. prisms for shrinkage tests.
3. Three 3-in. by 4-in. by 15-in. prisms for freeze-thaw durability tests.

All the specimens were consolidated, covered with wet burlap and a plastic sheet for 24 hours, removed from molds, and stored in at 74 ºF and a relative humidity of about 100% until testing.

4.2.7   *Hardened Concrete Tests*

Both types of batches, one prepared with manufactured clay coated aggregates and the other made with natural coated aggregates, were tested for strength, drying shrinkage, air voids and freeze-thaw durability. The tests used to determine these properties are summarize in Table 6.

Table 6 - Summary of Hardened Concrete Tests.

Test	Standard (ASTM)	Test x Batch	Duration of Curing
Compressive Strength	C39	4	28 days
Tensile Strength	C496	4	28 days
Drying Shrinkage	C490	3	14 days
Freeze-Thaw Durability	C666	3	28 days

The compressive strength was measured after 28 days of wet curing following ASTM C39. In order to compare the strengths 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 vs. air content relationship recommended by the American Concrete Institute (Popovics 1998).

Concrete tensile strength was measured after 28 days of wet curing using the split-cylinder tension test described in ASTM C496. No adjustment based on air content was made to the recorded values.

Drying shrinkage was assessed following the requirements of ASTM C490. After 14 days of wet curing, the specimens were kept in an environmental chamber at a temperature of 74 ºF and a relative humidity of 50%. Changes in length were recorded, relative to an initial reading, at a various ages between 14 and 120 days, using a length comparator gauge with a precision of 0.0001 in.

Freeze-thaw durability was measured in the samples in general compliance with ASTM 666 procedure A. The prisms were kept 28 days under wet curing conditions prior to commencing freeze-thaw testing. For each test batch, three specimens were kept immersed in a 3% NaCl solution and cycled between 1 ºF and 50 ºF in a freeze-thaw chamber at an average rate of 4.5 cycles per day. The weight and fundamental transverse frequency were recorded for each specimen every 7 days or roughly every 30 cycles.

4.2.8   *Hardened Air Void Analysis*

The air void content and the spacing factor of hardened concrete of the most representative batches were analyzed using an Optical Microscope Olympus BX40 at low magnifications. Specimens were sawed from the original concrete sample and observed 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 two-dimensional analysis in a profile of 0.22 in^2 (3570 mm^2) and image analysis software. The spacing factor was determined using profiles of approximately 1.2 in (30 mm) length by measuring the traverse length through 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 30 mm was significantly less than that required in ASTM C457. This deviation was partly compensated by examining three different specimens from the same concrete prism. Based on the results measured for the three specimens it was determined further specimens were not needed to determine spacing factor or air void for the purposes of this research.

4.2.9   *Microanalysis of Concrete Samples*

Several aspects of the concrete samples were studied using different techniques:

X-Ray Diffraction: several analyses were done in concrete samples following the same methodology described in the *Characterization of Natural Coatings* section. In this case this technique was used to identify typical hydration reaction products as though other possible new compounds due to the presence of microfines in the cement paste and also in the ITZ.

Scanning Electron Microscopy (SEM): the microstructure of the concrete samples was analyzed to correlate durability with microstructural properties of the samples. These analyses were performed in a JEOL 6100 Scanning Electron Microscope. Prior to microscope analysis, the samples were sawed, polished and carbon coated to estimate the degree of hydration in different concrete areas as cement paste and the ITZ of the concrete. The coated samples were observed

in the SEM under the following conditions: 15 kv of accelerating voltage and 15 mm of working distance (Mouret, Ringot and Bascoul 2001). The characterization of the ITZ and cement paste was done by taking 20 pictures of each area for all the samples selected. Each original image was 800 x 600 pixels with a resolution of 1,300 pixels/mm (400,000 pixels/inch), and the acquisition magnification was 1,900x. All the images were treated with a specific methodology to enhance the areas corresponding to pores and unhydrated cement (Werner and Lange 1999). Subsequently the volume of porous, unhydrated cement and hydration products were calculated (Igarashi, Kawamura and Watanabe 2004).

5.Results

5.1.Coatings on Coarse Aggregates

5.1.1   Clay Coatings

Results concerning the quantity of clay coated on the aggregate under different experimental conditions are reported in Figures 3 and 4 for the four clays employed in this study. The tested parameters in this experiment were the nature of the clay, the speed of withdrawing the aggregate from the clay suspension, the concentration of clay in the suspension and the number of coatings. The goal was to deposit a layer of clay that constituted between 1 and 1.5% of the weight of the coated aggregate, with the exception of the illite, where the targeted percentage was decreased to a 0.6%. Graphs 3a, 3b and 4a show that the coating thickness was obtained for NaM, CaM and kaolin, after four coating cycles. However, the concentration of clay in the suspension needed to achieve this coating level was different for each type of clay. In the case of the illite, the desired coating thickness was reached after 6 cycles.
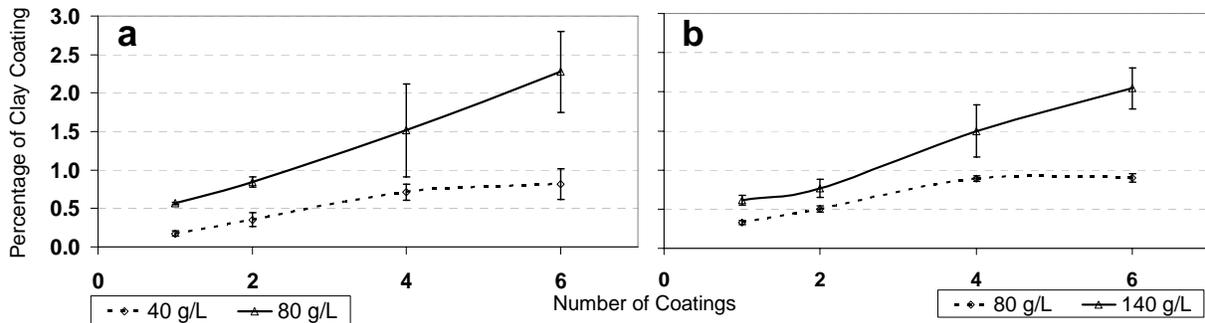
Figure 3 - Percentage of Clay Coating Attached to Aggregate Surface vs. Number of Coatings for (a) NaM and (b) CaMont

As expected, the quantity of clay deposited increases with an increase in the concentration of clays in suspension. It is interesting to note that the curves representing the quantity of coated clay versus the number of coatings show a saturation behavior for each of the clays. This saturation level is particularly noticeable when the concentration of clays in the coating suspension was 40 g/l for NaM and Illite, and 80 g/l for CaM and kaolin. This behavior may also be observed in the curves associated with the higher concentrations of clays in suspension (80 g/l for NaM, 140 g/l for CaM and 160 g/l for kaolin). However, this feature is

not so clearly visible due to the larger size of the error bars for these curves. It should be further noted, that the desired level of coating cannot be reached only by increasing the number of coating cycles but rather has to be through a combination of coating cycles coupled together with the concentration of clay in the coating suspension.
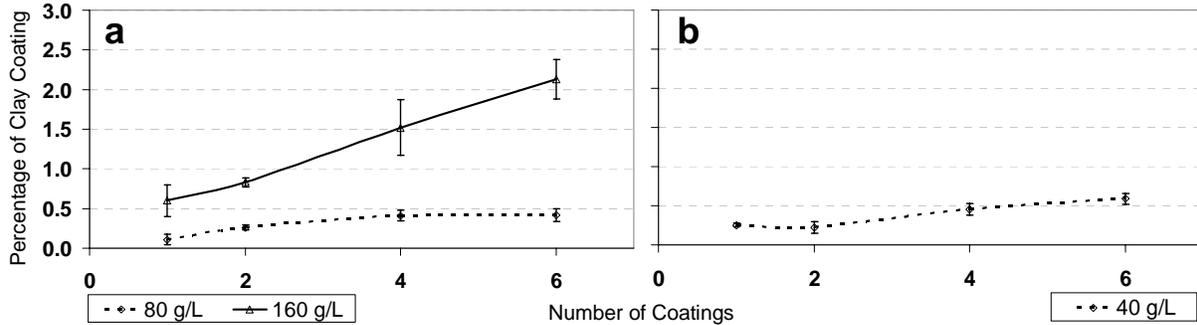
Figure 4 - Percentage of Clay Coating Attached to Aggregate Surface vs. Number of Coatings for (a) Kaolin (b) Illite

Unlike the case for most dip-coated films deposited on substrates, the thickness of the deposited layer (quantity of coated material) in this system is not related to the velocity withdrawal of the suspension. The thickness of the coated layer in this system is believed to be largely determined by the viscosity of the clay suspension. For example, the clay deposited after 4 coatings using a suspension of kaolin of 80 g/l is less than 0.5% versus 1.5% when using a suspension of NaM. This is due to the fact that the larger viscosity of the montmorillonite suspension leaves behind thicker films after coating. As the clays are only dried at 60 $^{\circ}$C between coatings, the saturation behavior may be explained if the attached clay re-suspends itself when exposed to a new coating cycle. As a cautionary comment, the layer of clay on the individual aggregates is not uniform, neither is it for the different aggregates (due to complex geometry of the coated material). However, the reproducibility with respect to the average thickness of coating is adequate to allow one to predict the set of coating conditions capable of delivering the desired percentage of clay on the coated aggregate.

Once the aggregates were coated with the clays, they were characterized with traditional monitoring tests such as, CCT and MBV before entry to the mixer. The results are shown in Table 7.

Table 7 - Results of Manufactured Clay Coating Characterization Tests.

Aggregate Coated	P200 (%)	Cleanness Value	MBV (mg/g)
NaM	1.45	66	15.8
CaM	0.79	94	106.7
Illite	0.4	95	6.67
Kaolin	0.68	94	6.76

As expected the NaM fines failed the CCT with the low cleanness value of 66 with a threshold value of 75 at the failure point. This is explained due to the tendency of this clay to exhibit a destacking process in water and forming a gel structure that does not sediment. This phenomenon is explained more in detail in *Properties of Clays in Water.* Also, this clay does not pass the MBV test since the measured index is above 10 mg/g. The same montmorillonite but with calcium instead of sodium as exchangeable cation is 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 is subjected to the methylene blue test the results are not as satisfactory. In this case the CaM fails with an MBV value of 106.7. Finally, the illite and kaolin have similar results for both monitoring tests. Both are characterized as displaying non crystalline swelling. Therefore they meet the requirements of CCT with an acceptable cleanness values, 95 and 94 respectively, and also meet the requirements of MBV with a slightly high value of 6.67 and 6.76 mg/L, respectively.

Recent studies have shown that microfines coatings with MBV index above 3 mg/g for dry sieving and 5 mg/g for wet sieving will provoke high water demand in concrete mixes (Quiroga, Ahn and Fowler 2006). Based on these facts all the clays should provoke an impact in the slump during the mixing process.

5.1.2 *Natural Coatings*

The mineralogies of the three natural coated coarse aggregate were analyzed by X-ray diffraction. The nature of the coatings and their principal compounds are delineated in Appendix I, however a summary of the principal findings are listed in Table 8.

Table 8 - X-Ray Diffraction Results for Natural Coatings.

Aggregate Source	Type of Coating	Principal Compounds
Black River Fall (BRF)	Carbonate/Dust	(Na, Ca)-Carbonate; (K, Al)-Silicate; (Ca, Mg, Al)-Silicate Hydroxide
Hw 53	Dust/Clay	Quartz; Amorphous silica; Chamosite (Chlorite)
Hw 64	Dust/Clay	(Ca, Al)-Silicate Hydrate; Ca-Silicate Hydrate (Montmorillonite)

The analysis of the coating attached to BRF sample reveals that the microfine is mostly sodium and calcium carbonate and dust, principally silicates with presence of potassium, aluminum, calcium and magnesium. The absence of clay minerals from the vermiculite or montmorillonite group is an indication of the low adhesion between the microfine and the aggregate surface. This means that the coating should be easily removed and suggests this aggregate source to be suitable as the control material for the project.

The other coatings for the two aggregates selected in the project are a mix of dust and clay materials. The analysis of coating from Hw53 aggregate reveals that the dust fraction is quartz and amorphous silica, and the clay detected is chlorite. This clay mineral group belongs to the subclass of phyllosilicates with typically CEC that ranges between 10-40 meq/100 g and a moderate water adsorption capacity. The coating from Hw64 aggregate has two different types of silicates: one calcium aluminum silicate hydrated with very low water adsorption capacity that is classified as dust and a clay type calcium silicate hydrated that belong to the group of montmorillonites with a high CEC and high water adsorption capacity.

The aggregate coatings were also characterized using the current monitoring methodology and the results are reported in Table 9. The BRF original material was washed and then characterized using CCT and MBV to ensure that the 0.1% of coating remaining is innocuous, and therefore the materials was suitable as the control. The P200 content for Hw53 and Hw64 aggregates varies from 0.76% to 1.47%, respectively.

Table 9 - Results of Natural Coating Characterization Tests.

Aggregate	P200 (%)	Cleanness Value	MBV (mg/g)
BRF[†]	0.1	100	0
Hw53	0.76	89	0.8
Hw64	1.47	91	6.67

[†] This characterization was done in our control material after washing the original coated aggregate

The CCT and MBV characterization obtained for Hw53 and Hw64 are in concordance with the mineralogy results. Both coatings are a mix of dust and clay. Both had cleanness values above 75 and MBV index below 10 mg/g, meeting the requirement of acceptable aggregates for the CCT and MBV, respectively. The presence of chlorite and dust in Hw53 provided an acceptable value in the CCT and also since both have low water adsorption, a low value of MBV index, 0.8 mg/g. The Hw64 aggregate shows a better CCT value, 91 vs. 89, but a significantly higher value of MBV, 6.67 mg/g due to the presence of a clay mineral from montmorillonite group with high water absorption capacity. Based on the high values of MBV (above 5 mg/g), it was expected that the presence of microfines from Hw64 aggregate will increase the water demand of the concrete mix (Quiroga, Ahn and Fowler 2006).

5.2.Detachment of Coatings during the Mixing Process

Clays may be present in suspension as the result of their detachment from the aggregate surface. Therefore, it would be useful to know the fraction of coating coming into the aqueous phase during the aggregate/water mixing stage in realistic concrete mixing conditions. However, even smaller commercial concrete mixers require samples of 5 Kg in size. To run only one sample at the time, we would require 200 Kg of aggregates for this study and a very long time frame to study all of the important variables in this process. Therefore we chose to agitate these mixtures in a mechanical shaker.

In order to determine the percentage of clays detached under real concrete making conditions we first employed the concrete mixer to study one of our clays, see appendix II. Results from this study allowed us to find the set of experimental conditions for the shaker that would deliver the same detachment level of clay as the laboratory mixer would produce. For this

study, we explored the variables: amount of aggregate; position and size of the vessel containing the aggregate; and time of the sample in the shaker (see appendix II).

The size of the sample in the range between 125 g and 500 g does not influence the quantity of detached clay. The position of the vessel in the shaker, whether it is parallel to the base of the shaker or has an inclination of 30°, also did not appear to be relevant. The size of the vessel for a given sample size (250 g: 500 ml to 4 L) did not produce a significant change in the amount of detached coating. The only variable tested that showed any influence upon the fraction of clay coating that could be detached was the time in the shaker. Detachment increased with increasing shaking time.

From these studies we were able to establish experimental conditions under which the shaker would yield the same percentage of detached clay coatings as that of the laboratory mixer. One set of variables that conforms to this requirement is: 250 g of coated aggregate in 1L capacity bottle and 15 minutes of shaking. These are the experimental conditions used in this study. The comparison between shaker experimental conditions vs. mixer normal conditions was represented in Figure 5.
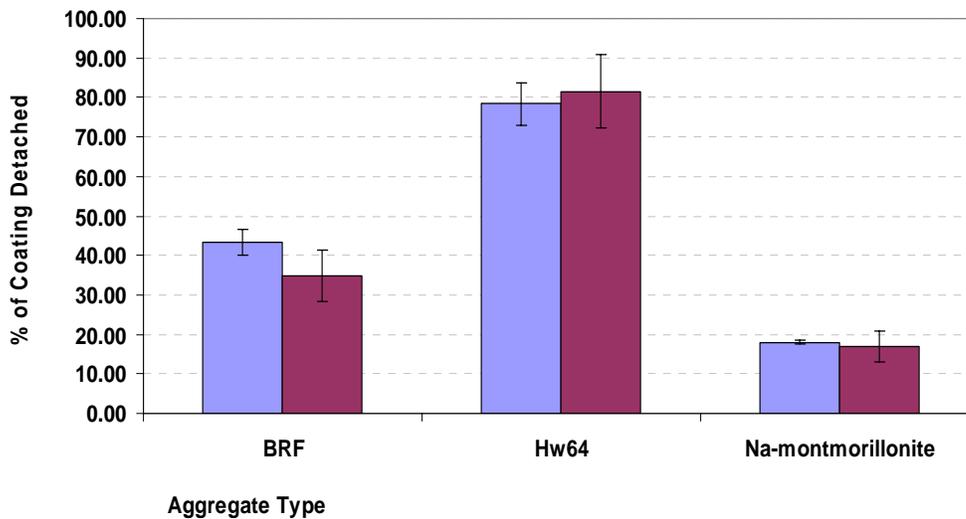
Figure 5 - Comparison of Coating Detached between (☐) Mixer and (■) Shaker Conditions.

It should also be noted that subsequent experiments to determine the detachment of clays were then performed at two different pH values: 7 and 12. The quantity of clay that was detached was measured gravimetrically as explained in the experimental section. The percentages of detached clay are represented in Figure 6. This figure shows that the degree of

detachment depends very much on the nature of the clay. In the case of NaM most of the coating remains on the aggregate upon mixing (10 and 20% detached). However, in the case of CaM and kaolin coatings most of these coatings detach and enter the water phase (CaM: 69 and 77%; kaolin: 50 and 79%).

