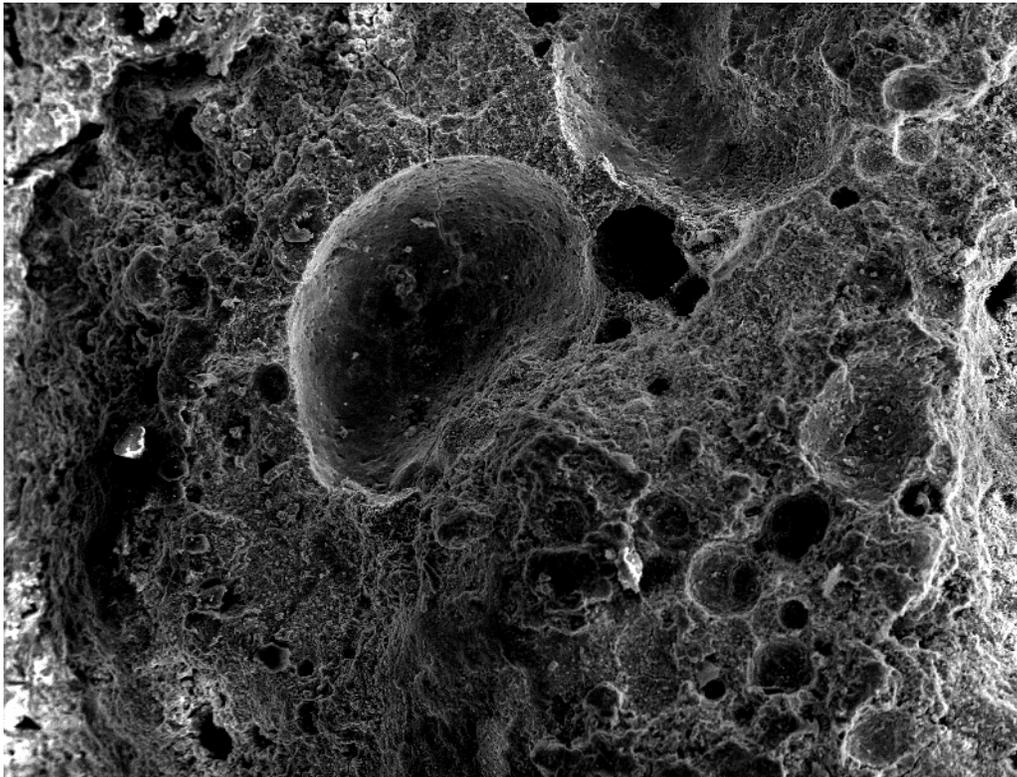An *IPRF* Research Report

Innovative Pavement Research Foundation

Airport Concrete Pavement Technology Program

Report IPRF-01-G-002-01-4.2

Effects of Coarse Aggregate Clay-Coatings on Concrete Performance

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Effects of Coarse Aggregate Clay-Coatings on Concrete Performance

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EXECUTIVE SUMMARY

Introduction

Due to the fact that aggregates comprise between 60-80 % of the total volume of concrete, and concrete failures have often been tied to the use of different aggregates, it would appear that one should characterize these aggregates and their surface chemistries in order to determine the roll of these materials on the final performance of concrete. Coarse aggregates often contain a layer of small particles bound strongly or weakly to the aggregate surface (a surface coating). Previous research associates the presence of some type of micro-fines on the surface of these aggregates with deleterious properties of concrete. A large fraction of micro-fine gravel coatings consist of clay minerals. Due to their small size and large surface areas as well as differing chemistries, these minerals likely can be expected to be major components of reactivity in concrete systems. It has been widely reported that presence of clays in cement reduces the compressive strength and increases shrinkage in the resulting concrete. However, the exact mechanism by which these clays affect these properties has not been established.

Our hypothesis as to how clays influence the evolution of the concrete is as follows: in the course of the mixing process, prior to the addition of cement, a fraction of the clay coating detaches from the aggregate surface and disperses into the aqueous phase. Thus, when the cement powder is added to this mixture, particles of clay will be incorporated into the matrix of the cement paste and affect hydration reactions. The other fraction of the coating will remain on the aggregate surface and influence the adhesion of the cement paste to the aggregates. The overall objective of this research project has been to establish which fraction of coating of three different types of clays (Na-montmorillonite, Ca-montmorillonite and Kaolin) detach from the surface of the aggregate, and how these detached particles of clays affect the pathway of the hydration reactions in the cement paste.

Research Approach and Results

In order to achieve the objectives mentioned above we have divided this project into three major areas of study:

1. Coating of previously cleaned aggregates with well characterized clays (Na-montmorillonite, Ca-montmorillonite and Kaolin)
In this phase of our research, we used a dip-coating technique to deposit the film of clay minerals on cleaned aggregates. The percentage by weight of clay in the coated aggregated was measured by extracting all of the clay from the aggregate with water and evaluating this amount gravimetrically. The tested parameters in this research were the nature of clay, the speed of withdrawal from the clay suspension, the clay concentration in suspension and the number of coatings.

In this part of our investigation, the following results can be reported: 1. The amount of clay deposited on the aggregates increased with increasing viscosity in the clay suspension for a given concentration of clay (depends on nature of the clay); 2. The amount of clay deposited also

increased with the number of coatings and the concentration of clay in suspension. From the results of these coating studies, we were able to establish the coating conditions required to prepare the desired coated aggregates.

2. Determine which fraction of clay-coating detaches from the aggregate surface and is dispersed into the water phase during the mixing stage of concrete fabrication.

We mixed the coated aggregate with water (at given water/concrete ratios), and shook this mixture under real concrete mixing conditions. In these studies, we used a coated aggregate having a 1.5 % weight in clay content, simulating real-world conditions. We discovered that the fraction of detached clay depends on the nature of the clay: Na-montmorillonite mostly remains in the aggregate upon mixing (10 and 20 % detached, at pH~7, and 12 respectively), Ca-montmorillonite and kaolin detached very readily and entered the water phase (Ca Montmorillonite: 69 and 77 % and Kaolin: 50 and 79 % for pH~7, and 12, respectively).

3. Study the influence of clays on the hydration reactions of cement paste.

We studied the evolution of cement pastes prepared with clay suspensions and that of a cement paste prepared with water (control) by using X-ray diffraction and Scanning Electron Microscopy. We employed the results of clay detachment resulting from the previous studies in order to determine the concentration of clays to be added to the suspension. These studies were performed in the early stages of hydration, 2h to 11 days. Results from these studies show that the presence of Ca-montmorillonite and Kaolin accelerate the rates of reaction with respect to the control. Reaction products such as ettringite, $Ca(OH)_2$ and CSH appear earlier. On the contrary, the presence of Na-montmorillonite tends to retard the hydration reactions, as indicated by the later appearance of the above mentioned reaction products and particularly by the lower rate of disappearance of the reactant Alite (C_3S).

Conclusions

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 given clay, this may depend on other variables, as for example 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 (Ca-montmorillonite) and no swelling (Kaolin) are easier to detach and increase the rate of the hydration reaction of the cement pastes.

1.   INTRODUCTION.

1.1.   OVERVIEW OF PROBLEMS IN THE PRODUCTION OF CONCRETE.

In the last few years, the ability to design alternative methods of producing concrete has greatly expanded [1] but so too has the level of complexity in determining which set of parameters provides superior pavement performance. Several factors contribute to this complexity: the use of different sources of materials (multiples sources of rock, sand and cements), the replacement of cement by new cementitious materials (fly ash, ground granulated blast furnace slag, etc), and the introduction of many new chemical additives that are claimed to produce a superior product [1]. Special significance has been given to the case of aggregates as they comprise between 60-80 % of the total volume of concrete. It has been well documented that the presence of micro-fines on aggregate materials has a significant impact on the ultimate quality of resulting pavements [2]. Defects such as spalling, D-cracking, longitudinal cracking, transverse cracking, and corner breaks have been in large part attributed to presence these micro-fines.

1.2.   TYPES OF MICRO-FINES COATINGS FOUND ON AGGREGATES.

Coarse aggregates commonly contain small particles (surface coatings) that are bounded strongly or weakly to the aggregate surface. These fine particles may partially or completely cover the surface of the aggregate. The coating usually appears as layers, blends, patches, or individual grains [3, 4]. The most universal types of coatings are clays, calcium carbonates, and dust or silt. Clay coatings originate by precipitating water-soluble materials from sand or gravel deposits; and are different from the rest of the coatings in that they strongly adhere to the surface of the aggregate. Clay minerals comprise a significant proportion of these finely divided materials and, as we shall also demonstrate, they are already known to cause deleterious effects in concrete.

