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# Thixotropic behavior of cement-based materials: effect of clay and cement types

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# Thixotropic behavior of cement-based materials: effect of clay and cement types

by

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# Abstract

In this thesis, effects of clay addition, clay replacement, and cement type on thixotropic behavior of cement-based materials are investigated.

Thixotropy is the property of certain fluid materials that are thick or viscous under normal conditions but flow or become less viscous over time when shaken, agitated, or otherwise stressed. Freshly-mixed cement pastes are thixotropic materials, which become fluid when agitated but restore its structural form at rest. This is because cement pastes experience microstructure change with time due to the particles flocculation and cement hydration.

The thixotropic behavior of cement-based materials is important in the modern concrete construction. Shape stability of concrete mixtures is often required for shotcrete and slip form construction so that the concrete mixture can adhere to the substrates or hold the shape right after casting and without support from formwork. Quick structural restore, or high thixotropy, of concrete can reduce formwork pressure in construction. Clay additions or replacement for cement often enhance concrete thixotropy and increase concrete shape stability.

In the present study, the typical hysteresis loop rheology test method is employed to evaluate thixotropy of various cement pastes. The pastes were made with different types of cement and with /without clay addition/replacement. The types of cement used are Ashgrove Type I, Lafarge Type I/II, Type IV, and High Alkali Type I cement. The clay

materials studied are Actigel, High Reactivity Metakaolin, and Ground Clay Brick. The rheology tests were performed at 0, 15, 30, 45, 60, and 75 minutes right after each paste was mixed. The rates of thixotropy change with time were analyzed for each mixture. The standard flow table tests (ASTM C230) were also conducted and the results were correlated with the rheological results. The rate of heat evolution of each paste studied is measured. The results indicate that clay addition and/or replacement for cement accelerates the rate of thixotropy change. The pastes made with different types of cement have different thixotropy changing rate. High Alkali cement has the highest thixotropy changing rate while both of Type IV and Ashgrove Type I cement have a lower thixotropy changing rate.  There is a clear relationship between thixotropy and flow test results. The faster the increasing rate of thixotropy, the faster the decreasing rate of flow can be expected. The rate of heat generation can be correlated with thixotropy increasing rate.

# Chapter 1 Introduction

## 1.1 General

Concrete which is composed of Portland cement, water and aggregates is the most widely used construction material. Advances in concrete materials have led to the use of supplementary cementitious materials and other admixtures. In fresh state of concrete, its method of placement, compaction and transportation generate high requirement of fresh concrete properties, such as workability. Concrete needs proper flowability or rheological performance to make sure that it gains enough workability. Concrete rheology is a quantitative measurement that cannot be used to characterize concrete flow but can be used to describe other aspects of concrete workability. During recent years, increasingly researchers put more emphasis on concrete rheology, because construction costs can be reduced by optimizing concrete workability to obtain easier placing ability. Additionally, different types of equipment and instrumentation have been developed to measure the concrete rheology. However, due to the complex composition of concrete, no standard measuring method is available for field construction.

Some models are available to describe the rheological properties of cement paste. One of the most popular ones is the Bingham model. The basic rheological parameters include yield stress, viscosity and thixotropy. Because aggregates can be considered as inert materials, researchers try to put more attention on the investigation of paste rheology properties. After mixing of paste, the chemical reaction between cement and water tends to change the structural degree of cement paste. Thus, the study of structural rebuilding after mixing will provide valuable information about rheological properties of cement based materials. Besides, the study of rate of structural rebuilding can be related to form pressure of concrete. In modern construction field, pre-cast concrete technology leads to development of special concrete, such as Self Consolidating Concrete (SCC). Concerning SCC, inappropriate estimation of formwork pressure might lead to formwork failure.

The thixotropy can be measured by a hysteresis loop and the area within the hysteresis loop can be described as the energy required to breakdown the structure of materials. The measurement of the variation of thixotropy with a period of time after mixing has the ability to provide useful information on structural rebuilding. In cementitious materials, thixotropy results from the time that cement takes to rearrange the microstructure of the paste matrix after introduction of shear energy. The phenomenon of structural rebuilding has a close relationship with aggregation, deflocculation of cement particles, dispersion of solid particles, rearrangement and reflocculation of cement particles. Thus combination of flocculation mechanism and structural rebuilding will improve the understanding about flow behavior of cement based materials.

In modern construction, different types of cement and cementitious materials are used for different purposes. The use of different admixtures has also become invaluable to enhance the properties of concrete to suit various construction requirements. The application of clay also provides opportunities to improve the performance of concrete, such as stability, durability and mechanical performance. Thus, more understanding about the structural rebuilding rate and flocculation mechanism of paste with clay addition/replacement or paste made with different types of cement will advance the knowledge about concrete flowability.

## 1.2 Research Objectives

The main purpose of this thesis is to investigate the influence clay addition/replacement and different cement types have on the structural rebuilding rate of cement based materials. To accomplish this main purpose, this thesis has the following objectives:

1. Evaluation of structural rebuilding rate of cement paste with different clay addition or replacement.
2. Evaluation of structural rebuilding rate of paste made with different types of cement.
3. Investigation of correlation between flow percent decreasing with structural rebuilding.
4. Study of relationship between heat generation rate and structural rebuilding rate.
5. Compressive strength for paste with clay addition/replacement and paste made with different types of cement

Three different types of clay (Actigel, High Reactivity Metakoalin and Ground Clay Brick) and four different types of cement (Ashgrove Type I, Lafarge Type I/II, High Alkali and Type IV cement) were used for this thesis. For the first two objectives, a systematic rheology test procedure based on the hysteresis loop was used. To accomplish the third objective, a flow table test was applied to measure the flow percent change with time. The fourth objective was achieved using isothermal calorimeter equipment which can measure the heat generation rate. The last objective was accomplished based on the procedure describe in ASTM C150.

## 1.3 Scope of Thesis

This thesis is divided into seven chapters including the literature review, experimental work, evaluation of structural rebuilding rate, rate of heat generation analysis and compressive strength analysis.

Chapter 1 provides the general information and background, research objective and thesis scope.

Chapter 2 provides a literature review based on basic rheology concepts, structural rebuilding rate and flocculation mechanism.

Chapter 3 describes the whole experimental program including material characterization, equipment and sample preparation procedures in detail.