The pH of the aqueous phase also plays a role in the detachment of the coating. The extraction of clay is significantly increased when the pH is raised to a value of 12. The influence of the pH is especially significant in the case of the NaM. The concentration of clay in the aqueous phase for each of the studied systems is reported in Table 10.
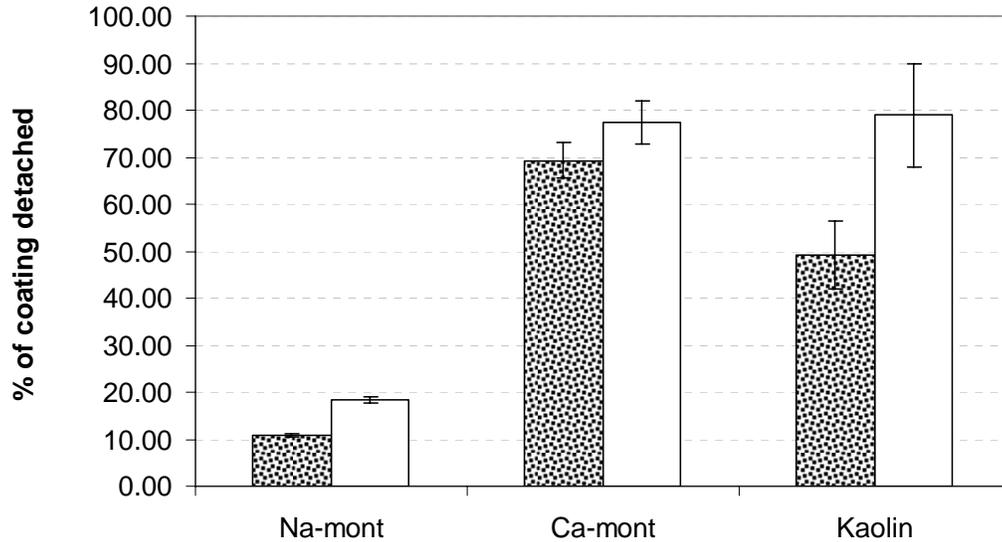
Figure 6 - Percentage of Clay Coating Removed with Respect to the Total Mass of Coating at Two Different pH Values at (▨) Natural Clay pH (~7) and (□)pH 12

Table 10 - Measured Concentration of Clays in Mixing Water.

Clay	Normal pH (~7)	pH =12
	g/L of clay in rinse water	g/L of clay in rinse water
NaM	8.95	14.5
CaM	27	30.83
Kaolin	24.4	36.56

5.3. Properties of Clays in Water

The four clays selected for these studies are different in structure as shown in Figure 7. The value of the net negative charge, as measured by the exchangeable capacity of cations, is very different, 2 meq/100 g for kaolin, 15 meq/100 g for Illite, and 76.4 meq/100 g for the Na and Ca montmorillonite. The major difference between the two montmorillonites is the nature of the cations, as the Ca sample was prepared from the Na sample by ionic exchange. Due to these structural differences, the reaction of the particles in aqueous media is expected to be very different. NaM should display macroscopic swelling; CaM crystalline swelling; and both kaolin and Illite no swelling at all. Therefore, one should expect these clays to display different stabilities (ability to sediment from solution) in aqueous media. Also, stable suspensions of these clays are expected to have different rheological properties as shown for such colloidal species as sols, isotropic gels, etc.
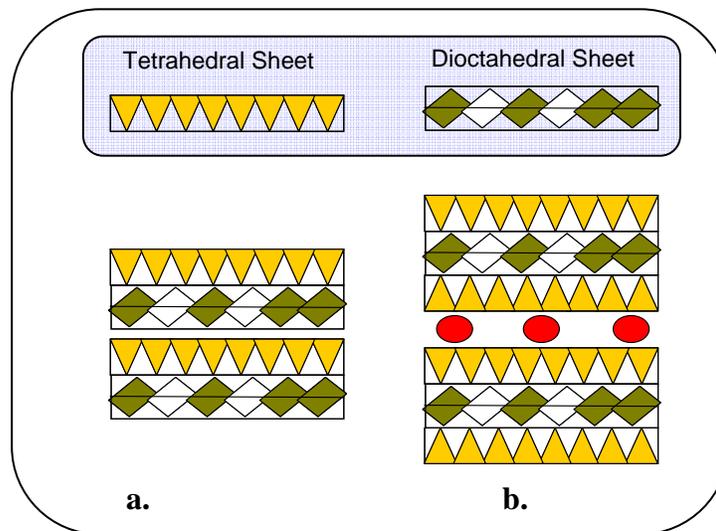
Figure 7 - Schematic Representation of the Structural Units of (a) Kaolin and (b) Na-M, Ca-M and Illite

Sedimentation studies of these clays were performed in pure water and 0.03 M Ca(OH)$_2$. Figure 8 shows the sedimentation behavior of these clays in presence of water. Kaolin and CaM sediment in 4 and 6 minutes respectively while the NaM does not sediment within 100 minutes. The explanation for these results is based on the hydration properties of these clays: NaM is expected to suffer macroscopic swelling (particles exfoliate). In this system the particles in suspension will likely be very thin and stable. Neither the particles of kaolin nor the ones of

CaM suffer exfoliation in water hence these particles remain in their original size and clays should be larger than that of NaM.

In the case of these three particular clays, the above explanation was confirmed by measuring the particle size of their suspensions using light scattering. We found out that the NaM formed isotropic gels. The average particle size in the suspension is 1.6 μm. Particles of this size do not flocculate and have fractal structures of low density. The formation of large fractals should be associated with a large degree of particle connectivity in the suspension. In other words, these suspensions should show gel-like characteristics.
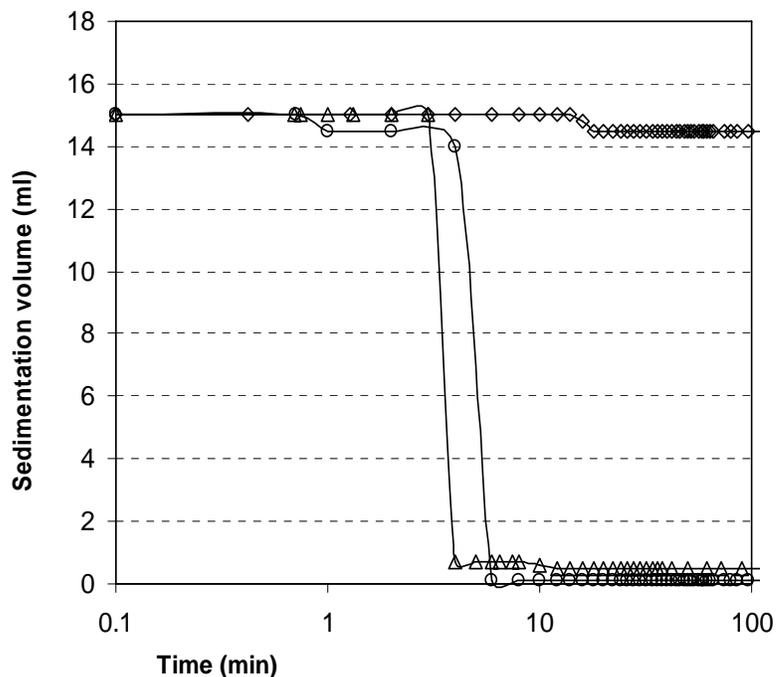
Figure 8 - Sedimentation Curves in Water for (◊) Na-M, (¤) Ca-M, and (Δ) Kaolin

The sedimentation is accelerated when the experiment is performed in presence of $Ca(OH)_2$ solution. Sedimentations occurred at 2 and 5 minutes earlier, in the case of kaolin and CaM, respectively. In the case of NaM, the clay sediments in presence of $Ca(OH)_2$. This happens because two Na^+ located in the interlayer of the clay are replaced by one Ca^{2+}.and this system now behaves as CaM.

Electrophoretic mobility measurements shown in Figure 9 also help to understand the sedimentation behavior of these clays. The electrophoretic mobility of a particle, for given solution conditions, is determined by a combination of shear plane potential and particle size. As

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both montmorillonites have the same exchange capacity, the surface charge should be practically the same, thus, differences in mobility should be attributed to differences in particle size.

Figure 9 - Electrophoretic Mobility of (◊) Na-M, (¤) Ca-M, and (Δ) Kaolin in Water as a Function of pH

5.4. Effects of Clay Aggregate Coatings in the Early Hydration Reaction of the Cement Paste

Once the studies of clay coating detachment during the mixing process and their behavior in the mixing water prior to the addition of cement were complete, the research group investigated the effects of clays in early hydration reactions in cement paste when they are suspended in the mixing water. Three clays were selected with very different hydration properties based on the earlier findings, kaolin, NaM and CaM. Kaolin had the smaller water absorption capacity of the three selected clays. Both CaM and NaM had a large capacity to absorb water and swell. When immersed in water the NaM suffered a destacking process.

To perform this study, three batches of cement paste were prepared for each clay, plus a control sample without clay. Each sample contained 150 g of cement powder with a water-cement ratio of 0.45, and each of the samples had a different clay concentration of 1.5, 2.5, or 5 percent weight. The total number of cement paste samples prepared and their compositions are reported in Table 11. First the clays were added to the water and stirred for 2 minutes.

Table 11 - Quantities of Clays Use to Prepared Cement Paste Samples.

Sample	% of Clay	Cement (g)	w/c Ratio	Clay Present in Water Mixing (g/L)
Control	--	150	0.45	--
Kaolin	1.5	150	0.45	2.25
	2.5	150	0.45	3.75
	5	150	0.45	7.5
CaM	1.5	150	0.45	2.25
	2.5	150	0.45	3.75
	5	150	0.45	7.5
NaM	1.5	150	0.45	2.25
	2.5	150	0.45	3.75
	5	150	0.45	7.5

The evolution of the samples was followed over a period of 6 weeks by X-ray diffraction. More precisely at 2 and 5 hours, 1, 2, 6, 14, and 42 days. Most of the measurements were performed during the first two days because this is when most of the hydration process takes place (preinduction, dormant and accelerating period). The methodology used was the same as that described in *Characterization of Natural Coatings*. The only difference was that an internal standard (IS), CaF_2, was mixed with the samples to obtain a semiquantitative analysis of the products, 2.5 percentage of the total weight of the sample. Judgment of the effect of the different clays in the early hydration reaction of the cement paste is attained from data on how early peaks of the most important hydration products, such as $Ca(OH)_2$, CSH and ettringite, become visible in the diffraction pattern. $Ca(OH)_2$ and CSH are followed by the peaks at 2θ values of 50.9 and 49.8, respectively. Ettringite was not always visible in the early stage of hydration, thus in this study, we only followed the peak growth of $Ca(OH)_2$ and CSH.

X-ray diffraction patterns of all the samples were obtained at 2h, 5h, 1, 2, 6, 14 and 42 days from mixing. A control paste was prepared without any clay to compare its evolution to those with kaolin and Ca/Na-M at 2.5% (wt). The intensity of all the peaks in all reported diffractograms is normalized with respect to the most intense peak of the IS. The IS has the

same weight percent in all samples, therefore, we should be able to compare in a quantitative manner the amount of $Ca(OH)_2$ and CSH present in the different cement pastes.
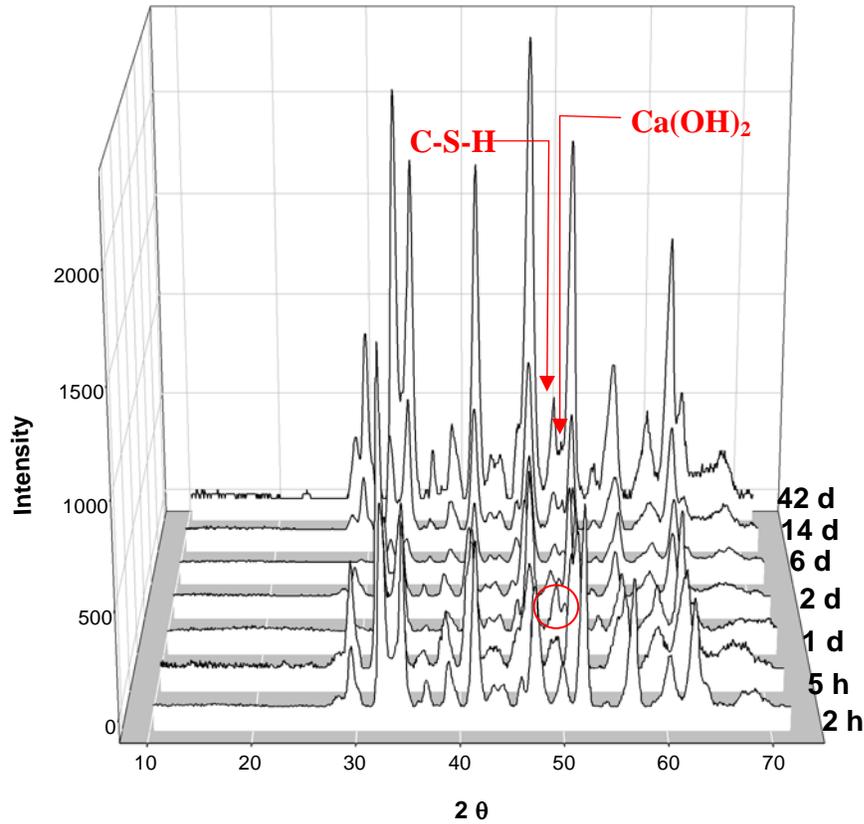
Figure 10 - X-Ray Diffraction Patterns for the Cement Paste Control at Different Aging Times

Figure 10 shows the evolution of the control paste with time. The major changes are detected between 2 and 5h of aging. Ettringite was detected in the 5 hours diffraction pattern while $Ca(OH)_2$ and CSH were only visible after 1 day of reaction. Differences among the diffraction patterns were smaller with increasing aging time.

The diffraction patterns in Figure 11 show that the evolution with time for samples containing kaolin are similar, to that of the control at early stage of reaction. The exception is the appearance of ettringite in the diffraction pattern of 2 hours old paste with kaolin. In both types of cement paste the peaks that correspond to alite maintain their sharpness during the whole study period, meaning that the hydration of the paste is very slow and thus the consumption is not noticeable during the expand time of our studies. Finally, both $Ca(OH)_2$ and CSH are visible in the one day pattern, the same as that in the control sample.
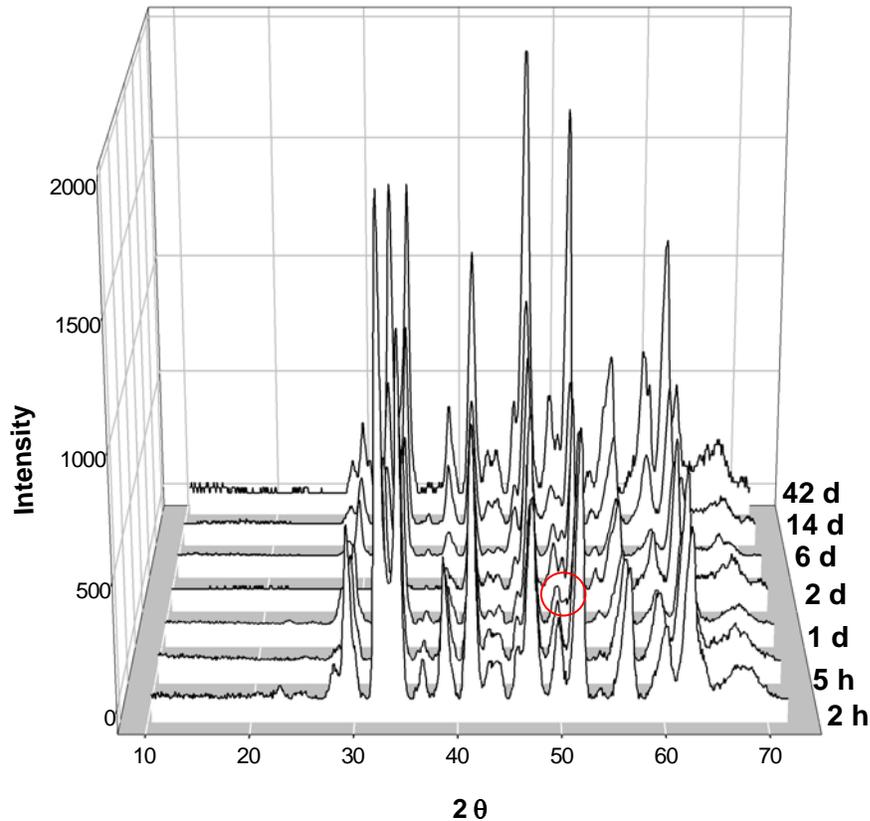
Figure 11 - X-Ray Diffraction Patterns for the Kaolin at 2.5% at Different Aging Times