1.3.   BRIEF DEFINITION OF CLAYS.

Following the definition given by the AIPEA (Association International Pour l´Étude des Argiles) committee in 1972 [10] clay minerals are phyllosilicates of small particle size (< 2 μm). They are formed by combining two basic *sheet* structures: one is a continuous two-dimensional *tetrahedral sheet* of individual tetrahedron sharing three corners and the fourth pointing in any direction. The central atom of the tetrahedron could be Si or Si/Al. The second sheet is an *octahedral sheet* built of octahedrons shearing edges with Al^{3+}, M^{g2+} or Fe^{3+} as the central atom. The different combinations of octahedral and tetrahedral sheets, that form the unit *layer* of the clay, generate different types of clays: when the unit layer is comprised of one tetrahedral sheet and one octahedral sheet the clay is classified as a *1:1 layer silicate*; if the unit layer of the clay consists of two outer tetrahedral sheets and an inner octahedral sheet the clay is classified as *2:1 layer silicate*.

Negative charge development on silicate clays is mainly due to isomorphous substitution in either sheet. In tetrahedral coordination, Al^{3+} substitutes for Si^{4+} and in octahedral coordination Mg^{2+}, Fe^{2+}, Fe^{3+} ions substitute for Al^{3+} [10, 11, and 12]. When the intra-layer charge balance of the 2:1 type silicates is incomplete, the net charge deficit is balanced by alkaline and alkaline earth cations situated between the layers. These cations can be easily exchanged. Table 1 shows a classification scheme for these clays minerals

TABLE 1. CLASSIFICATION SCHEME FOR PHYLLOSILICATES RELATED TO CLAY MINERALS.

Layer Type	Group (x = charge per formula unit)	Subgroup	Species
1:1	Kaolinite-serpentine	Kaolinite	Kaolinite, dickite, halloysite
	X ~0	Serpentine	Chrysotile, lizardite, amesite
2:1	Pyrophyllite-talc	Pyrophyllite	Pyrophyllite
	X ~0	Talc	Talc
	Smectite	Dioctahedral smectite	Montmorillonite, beidellite
	X ~0.2-0.6	Trioctahedral smectite	Saponite, hectorite, sauconite
	Vermiculite	Dioctahedral vermiculite	Dioctahedral vermiculite
	X ~0.6-0.9	Trioctahedral vermiculite	Trioctahedral vermiculite
	Mica	Dioctahedral mica	Muscovite, paragonite
	X ~1	Trioctahedral mica	Phlogopite, biotite, lepidolite
	Brittle mica	Dioctahedral brittle mica	Margarite
	X ~2	Trioctahedral brittle mica	Clintonite, anandite
	Chlorite	Dioctahedral chlorite	Donbassite
	X ~variable	Di, trioctahedral chlorite	Cookeite, sudoite
		Trioctahedral chlorite	Clinochlore, chamosite, nimite

1.4. EFFECTS OF WATER IN CLAYS.

The exchangeable cations in vermiculite and smectite type clays in the presence of water hydrate resulting in an increase in the space between clay layers. This phenomenon is known as the swelling of the clay. The amount of absorbed water in air is a function of the relative humidity and also of the quantity and nature of the exchangeable cations present in the clay. When these clays are immersed in water they can react in two different ways:

Endure crystalline swelling: the maximum expansion of the basal space in the clay is equal to that experienced in air at 100 % RH. For example, smectites, whose basal spacing when dehydrated is between 0.95 to 1.00 nm, upon hydration, passes to 1.9 nm.

Suffer macroscopic swelling: In the case of some clays, the basal spacings reach values larger than 4.0 nm upon their immersion in water. In this case, the unit layers start to separate from each other and the clay particles are said to be *destacked* or *exfoliated*. A clear example of this type of behavior is Na and Li smectites. In water or dilute solutions, these systems can swell macroscopically into a gel-like state in which the average layer separation is greater than 4.0 nm and increases in proportion to $1/\sqrt{c}$, where c is the electrolyte concentration in the liquid phase. This phenomenon is associated with the formation of a diffuse electrical double layer on each surface of the structural layer of the silicate.

1.5. EFFECT OF CLAY IN CONCRETE.

Many scientists have investigated the interaction of clays and cement as pozzolanic additives. These studies have revealed that the presence of some type of clays in the cement mixture produce a decrease in the strength and an increase in shrinkage. For example, Unikowski, found that the water demand, for making a workable cement mixture was related to the specific surface area of the clays present in the cement. He noted that a 3 % replacement of sand for montmorillonite decreased the compressive strength by nearly 40 % and doubled the amount of shrinkage [5]. Pike theorized that the loss of strength in clay-mortars was caused by clays adsorbing part of the water used for the cement forming "impermeable envelopes" around the cement grains slowing the rate of the pozzolanic reactions [6]. Moukwa M. et al. attributed the loss of strength in clay-mortars to a higher porosity in the hardened mixtures [7]. Changling He et [8]al studied the water demand, compressive strength, size distribution, and pozzolanic activity in six clays and came to the conclusion that since absorbed water has different physical properties than free water it should not be available for hydrating the reactive components of the cement. These authors also claimed that, when clays are present, the decrease in strength of the concrete can be correlated to the different bonding forces between the structural layers of the clay minerals and to the clay-cement adhesion properties. Fam M. A. et al studied bentonite- and attapulgite-cement slurries. They proposed that hydrated clays act as semipermeable membranes and temporally absorb intermediate products of the hydration reactions in cement chemistry [9].

It can be concluded that most of the authors believe that a significant amount of clay in a cement mixture reduces the amount of water available for the hydration reactions and thereby decreases its workability and also alters the course of the pozzolanic reactions. As a result, hardened cement containing clay minerals is expected to have different physical properties from that of cement fabricated without clays. It has been widely reported that presence of clays in cement reduces the compressive strength and increases shrinkage in the resulting concrete.

2. <u>WORKING HYPOTHESIS.</u>

In the process of making concrete, aggregate is mixed with water and sand prior to the addition of cement. The presence of water and the abrasion between sand particles and aggregates during this mixing process should provoke a fraction of the coatings on aggregate surfaces to detach and disperse into the water of this mixture. Thus, when the cement powder is added to this mixture, clay particles will be incorporated into the matrix of the cement paste. At present, the mechanism through which clays influence the physical properties of cement paste has not been conclusively established. Depending on the nature of the swelling in these clays we can envision two different scenarios upon adding the cement powder to the mixture:

a.   The dispersed clay has the ability of only crystalline swelling. Clay particles will absorb significant amounts of the water of the mixture leaving a quantity of *available* water that will yield water/cement ratios smaller than the best possible for hydrating the cement powder. Decreasing in water/cement ratio will reduce the workability of the cement and should also affect the quantity of entrapped air [8 and 9]. All of these parameters will modify the strength of the concrete.

b   The dispersed clay has the ability for macroscopic swelling. These particular types of clays, when placed in contact with water, experience an exfoliation of the stacked unit layers. The dispersion of these clays gives way to an aqueous suspension having a large number of very anisotropic nano-particles. Thus, the viscosity of the water of the mixture in these systems is expected to increase. These thin-layer particles may coat the un-hydrated cement compounds added to the concrete mixture and affect the kinetics of hydration. This may have an effect on the physical properties of the resulting concrete.

3. <u>OBJECTIVE.</u>

The overall objective of this research is to determine how clays affect the properties concrete. More precisely, we wish to investigate how these clays affect the path of the reactions in the early stages of hydration. In order to accomplish this objective we will address the following research aspects:

a.   Develop a methodology for preparing clay coated aggregates in our laboratories. The goal is to obtain a desired clay coated aggregate that is easy to reproduce.

b.   Measure the concentration of detached clay in the mixture of clay-coated aggregate /water upon mixing, the mixing process should be equivalent or closely simulate the one that takes place in the concrete making process before the addition of the cement powder. In addition, we will measure the state of aggregation of the clay in suspension. This will be done using light scattering techniques as well as sedimentation studies at different values of pH, different electrolytes and different electrolyte concentrations.

c.   Characterize by XRD the cement paste matrix resulting from mixing cement powder with water containing different types of clays. We will follow the kinetics of disappearance of unreacted cement and the formation of the early products of these cementitious reactions.

4. METHODOLOGY.

4.1. COATING OF CLEAN AGGREGATE WITH SELECTED CLAYS.

4.1.1. Aggregates and Clays.

The aggregate used was igneous gravel with a particle range size 4.0 and 25.0 mm. The "as received" materials were cleaned to remove potential fines coating. The washing was carried out by immersing the aggregate in water (200 g of aggregate/ 200 ml water), and sonicating the mixture for 24 hours. Next, the aggregate was separated from the suspension of fines by percolation. This operation was repeated until no fines appeared in the water.

Clays: in the coating of aggregates we used three different clays, kaolin (small water adsorption with no swelling of the clay structure), Ca-montmorillonite (large water adsorption producing crystalline swelling), and Na-montmorillonite (large water adsorption resulting in macroscopic swelling). All three clays were purchased from The Source Clays Repository that belongs to The Clay Minerals Society (CMS).

4.1.2. Method of Coating.

The clay film was deposited on the aggregates by the so call "dip-coating" method. For that, stable suspensions of the clays in water were prepared by adding the clay to MQ water and stirred until all the clay became a part of the stable suspension. In order to determine the desired coating thickness, we tried suspensions with different concentration of solids.