Chapter 4 discusses the influences of clay addition/replacement and different cement types on the structural rebuilding rate of cement paste and the correlation between flow table test results and structural rebuilding rate. The rheology test results were also analyzed by statistical software in order to build a regression model to describe the structural rebuilding rate of cement paste.

Chapter 5 investigates the relationship between heat generation rate and structural rebuilding rate.

Chapter 6 gives the analysis of mechanical performance of cement paste with clay addition/replacement and paste made with different types of cement.

Chapter 7 offers overall conclusions of this thesis and recommendations for future research.

# Chapter 2 Literature Review

## 2.1 Introduction

This chapter provides basic information in terms of rheology principles and rheological parameters for cement based material. Detailed information about thixotropy property and flocculation of cement based materials are given in order to advance understanding of structural rebuilding of cement based materials.

## 2.2 Basic rheology principles

Rheology is the science of studying the deformation and flow of matter under shear stress [1]. Investigating rheological properties places large emphasis on the response of materials under the application of shear rate, and the relationship between the shear rate and shear stress has been investigated. Scientists have developed many models, by which they can describe the flow and fluidity of concrete and cement paste. Two of them are very widely used. The first one is Newton's model, the other one is Bingham model.

Since rheology is a science of relationship between the shear stress and shear strain of the materials under shearing, the curve of shear rate versus shear stress is called flow curve. The flow curve is very important for analyzing rheological properties. For a fluid like water, it is characterized as Newtonian liquid. For such materials, the application of shear will not create a definite shear stress. The shear stress is linearly proportional to the shear rate. It obeys Newton's law of flow, which is shown as the following equation:

$$\tau = \eta \gamma$$

**Equation 2-1**

In this equation:

$\tau$ ------- Shear stress (Pa)

$\gamma$------- Shear rate ($s^{-1}$)

$\eta$ ------- Viscosity (Pa•s)

In Figure 2-1, Newtonian liquid is described with a plot of shear stress and shear rate, from which we can see a straight line going through the plot with a slope of η (Viscosity). This is because that Newtonian material will demonstrate a viscous and elastic property at the same time. Therefore the shear stress and shear rate have a linear relationship. The Newtonian material is a very diluted suspension of solids in a liquid and no interpaticle forces exist while the concrete and cement paste can be considered as very concentrated suspensions which have many interparticle forces. Thus, for such concentrated material which has forces acting between the solid particles, it obeys the Bingham model and can be described as the following equation:

$$\tau = \tau_y + \mu \gamma$$

**Equation 2-2**

In this equation:

$\tau$ -------Shear stress (Pa)

$\gamma$ ------- Shear rate ($s^{-1}$)

$\mu$ ------- Viscosity (Pa•s)

$\tau_y$ ------ Yield stress (Pa)

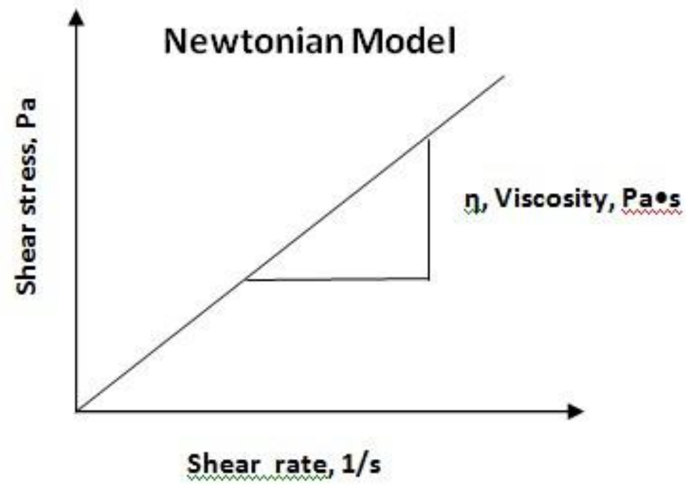



**Figure 2 - 1. Newtonian Model for fluid**

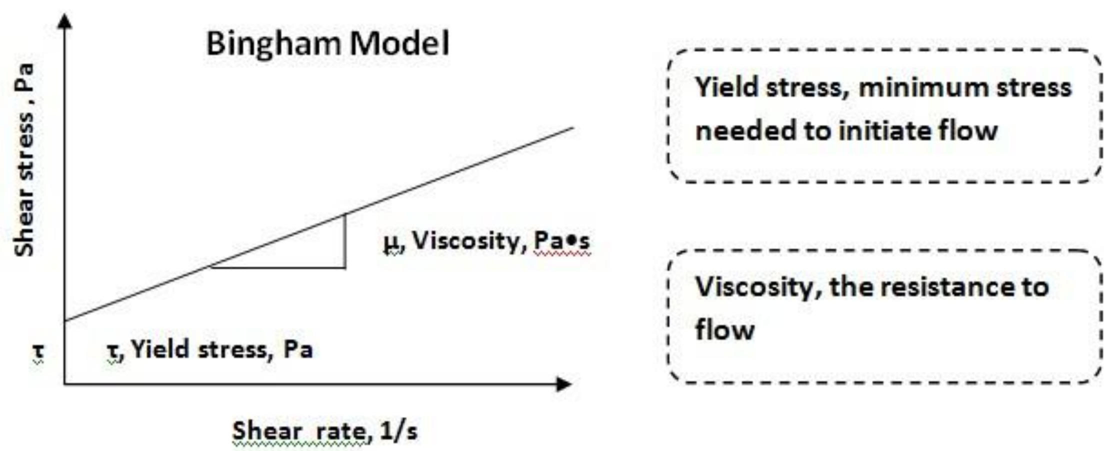
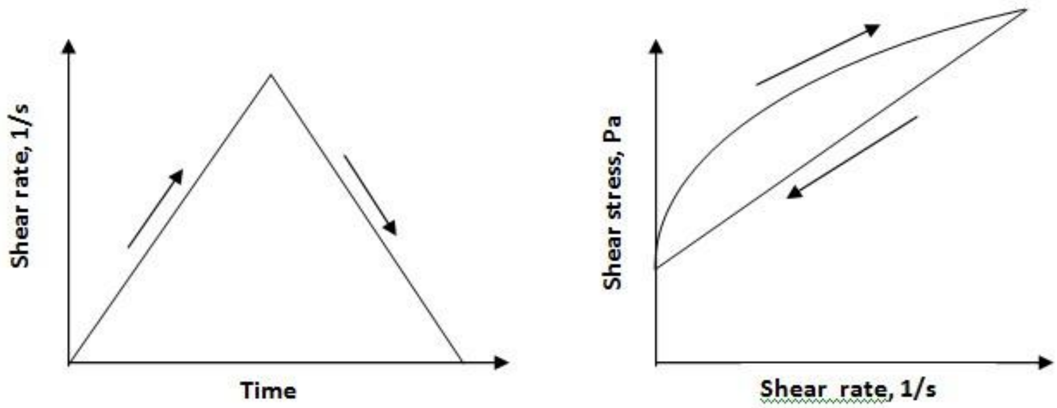