The diffraction patterns of the cement pastes containing CaM (figure 12) reveal that ettringite is formed during the first 2 hours of reaction. Calcium hydroxide is detected in the patterns of the 1 day old pastes, as happen in the control paste and in the pastes with kaolin. It is also note worthy that in diffraction patterns of pastes containing CaM the peak of $Ca(OH)_2$ has higher intensity than the one of CSH, unlike in the control or the pastes with kaolin. This is especially pronounced in the 6 week diffractogram. We believe that the higher intensity of the $Ca(OH)_2$ peak was due to the additional quantity of calcium added to the system as CaM.
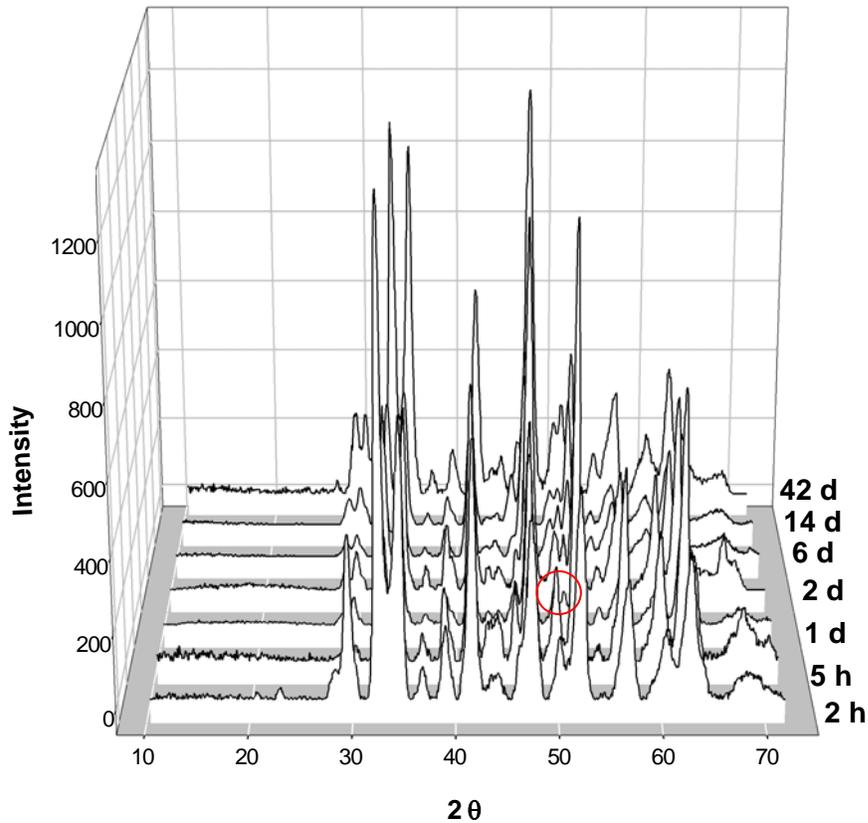
Figure 12 - X-Ray Diffraction Patterns for the CaM at 2.5% at Different Aging Times

The diffractograms of the cement pastes containing NaM (Figure 13) show a distinct evolution when compared with the rest of the systems in this study. The hydration reactions appear to go slower, especially during the first days. The peaks of $Ca(OH)_2$ and CSH are visible only after 2 days of reaction. Respect to the ettringite the NaM samples show the same pattern as the rest, this means that the ettringite is also detected after 2 hours of reaction.
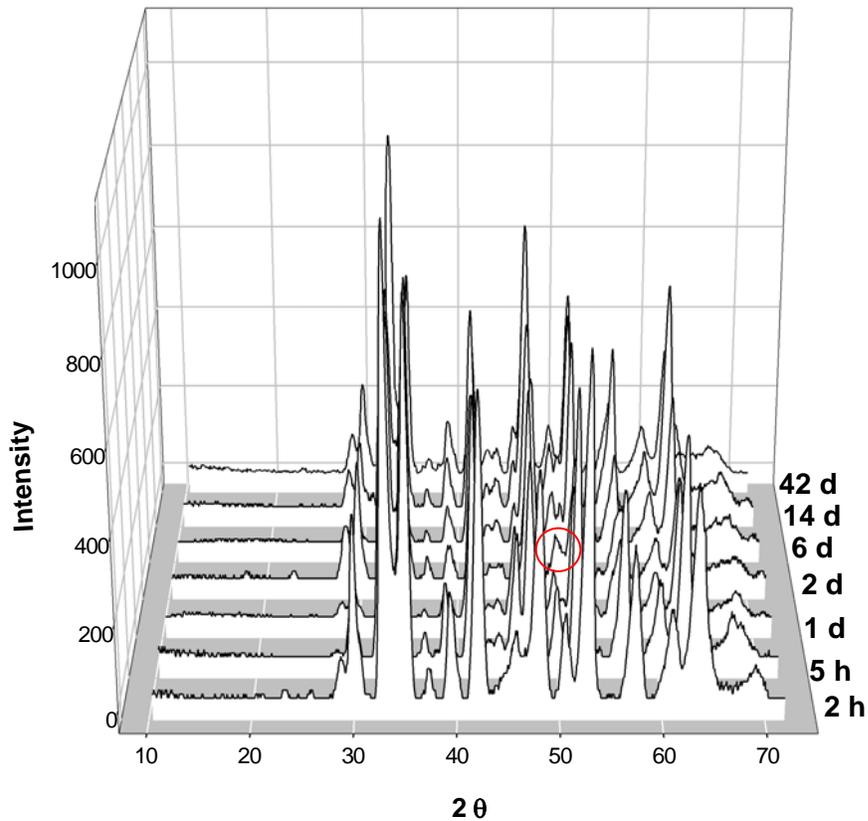
Figure 13 - X-Ray Diffraction Patterns for the NaM at 2.5% at Different Aging Times

A summary of all the findings obtain from the comparison of the four samples is presented in Table 12.

Table 12 - Time of Appearance of Principal Hydration Products in the Samples.

Sample	Ca(OH)$_2$	C-S-H
Control	1 day	1 day
Kaolin	1 day	1 day
CaM	1 day	1 day
NaM	2 days	2 days

In order to identify how the concentration of clay in the cement paste affects the rate of formation of hydration products, we also study cement pastes containing 1.5 and 5% in weight of the clays. The histograms of Figure 14a and b show the intensity of the peaks (relative to the IS)

of the hydration products (calcium hydroxide and CSH) in the diffractogram of samples 6 weeks old for cement pastes containing the different clays in three different concentrations (1.5, 2.5 and 5%).

Figure 14a shows that the control sample (0% clay) exhibits the highest amount of $Ca(OH)_2$. According to the literature, this effect could be due to the pozzalonic effect of some clays, which tends to decrease the final amount of $Ca(OH)_2$ present in cement paste (He, Osbaeck and Makovicky 1995). The exception is the sample made with 5% of CaM which presents a higher amount than the control. This could be explained by the extra amount of calcium introduced by the clay. Cement pastes with Na-M are the with ones the less $Ca(OH)_2$ after 6 weeks. The amount of $Ca(OH)_2$ in both, pastes with kaolin and CaM increases with increasing clay concentration. While this phenomenon is easy to understand for the pastes with CaM and still can be attributed to the pozzolanic effect of this clay, it is paradoxical in the case of kaolin containing pastes.

Figure 14b represents the relative concentration of the CSH for all systems studied at 6 weeks from mixing. Samples containing kaolin show a larger concentration of CSH than the control and the quantity increases with increasing concentration of this clay. These results, in conjunction with those for $Ca(OH)_2$, seem to indicate a pozzolanic effect of the kaolin and faster hydration kinetics than in the control. In the case of pastes containing the highest concentration of CaM (5%) the amount of CSH was higher than in the control and kaolin samples. Therefore, the higher concentration of $Ca(OH)_2$ in these pastes after 6 weeks may be primarily attributed to the paste being more fully hydrated than the control and not from the Ca contained in the clay. The NaM containing samples showed similar results for CSH concentration to those obtained for $Ca(OH)_2$. The concentration of CSH tended to decrease with the increase of clay concentration, leading to the belief that this clay retards the hydration of cement pastes.
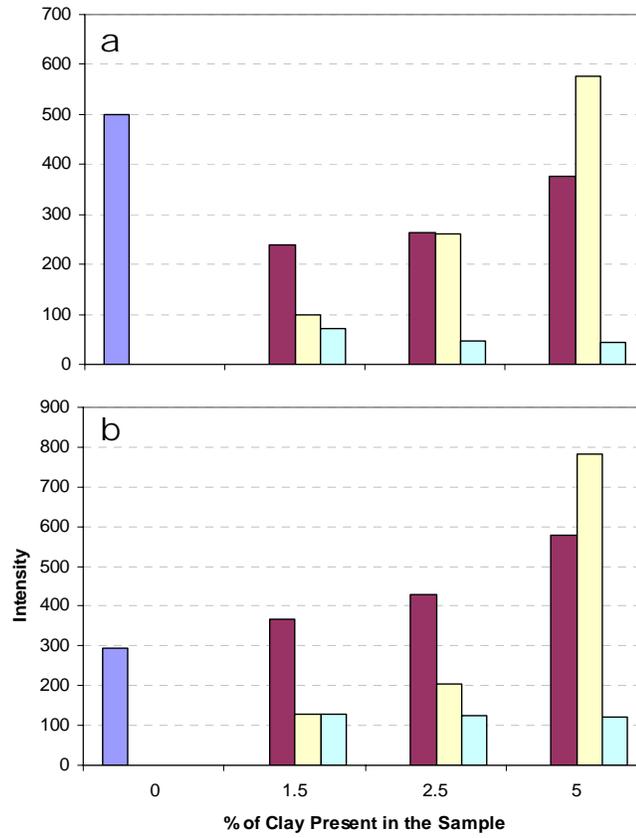
Figure 14 - Relative Intensity of the Ca(OH)$_2$ peak (a) and C-H-S peak (b) in Six Weeks Old Cement Pastes Prepared with Different Clays and Clay Concentration. ☐ **Control;** ☐ **Kaolin;** ☐ **Ca-M;** ☐ **Na-M**

5.5. Impact of Clay and Natural Coatings on the Physical Properties of Concrete

5.5.1   *Effect on Fresh Concrete Properties*

Once the concrete mixes were prepared, certain parameters such as air entrainment, slump, unit weight, and air content, were monitored to understand and quantify the impacts of clay and natural coatings on fresh concrete properties. The values are reported in Table III.1, see Appendix III. The slump results and a comparison between AEA and air content are shown in Figures 15 and 16 respectively.

Natural Coating Samples: The two selected samples resulted in different effects on the slump depending on the nature and the amount of the coating. There was no significant difference in slump between the Hw53 coating and the control since the difference between both values was only ¼-in. This type of coating, a mix of dust and chlorite, with a P200 value of

0.76% did not have an impact on slump. The Hw64 coating, also a mixture of dust and a clay from the montmorillonite group with a P200 of 1.47%, significantly decreased the slump of the mixture when compared with the control (1-¾ in vs. 3 in, respectively). This difference in behavior between the two natural coatings could be explained by the fact that the clay present in Hw64 had a high water adsorption capacity and also because its P200 value was approximately twice that of the Hw53 coating. The influences of these coatings in the amount of air entraining agent needed to reach desirable air content (6 % ± 1%) and the final air content obtained is represented in Figure 16. The Hw53 microfine appeared to decrease the necessary amount of air entraining agent to reach the same final air content as control, 26 vs. 37 ml, respectively. The coating in Hw64 sample demanded the same amount of air entraining agent as the control, however the final amount of air content obtained was slightly different (5.0% for Hw64 and 5.8% for control).
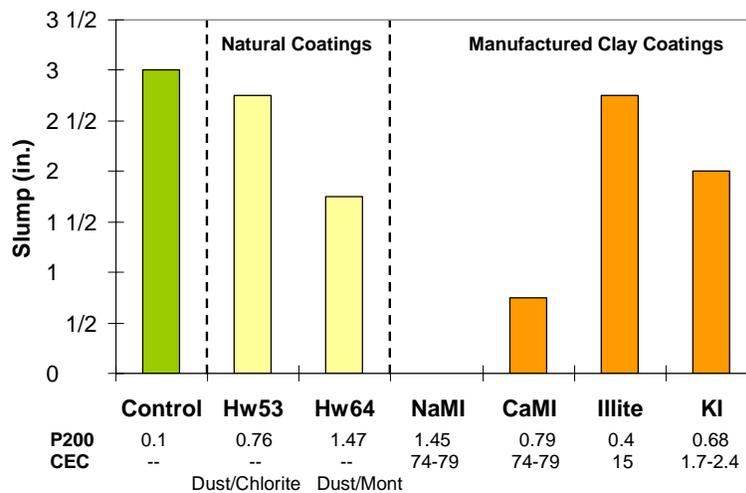
Figure 15 - Slump Values for Concrete prepared with Coated Aggregates

Manufactured Clay Samples: The manufactured clay coatings decreased the slump with the exception of the illite. The most dramatic decreases are registered for the NaMI and CaMI, where the first one produced a stiff mixture with no slump and the second one only had a ¾ in slump. The 0.70% of kaolin coating produced a decrease in slump of 1 inch with respect to the control. And finally, the coating of illite with a P200 of 0.40% did not change the slump of the mixture. This could be due to the convergence of two factors: 1) the low amount of coating present in the aggregate, reflected by a P200 less than 0.5% and 2) the low CEC value and

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therefore the low water adsorption capacity of the illite. As in the previous samples, the influence of the clay coatings on 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 the similar value of P200, around 0.70%, but different CEC and therefore different water adsorption capacity. The results show that the decrease in slump is higher in clays with high CEC and therefore high water adsorption capacity. Some of the natural clay coatings have an impact in the required air entrainment dosage and the final amount of air achieved. The higher impact is produced by the coatings with higher water absorption capacity such as NaMI and CaMI. In both samples, the addition of high amounts of AEA, 85 and 100 ml respectively, produced batches with air contents still under the target range proposed for this study. More precisely, the air content achieved in batch NaMI was 4% and only 2.5% in batch CaMI. These two batches were only able to meet the air content requirements when extra water was added to them to keep workable. For the NaMII batches 20% extra water was added and for the CaMII batches 40% extra water was added. The addition of 90 ml of AEA in batch NaMII was enough to produce an air content of 5.5%. In CaMII, with only 35 ml of AEA the resulting air content was 7%. The 4.4% of extra water added in batch KII, made it possible to achieve a higher air content than KI, 6.5% vs. 5.6% respectively, despite less AEA, 35 vs. 45 ml.
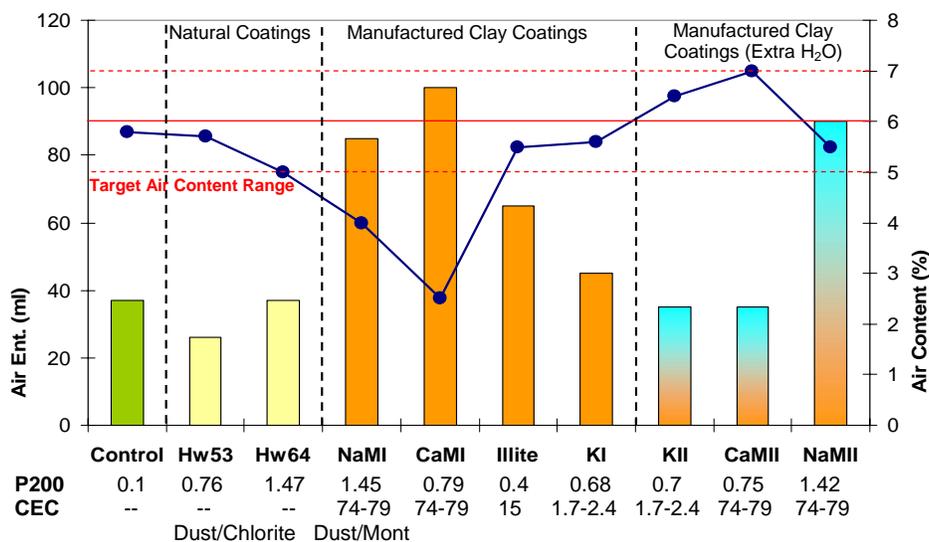
Figure 16 - Effects in (Bars) Air Entrainment and (●—●) Air Content of Aggregate Coatings

5.5.2   Effect on Compressive Strength

The compressive strength of the samples was measured at 28 days of curing for all the batches and the results are presented in Figures 17 and 18.

Natural Coating Samples: A statistical analysis of the natural coated batches revealed no statistical difference between the compression values of these samples and the control under the applied curing conditions.
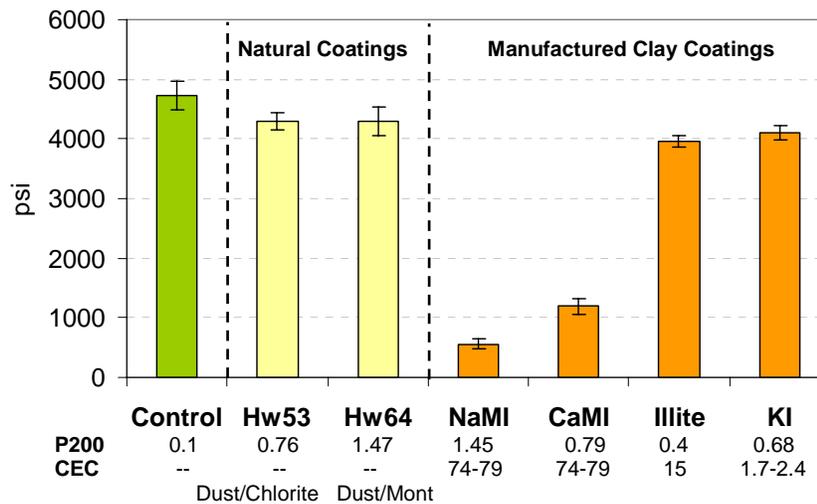
Figure 17 - Values of Compressve Strength (28 days) for Natural and Manufactured Coating Batches

Manufactured Clay Samples: The effect on compressive strength was divided between clays with strong impact and clays with virtually no impact. NaM and CaM clays belong to the first group and the corresponding batches produced a pronounced decrease in the compressive strength, about 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 with a resulting disruption to normal hydration of the cement paste. The possible result in both cases was a concrete with such low content of hydrated cement paste that cohesion between the coarse aggregates was not achieved. For these cases, the addition of extra water during the mixing process increased the compressive strength but always resulted in values lower than the control as shown in Figure 18. The comparison between batches NaMI and NaMII, with 20% extra

water, reveals an increase in compressive strength from 563 to 2194 psi. A similar pattern can be observed when comparing batches CaMI and CaMII, 40% of extra water increased the compression strength from 1189 psi (CaMI) to 2495 psi (CaMII).