Coating device: 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 15 of cm/min in the large cylindrical container.

Two different values of concentration were used for each of the three clays; values for these concentrations are reported in table 2. Also, aliquots of the aggregate were subjected to different numbers of coating cycles (1, 2, 4 and 6).

TABLE 2. 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

4.1.3. Amount of Clay in the Coatings.

To evaluate the quantity of clay deposited after each coating cycle the coated aggregate was subjected to the same procedure used for cleaning the aggregate. Finally, the suspensions of clays were dried in an oven at 60 ^{o}C and then weighed.

4.2. DETACHMENT OF CLAY COATINGS DURING THE MIXING STAGE OF AGGREGATE, SAND AND WATER IN THE CONCRETE MAKING PROCESS.

The study of the detachment of clays during the mixing process was performed in a cement mixer of 3 ft^3 for one of the clays, at one pH value. In this experiment 5 kilograms of clay-coated aggregate was placed in the mixer with 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 clay detachment. 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, we could study several samples 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 cement mixer. We studied the detachment of clays at two different pH values (~7, which is about 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, we were able to find the conditions of time and shaking strength for the Incubator Shaker Model G-27 that would yield the same clay detachment as that in the cement 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.

4.3. CHARACTERIZATION OF CLAYS IN WATER.

Sedimentation studies were conducted to determine the stability of the three clays in water at pH 7 and pH 12. The experiments were performed in 15 ml test tubes, using 100 min of total settling time. The samples were prepared using the following protocol: 0.01 g of clay was added to 20 ml of solution and left to mix for 12 hours in a shaker followed by 15 min of sonication.

The size of the suspended clay particles was determined by light scattering. These measurements were performed in clay suspensions equivalent in preparation to those samples used in the sedimentation studies.

Electrophoretic mobility measurements were also performed on the suspended clays by using a Zetasizer 3000 HAS. For these measurements the concentration of clay in the suspension was of 0.2 g/L. Previous to measuring electrophoretic mobility, the suspensions of clays were equilibrated at different pH values for 2 hours. NaOH and HNO_3 solutions were used to obtain the desired pH value.

4.4. PREPARATION OF CEMENT PASTE.

Samples of 150 g of cement were mixed with water or clay suspensions, and manually stirred for 3 minutes, then left to rest for 2 minutes and finally stirred again for 2 more minutes. Cement pastes containing clays were prepared using two different water/cement ratios: 0.45 (the ratio usually used to prepare cement) and the ratio that provides the paste with the desired workability. The amount of clay added to the water was not the same for each of the three clays, but it was calculated based on the values obtained for the percentage of detached clay produced in the experiments described above. To make these calculations, we assume that the aggregates contain a 1.5 % of clay in weight. This value of coating was selected because it is the actual maximum of fine particle content allowed in road construction aggregate in Wisconsin. The w/c ratio and the amounts of clay used to prepare the cement paste samples are shown in table 3.

TABLE 3. QUANTITIES OF CLAY USED TO PREPARED CEMENT PASTES.

Clay	W/C ratio	Total mass of clay in coating (g)	% detachment of clay during mixing	Clay present in water mixing (g)
No clay	0.45	--	--	--
Na-Montmorillonite	0.45	7.575	11	0.83
	0.65	7.575	11	0.83
Ca-Montmorillonite	0.45	7.575	70	5.30
	0.53	7.575	70	5.30
Kaolin	0.45	7.575	50	3.79
	0.50	7.575	50	3.79

4.4.1. Cement Paste Characterization.

By using a High Start 2-D X-ray diffractometer, over a 11 day sampling period, we were able to follow the evolution of the cement paste. We also analyzed the differences in the mineral phases and microstructure of the cement pastes with different clays using the scanning electron microscope (SEM). In this study we used a .JEOL 6100 Scanning Electron Microscope. The SEM studies were performed on 4 days old cement pastes.

5. RESULTS

5.1. COATING OF AGGREGATE WITH CLAYS

Results concerning the quantity of clay coated on the aggregate under different experimental conditions are reported in Figures 1-3 for the three 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 1.5 % of the weight of the coated aggregate. Graphs in Figures 1-3 show that this coating thickness was obtained for each of the clays after four coating cycles. However, the concentration of clay in the suspension needed to reach this coating level is different for each type of clay.

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 Na-montmorillonite and 80 g/l for Ca-montmorillonite and kaolin. This behavior may be also operative in the curves associated with the higher concentrations of clays in suspension (80 g/l for Na-montmorillonite and 140 g/l for Ca-montmorillonite 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 reach 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. This is unfortunate because, as Figures 1-3 indicate, more dilute suspensions yield a better reproducibility of data.

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. We believe that the thickness of the coated layer in this system is 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 Na montmorillonite. This is due to the fact that the larger viscosity of the montmorillonite leaves behind thicker films after coating. As the clays are only dried at 60 ^{o}C between coatings, the saturation behavior may be explained if the attached clay resuspends itself when exposed to a new coating cycle. As a cautionary comment, we note that 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.
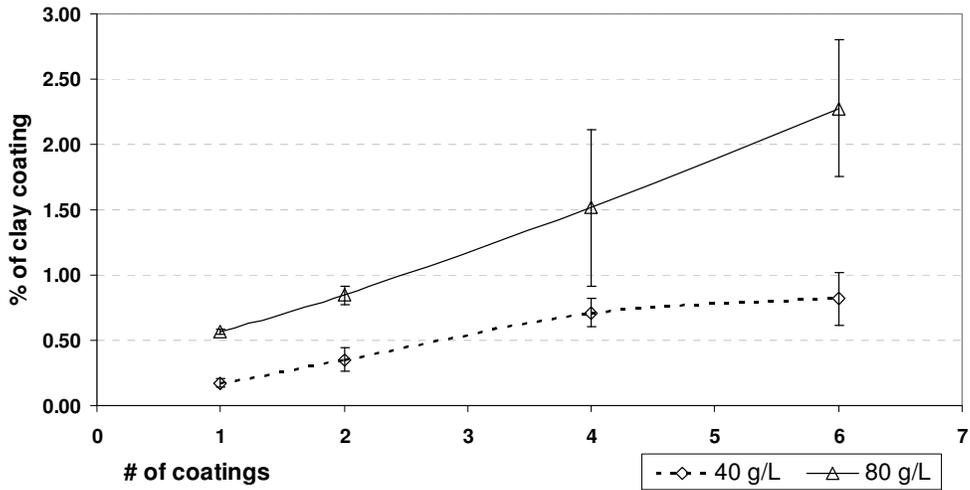
FIGURE 1. PERCENTAGE OF CLAY COATING ATTACHED TO AGGREGATE
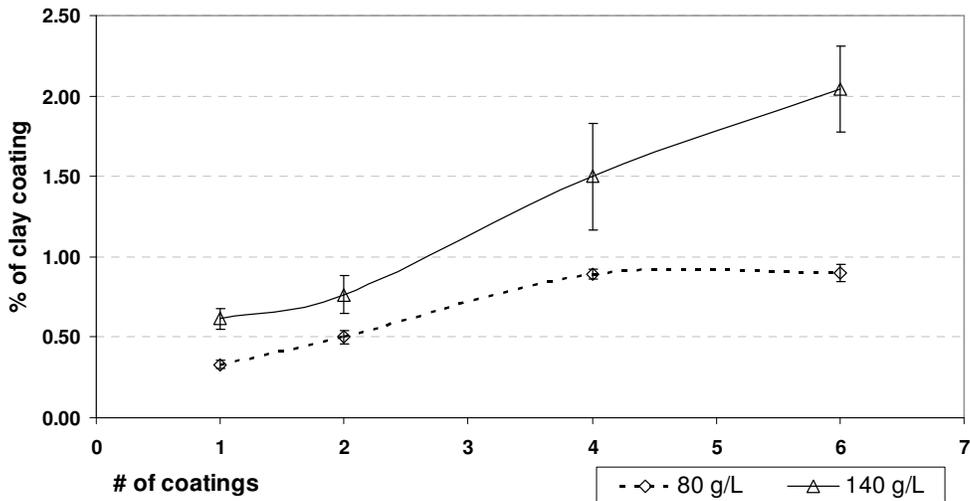SURFACE VS. NUMBER OF COATINGS FOR Na-MONTMORILLONITE.