**Figure 2 - 2.Bingham Model for fluid**

A Bingham fluid has one more rheological parameter which is named as yield stress. The yield stress indicates the smallest energy required to initiate the flow of materials. Due to some materials with same viscosity might not have same yield stress, both of these two parameters should be used to describe the flow of materials. The measurement of rheological parameters is attractive to the scientists for the reason that it will be very important and valuable to predict the properties and flowability of fresh concrete and cement paste. To determine the Bingham parameters, there are two possible methods: 1)

Slowly increase the shear rate and measuring the shear stress. The stress where materials start to flow is yield stress and the slope of the flow curve is viscosity; 2) High shear rate is applied before test. Then, the shear rate will slowly decrease and the shear stress is measured. The plot of shear stress versus shear rate indicates the yield stress which is the zero intercept of shear rate and viscosity is the slope.




(a) Shear rate versus Time (b) Shear rate versus Time

**Figure 2 - 3.Thixotropy measurement and hysteresis loop**

Another important parameter for rheology is thixotropy. Figure 2-3 describes the measurement of thixotroy. The plot of shear rate versus time indicates the shear history needed for the measurement of thixotropy. The shear rate ramps up from zero to a pre-determined value. Once the shear rate increases to this point, it will ramp down back to zero. From the plot of shear stress versus shear rate, we can tell that the up curve lies above the down curve and the area between up and down curve is thixotropic value. This phenomenon results from the decreasing viscosity during shearing with time. Thixotropy can be described as the energy needed to break down structure of material. Generally, the combination of the up and down curve is called the as "hysteresis loop" and the larger the area for the hysteresis loop, the higher degree that the material structure is broken down.

## 2.3 Concrete Rheology

Due to the fact that concrete is usually put into place when it is plastic, the rheological properties of concrete are very significant to the cosnstruction industry. But unfortunately, because of the complicated composition of the concrete materials, no standard methods of measuring the flow and rheological properties are available. Besides, a large range of particle sizes can be found in concrete (the large differences in terms of particle size of aggregates and cement), thus even the characterization of concrete rheological parameters is not easy to achieve. Usually, measurement of concrete rheology just applied one of the many available test methods. However, the intrinsic flow properties of concrete are just partially measured and only limit information can be obtained from such flow tests. Therefore, more understanding of concrete rheological properties is needed to help us predict the flowability of concrete.

In the civil engineering field, many of the terms such as workability and flowability are used for describing the rheological behavior of concrete. Tattersall [1] explained concrete workability as "the ability of concrete to flow in a mold or formwork, perhaps through congested reinforcement, the ability to be compacted to a minimum volume, perhaps the ability to perform satisfactorily in some transporting operation or forming process, and maybe other requirements as well" [1]. There are also some definitions available for describing concrete rheology and workability, however, there is not total agreement among them. It is possible that these definitions are based on feeling of researchers rather than intrinsic rheological behaviors of concrete materials.

## 2.4 Measurement of Concrete Rheological Properties

The hysteresis loop method described in the previous section is the commonly used method for measuring the thixotropy. However, there are more techniques to investigate the thixotropy behavior in colloid materials.

Firstly, two samples can be prepared at the same time after mixing and two hysteresis loops can be conducted at 0min and 15 min after mixing. As described in Figure 2-4, the area between up and down curve of each hysteresis loop will be calculated and the ratio between them is called thixotropic ratio which can be used for investigating the thixotropic changing for mixtures 15mins after mixing.

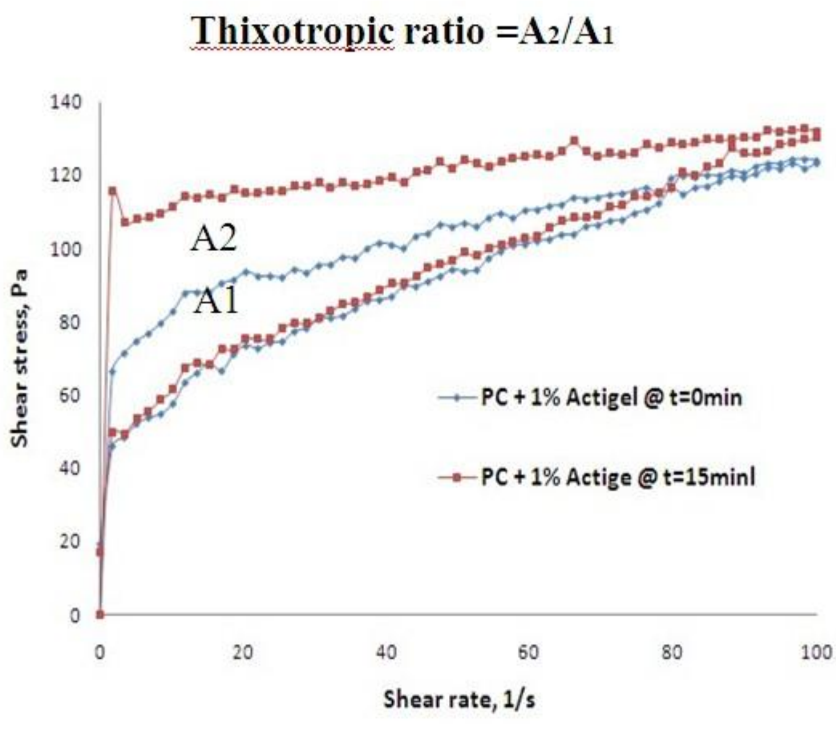



**Figure 2- 4. Thixotropic ratio measurement (two hysteresis loop)**

Secondly, another thixotropic ratio measurement is described in Figure 2-5. The shear rate is increased from 0 to a pre-determined value and shear rate is kept at such value for

3mins in order to break-up the microstructure. Then, the shear rate is ramped down to a much lower value (10 $S^{-1}$) and such value is kept for 15mins. It is assumed that the microstructure of mixture is able to rebuild with a low enough shear rate. Therefore, the generated flow curve can be used for calculating break-up area and re-build area. The ratio between them can also be used for investigating the thixotropic changing of the colloid materials.