	Control	NaMI	CaMI	KI	KII	CaMII	NaMII
P200	0.1	1.45	0.79	0.68	0.70	0.75	1.42
CEC	--	74-79	74-79	1.7-2.4	1.7-2.4	74-79	74-79
Extra Water (%)					4.4	40	20
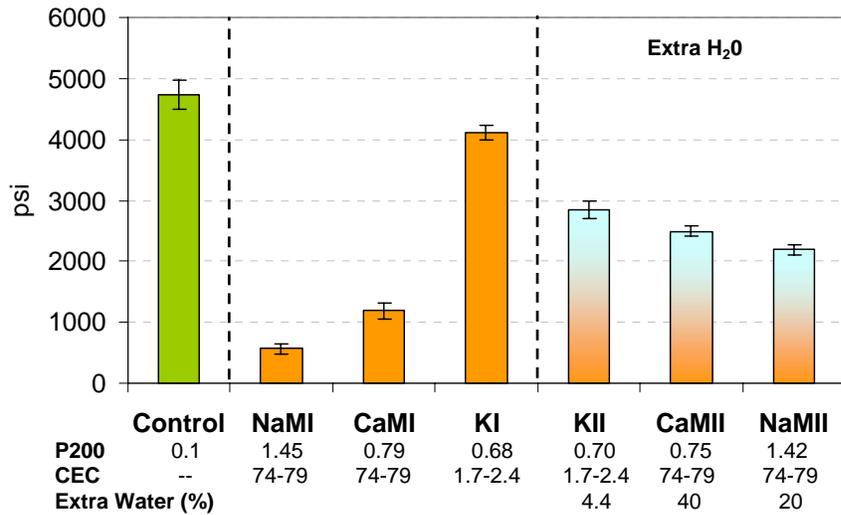
**Figure 18 - Effect of Extra Water Addition on Compressive Strength (28 days)
for Batches with Manufactured Coatings**

The second group of manufactured clays is characterized by batches made with kaolin and Illite coatings. The statistical analysis reveals weak evidence that results from coated batches and control are equal. This means that clays with low water absorption capacities have in the worst of the cases small impact on concrete compressive strength. In contrast with the previous group of clays, the addition of extra water in these mixes was detrimental to compressive strength. For KII, with 4.4% more of water than KI, a decrease of 30% in the overall compressive strength at 28 days of curing was observed (Fig. 18).

5.5.3 *Effect on Tensile Strength*

The 28-day tensile strength values for all batches are presented in Figures 19 and 20.

Natural Coating Samples: As with the compressive strength the presence of the natural coatings did not affect the tensile strength of the batches. The statistical analysis revealed that the results, shown in Figure 19, for batches of Hw53 and Hw64 are not different from the control.
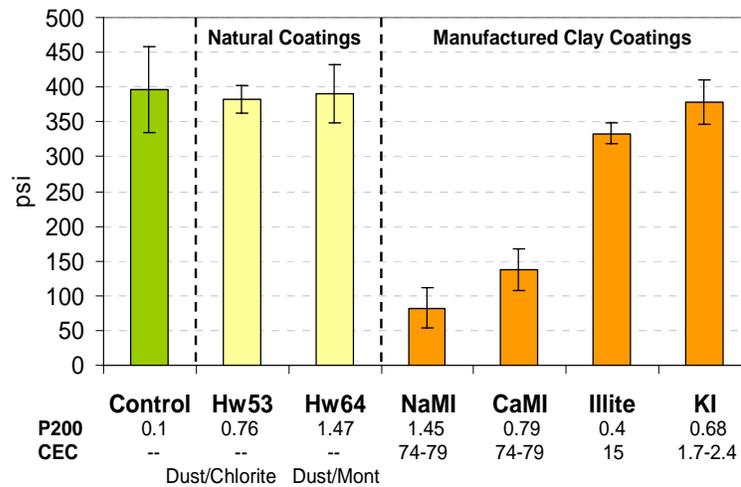
Figure 19 - Values of Tensile Strength for Natural and Manufactured Coating Batches

Manufactured Clay Samples: The tensile strength of manufactured clay samples showed a similar behavior as observed for compressive strength. Two of the clays with high impact on compressive strength also dramatically decreased the tensile strength. The tensile strength loss was 80% in batch NaMI and 65% in batch CaMI with respect to the control. The reasons for these significant decreases are the same argued for the compressive strength. The negative effects of both coatings are partially ameliorated by the addition of extra water. The tensile strength rose from 82 psi in NaMI batch to 255 psi in NaMII batch, and from 138 psi to 236 psi in batches CaMI and CaMII, respectively.
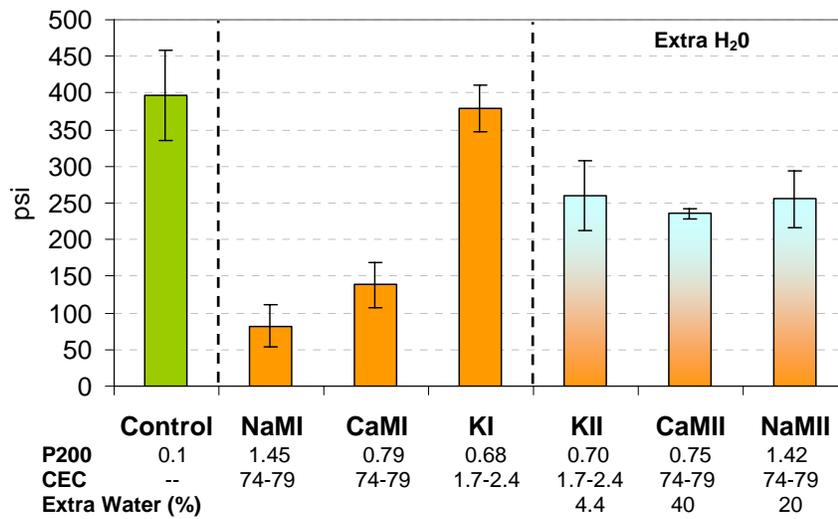
Figure 20 - Effect of Extra Water Addition on Tensile Strength for Batches with Manufactured Coatings

The other two clays, kaolin and illite, did not appear to impact the tensile strength of the concrete. The analysis with the T-test strongly indicates that the kaolin and control are not different, although the same comparison between illite and the control did not show such strong evidence. The addition of 4.4% of water in KII significantly decreased the tensile strength with respect control ($p = 0.013$) as shown in Figure 20.

5.5.4   *Effect on Drying Shrinkage*

The drying shrinkage of all the batches was monitored during 3 months. Figures 21 and 22 show the shrinkage suffered by the concrete samples at 56 and 120 days.

Natural Coating Samples: The drying shrinkage measured for batches made with natural coatings is the same as control, no significant difference was found under the curing conditions used. All the shrinkages fell in the range of 400 to 650 microstrain .
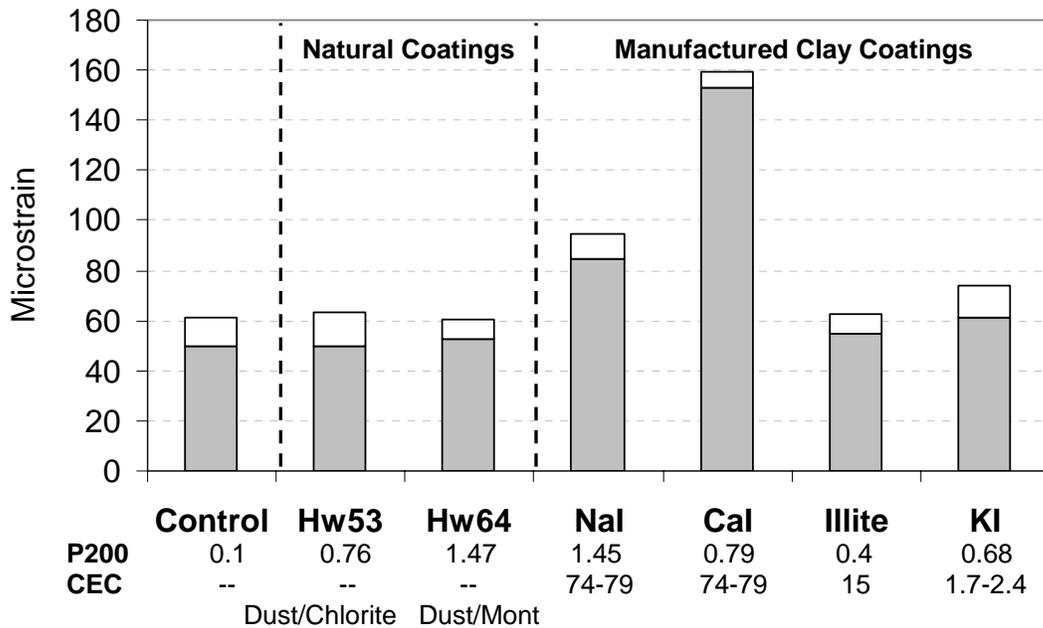
Figure 21 - Drying Shrinkage Values for Natural and Manufactured Coatings, (▨) 56 Days and (☐) 120 Days

<u>Manufactured Clay Samples</u>: The shrinkage of the four types of manufactured clay samples fell within a wide range, between 600 microstrain for the innocuous clay, up to 1600 microstrain for the most harmful clays. The 0.4% P200 value for the illite coating did not produce significant changes with respect to the control shrinkage. That was not the case for the kaolin clay, where only 0.3% more coating than with Illite, produced a significant increase of 15% in the shrinkage at 120 days with respect to the control (p = 0.016). Nevertheless, the greatest increases in shrinkage were registered for the NaMI and CaMI batches. At 120 days, the shrinkage increased from 660 microstrain in the control up to 940 microstrain in NaMI batch and to 1600 microstrain with the CaMI batch. This last case was significant especially when almost half of the amount of CaMI coating (0.79%) with respect to NaMI coating (1.49%) coating was able to instigate a significantly higher shrinkage. Both clays have similar structure and CEC capacity. The only difference resides in the nature of the exchangeable cation. This difference will determine the behavior in water, for example NaM will suffer a destacking or defoliation process in water known as "macroscopic swelling" while the CaM in the presence of water will tend to increase the size of its particles in one direction due to the incorporation of water molecules in between the layers of its structure. This process is called "crystalline swelling".

The final values of shrinkage at 120 days suggest that the crystalline swelling process has a higher impact than the macroscopic swelling.

	Control	NaI	CaI	KI	KII	CaII	NaII
P200	0.1	1.45	0.79	0.68	0.70	0.75	1.42
CEC	--	74-79	74-79	1.7-2.4	1.7-2.4	74-79	74-79
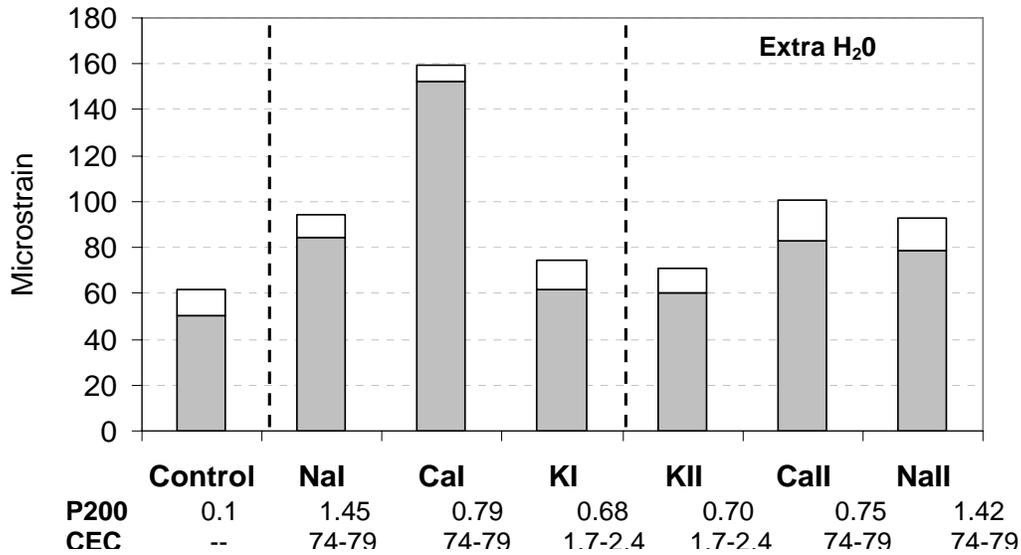
Figure 22 - Effect of Extra Water on Drying Shrinkage for Manufactured Clay Coatings, (▧) 56 Days and (☐) 120 Days

The effect of extra water on the shrinkage is represented in Figure 22. In contrast to what would be expected, the additions of extra water in the batches did not increase the amount of shrinkage. The addition of 4.4 and 20% extra water in KII and NaMII batches respectively, did not change the value of drying shrinkage at 120 days registered in batches KI and NaMI. However the addition of 40% extra water in the CaM decreased the shrinkage by 37% at 120 days. The analysis of the shrinkage histogram for manufactured clay coatings presented in Figure 23 brings additional information about the drying shrinkage mechanism with extra water in the batches.
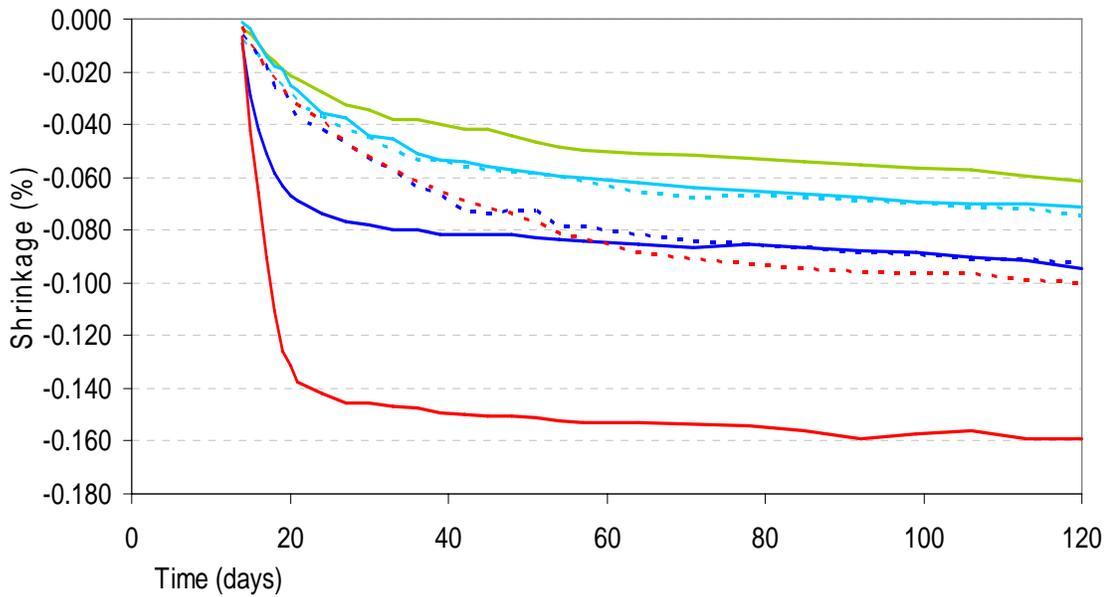
Figure 23 - Drying Shrinkage Evolution of Batches control (▬▬), KI (▬▬), KII (••••), NaMI (▬▬), NaMII (••••), CaMI (▬▬), and CaMII (••••)

The batches made 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, while in batch NaMII, with 20% more water, the same amount of shrinkage was achieved after 57 days of testing. A similar effect was observed in batch CaMI where 92% of the total shrinkage was reached at 27 days vs. batch CaMII where, with 40% of extra water, 92% of the shrinkage was attained only after 78 days of testing.

5.5.5 *Effect on Freeze-Thaw Durability*

The study of freeze-thaw durability was performed on a total of four batches plus the control: 1) two sets of samples were from batches made with natural coated aggregates and 2) two sets of samples were from batches made with two different clay coated aggregates. Kaolin and NaM were selected since both clays present opposite behavior patterns in concrete. Kaolin represents those clays with low water adsorption, high detachment from the aggregate surface during the mixing process, no significant impact on compression and tensile strengths, and low air dry shrinkage. NaM represents those clays with high water adsorption, low detachment from the aggregate surface during the mixing process, and high impact on mechanical properties of the

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concrete. The stiffness and weight degradation of the samples were monitored during 420 freeze-thaw cycles. Results of these studies are illustrated in Figures 24 and 25.
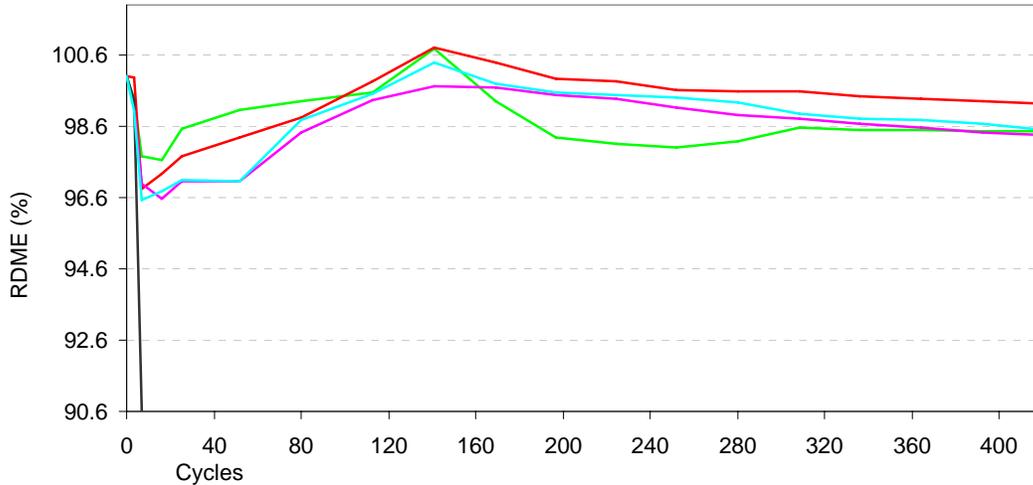
Figure 24 – Stiffness Durability of Batches control (▬▬), Hw53 (▬▬), Hw64 (▬▬), KI (▬▬), and NaMI (▬▬)
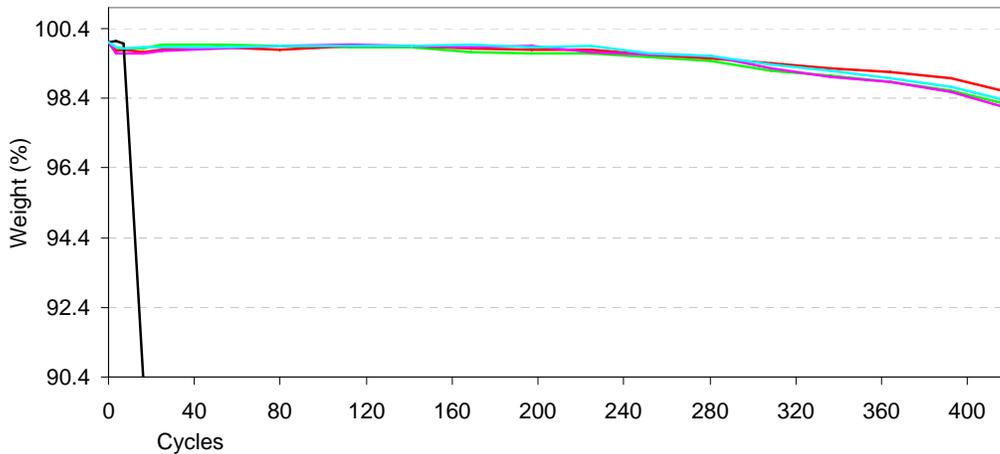
Figure 25 - Weight Durability of Batches control (▬▬), Hw53 (▬▬), Hw64 (▬▬), KI (▬▬), and NaMI (▬▬)

<u>Natural Coating Samples</u>: There was no statistical difference in freeze-thaw durability results between samples with natural coatings and the control, under these experimental conditions, curing for 28 days at 100% relative humidity and 420 cycles of freeze-thaw. As seen

in graphs 24 and 25, Hw53 and H64 samples showed similar evolution of stiffness and weight loss as the control during the entire experiment.