FIGURE 2. PERCENTAGE OF CLAY COATING ATTACHED TO AGGREGATE
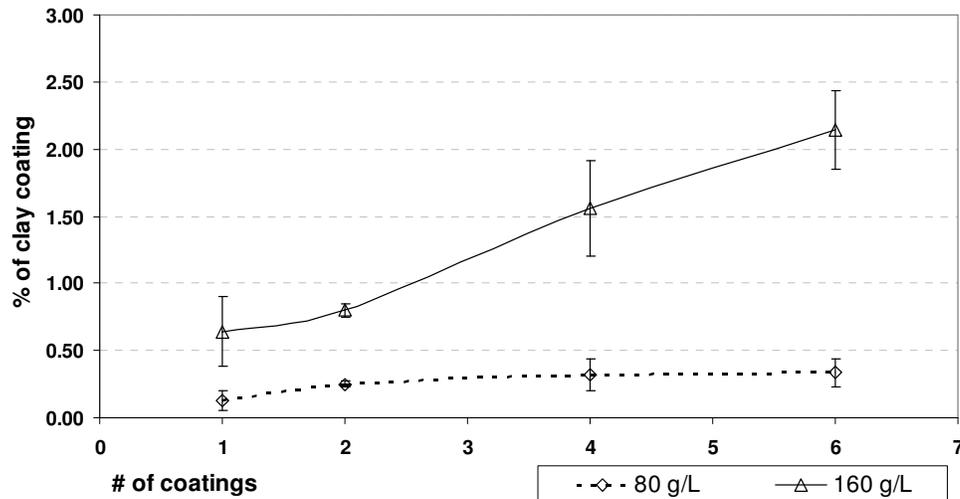SURFACE VS. NUMBER OF COATINGS FOR Ca-MONTMORILLONITE.

FIGURE 3. PERCENTAGE OF CLAY COATING ATTACHED TO AGGREGATE SURFACE VS. NUMBER OF COATINGS FOR KAOLIN.

5.2. DETACHMENT OF CLAYS DURING THE GRAVEL, SAND AND WATER MIXING STAGE OF THE CONCRETE MIXING PROCESS.

Clays may be present in suspension or may arise from the detachment of the clays from the aggregate surface. Therefore, it would be nice to know the fraction of coating coming into the aqueous phase during the aggregate/water mixing stage in real concrete mixing conditions. However, even smaller commercial concrete mixer requires 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. Results from this study allowed us to find the set of experimental conditions for the shaker that would deliver the same detachment of clay. For this study, we explored the variables: amount of aggregate; position and size of the vessel containing the aggregate; time of the sample in the shaker; and velocity of agitation.

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 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: 250ml to 2L) did not produce a significant change in the amount of detached coating. Furthermore, the velocity of the shaker had no influence on the total amount of coating detached. 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 cement mixer. One set of variables that conforms to this requirement is: 250 g of coated aggregate, 1L bottles and 15 minutes of shaking. These are the experimental conditions used in this study. It should also be noted that subsequent experiments 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 4. This Figure shows that the degree of detachment depends very much on the nature of the clay. Na-montmorillonite behaves the most different, and most of the coating remains on the aggregate upon mixing (10 and 20 % detached). However, in the case of Ca-montmorillonite and kaolin coatings most of these coatings detach and enter the water phase (Ca-montmorillonite: 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 Na-montmorillonite. The concentration of clay in the aqueous phase for each of the studied systems is reported in Table 4.
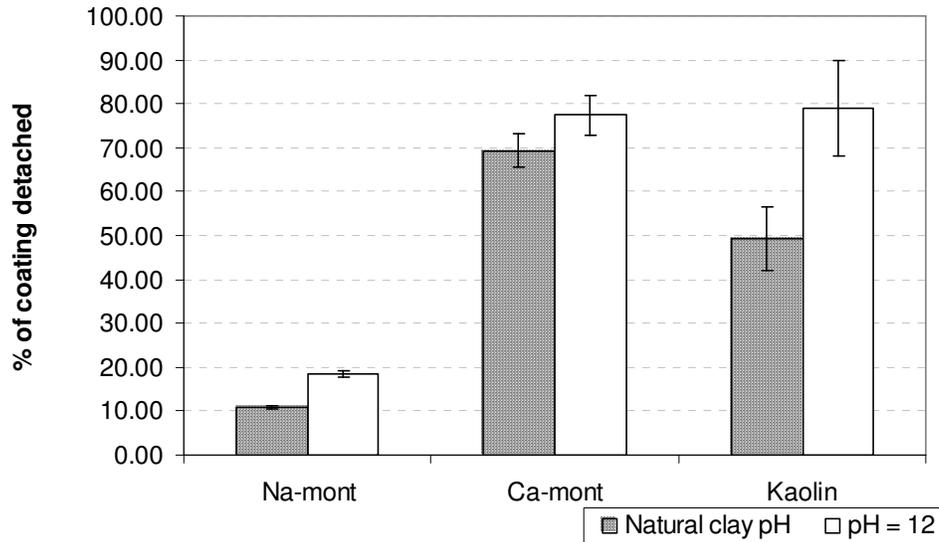

FIGURE 4. PERCENTAGE OF CLAY COATING REMOVED WITH RESPECT TO THE TOTAL MASS OF COATING AT TWO DIFFERENT PH VALUES.

TABLE 4. MEASURED CONCENTRATION OF CLAYS IN MIXING WATER.

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

5.3. PROPERTIES OF THE CLAYS IN WATER.

The three clays selected for these studies are different in structure as shown in Figure 5. The value of the net negative charge, as measured by the exchangeable capacity of cations, is very different, 2 meq/g for kaolin versus 76.4 meq/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. Na montmorillonite should display macroscopic swelling; Ca montmorillonite crystalline swelling; and kaolinite 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.
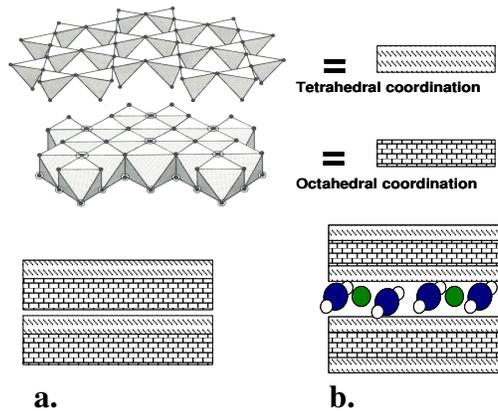

FIGURE 5.   SCHEMATIC REPRESENTATION OF THE STRUCTURAL UNITS OF (a) KAOLIN AND (b) SODIUM AND CALCIUM MONTMORILLONITE.

We performed sedimentation studies of these clays in: pure water, and 0.03 M $Ca(OH)_2$. Figure 6 shows the sedimentation behavior of these clays in presence of water. Kaolin and Ca-montmorillonite sediment in 4 and 6 minutes respectively while the Na-montmorillonite does not sediment within 100 minutes. The explanation for these results is based on the hydration

properties of these clays: Na-montmorillonite 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 Ca-montmorillonite suffer exfoliation in water hence these particles remain in their original size and clays should be larger than that of Na-montmorillonite.

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 Na montmorillonite 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 characteristics.
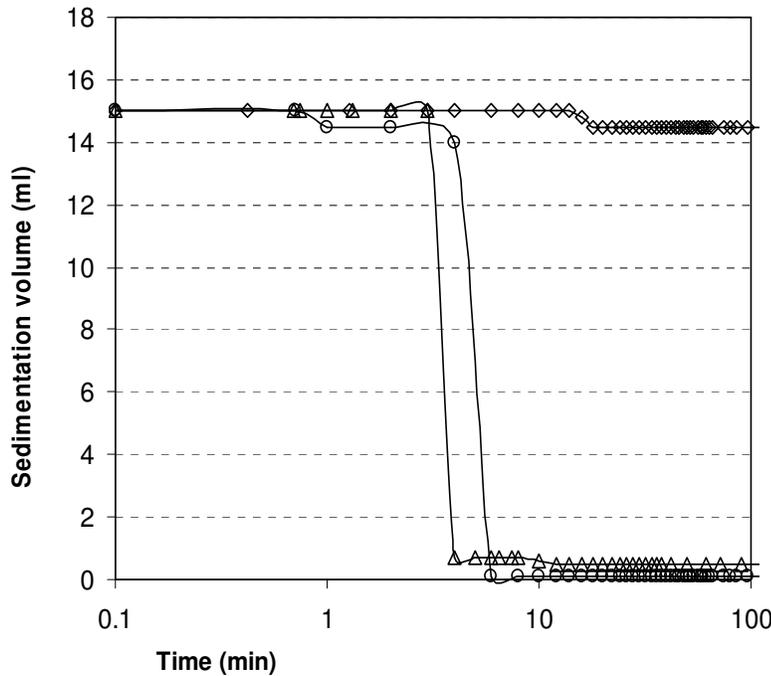

FIGURE 6. SEDIMENTATION CURVES IN WATER FOR (◊) Na-MONTMORILLONITE, (¤) Ca-MONTMORILLONITE, AND (Δ) KAOLIN.

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 Ca-montmorillonite, respectively. In the case of Na-montmorillonite, 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 Ca-montmorillonite.