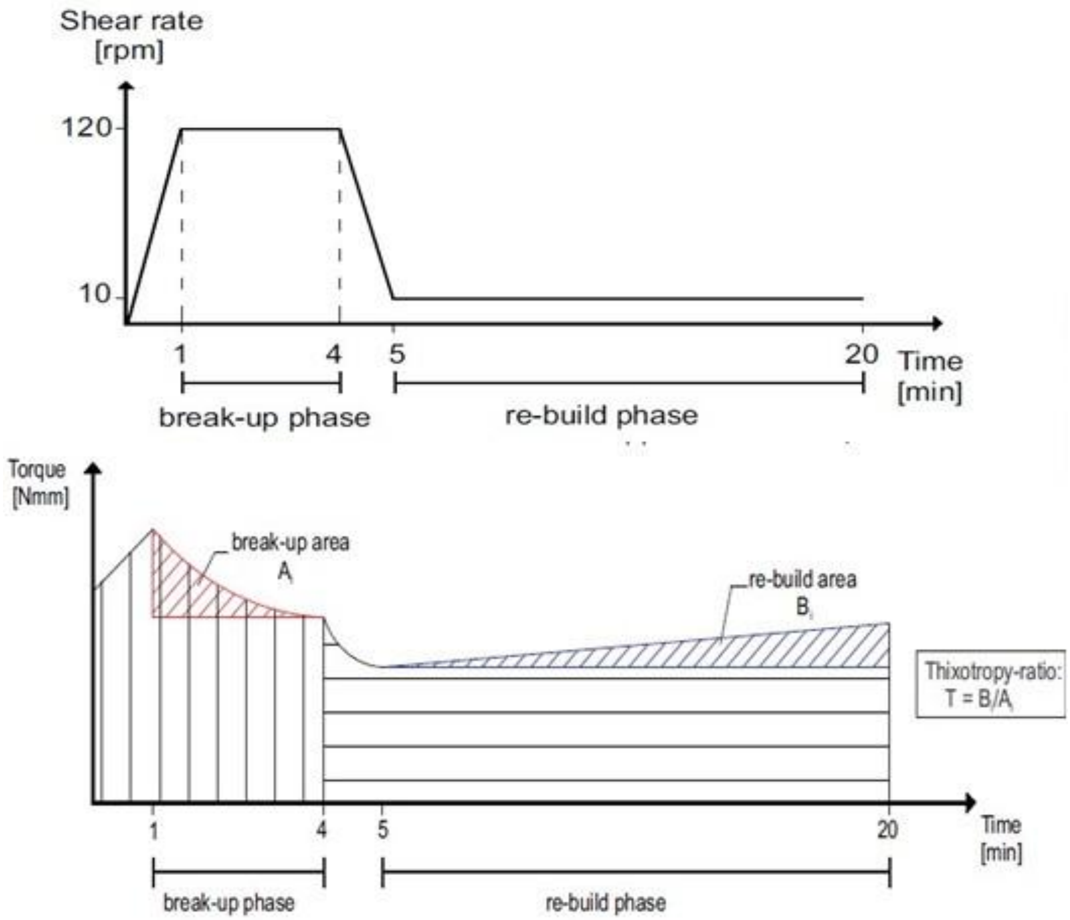



**Figure 2- 5. Thixotropic measurement method (break and rebuild)**

Besides, some researchers [23] tried to evaluate the structural rebuilding rate of materials by conducting multiple hysteresis loops after mixing. The method can be described as Figure 2-6. Before the mixing, they increased the shear rate to pre-determined value and keep this value for 8 minutes to generate an equilibrium state and then decrease the shear rate back to zero. Only one sample will be prepared after mixing and hysteresis loop are conducted every 10 mins after mixing. The area between up curve of each hysteresis loop and down curve of equilibrium curve will be calculated and plotted versus time. The slope of the curve can be used for indicating the structural rebuilding rate of colloid materials.