Manufactured Clay Samples: As with the natural coatings, no statistical differences were found between the kaolin sample and the control with regard to freeze-thaw durability measures. The presence of this coating had no effect in stiffness and weight durability under these experimental conditions. A much different result was attained when the sample contained the NaM coating. After 16 cycles the stiffness durability dropped under 60% of the initial stiffness and the test was aborted consistent with ASTM C666. Coatings with high water absorption capacities produce a concrete with low durability characteristics.

5.5.6   *Air Void System Results*

The determination of air content in hardened concrete was conducted for 7 samples. These samples were divided in four groups: 1) one batch prepared with cleaned coarse aggregates, control; 2) two batches prepared using natural coated aggregates; 3) two batches using manufactured clay coated aggregates, NaM and kaolin and water /cement ratio of 0.45; and 4) batches prepared using the clay coated aggregates of group 3) but using extra 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 13.

Table 13 – Fresh, Hardened Air Content and Spacing Factor

Batch	P200 (%)	Fresh Air Content (%)	Hardened Air Content (%)	Spacing Factor (mm)	Standard Deviation
Control	0.1	5.8	6.9	0.10	0.02
Hw53	0.76	5.7	6.8	0.10	0.02
Hw64	1.47	5.0	4.6	0.12	0.02
NaMI	1.45	4.0	28.2	0.32	0.04
NaMII	1.42	5.5	4.9	0.17	0.04
KI	0.68	5.6	4.9	0.22	0.05
KII	0.7	6.5	7.0	0.07	0.02

Natural Coating Samples: The value of air content in Hw53 hardened concrete batch was significantly higher than that from the plastic mix. This concrete batch showed very similar features with respect to air content as the batch prepared with cleaned aggregates (control). These results agreed with the observed AEA demand values for these two concrete batches. The microfine coating of Hw53 did not increase the AEA volume needed to reach the desired fresh air content. In the case of the Hw64 batch, the air contents in the hard and fresh concrete batches were similar. Moreover, the quantities of air content in fresh and hard concrete were smaller than the one achieved in the control or in Hw53 for the same amount of AEA used. Thus, one can postulate that the presence of clay (from montmorillonite group) in the aggregate coating partially inhibits the AEA effect.

The values of air void spacing factor obtain for both natural samples were similar to control, there was no statistical differences between them. The values were below the recommended range for durability in moderate and severe environments. These values were in accordance with the freeze-thaw durability results, where no differences were observed between control and concrete with natural-coated aggregates, see Figure 24. All displayed excellent freeze-thaw durability.

Manufactured Clay Samples: The most striking result is the high value, 28.2%, for the air content measure in NaMI hard concrete batch (w/c = 0.45). This was due to the high quantity of entrapped air voids. This high level of entrapped air was attributed to the high water absorption of the NaM coating resulting in a large increase in the viscosity of the mixture. The lack of plasticity in the mixture prevented the concrete from achieving good compaction and therefore, a high amount of air was entrapped. 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 (from 28.2% to 4.9%). The effectiveness of the AEA increased, as the air content in fresh concrete was slightly higher for the NaMII batch (5.5% vs. 4.0%). Finally, the air voids contained in hardened concrete for both kaolin coated batches, one at 0.45 w/c ratio 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 AEA, the mix demanded more AEA than the control mix 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 the results shown in Table 13, 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 analysis of variance (ANOVA) test showed significant differences between clay samples and control. A statistically significant increase in the spacing factor was registered for the NaM coatings, from 0.10 to 0.32 (p = 0.003), 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 = 0.027) and the value was close to that recommended for a durable concrete. As for the natural coating, the spacing factors obtained were in agreement with freeze-thaw durability measurements, see Figure 24. 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 type of clay coatings could be explained by the tendency of these materials to decrease the effectiveness of AEA, as explained in section 5.5. These clays tend to absorb mixing water so the ability of AEA to created bubbles was potentially reduced.

Finally the effect of the addition of extra water on spacing factor was determined by studying samples 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.

5.6. SEM Analysis of Cement Paste and Interfacial Transition Zone of Concrete Samples

The SEM analyses were conducted for the natural-coated samples and the most representative clay-coated aggregates, kaolin and NaM at 0.45 w/c ratio. Results are shown in Figure 26 and Table 14, respectively. Generally, all coated samples, with the exception of Hw53, and the control had a higher porosity in the ITZ than in the bulk paste. For this project the ITZ was considered those cement paste regions located no further than 25 µm from the coarse aggregate. Bulk paste was considered all the cement paste areas in between 25 and 70 µm from the coarse aggregate.

Natural Coating Samples: The distribution of volume fractions analyzed in Hw53 and Hw64 revealed that both coatings provoked an increase in the bulk porosity in comparison with control sample. This could be explained by the fact that these microfines dispersed in concrete and therefore their impacts were located mostly in the cement paste. The dispersion studies revealed that around 80% of the Hw64 microfines tend to be dispersed in the cement paste

during mixing conditions (see Figure 5). There are not specific data for Hw53 on that respect but base on its nature, where only chlorite clay was detected, it is expected that these microfines will have also a high tendency to get dispersed in the cement paste. In contrast they show a slight decrease in the ITZ porosity and in the amount of unhydrated cement in both, ITZ and bulk, with respect to the control.
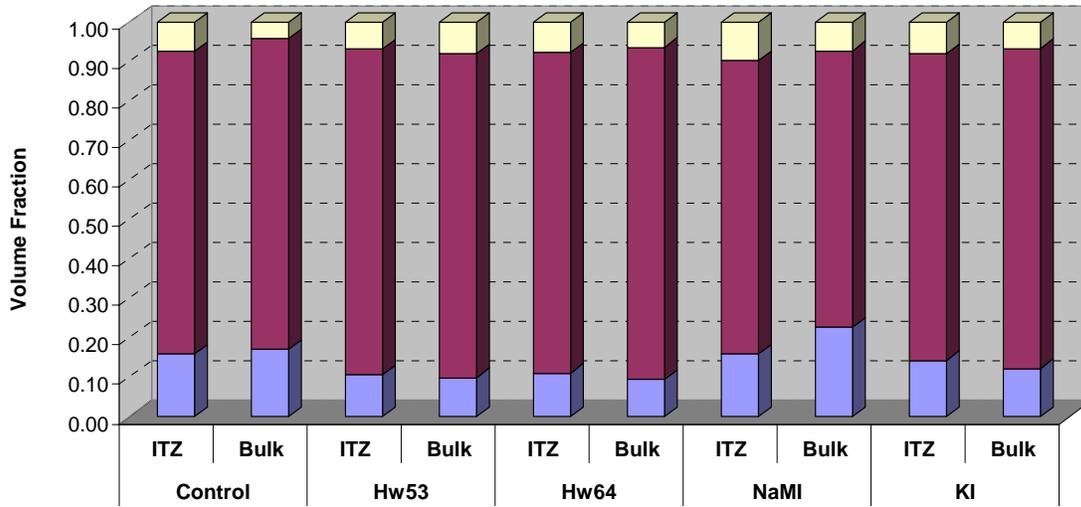
Figure 26 – Volume Fraction of (☐) Unhydrated Cement, (■) Hydration Products, and (☐) Pores in Concrete Samples

Manufactured Clay Coatings Samples: The presence of a NaM coating on the coarse aggregates caused an increase in the porosity of both the ITZ and bulk cement paste. Figure 5 shows that this type of microfine tends to remain attached to the aggregate during the mixing process and therefore should be concentrated in the ITZ, however the increase in porosity when compared with the control concrete is proportionally larger in the bulk paste, thus the increase in porosity does not correlate with the location of clay concentration. The presence of NaM appeared to have a larger effect on the rate of hydration of the cement, its presence decreases the volume fraction of hydrated cement in both the bulk paste and the ITZ. The retardation of the cement hydration caused by the presence of NaM coatings has been also observed by the use of XRD in samples of cement containing NaM (Figure 14). Finally, the kaolin did not show any noticeable change with respect to the control sample in the ITZ or in the bulk with respect to porosity or degree of hydration.

Table 14 – Measured Volume Fraction in Concrete Samples.

Sample	Area of Analysis	Volume Fraction		
		Unhydrated Cement	Hydration Products	Pores
Control	ITZ	0.16	0.77	0.07
	Bulk	0.17	0.79	0.04
Hw53	ITZ	0.11	0.83	0.07
	Bulk	0.10	0.82	0.08
Hw64	ITZ	0.11	0.81	0.08
	Bulk	0.09	0.84	0.06
NaMI	ITZ	0.16	0.74	0.10
	Bulk	0.23	0.70	0.07
KI	ITZ	0.14	0.78	0.08
	Bulk	0.12	0.81	0.07

6. Evaluation of Monitoring Aggregate Cleanness Tests

In this section we examine the ability of the most common tests used to predict the deleterious effects of microfine coatings to foresee the influence of the aggregate coatings of this study in the quality of concrete. Following the work reported by Gullerud and Cramer in 2002 (Gullerud 2002), the evaluation was done 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 ratio (0.45) to eliminate the effect of extra water addition. As in the Gullerud and Cramer report the tests under evaluation were ASTM C117, California Test 227, ASHTO TP57, and the modified methylene blue value index (MMBV) which related results from ASTM C117 and ASHTO TP57. Results from these analyses are reported in Table 15.

Table 15 - Correlation Coefficients (R) for Batches with 0.45 w/c Ratio

Test	Slump (in.)	AEA (ml)	Fresh Air Cont (%)	Strength (psi)		Shrinkage	Stiffness	Weight
				Compressive	Tensile	120-day	300 Cycles	300 Cycles
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

The values of correlation coefficients reveal that P200 value of ASTM C117 test is the poorest predictor of all the concrete properties analyzed except for the slump. The correlation coefficient value ranges between 0.15 and 0.52 for AEA demand, fresh air content, and concrete strength and durability while for slump the correlation coefficient increases in magnitude to -0.72. The California Test 227 anticipates 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. It is worth mentioning the lack of correlation between the values for this test and the values for shrinkage (R= -0.09). 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 goes 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 (see Table 7), suffered a very large drying shrinkage (see Figure 21). Thus, one can say that the California test is not a good predictor of the deleterious character of CaM microfines. Particles of CaM were large enough to easily sediment in aqueous media resulting in high CV values. This clay in water suffers crystalline swelling, however, and as reported before, most of the CaM microfines detach from the aggregate during the mixing process and pass to the mixing water ending in the cement paste. The fact that these clay particles were able to adsorb mixing water in 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 the concrete sets the environment of the clay particle gets drier, and thus, the clay particles desorb water and contract. The contraction of the particle is manifested as a high shrinkage in the overall concrete structure. Base on these facts, it can be said that the California Test 227 is unable to detect the impact of clay coatings on shrinkage with crystalline swelling.

In comparison with California Test 227, the Methylene Blue Value (MBV) is an excellent indicator of shrinkage and fresh air content, with a 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 Modified Methylene Blue Value (MMBV) indicates that in general this index was the best indicator when it can be conducted in a repeatable manner. It showed strong

correlations fresh air content, shrinkage, concrete durability, AEA demand and both compression and tensile strengths.

7. Database of Studied Coatings

One of the original objectives of this project was to determine the frequency and source of deleterious coating in Wisconsin. It was expected that WisDOT would run the California Cleanness Test 227 on No. 1 coarse aggregates qualifying for use in concrete pavement construction projects. The results were expected to be analyzed by this research group and complimented with a mineralogical characterization of the microfines by X-Ray diffraction. A significant amount of data was expected to be collected and used to create a mineralogy database of coating in Wisconsin. Base on this planning, originally it was proposed to create a database limited to the following list of properties/criteria for simplicity:

- Aggregate source
- Aggregate size
- P200
- California Cleanness value.

All samples with results near or below 85 in the California Cleanness Value were intended to be selected for final studies. Difficulties within WisDOT on aggregate monitoring and the collection of data prevented this work as projected from proceeding and the work plan was adjusted accordingly. In February 2005, the WisDOT sent a preliminary analysis of samples from coarse aggregate monitoring used during the 2004 construction season. A total of 61 coarse aggregate samples were analyzed to determine the P200 content and the California Cleanness Value (see Appendix 11.6). Only one of the 61 had an index below 85 and two more were just slightly above this threshold with a value of 86. These three samples were the only ones that appeared suitable for further study. Unfortunately it was not possible to gather more material for further analysis. As a consequence only two natural samples were selected for the final stage of the study. Study on the impacts of clay coatings and the natural selected microfines on concrete performance have been extremely valuable to support development of a database that could help to prevent and/or identified problems in concrete performance related with presence of

microfines, and an example can be seen in Appendix IV. Based on our knowledge we recommend that the data base should contain at least three different levels of information with their corresponding data:

1)   Identification of the samples: where the aggregate came from and in which project it was used.

2)   Characterization of the coating: aggregate source and size, P200, MBV or CV results, and mineralogy of the coating.

3)   Construction records. This section would gather data related to mixing, construction and curing conditions during the project. All of these data could be relevant in order to prevent or identify problems in concrete performance.

8. Summary and Conclusions

The major observations from this study of the effects of manufactured clay and natural coating of coarse aggregates in concrete are summarized in Tables 16 and 17 respectively.

Table 16 - Summary of Findings for Manufactured Clay Coatings of Coarse Aggregates

Batch	Microfine Characterization	Impacts
NaMI	• Microfine: sodium montmorillonite (NaM). • Monitoring Tests: Microfine with a **P200** of **1.45**, **failed CV** with a **66** and **high value of MBV** (15.8 mg/g). The clay has a **high CEC** (74-79 meq/100 g). • Behavior in Water Suspension: The clay does not sediment in water (see Figure 8). • Dispersion in Concrete: the distribution studies done indicate that this clay tends to **remain attached to the surface of the aggregates** and therefore disrupt the ITZ of the concrete.	▪ Early Hydration Reaction: **decreases hydration reaction and lowers the concentration of CSH and Ca(OH)$_2$.** ▪ Slump: dramatically **decreases workability** ▪ AEA demand: needed **high amounts of AEA** to achieve **low fresh air content** in the mixture ▪ Air Void System: the AEA is unable to create bubbles due to lack of available mixing water and possibly due to a specific absorption between the clay and the molecule of AEA. The stiffness of the mixture inhibits the formation of air void system. ▪ ITZ and Bulk: **increases the porosity in the ITZ**. **Higher concentration of unhydrated cement** in the bulk. ▪ Hard Properties: **decreases in compression and tensile strength. High drying shrinkage. Very low freeze-thaw durability**.
NaMII	• Batch prepared with same microfine as NaMI but adding 20% of extra water to maintain workability.	▪ AEA demand: **high amounts of AEA** to achieve **low fresh air content** in the mixture ▪ Air Void System: improved the effectiveness of the AEA, but the fresh air content achieved were still under limits of the study (see Figure 16). The mixture presented a more cohesive and plastic mix ▪ Hard Properties: **Improved compression and tensile strength** with respect batch NaMI but always under the control levels. **Same drying shrinkage** as NaMI.