Electrophoretic mobility measurements shown in Figure 7. 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 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.
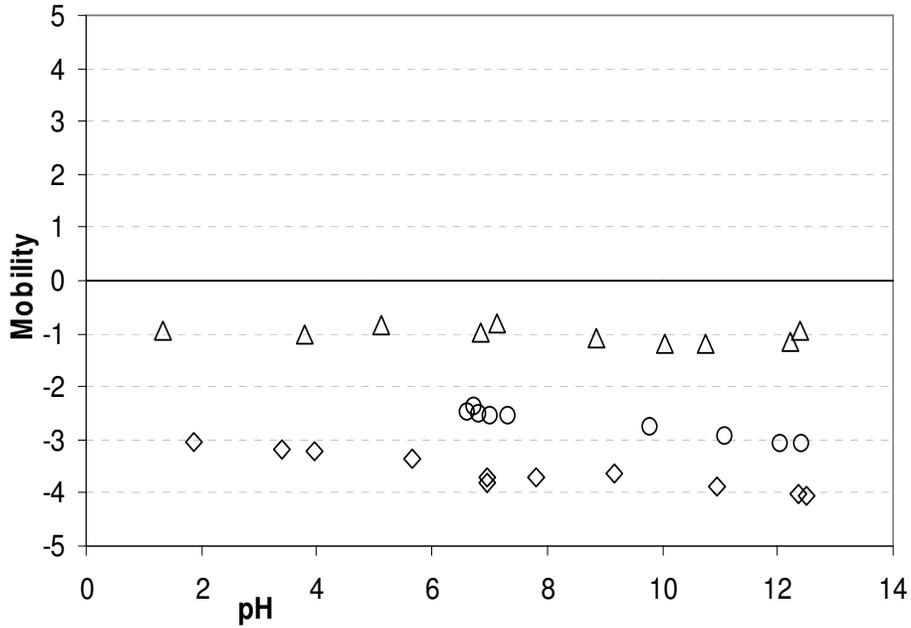

FIGURE 7. ELECTROPHORETIC MOBILITY OF (◊) Na-MONTMORILLONITE, (¤) Ca-MONTMORILLONITE, AND (∆) KAOLIN IN WATER AS A FUNCTION OF PH.

5.4. INFLUENCE OF CLAYS IN THE EARLY STAGES OF THE HYDRATION REACTION OF CEMENT PASTE.

To learn more about how the presence of clays in concrete affect its properties, through the interphase or by affecting the hydration reactions in the bulk of the cement we have prepared cement pastes using either water or a suspension of one the three clays of this study. We followed the kinetics of these hydration reactions using X-Ray diffraction (XRD) techniques. Figure 8 shows the diffractogram of the cement powder that was used in these studies.
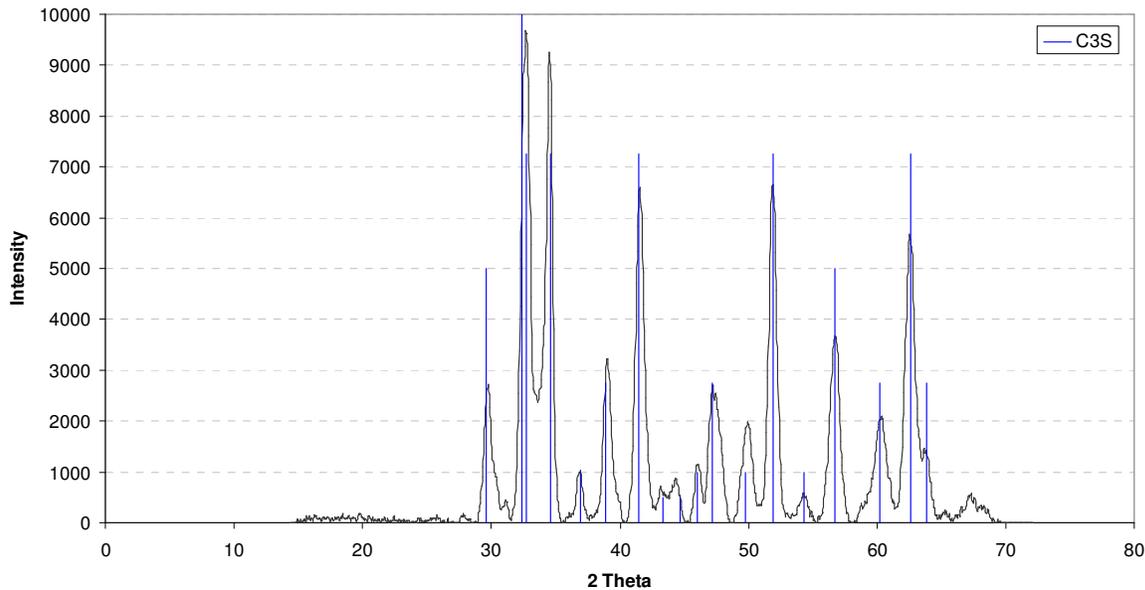

FIGURE 8. X-RAY DIFFRACTION PATTERN OF THE CEMENT POWDER.

All peaks in this diffraction pattern could be identified as coming from one compound, Alite (C_3S) [13]. This compound is the major constituent of the cement powder (50-70 % [14] in weight). Although C_2S comprises from 15 to 20 % of the cement powder it is not clearly visible in the diffratgram as its peaks appear at 2θ values very close to the ones of Alite. The aluminoferrite (C_4AF) (5-15 %) and the gypsum are in smaller concentrations and are not visible in the diffractogram, in part due to the overlapping of the major peaks with those of Alite.

X-ray diffractograms of the different pastes were acquired at 2h, 5h, 1, 2, 3, 4 and 11 days from the preparation. In these diffractograms we were able to detect the presence of the most important hydration products, such as calcium hydroxide, ettringite and calcium silica hydrate (CSH). In the case of all four pastes, the first detectable reaction product in time was ettringite, followed by the CSH and finally the calcium hydroxide.

Figures 9 to 12 show the diffractograms of each of the cement pastes, without clay (control paste) combined with either kaolin, Na or Ca montmorillonite, for different aging times. In order to track the evolution of reaction products we have chosen peaks present in the diffractogram for each reaction product that do not overlap with peaks of other products. As mentioned above, ettringite appeared as the first product of these reactions that becomes visible. This is evidenced through a peak at 22.9 2θ. Calcium hydroxide was monitored using peaks at 18.1 and 50.9 2θ angles, respectively. Finally the evolution of CSH was performed following the peak at the 49.8 2θ angle.

Only one of the reactants, alite, was clearly detectable in these diffractograms. In all 4 cases, the disappearance of alite could be noticed by the decrease in the intensity of its peaks and increase of the half width. This is especially visible following peaks between 39 and 62 2θ. These changes indicate that the particles of alite decrease in size along with the progress of the hydration reactions.

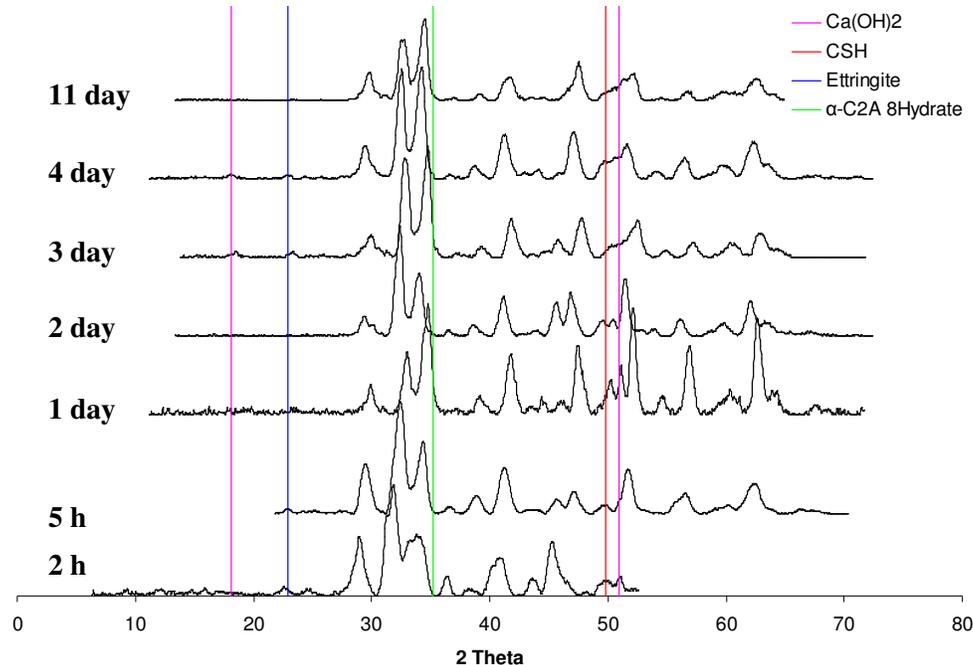In Figure 9, we show the evolution of the diffractograms for the control sample.

FIGURE 9. X-RAY DIFFRACTION PATTERNS FOR THE CEMENT PASTE CONTROL AT DIFFERENT TIMES OF AGING.

In the control samples, the peaks of ettringite are already present in the 2 hours old sample. However, this product is not visible in the diffractograms of 5h, 1 and 2 day old samples and it reappears again in the diffractograms of the samples 3 and 4 days old. The calcium hydroxide is visible in the patterns of samples older than 1 day. The CSH is clearly detected between the first and second day of reaction.