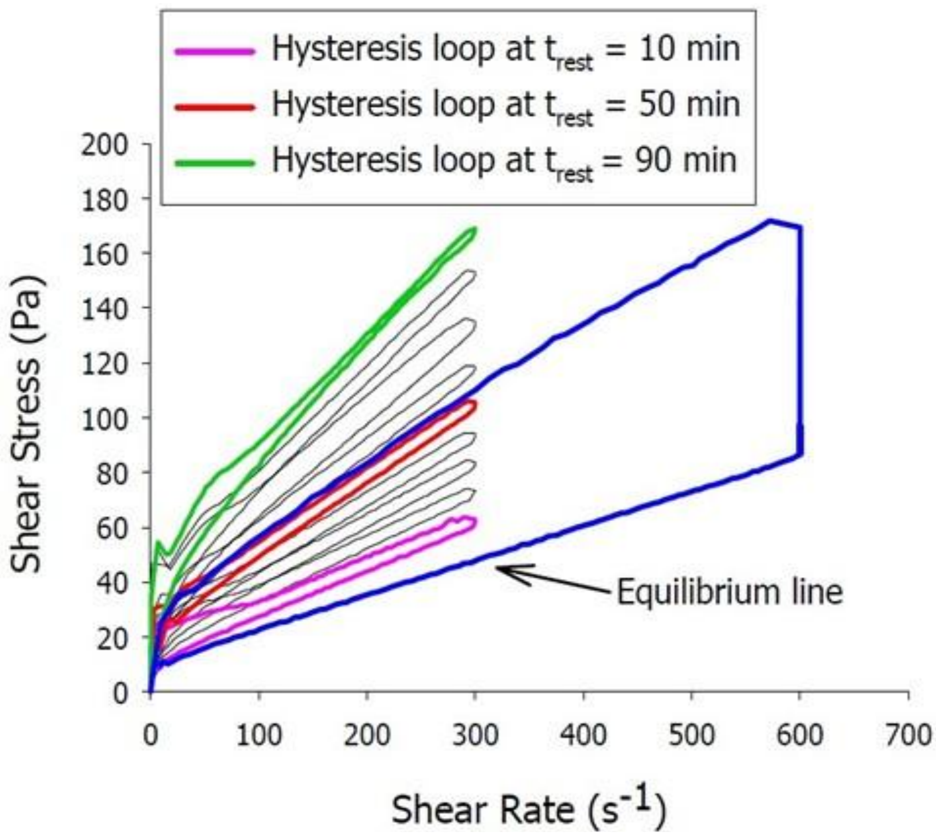



**Figure 2- 6. Mutiple hysteresis loops for evaluating structural rebuilding rate**

There are many test techniques and types of equipments available to characterize the rheological parameters of concrete in the construction field. However, it is very important to choose the most appropriate method to test the rheological properties because that it is meaningful and valuable to use this method to predict and investigate the workability and flowability of fresh concrete. It is noted that the basic parameters used to describe concrete rheological properties are yield stress and viscosity. Therefore, the methods that can appropriately indicate both of these parameters can be used for field construction. However, most of the test techniques and equipment can just measure one of these two parameters, either yield stress or viscosity, which is not enough to give an indication of the natural fundamentals of concrete. Thus, it is necessary to develop the best method to characterize the rheological properties of concrete and cement paste. In the last several decades, some test methods were developed by the researchers in order to obtain rheological parameters of concrete materials. Considering whether results of test techniques are based on one parameter or two parameters, the test methods can be divided into two categories, one parameter measuring and two parameters measuring method.

**Table 2 - 1. Tests that measure only one parameter, either yield stress or viscosity**

| Test method | Application of stress | Relation to rheological parameters |
|---|---|---|
| Slump | Self Gravity | Yield stress |
| Ve-Be Time | External Vibration | Yield stress |
| Flow cone | Self Gravity | Yield stress |
| Turning tube viscometer | Self Gravity | Viscosity |

Table 2-1 describes some test methods that measure only one of the two parameters, either yield stress or viscosity. About these methods, the basic parameters needed to characterize concrete rheology cannot be calculated from the test results. However, some relationships between rheological parameters and workability might be performed.

For the two parameters measuring methods, they can better reflect the basic concrete rheological parameters. Some popular test methods include: Two-point test, Bertta apparatus, BTRHEOM rheometer, modified slump cone test, IBB rheometer, vibration slope apparatus and BML viscometer.

Rheometer is one of the most popular measuring methods for characterizing the rheology of concrete. To achieve this purpose, different combinations of shear history are applied to concrete or cement paste and both the viscosity and yield stress can be analyzed from the resultant plot of shear rate versus shear stress. Generally, the rheometers can work in the following two mechanisms. Firstly, the imposed shear rate will be controlled by researchers and the reflection of shear stress will be measured. Secondly, the shear stress will be controlled and the resulting shear rate will be measured. Therefore, the former one is called a controlled-rate rheometer and the later one is called a controlled-stress rheometer.

Researchers usually try to relate the rheological properties of concrete with the cement paste/mortar. Because the aggregates are usually considered as intrinsic materials in concrete [2,3]. It is also easier and less labor intensive to measure the rheological parameters of cement paste than fresh concrete. A wide range of rheometers are commercially available, most of which can be used for measuring cement paste and mortar.

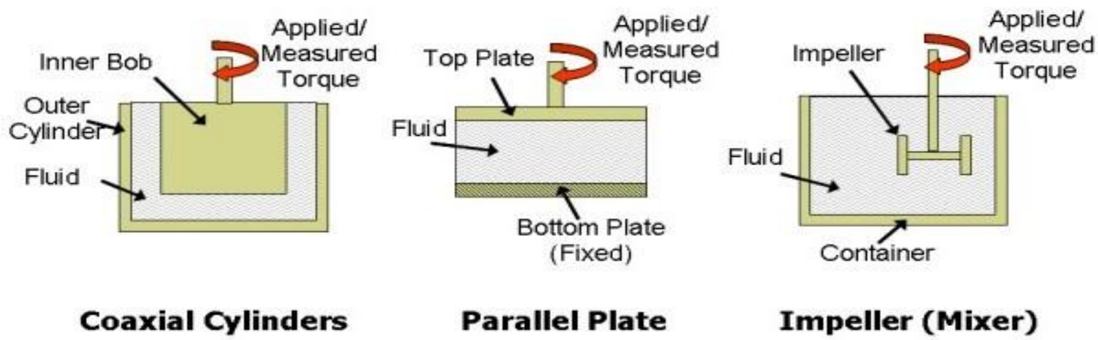



**Figure 2 - 7.Three categories of rheometers**

As shown in Figure 2-7, rheometers for concrete, cement paste and mortar can be divided into the following three categories: coaxial cylinders, parallel plate and impeller-type.

## 2.5 Factors Affecting Concrete Rheology

Prediction of evolution of rheological parameters is becoming more and more important for fresh properties of new generation concretes, such as Self Consolidating Concrete (SCC). Most of fresh properties of concrete are determined using concrete rheological parameters. Concrete rheology is influenced by all of the components of concrete and all factors during concrete mixing and placing. The following section will discuss the factors affecting concrete rheology properties in more detail.

### 2.5.1 Water Content

Water content has a very significant role to play in determining the rheological properties of concrete. When other components of concrete are controlled, increasing the water content has the ability to decrease the yield stress and viscosity of fresh concrete. However, the increasing content of water also tends to result in more bleeding and segregation of concrete. Much emphasis is put on the investigation of the relationship between concrete rheology and water content. Jones and Taylor [2] developed an empirical equation based on flow curves in order to describe the correlation between rheological parameters of cement paste and water to cement ratio. Also, Banfill [3] pointed out that increasing the amount of water contributed a higher slump and less Vebe testing time.

### 2.5.2 Temperature and Elapsed Time

The development of water reducing agents and superplasticizers advanced the application of modern concrete technologies. Temperature affects efficiency and incompatibility of water reducing agents with the cementitious materials and other admixtures [4, 5 and 6]. It is shown that the rheological properties of mortars including High Range Water Reducing Agent are significantly influenced by temperature [7]. Mixture temperature can increase the yield stress and decrease the initial plastic viscosity. If the mixture temperature increases from 10 to 30 ℃, the initial plastic viscosity will decrease while the plastic viscosity will linearly increase with time. The decrease in mixture temperature is related to a reduction of cement hydration rate and water reducing agent adsorption. At the same time, the duration of the dormant period of concrete will be lengthened [7 and 8].