Batch	Microfine Characterization	Impacts
CaMI	- Microfine: calcium montmorillonite (CaM). - Monitoring Tests: Microfine with a **P200** of **0.79**, **pass CV** with a **94** and **high value of MBV** (106.7 mg/g). The clay has a **high CEC** (74-79 meq/100 g). - Behavior in Water Suspension: Clay in water tends to sediment (Figure 8). This is explained by the fact that although the particles tend to incorporate water molecules in between the clay layers they do not suffer destacking. They suffer an expansion in one direction as **crystalline swelling**. - Dispersion in Concrete: the distribution studies indicate that this clay tends to detached from the surface of the aggregates and are **dispersed in the bulk**. Its impacts will be located mostly in the cement paste.	- Early Hydration Reaction: **Increases rate of hydration** (especially in concentrations equal or lower than 2.5%). - Slump: Dramatically **decreases workability** by "capturing" the mixing water. - AEA demand: Needed **high amounts of AEA** to achieve **low fresh air content** in the mixture - Air Void System: The AEA is unable to create bubbles due to lack of mixing water available and probable due to a specific absorption between the clay and the molecule of AEA. The stiffness of the mixture inhibited the accumulation of significant amount of air voids. - Hard Properties: **Decreased compression and tensile strength**. **Higher drying shrinkage**.
CaMII	Batch prepared with same microfine as CaMI but adding 40% of extra water to maintain workability.	- AEA demand: **High amounts of AEA** were needed to achieve **low fresh air content** - Air Void System: Improved the effectiveness of the AEA. The mixture presented a more cohesive and plastic mix and therefore no significant amount of air was entrapped. - Hard Properties: **Improved compressive and tensile strength** with respect batch CaMI but always under the control levels. It showed **smaller drying shrinkage** compared to CaMI at the end of 120 days.
KI	- Microfine: Kaolin. - Monitoring Tests: Microfine with a **P200** of **0.68**, **pass CV** with a **94** and **medium value of MBV** (6.76 mg/g). The clay has a **low CEC** (1.7-2.4 meq/100 g). Low water adsorb tendency. - Behavior in Water Suspension: as CaM, the clay easily sediment (Figure 8). The clay particles do not have crystalline swelling. - Dispersion in Concrete: Clay tends to detach from the surface of the aggregates and is **dispersed in the bulk**. The impacts will be primarily located in the cement paste.	- Early Hydration Reaction: **Increased the rate of hydration** (at any studied concentration). - Slump: **Decreased workability**. - AEA demand**: Increased the amount of AEA** needed to achieve the same air content as in control. This could be explained by a specific absorption between the clay and the molecule of AEA. - Air Void System: **No impact was observed in the hardened air void system**. - ITZ and Bulk: Volume fraction of pores, unhydrated cement and hydration products in both areas are similar to the ones measured in control sample. - Hard Properties: **Possible decrease in compressive strength**. **No effect in tensile strength**. **Moderate drying shrinkage. Good freeze-thaw durability**

Batch	Microfine Characterization	Impacts
KII	• Batch prepared with same microfine as KI but adding 4.4% of extra water to maintain workability.	▪ AEA demand: Extra water addition decreased the AEA demand. The same amount of AEA was needed as in control to reach the desired level of fresh air content. ▪ Hard Properties: **Decreased compressive and tensile strength** with respect KI batch. **Same drying shrinkage** as KI.
Illite	• Microfine: Illite. • Monitoring Tests: Microfine with a **P200 of 0.4**, **pass CV** with a **95** and **medium value of MBV** (6.67 mg/g). The clay has a **low CEC** (15 meq/100 g). Low water adsorb tendency. Behavior in Water Suspension: Not done. Based on its characteristics is expected to behave as kaolin • Dispersion in Concrete: Not done, but it is expected to behave as kaolin.	▪ Slump: **No effect in workability** (for this amount of P200) but could have a modest influence on workability. ▪ AEA demand: **Increased** the **amount of AEA** needed to achieve same fresh air content as control. ▪ Air Void System: Not done, but no impact is expected in the hardened air void system. ▪ Hard Properties: **Possible decrease in compressive strength**. **No effect in tensile strength**. **No effect in drying shrinkage**.

Table 17 - Summarize of Findings Natural Coatings of Coarse Aggregates

Batch	Characterization	Impacts
Hw53	• Microfine: Dust/Clay (Chlorite). • Monitoring Tests: Microfine with a **P200 of 0.76**, **pass CV** with **89** and **very low value of MBV** (0.8 mg/g). • Dispersion in Concrete: This microfine is expected to be dispersed in the cement paste during the mixing process.	▪ Slump: The microfine at this P200 **does not affect the workability**. ▪ AEA demand: a slight decrease in AEA demand was detected. ▪ Air Void System: **No observed impact** of the microfine on the **air void system**. The hard and fresh air content results are in agreement with control. ▪ ITZ and Bulk: Volume fraction of pores, unhydrated cement and hydration products in both areas are similar to those of the control. ▪ Hard Properties: **No effect in compressive and tensile strengths**. **No effect in drying shrinkage. Good freeze-thaw durability**.

Batch	Characterization	Impacts
Hw64	• Microfine: Dust/Clay (Montmorillonite). • Monitoring Tests: Microfine with a **P200** of **1.47**, **pass CV** with a **91** and **medium value of MBV** (6.67 mg/g). • Dispersion in Concrete: The distribution studies done indicate that this microfine easily detaches from the surface of the aggregates and **disperses in the bulk**.	▪ Slump: **Decreased workability**. ▪ AEA demand: Slightly increased the amount of AEA needed to achieve the same air content as in control. This could be explained by a specific absorption between the clay fraction of the microfine and the molecule of AEA. ▪ Air Void System: No observed **impact** of the microfine in the **air void system.** ▪ ITZ and Bulk: No significant impacts in volume fraction of pores, unhydrated cement and hydration products were detected in both areas ▪ Hard Properties: **No effect in compression and tensile strength. No effect in drying shrinkage. Good freeze-thaw durability**.

Several conclusions are extracted from the current research project. In general, the conclusions reinforce those by Gullerud and Cramer in the previous report but add some new discoveries (Gullerud 2002). The major conclusions are listed below and divided in three sections:

I. Study of the effect of clay coatings in concrete.

*W*hen aggregates with clay coatings are used in the preparation of concrete, a fraction of the clay will enter the water phase before the dry cement is added. The degree of detachment depends on the nature of the clay. But clay detachment may also depend on other variables not explored in this study, such as particle size. The concentration of clay in the water phase before the dry cement is added will be a function of the nature of the clay and the original clay content of the aggregate. The presence of clays in the cement paste influences the rate of the hydration reactions. The clay with macroscopic swelling (NaM) is the most difficult to detach and decreases the rate of hydration. Clays with crystalline swelling (CaM) and no swelling (kaolin) are easier to detach and increase the rate of the hydration reactions.

The effect of clays in early hydration reactions depend on the nature of the clay. Pastes with NaM decrease the rate of hydration. CaM cement paste tends to increase the rate of hydration in concentrations equal or lower than 2.5% and decrease this rate when the concentration of clay is equal or larger than 5%. The presence of kaolin accelerates the hydration reaction in cement paste at any of the studied concentrations.

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 of 1.5%. The extent and nature of the impact depends on the nature and the quantity of the clay. Clays with higher Cation Exchange Capacity (Na and Ca montmorillonite) produce the higher impacts in fresh and hardened concrete properties. Montmorillonite group clays, with a 0.76% P200 value, tended to adsorb high amounts of water and increase the stiffness of the plastic concrete mixtures. This stiffness in the mixture inhibits adhesion between cement paste and coarse aggregate. These effects lead to concretes with lower compressive and tensile strengths, and higher shrinkage and lower freeze-thaw durability. The addition of extra water in mixes 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 low CEC (kaolin) and with a 0.70% P200 value only affected workability by decreasing the slump. The other clay, illite, with a smaller P200 value did not affect workability. However, the analysis of compressive strength in mixes with both clays shows weak evidence that their results are equal to the control, meaning that higher P200 values of these two clays could lead to a decrease in compressive strength. The addition of extra water in the batch containing kaolin coatings produced a deterioration of both strengths of the concrete.

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

Finally, an increase in the AEA 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 appear to be inhibited by the presence of these clays since 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 adsorption capacity of these clays lead

to insufficient mix flow for the AEA to stabilize air bubbles and 2) a specific interaction between AEA molecules and clay particles inhibits the AEA molecules to stabilize air bubbles.

II.   *Evaluation of the current monitoring method to detect microfine coatings.*

Four main conclusions can be drawn from the evaluation of the current methods for detecting or limiting microfines. 1) The P200 index is a quantitative measure that does not reflect the detrimental or innocuous nature of the coatings. The extent and impact of microfines in concrete not only depends on quantity but also in the nature of the microfines. 2) It is demonstrated that both CV and MBV are better indicators than P200 index. 3) CV index is unable to detect shrinkage with concrete which possesses coatings with clays having crystalline swelling. 4) the MMBV is the method that best predicted the quality measures of the concrete in this study.

III.   *Characterization of properties from concrete made with real Wisconsin Aggregates*

Two different coarse aggregates containing microfines were analyzed. Both microfines were a mix of dust and clays. The clays detected were chlorite for one microfine and montmorillonite for the other sample. No significant impacts were detected in the fresh and hardened concrete properties analyzed under the curing conditions of the tests. The sample containing montmorillonite had an observable decrease in workability and the slump of the concrete.

9. Recommendations

Both reports, the one previously elaborated by Gullerud and Cramer and this one, clearly demonstrate that the effects of microfines in concrete are not only dependent on the amount of microfines but also on their nature. Based on this assertion, the current monitoring situation in Wisconsin is unnecessarily limited since it is only based on P200 values. This situation can easily allow potentially harmful microfines to be accepted and may over limit other microfines that are innocuous or even beneficial. The first recommendation is to update the monitoring protocol by complimenting the P200 test with another test. While the P200 test combined with the MMBV test provides the best available prediction of concrete properties, the Methylene Blue test is susceptible to variations resulting from operator technique and interpretation. Neither the California Test 227 nor the MMBV are trivial in the time requirements to conduct the test. Not including specimen preparation time, the California Test 227 requires 20 to 30 minutes to conduct and similar time is required for MMBV test. Given this situation neither of these tests can be strongly recommended to WisDOT for implementation. Essentially, the complimentary test needed does not exist and requires development.

The second recommendation is to review the actual limits of microfine content coarse aggregates. The current standard only allows 1.5% of microfines on coarse aggregate if deleterious materials are not present. The research group recommends that these limits should be reviewed based on the nature of the microfines. Not all microfines have the same impact on concrete, so their limits should not be the same. For example, clays with low CEC such as kaolin and illite only have an impact in concrete on P200 values higher than 0.70%. The P200 limit could vary according to the nature of the microfine if a suitable screening test could be identified and implemented to differentiate the nature of the microfines.

Finally, the last recommendation is the creation of a database of coarse and fine aggregates as the one proposed in this research. This database will be useful not only to prevent possible problems due to presence of microfines but also will be a valuable tool to identify the causes of premature deterioration symptoms.

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11. Appendices

11.1   Appendix: X-Ray Diffraction Data

<u>Black River Fall Coarse Aggregate</u>
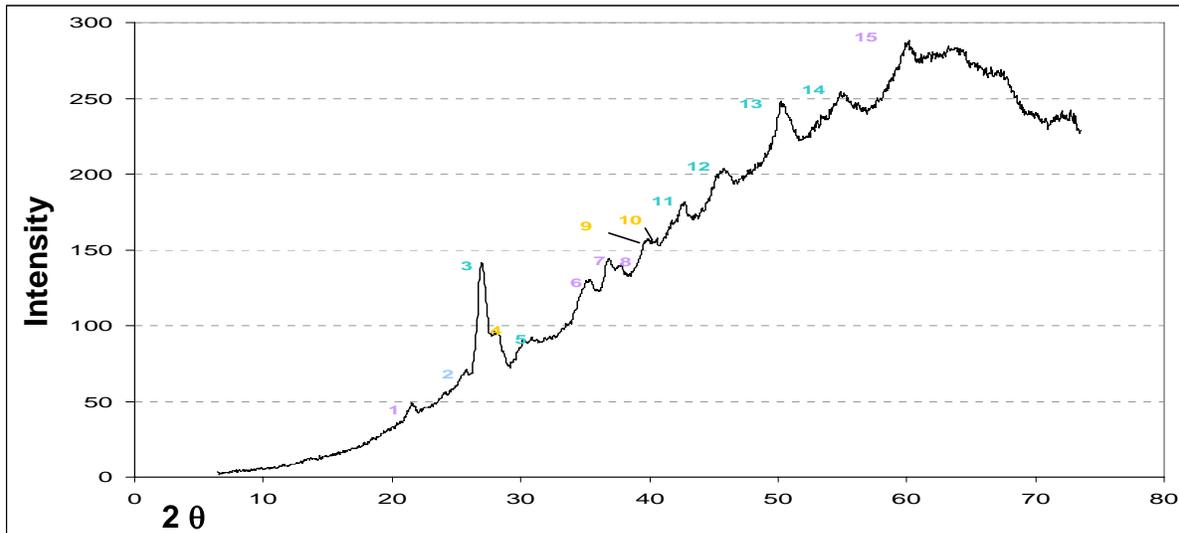
Figure I.1 – Diffractogram of Natural Coating from Black River Falls Coarse Aggregate

Table I.1. - Peak Identification for Black River Falls Coating

Peak	2θ	d (A)	Intensity	2θ	Intensity	Compound
1	21.8	4.183	46.54	21.956	4	Ca Mg Al Silicate Hydroxide
2	26.25	3.483	69.68	26.75	100	K Al Silicate
3	27.1	3.376	138.95	27.165	60	
4	28.35	3.230	93.18	28.037	100	Na Ca Carbonate
5	30.7	2.988	89.41	30.71	14	K Al Silicate
6	35.55	2.591	127.81	35.452	5	
7	37	2.493	141.35	36.853	10	Ca Mg Al Silicate Hydroxide
8	37.95	2.432	139.29	37.884	6	
9	40.3	2.296	155.11	39.673	10	Na Ca Carbonate
10	41	2.258	155.25	40.991	60	
11	42.85	2.165	179.22	42.675	2	
12	46.2	2.016	200.07	45.961	8	K Al Silicate
13	50.55	1.852	244.44	50.315	3	
14	55.45	1.700	250.32	55.55	2	
15	60.2	1.577	287.02	60.005	1	Ca Mg Al Silicate Hydroxide

Highway 53 Coarse Aggregate in Eau Claire (Eau Claire County)
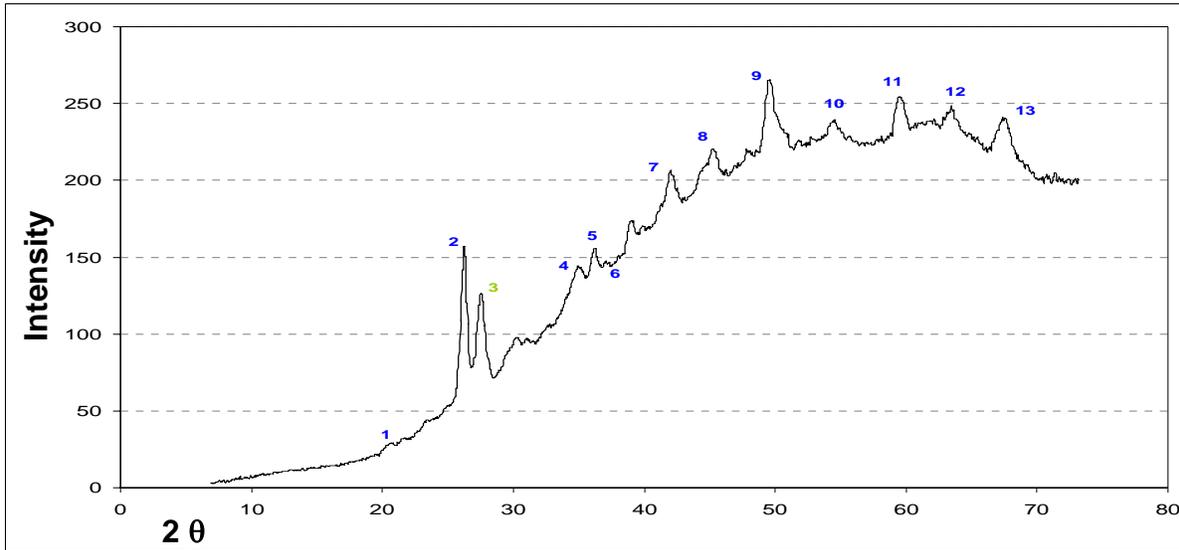
Figure I.2 – Diffractogram for Sedimentable Fraction of Natural Coating from Highway 53
Coarse Aggregate

Table I.2. – Peak Identification for Sedimentable Fraction of Highway 53 Coating

Peak	2θ	d (A)	Intensity	2θ	Intensity	Compound
1	21	4.340		20.850	22	Quartz
2	26.25	3.483	157.1853	26.652	100	
3	27.55	3.322	126.5536	28.871	20	Calcium Chlorate
4	36.15	2.549	155.7189	36.542	8	
5	39.2	2.358	172.587	39.456	8	
6	40.3	2.296	169.6576	40.284	4	
7	42.05	2.204	206.7014	42.470	6	
8	45.45	2.047	218.6491	45.809	4	Quartz
9	49.7	1.882	262.7996	50.141	14	
10	54.7	1.722	237.234	54.869	4	
11	59.7	1.589	252.4605	59.948	9	
12	63.65	1.500	245.8048	64.001	1	
13	67.7	1.420	239.7841	67.750	6	
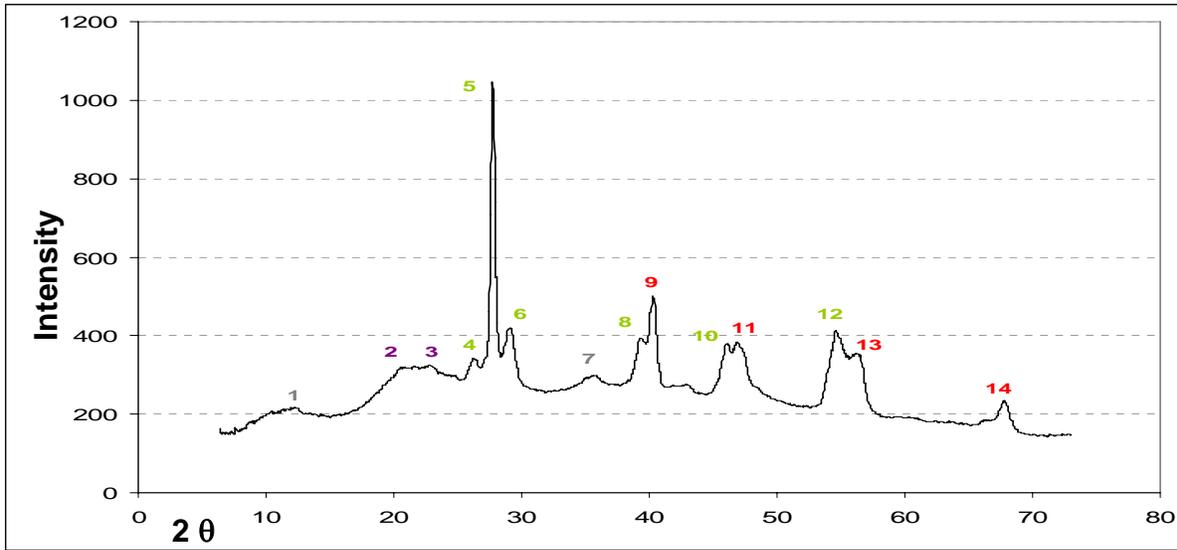
Figure I.3 – Diffractogram for Suspended Fraction of Natural Coating from Highway 53 Coarse Aggregate