The diffraction patterns in Figure 10 indicate that the cement paste with Na-montmorillonite evolves very similarly to the "control" paste at least during the first four days. However, the diffraction pattern of the 11 days old sample containing Na-montmorillonite is very different to that of the control paste as the most intense peak of the diffractogram is associated with the ettringite. The evolution of the peaks associated with alite seems to indicate a slower reaction in the case of the clay containing paste.
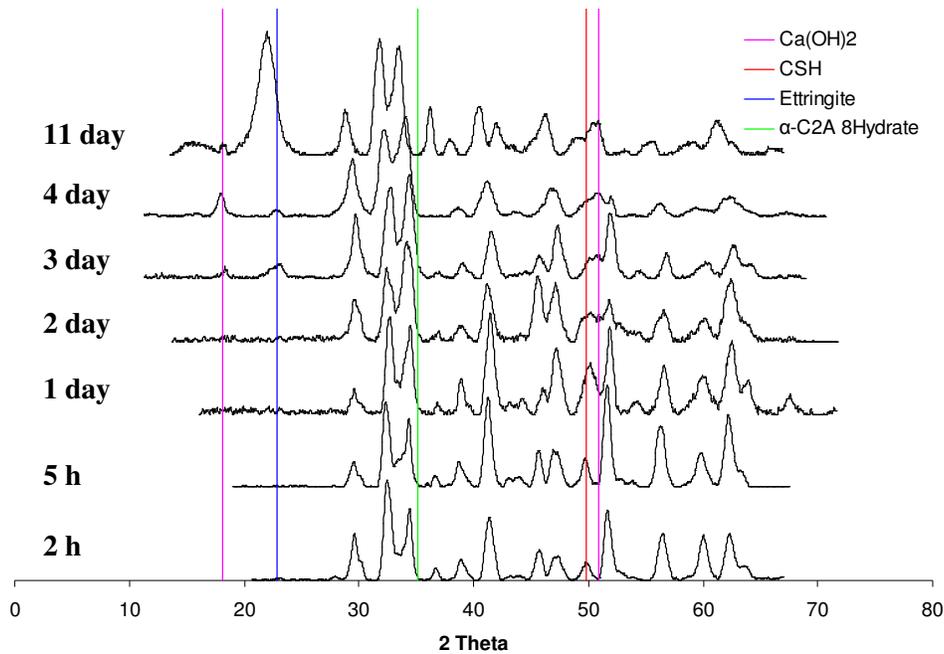

FIGURE 10. X-RAY DIFFRACTION PATTERNS FOR CEMENT PASTE WITH Na-MONTMORILLONITE AT DIFFERENT TIMES OF AGING.

The analysis of the diffractogram for the cement paste containing Ca-montmorillonite, Figure 11 reveals that ettringite is present after one day of reaction. It is interesting to note the evolution of this compound as a function of aging time. During the 11 days of this study it reached two maxima, one for the 2 days old sample the other after 4 days. Figure 11 shows that intense peaks of ettringite coincide with the disappearance of the ones associated with α-C$_2$A 8 hydrate, the intense peak at 35.2 2θ in the 1 and 3 day old pastes is not present in the diffraction patterns of

the 2 and 4 day old pastes. The ettringite peak at 22.9 2θ of the sample at 11 days is very weak as it seems that the concentration of this compound has decreased once again. The XRD data seems to indicate that α-C_2A 8 hydrate is an intermediate reaction product in the formation of ettringite. Calcium hydroxide and CSH already is evident in pastes only 1 day old.

From the evolution with time of the intensity of the peaks associated with C_3S, one can argue that the hydration reactions in the paste containing Ca-montmorillonite is faster than that of the control.
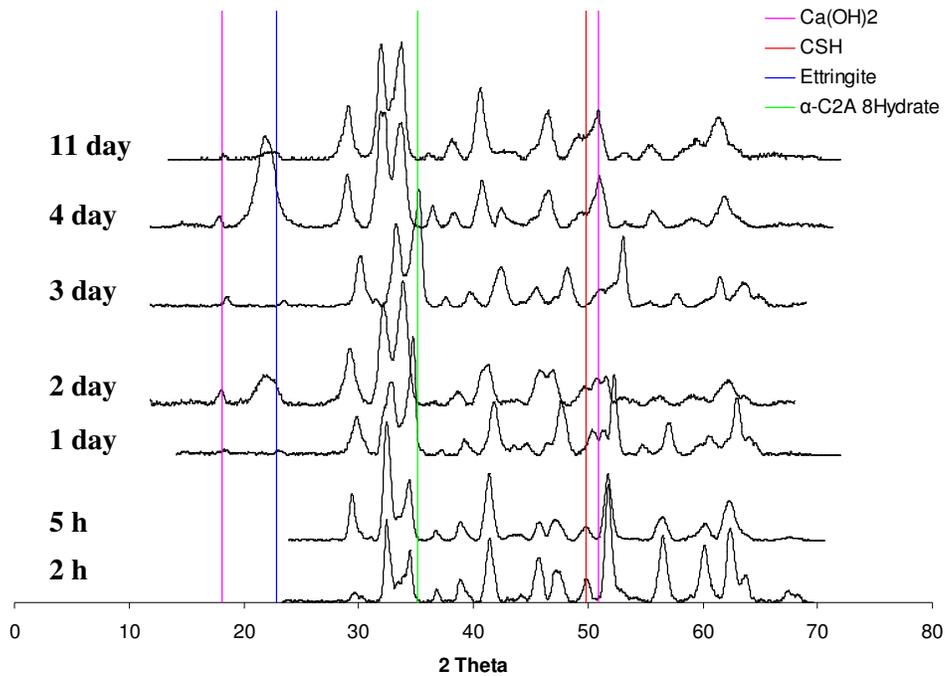

FIGURE 11. X-RAY DIFFRACTION PATTERNS FOR CEMENT PASTE WITH Ca-MONTMORILLONITE AT DIFFERENT TIMES OF AGING.

The Kaolin containing pastes evolve very similarly to the pastes containing Ca-montmorillonite (see Figure 12) Also, the ettringite peak at 22.9 2θ reaches the maximum intensity in the diffractograms for 2 and 4 day old samples and the α-C_2A 8 hydrate appears as a precursor of the ettringite. The major difference is that all of the reaction products are detectable after five hours of reactions.
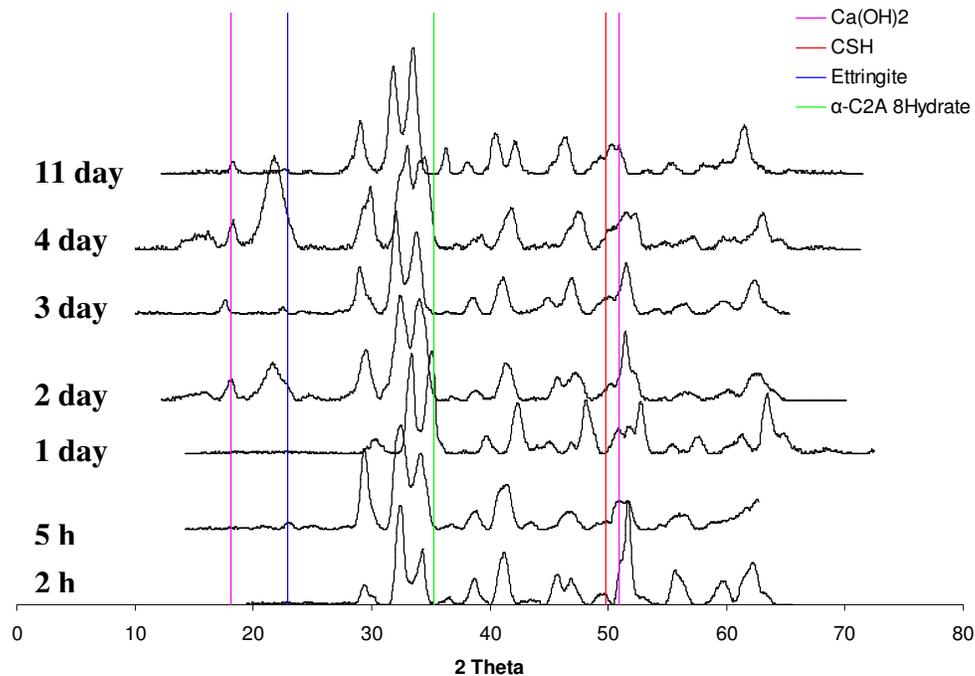
FIGURE 12. X-RAY DIFFRACTION PATTERNS FOR CEMENT PASTE WITH KAOLIN
AT DIFFERENT TIMES OF AGING.