It is known that the combination of mineral admixtures and chemical admixtures are used for improving workability of concrete and cementitious materials. However, the efficiency of such combination also depends on the temperature of the mixture. Petit [9] investigated the effects time and temperature have on yield stress and plastic viscosity of mortar mixtures obtained from SCC with addition of High Range Water Reducing

Agents. He also developed general equations in order to indicate the relationship between temperature/time with yield stress and viscosity, which were very useful to predict the rheological parameters for concrete.

### 2.5.3 Chemical Admixtures

It is well known that chemical admixtures have the ability to change the yield stress and viscosity of concrete which have an important role to play in the rheology properties of concrete. Air entraining agent (AEA) and water reducing agent are applied in order to improve the concrete workability. The addition of AEA has the ability to lead to an increase of paste volume and improve the consistency of the concrete while reducing bleeding and segregation. Chia and Zhang [10] indicated that the AEA addition will reduce the plastic viscosity without changing yield stress due to the reason that the small air bubbles have the ability to lubricate the cement structure. However, Struble and Jiang [11] stated that the addition of AEA results in a decrease of viscosity but an increase of yield stress.

In the fresh state of concrete, cement particles will contact together to form flocculation and some water will become trapped into the flocs of cement particles. The water reducing agents can attach to the cement particles' surface and disperse the flocs, releasing the trapped water and improving the workability of concrete. Cry et al [12] investigated the influences high range water reducer has on the rheology of cement paste. They found that high solid concentration and repulsive forces between cement particles resulted in a shear thickening fluid. It is also expected that the water reducing agents will reduce the yield stress but viscosity of fresh concrete might not be significantly affected

[9] while some other researchers indicated that the yield stress will decrease with the increase of viscosity at the same time. In addition, Perret [13] found that different combinations of cement and HRWR will improve the concrete rheological properties at different levels.

Viscosity Modifying Admixture (VMA) is commercially used for self consolidating concrete (SCC). VMA has been proved to have the ability to increase the viscosity of concrete and advance the stability of fresh mixing concrete [14]. Some VMAs are high molecular weight polymers with a high affinity to water. The functional groups of VMA molecules tend to interact with surfaces of cementitious particles and water, by which a three dimensional structure in the liquid phase of the mixture will be built up. Therefore, viscosity and yield stress will increase. The degree/strength of this three dimensional structure determines the extent to which the yield stress and viscosity is increased. Some other VMAs are inorganic materials, for example, colloidal silica. Their particles are amorphous, insoluble, non-diffusible and small enough to keep suspended in water system without setting. A three dimensional gel structure is formed due to the ionic interaction of silica and calcium of cement, by which the viscosity and yield stress will increase. The homogeneity of cement based materials can be improved by addition of VMA and a more uniform fluid can be expected. Comparing with concrete without addition of VMA, concrete with VMA addition is expected for higher thixotropy [15]. It is also found that the addition of VMA will lead to a higher value of both the yield stress and viscosity of fresh concrete [16]. The combination of appropriate amount of VMA and high range water reducer can dramatically produce a high performance concrete with high flowability and high cohesive ability in order to reduce the water dispersion [17 and

18].What's more, the time of addition of chemical admixtures will also affect the flow properties of fresh concrete. It is found that delaying the addition of High Range Water Reducer is advantageous to get a better dispersion of cement particles [19].

### 2.5.4 Supplementary Cementitious Materials

The supplementary cementitious materials are used to improve the strength, permeability, flowability and shrinkage of concrete. Rudzinski indicated that the addition of Fly Ash has the ability to increase the flowability of fresh concrete [20] because fly ash has spherical particles and a smooth surface texture, by which it can be considered as small ball bearings that can lubricate the fine particles and reduce the friction between cement particles. It is believed that the size distribution of particles, density and particle morphologies of fly ash are the major factors influencing the flowability of fresh concrete [21]. Also, both of yield stress and viscosity of cement based materials will decrease due to the replacement of fly ash. However, unlike fly ash, some mineral admixtures made with very fine particles, such as Silica Fume, will increase the water demand and reduce workability of fresh concrete. Cry et al. pointed out that the silica fume will have a very strong negative effect on water demand and hence workability [12]. Actually, the silica fume increases the amount of superplasiticizer needed to remain a constant rheology level. However, comparing with silica fume, ground silica or limestone dust will not increase water demand significantly. This suggests that high surface area is not the only factor related to higher amount of superplasticizer demand, and silica fume may have a strong affinity to superplasticizer molecules [22].

### 2.5.5 Aggregate

The particle size of aggregates will affect the workability of fresh concrete. More water will be needed to keep a constant slump of concrete if the particle size of aggregate is high. Besides, with the same water to cement ratio, the complicated shape and texture of fine sands will increase the water demand. Therefore, fresh concrete is expected to obtain a worse flowability with larger aggregates. In addition, the shape and texture of both fine and coarse aggregates have a significant effect on the rheological properties of fresh concrete. Usually aggregates with spherical shape are helpful to improve the workability. What's more, the gradation of fine and coarse aggregates also affects concrete rheology [91].

### 2.5.6 Clay Addition

Modern processing technologies have lead to the generation of modern concrete such as Self Consolidating Concrete (SCC). The change of microstructure of SCC during/after mixing and placing has been investigated recently in order to advance understanding of processing techniques. Considering SCC, its high flowability can be obtained with an increasing formwork pressure. SCC needs enough flowability to complete consolidation without the application of external vibration. It is also very important for other types of SCC, such as semi-flowable SCC, to obtain enough shape holding ability (shape stability) in order to remain its original shape after slipform paving [32]. Some research stated that modification in terms of microstructure of fresh concrete might increase the flowability without reducing the formwork pressure of fresh concrete [23]. The microstructure change is a reflection of the flocculation degree of the cement particles. Cement paste has a high inherent solid concentration. When water and cement contact with each other, cement particles rapidly form into flocs due to the frequency of particle collisions significantly increasing [24].There will be a constant formation and breakage of flocculation of cement paste during mixing. Applied with a constant mixing speed, the floc size will reach an equilibrium state based on a function of the flocculation strength. Higher flocculation strength can obtain larger flocs [25]. If mixing speed is high enough, a maximum solid volume fraction can be expected as a function of flocculation strength as well as the distribution of particle size and particle shape [26]. The yield stress is dependent on both the flocculation strength and structure of the suspension [27]. If the larger flocs are separated into smaller flocs under the application of shear rate, the flow of cement paste will be initiated when the reflective shear stress is larger than yield stress. The trapped water will be released into the cement paste and lubricate the particles of cement paste. As a result, the viscosity begins to decrease, which explains the shear-thinning behavior of cement pastes [28, 29]. The floc strength is also a determinative factor for shape holding ability of fresh concrete.