Table I.3. – Peak Identification for Suspended Fraction of Highway 53 Coating

Peak	2 θ	d (A)	Intensity	2 θ	Intensity	Compound
1	12.55	7.053	214.93	12.540	100	Chamosite
2	21.1	4.211	317.69			Amorphous Silica
3	23.3	3.818	316.47			
4	26.5	3.364	336.92	26.587	12	
5	27.75	3.215	1042.87	27.594	100	Calcium Chloride
6	29.25	3.053	411.31	28.871	20	
7	36.4	2.468	292.00	36.580	70	Chamosite
8	39.75	2.268	379.81	39.312	20	Calcium Chloride
9	40.4	2.233	496.00	40.750		Silica Wafer
10	46.25	1.963	373.41	45.790	10	Calcium Chloride
11	47	1.933	378.07	47.500		Silica Wafer
12	54.8	1.675	403.75	54.582	4	Calcium Chloride
13	56.6	1.626	348.52	56.500		Silica Wafer
14	68	1.379	225.92	68.500		
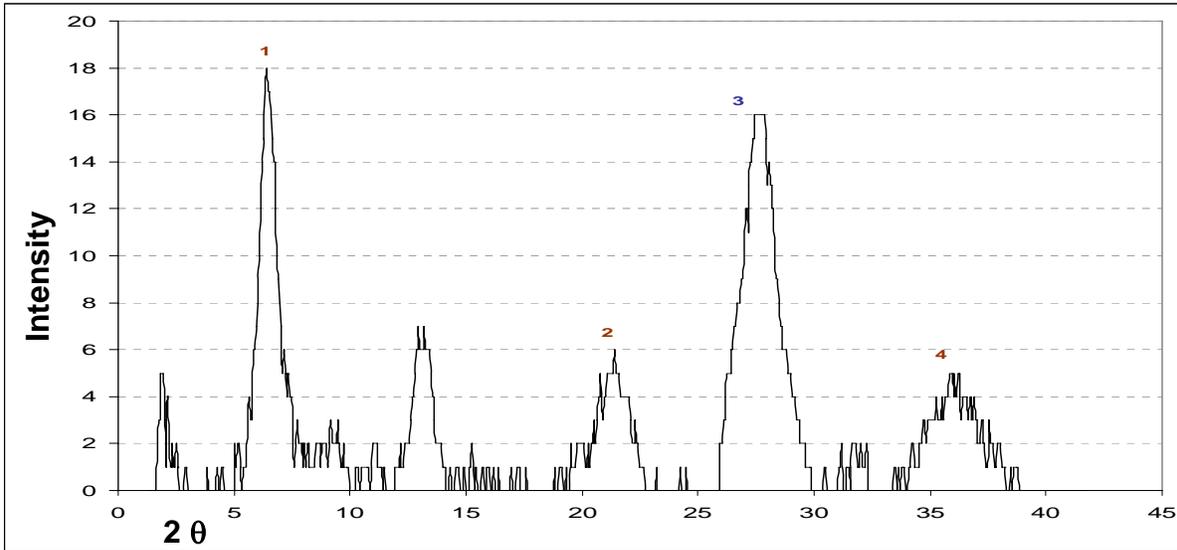
Figure I.4 – Diffractogram of Natural Coating from Highway 64 Coarse Aggregate

Table I.4. – Peak Identification for Highway 64 Coating

Peak	2 θ	d (A)	Intensity		2 θ	Intensity	Compound
1	6.612	13.368	18		6.955	100	Ca Al Silicate Hydrate
2	21.4	4.152	6		21.42	10	Ca Al Silicate Hydrate
3	27.7	3.220	16		27.507	50	Calcium Silicate Hydrate
4	36.05	2.491	5		36.026	20	Ca Al Silicate Hydrate

11.2   Appendix: Study for Simulation of Coating Detachment

Studied Variables in the Shaker Model G-27:

1 – Amount of Aggregate and Vessel Position
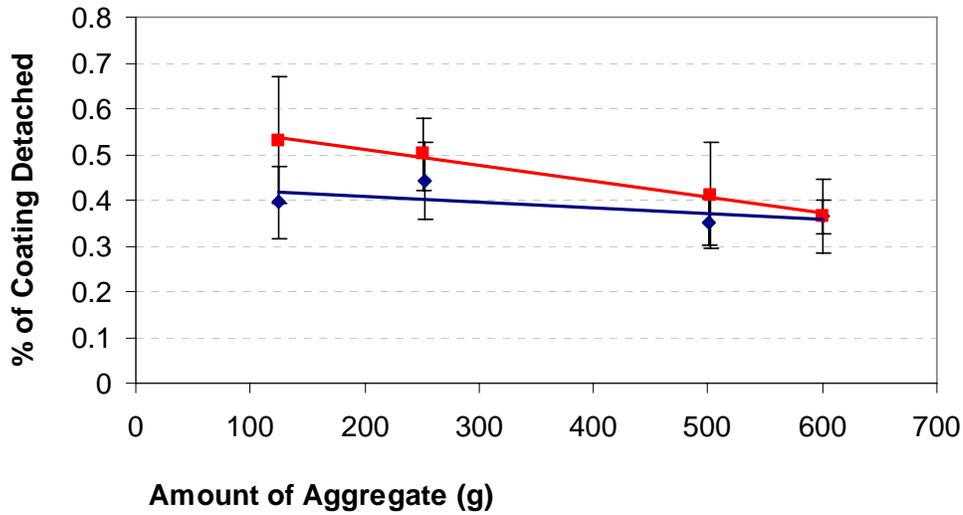
Figure II.1 – Influence of Amount of Aggregate and Vessel Position in the Detachment of Coatings for (■) Horizontal and (▲) 30º Inclined Samples.

2 – Volume of the Vessel
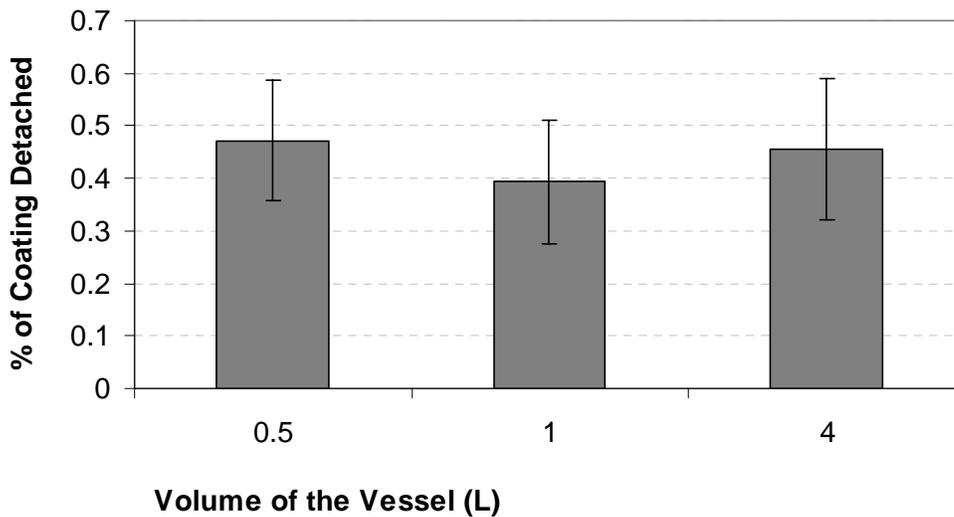
Figure II.2 – Influence of Vessel Size in the Detachment of Coatings.
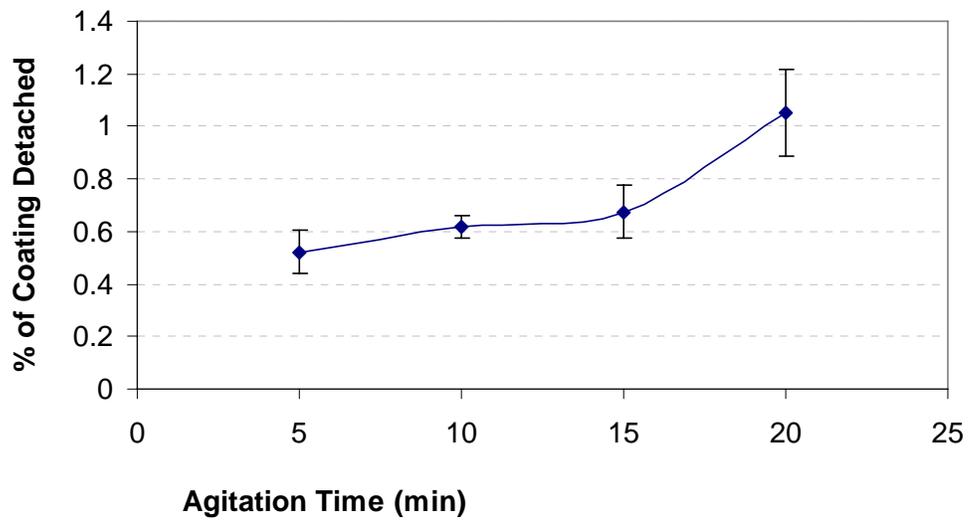
Figure II.3 – Influence of Agitation Time in the Detachment of Coatings.

11.3   Appendix: Concrete Properties of Batches

Table III.1. – Fresh Concrete Properties

Batch Id	Type coating	P200 (%)	Air ent (ml)	Slump (in.)	Unit Weight (lb/ft^3)	Fresh Air Content (%)
Control	Clean	0	37	3	143.68	5.8
H53	Dust (Quartz)/ Clay (Chlorite)	0.76	26	2 3/4	143.92	5.7
H64	Dust/Clay (Montmorillonite)	1.47	37	1 3/4	145.84	5
NaMI	Clay Na-M	1.45	85	0	140.72	4
NaMII	Clay Na-M	1.42	90	1/2	164.8	5.5
CaMI	Clay Ca-M	0.79	100	3/4	142.8	2.5
CaMII	Clay Ca-M	0.75	35	7	155.2	7
Illite	Clay Illite	0.40	65	2 3/4	164.8	5.5
KI	Clay Kaolin	0.68	45	2	165.76	5.6
KII	Clay Kaolin	0.70	35	4	157.2	6.5

Table III.2. – Average Batch Compressive Strengths

Batch Id	Air Content (%)	Compressive Strength (psi)		Tensile Strength (psi)
		Uncorrected	Corrected	
Control	5.8	4803	4735	397
H53	5.7	4385	4293	382
H64	5	4599	4293	390
NaMI	4	644	563	82
NaMII	5.5	2272	2194	255
CaMI	2.5	1486	1189	138
CaMII	7	2317	2495	236
Illite	5.5	4101	3960	333
KI	5.6	4226	4108	379
KII	6.5	2744	2846	260

Table III.3. – Air Dry Shrinkage Absolute Values

Days	Shrinkage (%)									
	Control	Hw53	Hw64	NaI	NaII	CaI	CaII	Illite	KI	KII
14	0.004	0.006	0.002	0.009	0.006	0.007	0.003	0.002	0.008	0.001
15	0.005	0.010	0.005	0.029	0.009	0.043	0.010	0.005	0.011	0.004
16	0.009	0.013	0.011	0.042	0.014	0.066	0.014	0.010	0.014	0.009
17	0.013	0.015	0.015	0.051	0.018	0.090	0.019	0.015	0.019	0.014
18	0.016	0.019	0.018	0.059	0.026	0.111	0.023	0.018	0.022	0.018
19	0.019	0.020	0.019	0.063	0.026	0.126	0.026	0.021	0.026	0.019
20	0.021	0.024	0.021	0.067	0.032	0.132	0.031	0.024	0.028	0.025
21	0.023	0.026	0.024	0.069	0.037	0.137	0.032	0.027	0.032	0.027
24	0.028	0.030	0.029	0.074	0.042	0.142	0.039	0.031	0.037	0.036
27	0.032	0.034	0.033	0.077	0.047	0.146	0.047	0.036	0.042	0.038
30	0.034	0.037	0.036	0.078	0.053	0.146	0.052	0.039	0.045	0.044
33	0.038	0.041	0.039	0.080	0.057	0.147	0.057	0.041	0.050	0.046
36	0.038	0.042	0.040	0.080	0.064	0.148	0.061	0.044	0.053	0.051
39	0.040	0.043	0.041	0.082	0.066	0.149	0.065	0.045	0.053	0.054
42	0.042	0.047	0.044	0.082	0.073	0.150	0.069	0.048	0.056	0.054
45	0.042	0.046	0.046	0.082	0.074	0.151	0.071	0.050	0.057	0.056
48	0.044	0.048	0.047	0.082	0.073	0.150	0.074	0.050	0.058	0.057
51	0.047	0.050	0.047	0.083	0.073	0.151	0.077	0.051	0.059	0.058
54	0.049	0.050	0.051	0.083	0.078	0.152	0.081	0.053	0.060	0.060
57	**0.050**	**0.050**	**0.052**	**0.084**	**0.079**	**0.153**	**0.083**	**0.055**	**0.061**	**0.060**
64	0.051	0.052	0.053	0.086	0.082	0.153	0.089	0.056	0.066	0.062
71	0.052	0.053	0.054	0.086	0.084	0.153	0.091	0.058	0.067	0.064
78	0.053	0.055	0.056	0.086	0.085	0.154	0.093	0.059	0.067	0.065
85	0.054	0.056	0.056	0.086	0.087	0.156	0.095	0.060	0.068	0.066
92	0.055	0.058	0.056	0.088	0.089	0.159	0.096	0.061	0.069	0.068
99	0.056	0.059	0.059	0.089	0.089	0.157	0.096	0.061	0.070	0.070
106	0.057	0.061	0.059	0.090	0.091	0.156	0.096	0.061	0.071	0.070
113	0.059	0.061	0.059	0.091	0.091	0.159	0.097	0.062	0.072	0.070
120	**0.061**	**0.063**	**0.060**	**0.094**	**0.093**	**0.159**	**0.099**	**0.062**	**0.074**	**0.071**

Table III.4. – Stiffness Durability Values

Cycles	Control Average	Control Std dev	Hw53 Average	Hw53 Std dev	Hw64 Average	Hw64 Std dev	NaI Average	NaI Std dev	KI Average	KI Std dev
0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	0.0
3	99.3	0.4	100.0	0.2	99.2	0.2	99.3	0.2	99.0	0.7
7	97.8	1.1	96.8	0.5	97.0	0.9	90.6	0.0	96.5	0.4
16	97.6	0.9	97.2	0.9	96.6	1.3	4.0	5.8	96.8	1.2
25	98.5	0.8	97.8	0.9	97.0	1.1	0.0	0.0	97.1	1.2
52	99.0	1.0	98.3	0.8	97.0	1.1	0.0	0.0	97.0	0.6
80	99.3	0.4	98.9	0.5	98.4	0.5	0.0	0.0	98.8	0.5
113	99.5	0.4	99.9	0.1	99.3	0.8	0.0	0.0	99.5	0.3
141	100.8	0.5	100.8	0.6	99.7	0.8	0.0	0.0	100.4	0.8
169	99.3	2.2	100.4	0.8	99.7	0.8	0.0	0.0	99.8	0.7
197	98.3	1.5	99.9	0.7	99.5	0.9	0.0	0.0	99.6	0.8
225	98.1	1.6	99.9	0.7	99.4	1.0	0.0	0.0	99.5	0.8
252	98.0	1.7	99.6	0.7	99.1	1.1	0.0	0.0	99.4	0.8
280	98.2	1.4	99.6	0.7	98.9	1.1	0.0	0.0	99.3	0.9
308	98.6	0.3	99.6	0.7	98.8	1.0	0.0	0.0	98.9	1.2
336	98.5	0.4	99.4	0.7	98.7	1.0	0.0	0.0	98.8	1.1
364	98.5	0.4	99.4	0.7	98.6	1.0	0.0	0.0	98.8	1.2
392	98.5	0.4	99.3	0.7	98.4	0.9	0.0	0.0	98.7	1.2
420	98.5	0.4	99.2	0.7	98.3	0.9	0.0	0.0	98.5	1.1

Table III.5. – Weight Durability Values

Cycles	Control Average	Control Std dev	Hw53 Average	Hw53 Std dev	Hw64 Average	Hw64 Std dev	NaI Average	NaI Std dev	KI Average	KI Std dev
0	100.0	0.0	100.0	0.0	100.0	0.0	100.0	57.7	100.0	0.0
3	99.8	0.1	99.7	0.1	99.7	0.2	100.0	57.2	99.9	0.1
7	99.8	0.0	99.8	0.1	99.7	0.1	100.0	51.6	99.8	0.2
16	99.8	0.0	99.7	0.0	99.7	0.1	90.4	1.6	99.8	0.1
25	99.9	0.0	99.8	0.1	99.8	0.1	0.0	0.0	99.8	0.1
52	99.9	0.0	99.8	0.0	99.8	0.1	0.0	0.0	99.9	0.1
80	99.9	0.0	99.8	0.0	99.9	0.1	0.0	0.0	99.9	0.0
113	99.9	0.1	99.9	0.0	99.9	0.1	0.0	0.0	99.9	0.1
141	99.9	0.1	99.9	0.0	99.9	0.1	0.0	0.0	99.9	0.1
169	99.7	0.2	99.8	0.1	99.9	0.1	0.0	0.0	99.9	0.0
197	99.7	0.1	99.8	0.0	99.9	0.1	0.0	0.0	99.9	0.1
225	99.7	0.1	99.8	0.1	99.7	0.1	0.0	0.0	99.9	0.1
252	99.6	0.1	99.7	0.1	99.7	0.1	0.0	0.0	99.7	0.1
280	99.5	0.2	99.6	0.1	99.6	0.2	0.0	0.0	99.6	0.2
308	99.2	0.3	99.4	0.1	99.3	0.2	0.0	0.0	99.4	0.2
336	99.0	0.4	99.3	0.1	99.0	0.2	0.0	0.0	99.2	0.3
364	98.9	0.5	99.1	0.1	98.9	0.2	0.0	0.0	99.0	0.5
392	98.6	0.6	99.0	0.2	98.6	0.3	0.0	0.0	98.7	0.6
420	98.2	0.7	98.5	0.3	98.1	0.4	0.0	0.0	98.3	0.7