In order to maintain the workability of the cement, we also studied pastes containing clays with higher water content. The water to clay (w/c) ratio for those samples was increased, from 0.45 to 0.65, 0.53 and 0.50 for Na-montmorillonite, Ca-montmorillonite and kaolin containing pastes respectively. The diffractograms from these samples showed the same products that as those from the pastes with a w/c ratio = 0.45. The major differences are related to how early the reaction products become visible which corresponds to the rate of the reactions. For example, in the case of the Na-montmorillonite containing paste, the ettringite was detected after two hours for pastes with w/c ration = 0.65 instead of the 3 days it took to appear when the w/c ration is equal to 0.45. The calcium hydroxide was also detected one day earlier in the former paste. In the case of calcium montmorillonite containing pastes, the increase in the water ratio accelerated only the appearance of ettringite (the peak of this compound was detected after only 5 hours of reaction instead of 1 day). Finally, in the case of kaolin, the effect of the small increase in the water content of the paste did not appear to influence the diffraction patterns of the samples. A summary of these results is shown in table 5.

TABLE 5. VALUES FOR THE APPEARANCE OF PRODUCT PEAKS IN DIFFERENT SAMPLES.

Sample	W/C ratio	pH cement paste	Ettringite	Ca(OH)$_2$	CSH
Control	0.45	13.13	2 hours & 3 days	2 days	2 days
Na-mont	0.45	13.12	3 days	3 days	2 days
	0.65	12.90	2 hours	2 days	2 days
Ca-mont	0.45	12.35	1 day	1 day	1 day
	0.53	12.45	5 hours	1 day	1 day
Kaolin	0.45	12.70	5 hours	2 days	5 hours
	0.50	12.69	5 hours	2 days	5 hours

The four different cement pastes studied by XRD were examined under the SEM microscope after four days of aging. These pastes were prepared using a W/C ratio of 0.45. The aging time was chosen based on the maximum in ettringite peaks detected by XRD.
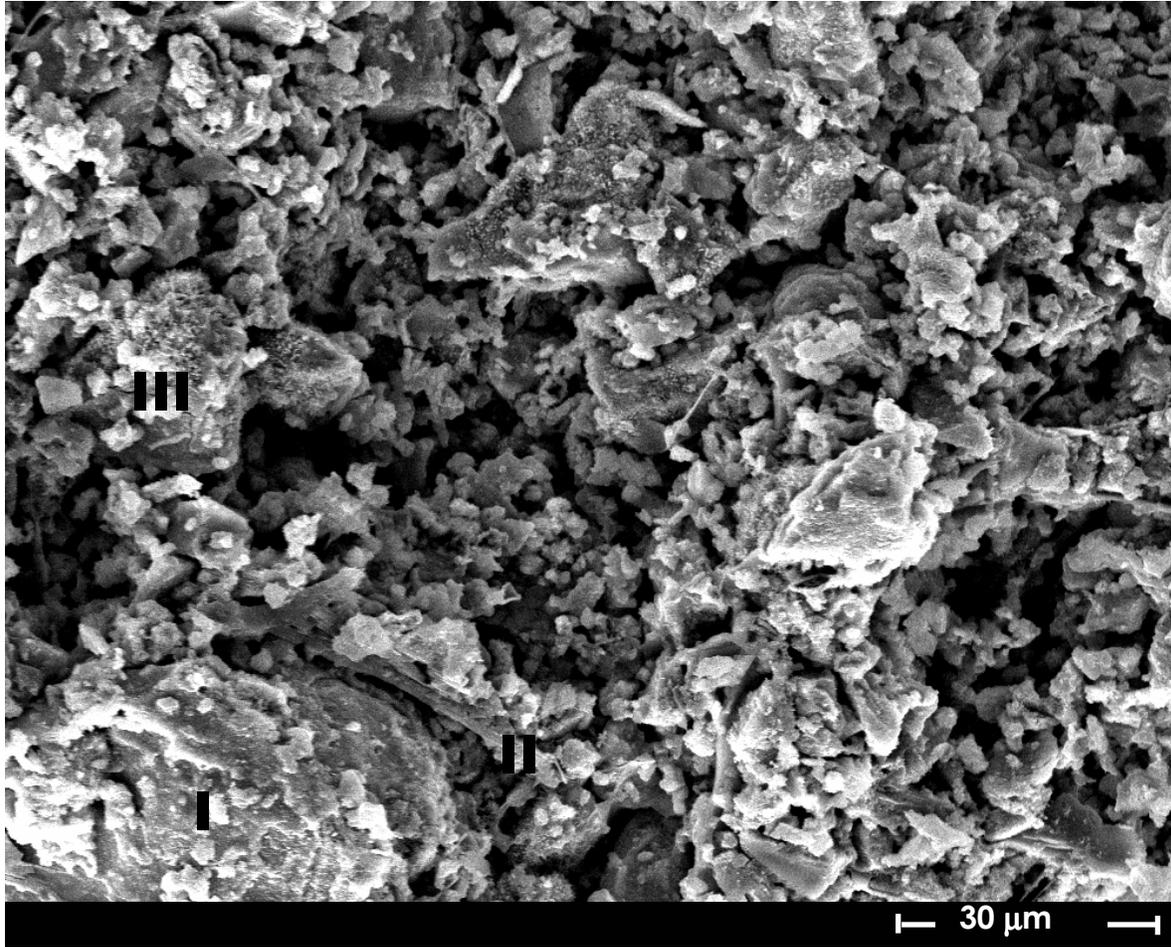
FIGURE 13. SEM PICTURES OF CEMENT PASTE AFTER FOUR DAYS OF AGING.

In figure 13, that corresponds to the control sample, one can identify several different structures. Particles of alite are present (i.e. structure I). The size of these particles varies from 60 to 10 μm. Some other products are also visible, as planar compounds that correspond to $Ca(OH)_2$ (structure II) and also some ettringite growing on the surface of C_4AF particles (structure III).
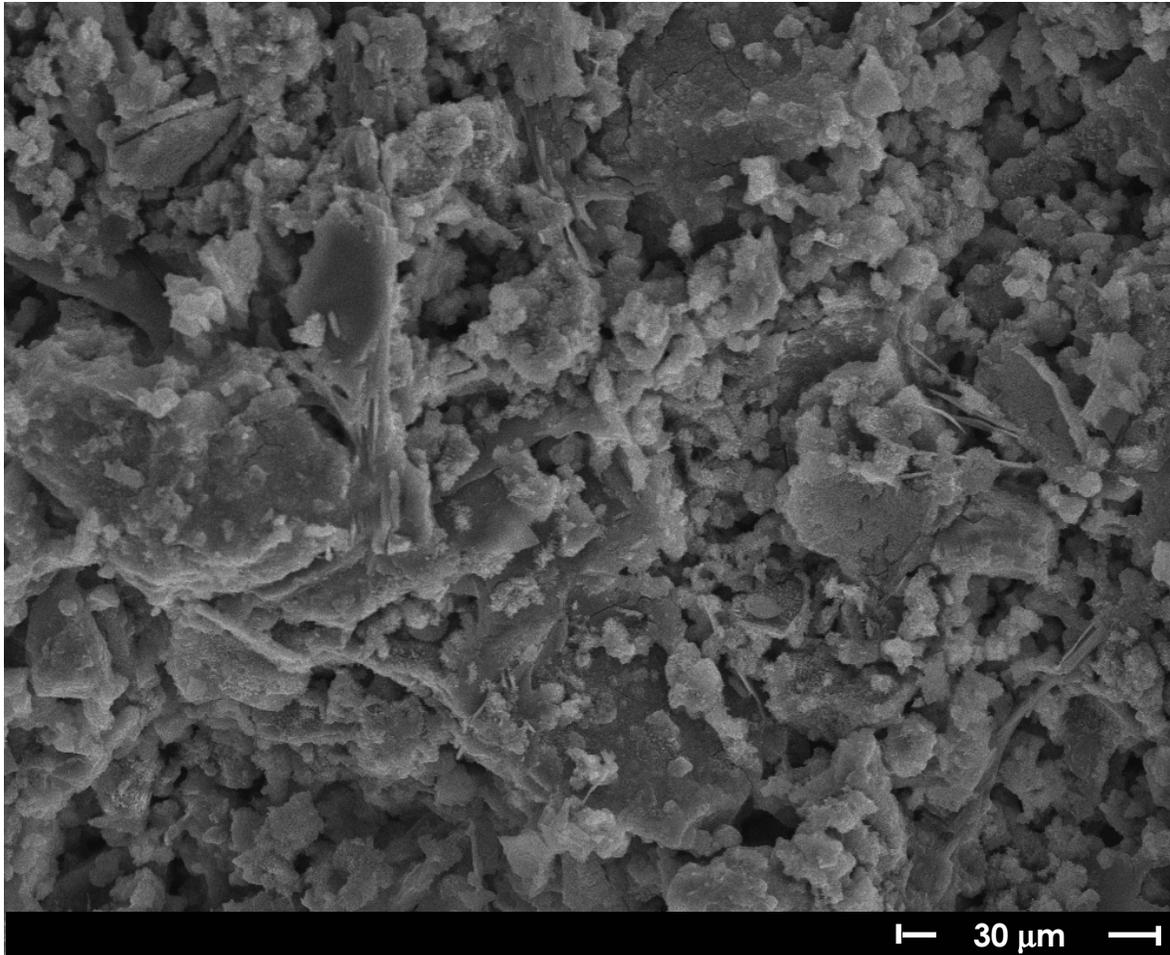
FIGURE 14. SEM PICTURES OF CEMENT PASTE WITH Na-MONTMORILLONITE AFTER FOUR DAYS OF AGING.