It has been demonstrated that with small addition of clay (less than 1% by mass of cement), substantial improvements on the shape-stability of SCC can be made. Small dosage of Clay addition has also been proved to improve the cohesiveness of cement-based materials [30, 31].

Tregger [32] tried to quantify how clay admixtures affect the strength of microstructure based on rheological theory. He applied different rheological techniques including shear and compressive rheology techniques in order to measure the effects of solids volume fraction of cement paste suspensions with different clay admixtures on shear stress. By which, he measured the shape holding ability of cement paste and investigated the effects of clays added into the mixture on ability to keep balance between flowability and formwork pressure. He also tried to take advantage of green strength test to check if the results were consistent with the results obtained from rheological investigation of cement paste. The cement and clay used in his research are shown in the table2,

**Table 2 - 2. Description of cement and clays [32]**

| Material | Particle size, µm (µin) | Description |
|---|---|---|
| Cement (CM) | 14.8 (582) | Type I |
| Fly ash (FA) | 23.5 (925) | Class C |
| Clay 1 (C1) | 65.2 (2567), 1.75 (68.9) | Purified magnesium alumino silicate |
| Clay 2 (C2) | 13.0 (512), 0.50 (19.7) | Kaolinite, illite, quartz |
| Clay 3 (C3) | 3.54 (139), 1.20 (47.2) | Purified calcined kaolinite |

Based on the previous testing methods, he concluded that both shear and compressive rheology method can provide information about the effect different clay admixtures has on the green strength. The testing results indicated that both shear and compressive strength will be improved by addition of clay admixtures. Besides, the addition of HRWR and fly ash replacement tended to lead to a higher maximum packing fraction and also a significant change in packing fraction. However, the addition of clay admixtures showed a totally opposite result. Among the three clay admixtures, the nanoclay, C1, which is purified magnesium alumino silicate clay, was most effective in improving the shape-holding ability. A close relationship between micro and macro behaviors in terms of microstructural flocculation strength and green strength was demonstrated. Thus, modification of microstructure of cement paste can be accomplished by addition of nano clay admixtures and flocculation behavior will be improved. It is expected that we may develop modern concrete with better shape holding ability by taking advantage of nano clay application.

### 2.5.7 Others

There are still many other factors affecting the rheology of concrete, such as fiber addition, mixing procedures and vibration, anyone of which will also has an important role to play in rheology of concrete.

For fiber addition, it has a very positive effect on the rheological properties of fresh concrete and the degree of effect depends on the aspect ratio of fibers [95]. The aspect ratio is defined as the value of fiber length divided by diameter. The amount of fibers added into concrete will also affect the rheological properties of concrete. With increasing amount of fibers addition, both the yield stress and viscosity will increase obviously at the same time. From the macroscopical point of view, the slump of fresh concrete will decrease because of the increasing viscosity and yield stress. It has been demonstrated that there is a critical amount of fiber addition, above which the concrete will not flow due to the fact that the fibers will connect and interlock with each other [95]. It leads to a much larger structural connection and more energy required to break down the structure. Because some metal fibers have complicated shape and hard to be sheared, it will be very difficult to measure the rheological parameters of fiber reinforced concrete using the same measurement of cement paste. However, it is very important to understand more information about the effect of fiber addition on rheological properties of concrete, by which we can take advantage of fibers to improve the other properties of concrete.

Before placing, the concrete will be mixed in the trucks for field construction. It is obvious that the mixing procedure will dramatically affect the rheological properties of concrete, among which, the shearing rate is the most important factor. High shear rate during mixing will break down the structural flocculation and agglomerates of cement particles. High shear rate has ability to result in an irreversible structural breakdown. Tattersall and Banfill stated that the agglomerates and flocculations of cement share the same hydrate membrane which will be broken by the high shear rate during mixing and another new membrane will immediately generate and attach around the particles of cement. The membrane will protect the cement particles from agglomeration and flocculation [33]. This theory is supported by environmental scanning electron microscopy [34, 35]. The high shear rate will decrease both the viscosity and yield stress of concrete [36]. In addition, the area between the up and down curve of hysteresis loop will also reduce [37, 38]. The increasing shear rate will result in more structural breakdown, but the hydration products during high shearing will form to fill intervals of cement flocculation and lead to an increasing viscosity and yield stress. Normally, people measure the rheological parameters of concrete buy testing the mortar extracting from the concrete, by which they try to figure out the effects of shearing and mixing on rheology of concrete [39]. However, the mortar sieving from concrete cannot keep the same initially structural nature, therefore there are no informative research about the effects of shear mixing on concrete rheology and most of research aim to test the effect of mixing on cement paste or mortar. It is shown that shear during the first two hours will significantly influence the rheological properties of cement paste [40]. Actually, hand mixing will result in a higher and faster peak stress comparing with the high shearing methods. What's more, it is also proved that yield stress and plastic viscosity will decrease as the increase of mixing duration.

The low yield stress and viscosity are two major characterizations of SCC. However, the situation is ideal for SCC and deviations always occur in the real construction field. For normal or high strength concrete, the vibration is necessary. Thus, vibration also has an important role to play to determine the rheological properties of concrete. During vibration, the yield stress of fresh concrete will significantly decrease while no pronounced effect on the viscosity [41]. De Larrard, Krstulovic and Banfill investigated the influence of vibration on concrete rheology [42, 43, 44]. They indicated that the workability of fresh concrete has close relationship with frequency of vibration. There velocity of vibration has a critical value, below this value the workability of concrete is linearly increase as the increase of vibration velocity and lower viscosity and yield stress can be expected. Once the velocity is above the critical value, the workability of fresh concrete will not have an obvious increase.