11.4   Appendix: Hardened Air Void Profiles
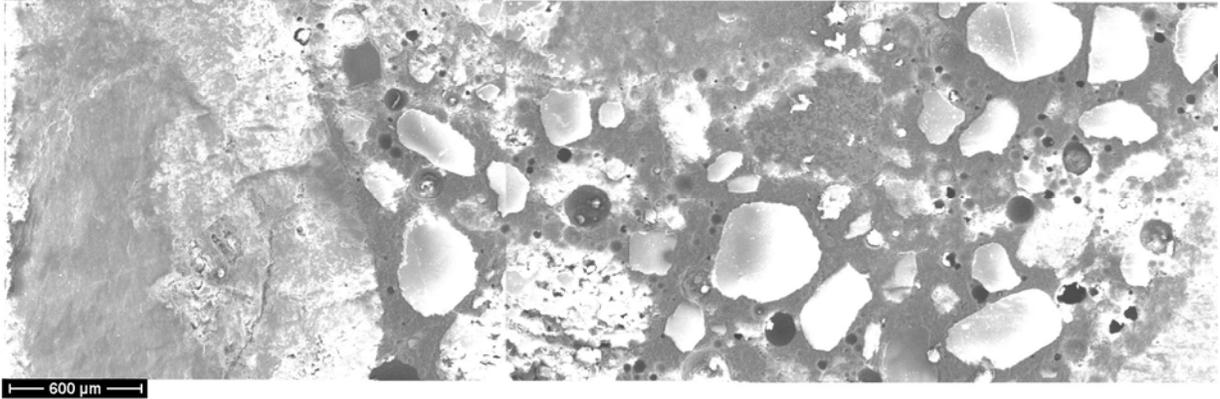
Figure IV.1 – Hardened Air Void Distribution of Control Sample
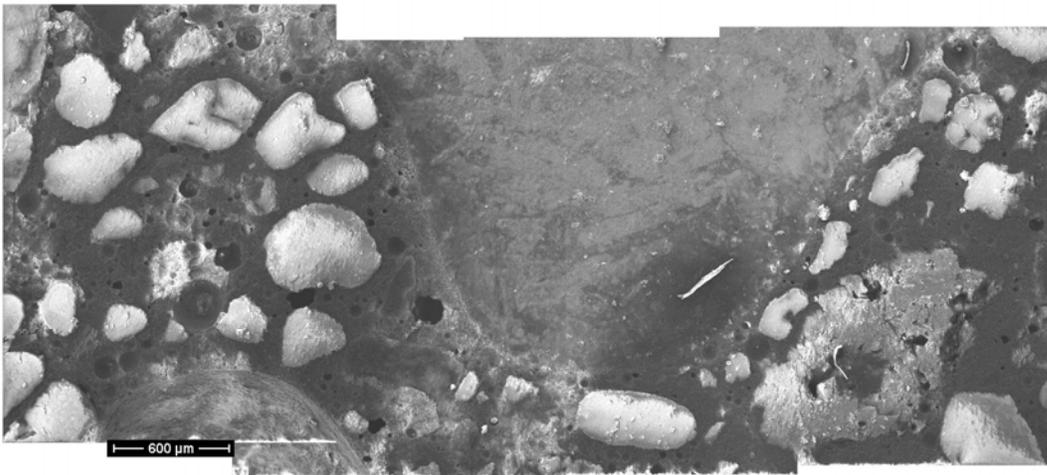
Figure IV.2 – Hardened Air Void Distribution of Hw53 Sample
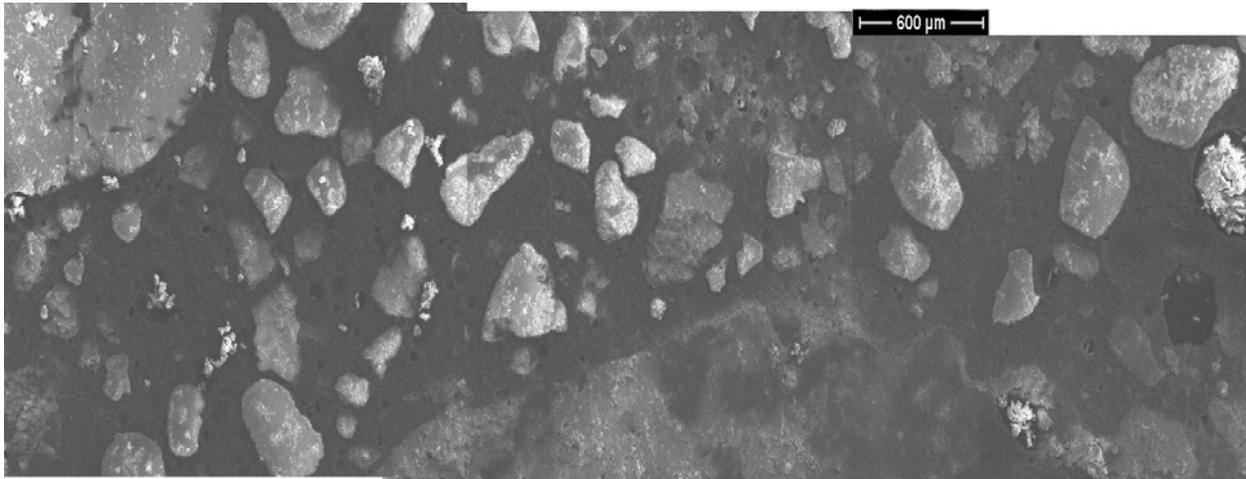
Figure IV.3 – Hardened Air Void Distribution of Hw64 Sample
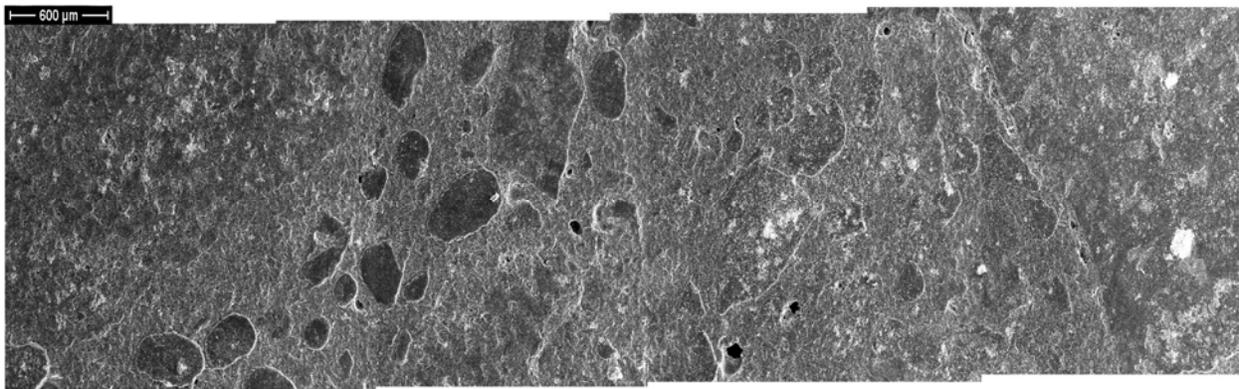
Figure IV.4 – Hardened Air Void Distribution of NaMI Sample
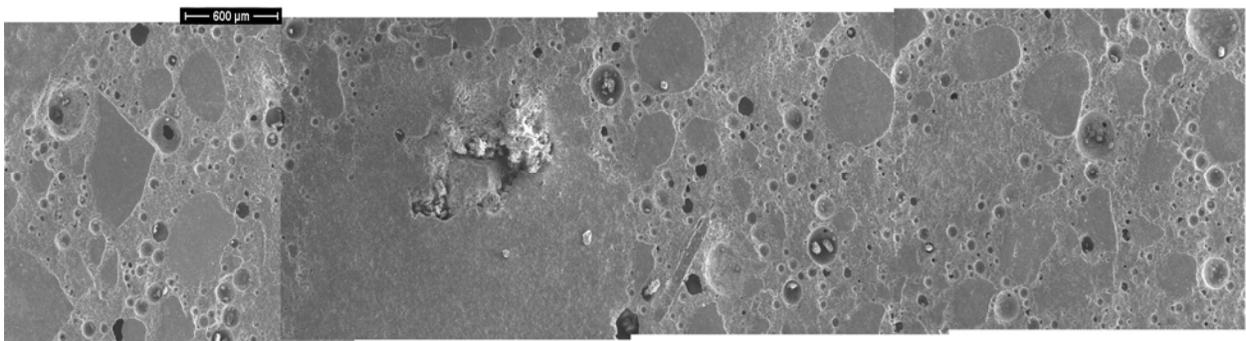
Figure IV.5 – Hardened Air Void Distribution of KI Sample

11.5 Appendix: Database of Concrete Aggregates

I. Sample Identification			
Project Name			
Highway			
County		Year of Construction	
Quarry Location:		Quarry Description:	
II. Coating Characterization			
Type of Aggregate		Size of Aggregate (in.)	
Rock type:		Microfines	Yes ☐ No ☐
P200:		MBV or CV	
Microfine Mineralogy			
Detected Anomalies	Yes ☐ No ☐	Description:	
III. Construction Information			
III.a. Mixing Data			
Cement Proportion (lb/yd^3)			
Pozzolanic Additives	Yes ☐ No ☐		
Type		Proportion (lb/yd^3)	
III.b. Curing Conditions			
Curing Compound Use		Time between concrete placement and curing compound applying	
Temperature		Relative Humidity	
Wind Intensity			

11.6 Appendix: California Cleanness Database Performed by WisDOT

Test #	Date Tested	Aggregate Source	Q/P	QRT	QRT	section	Town	Range	County	t-11 P200, %	cv P200, %	Sediment Height	CV
CV-1	10/11/04	Brock	P		NE	29	31N	7E	Lincoln	0.32	0.31	1	97
CV-2	10/11/04	Lund	P	SW	SW	6	36N	8E	Onieda	0.17	0.38	2	94
CV-3	10/12/04	Flannery	P	SW	SE	33	36N	13E	Forest	0.55	0.60	3	91
CV-4	10/13/04	Cross road	P	SW	NE	1	34N	6E	Lincoln	0.22	0.38	2	94
CV-5	10/13/04	Schallack	P	SE	NE	36	36N	12E	Forest	0.31	0.50	2	94
CV-6	10/13/04	Olynick	P	NW	NE	16	35N	6E	Rusk	0.16	0.24	1	97
CV-7	10/15/04	Bohl	P	SW	SE	10	32N	11W	Barron	0.06	0.24	1	97
CV-8	10/15/04	Peterson "CC"	P			32	28N	19E	Oconto	0.13	0.34	1	97
CV-9	10/15/04	Somer's	P	NE	NE	29	23N	R9E	Portage	0.16	0.23	1	97
CV-10	10/18/04	Alby's Matls-Waterford	P	SW	SW	28	4N	19E	Racine	0.22	0.34	2	94
CV-11	10/18/04	Michels-Marblehead	P	NE	NE	7	14N	18E	Fondulac	0.79	0.92	6	84
CV-12	10/18/04	Gen Agg Corp-Genesse	P		NW	28	6N	18E	Waukesha	0.19	0.25	1	97
CV-13	10/18/04	Michels-Ketter	P		SW	4	13N	19E	Fondulac	0.23	0.42	1	97
CV-14	10/19/04	Michels-Rudinger	Q		NW	11	14N	17E	Fondulac	0.42	0.47	2	94
CV-15	10/19/04	Michels-Waupun	Q	SE	NW	36	14N	14E	Fondulac	0.67	0.87	3	91
CV-16	10/19/04	Michels-Hamiton	Q		NW	10	14N	17E	Fondulac	0.80	1.18	5	86
CV-17	10/20/04	J.W. Peters-Burlington	P		NE	6	2N	19E	Racine	0.19	0.38	3	91
CV-18	10/20/04	Brock	P		NE	29	31N	7E	Lincoln	0.01	0.11	1	97
CV-19	10/20/04	Sussex	Q		NW	36	8N	19E	Waukesha	0.42	0.45	2	94
CV-20	10/21/04	Pound	P	NE	NW	1	30N	20E	Marinette	0.08	0.16	1	97
CV-21	10/21/04	Neva	P	S	NE	29	32N	11E	Langlade	0.19	0.37	1	97
CV-22	10/21/04	NLC Eagle	P							0.30	0.54	2	94
CV-23	10/21/04	Randt-Shoto	Q	SE	SW	20	20N	24E	Manitowwoc	0.12	0.31	3	91
CV-24	10/21/04	Rib River	P		SW	36	29N	5E	Marathon	0.17	0.23	1	97
CV-25	10/25/03	North Lake Sand and Gravel	P	N	SW	10	8N	18E	Waukesha	0.30	0.35	1	97

Test #	Date Tested	Aggregate Source	Legal Description							t-11 P200, %	cv P200, %	Sediment Height	CV
			Q/P	QRT	QRT	section	Town	Range	County				
CV-26	10/26/04	Wagner	Q		NW	17	33N	22E	Marinette	1.11	1.12	4	89
CV-27	10/26/04	Carew-Brussels	Q	NW	NW	21	26N	24E	Door	0.62	0.74	3	91
CV-28	10/27/04	Town of Lake	P	NW	SE	10	31N	21E	Marinette	0.27	0.39	1	97
CV-29	10/27/04	Custer	P		E	4	23N	9E	Portage	0.12	0.15	1	97
CV-30	10/27/04	3M	Q/P	NE	SW	11	29N	R7E	Marathon	0.23	0.25	2	94
CV-31	10/27/04	Lutzke	P	SE	SE	20	T18N	22E	Manitowoc	0.37	0.37	1	97
CV-32	10/28/04	Easton	P	SW		23	29N	9E	Marathon	0.09	0.26	1	97
CV-33	10/28/04	NLC - Woodruff	P	NW	SE	14	40N	6E	Vilas	0.10	0.14	1	97
CV-34	10/28/04	Aggrecon	P		SE	33	17N	21E	Manitowoc	0.35	0.52	2	94
CV-35	10/28/04	Geiter	P	NW	NW	18	34N	15E	Forest	0.90	1.10	1	97
CV-36	10/28/04	Vulcan	Q		NE	27	18N	16E	Winnebago	0.17	0.27	1	97
CV-37	10/29/04	Ruzic/Olynick	P	NE	SE	14	33N	4W	Taylor	0.16	0.19	1	97
CV-38	10/29/04	New London	Q			30	22N	15E	Outagamie	0.85	0.95	4	89
CV-39	10/29/04	Radandt "Q"	P			33	21N	23E	Manitowoc	0.27	0.37	1	97
CV-40	10/29/04	Bloomer 124	P	SW	SW	7	30N	8W	Chippewa	0.23	0.28	2	94
CV-41	11/01/04	Superior-Duluth-Arrowhead S&G	P	S	NW	11	52N	17W	St. Louis Co., MN	0.26	0.24	1	97
CV-42	11/01/04	Haugen	P	NW	SW	18	36N	11W	Barron	0.04	0.18	1	97
CV-43	11/01/04	Casey	P		SE	16	30N	17E	St. Croix	0.12	0.15	1	97
CV-44	11/02/04	American Materials Pit 58	P			15	28N	14W	Dunn	0.61	0.62	2	94
CV-45	11/02/04	Cook-Mollet	Q	NE	SE	4	12N	4W	Vernon	0.69	0.89	4	89
CV-46	11/03/04	Marsolek	Q	NW	SE	36	23N	10W	Buffalo	0.73	0.68	3	91
CV-47	11/03/04	Dousman	P	SE	SW	1	6N	17E	Waukesha	0.31	0.38	2	94
CV-48	11/03/02	Colgate	P	S	NW	3	8N	19E	Waukesha	0.22	0.31	1	97
CV-49	11/03/04	Vulcan-Dousman	P		NE	1	6N	17E	Waukesha	0.42	0.62	3	91
CV-50	11/03/04	Hillview	P		SE	8	8N	19E	Waukesha	0.19	0.23	1	97
CV-51	11//08/04	Waubesha Sand and Gravel	P						Buffalo	0.25	0.44	1	97
CV-52	11/08/04	Duessing	P	N	SW	33	32N	1E	Taylor	0.76	0.98	2	94
CV-53	11/09/04	Yellow River	P	SE	SW	21	37N	17W	Polk	0.46	0.44	2	94
CV-54	11/09/04	Householder	Q	NW	SE	15	10N	1E	Richland	0.98	0.97	5	86
CV-55	11/10/04	Media	P		SW	19	21N	16E	Outagamie	0.27	0.21	1	97

Test #	Date Tested	Aggregate Source	Legal Description							t-11 P200, %	cv P200, %	Sediment Height	CV
			Q/P	QRT	QRT	section	Town	Range	County				
CV-56	11/10/04	Carew-Freedom	Q	SW	NE	10	22N	18E	Outagamie	0.63	0.62	3	91
CV-57	11/10/04	Mackville	Q	SW	NE	33	22N	17E	Outagamie	0.55	0.67	2	94
CV-58	11/11/04	Prarie Sand and Gravel	P			19	7N	6W	Crawford	0.26	0.29	1	97
CV-59	11/11/04	Krueger	Q			6	27N	20E	Oconto	0.39	0.46	2	94
CV-60	11/11/04	Carew-Rock Road	Q	NE	NW	20	22N	17E	Outagamie	0.56	0.61	3	91
CV-61	11/11/04	Kust	P	NW	SE	15	30N	20E	Marinette	0.53	0.57	2	94