In the micrography of the cement paste containing Na-montmorillonite (Figure 14) it is also possible to observe the presence of large particles of alite. There also seem to be more defined needles of ettringite and bigger particles of $Ca(OH)_2$. The microstructure of this paste is very different from that of the one of the control - it is less porous.

In the micrographs for Ca-montmorillonite and kaolin containing pastes (Figure 15 and 16) the size of the alite particles is smaller than in the control. The biggest particles observed in this paste have a diameter of around 20 μm. This is a sign that the hydration reaction is more advanced. As in the SEM pictures of the control, it is also possible to observe crystals of $Ca(OH)_2$ and incipient structures of CSH (structure marked as I).
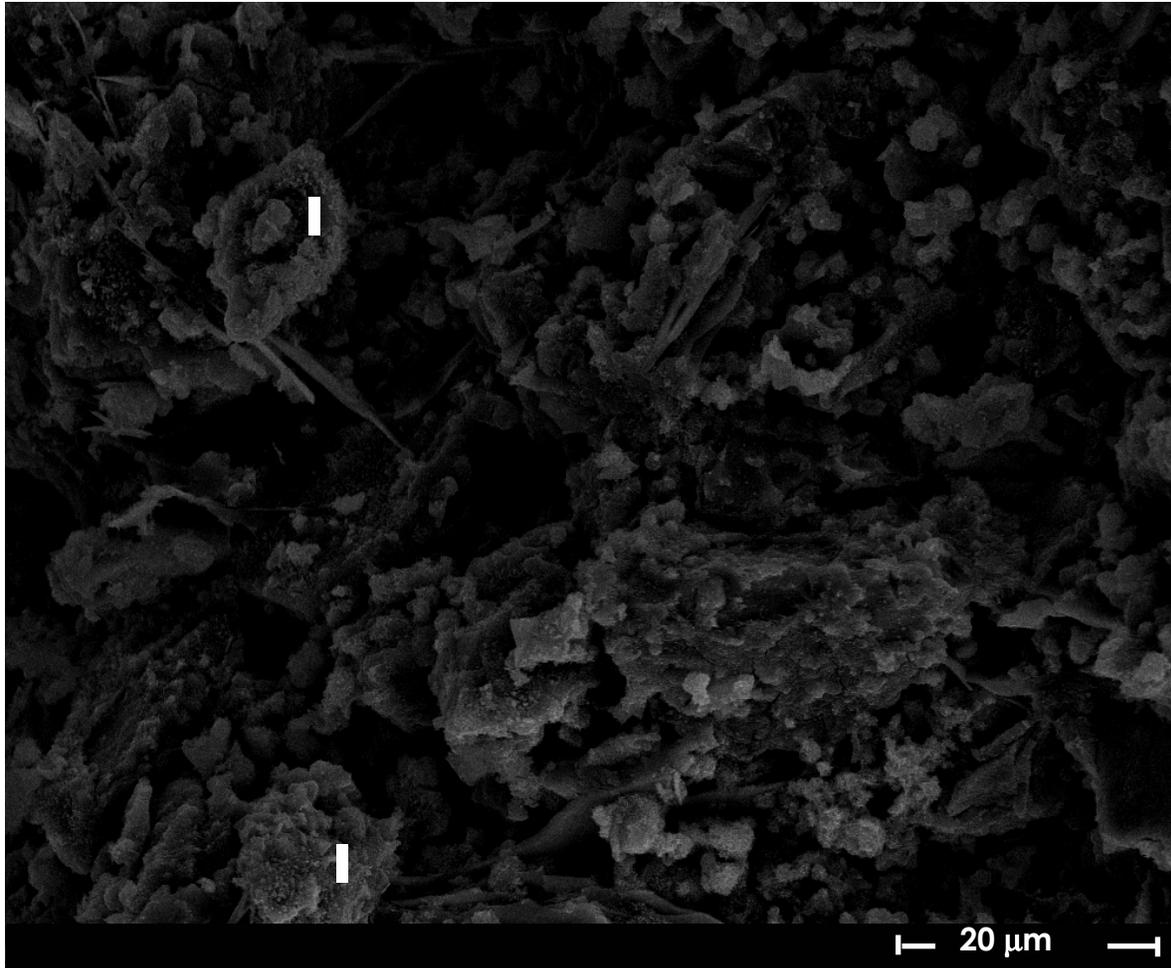
FIGURE 15. SEM PICTURES OF CEMENT PASTE WITH Ca-MONTMORILLONITE
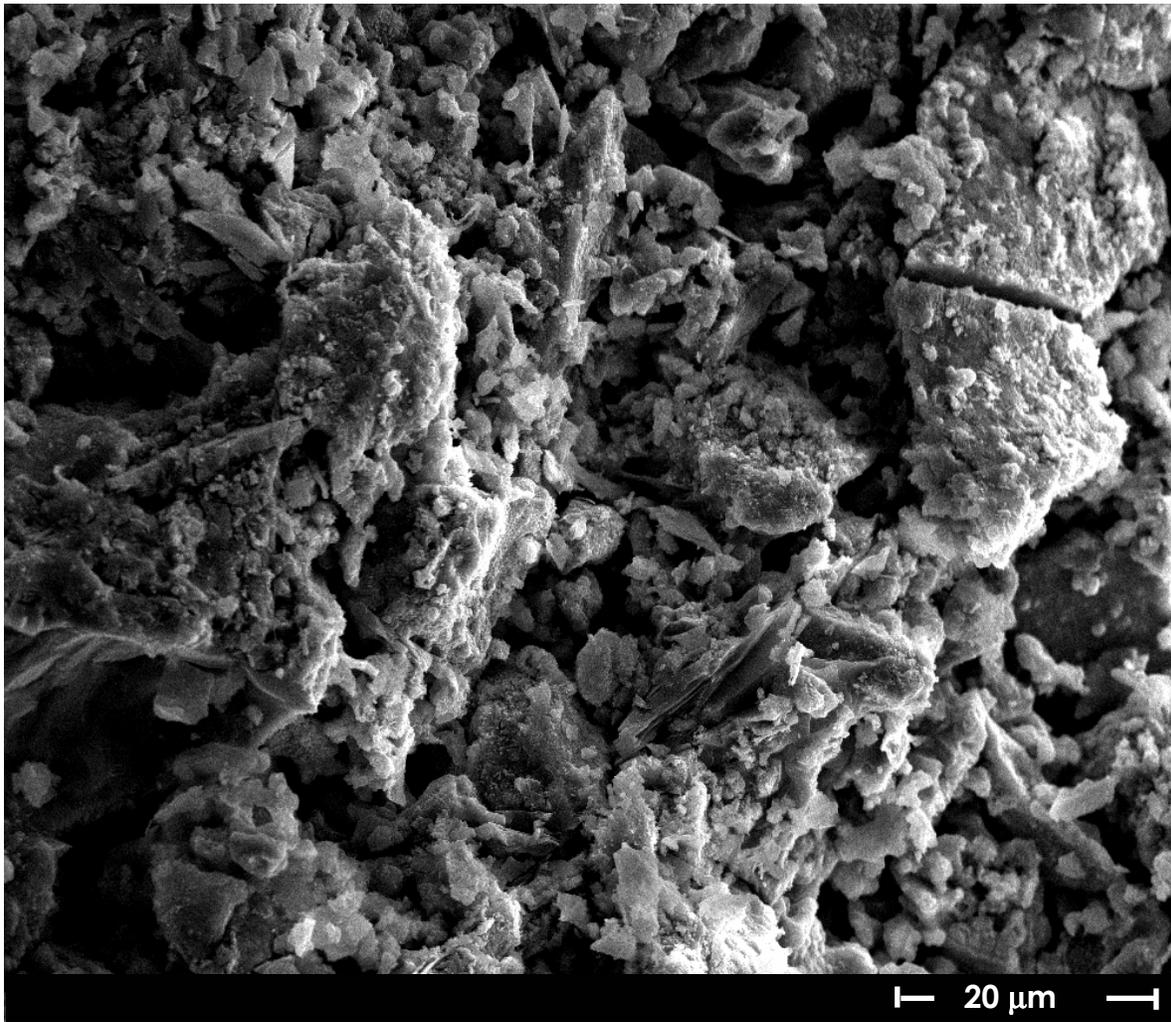AFTER FOUR DAYS OF AGING.

FIGURE 16. SEM PICTURES OF CEMENT PASTE WITH KAOLIN AFTER FOUR DAYS
OF AGING.

6. <u>CONCLUSIONS.</u>

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 given clay this may depend on other variables, as for example 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 (Ca-montmorillonite) and no swelling (Kaolin) are easier to detach and increase the rate of the hydration reaction of the cement pastes.

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