All the factors previously discussed will affect the concrete rheology in different points of aspects. The different combinations of all these factors tend to dramatically affect the rheological parameters of fresh concrete. If single change of any of these factors is conducted, the others have to be adjusted at the same time in order to keep the same flowability.

## 2.6 Thixotropy

### 2.6.1 The Origin of Thixotropy

In the field of colloid science, the property of thixotropy is the most famous rheological phenomenon, which is very attractive to researchers. However, the research about the thixotropy is very challenging and even confusing. Although the phenomenon of thixotropy is widely applied in the modern engineering and industrial systems, the complex information of thixotropy due to microstructral changes of materials are not understood very well. Thus, there is still no standard method for fully indicating thixotropical behavior.

People used to observe that, with shaking into a liquid sol, some gels (dispersions of aqueous $Fe_2O_3$) could be changed. However, this type of gel generated again when the samples were placed without shaking and this transformation could be repeatable many times [45, 46 and 47]. Therefore, this transformation is the major contribution to the thixotropy of colloidal materials. Due to the development of material rheology, the phenomenon of thixotropy has been advanced. Many researchers put more attention on the differences in thixotropy between the Newtonian Behavior and Bingham Behavior. The definition of thixotropy can be described as following: the decrease of viscosity with time by application of shear and the recovery of viscosity when the material is at rest. The definition is based on viscosity and it is a time dependent change. Besides, viscosity changing is reversible.

The understanding of the thixotropy is based on the microstructure of the fluid. The existence of weak interparticle forces will create a network structure and lead to the flocculation of particles. However, such weak interparticle forces cannot exist when there is not outside mechanical shear, which break the flocculation and also decreases yield stress and viscosity. Once the fluid is placed at rest, the flocculation and the microstructural network will start again because of the interparticle forces.

## 2.6.2 Origin of Thixotropy of Cement Paste

The basic physical description for thixotropical properties cannot fully indicate the nature of thixotropical properties of cementitious materials since the hydration of cement will result in different phases and states of cementitious materials. The development of thixotropy of cement paste is due to the changes of materials from one phase to another phase. Therefore, based on the microstructural point, the thixotropy for cement paste comes from the break of flocculation or connected particles [48].The physical description of thixotropic behavior is as shown in Figure 2-8.  As shown in figure (a), the smallest potential energy lead to a balance position for each cement particle. Once small external energy is applied into the materials, $\Delta E$ will not be enough to make the particle move from this position, as show in (b), the particle will move back to its initial position. However, if the external energy is larger than certain value, the particles will move outside of the energy well, as shown in (c), and the flow initiates. For thixotropic behavior of cementitious materials, the energy required for cement paste to leave the energy well increases due to change of interactions of particles and cement hydration. As shown in (d), after the particles leaving the energy well, the energy well will return to its initial depth.

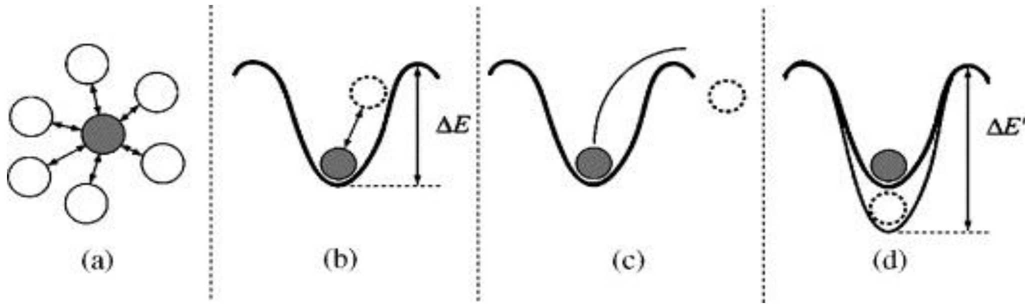



**Figure 2- 8.Physical description of the thixotropic behavior of cementitious materials [48]**


**Figure 2 - 9.Visualization of thixotropic behavior of cement paste [49]**

Figure 2-9 gives another description of thixotropic behavior of cement paste. The thixotropy of cementitious materials can be considered as the coagulation of particles when shearing is not applied to the cement particles. Once the external shearing is applied into the paste, the particles will be separated. It is noted that the reversible behavior of coagulation, separation and coagulation of cement particles contribute to thixotropic behavior of cement paste [49]. The decrease of viscosity of cement paste during the mixing with time is contributed by change of microstructure. When the microstructure is sheared, the viscosity of cement paste will decrease up to a certain steady value. During the shearing, the particles will form into lines parallel to the shear direction. The deflocculation and dispersion of cement paste particles will happen, coming with the decrease of viscosity. Once the paste is at rest, the re-connection and recoagulation of particles come with the increasing viscosity again. The yield stress properties come with the change of thixotropy and thixotropy has a significant role to play to affect the yield stress beacuse it takes some time to rebuild the microstructure of cement paste. The yield stress of cement paste will increase as the resting time after shearing and it is noted that the longer the resting time, the higher the yield stress will be. Thus the rate of change of yield stress with resting time is very useful for characterizing the thixotropy of cement paste [50]. Pierce used to investigate the thixotropic behavior of cement paste with testing gel strength of paste by applying some cycles of shearing and rest [51]. Khayat studied the effects of thixotropy on cement paste and the variation of peak stress and minimum stress [52]. They also developed an important method to study the rate of microstructural rebuilding of cement paste by measuring the thixotropic value of cement paste 1, 2 and 3 hours after mixing [52].

### 2.6.3 Experimental Quantification of Thixotropy

Concrete and cement paste are thixotropic materials. There are several experiments available for measuring and characterizing the thixotropy. Two of them are very popular and both of them are based on a rheological test. One of them takes the application of a constant shear rate and the other one is applying different shear rates on the fluid. For cementitious materials, the thixotropy is often quantified by measuring the area between the up and down curve of thixotropic loop which is also called a “Hysteresis loop”. The hysteresis loop method still has some problems because it is very dependent on testing procedures and equipments [53]. The shearing procedures can be described as follow: The shear rate will increase from zero up to a pre-determined point and it will decrease back to zero. Then, the shear stress versus shear rate will be plotted. A typical hysteresis loop is show in the Figure 2-10.

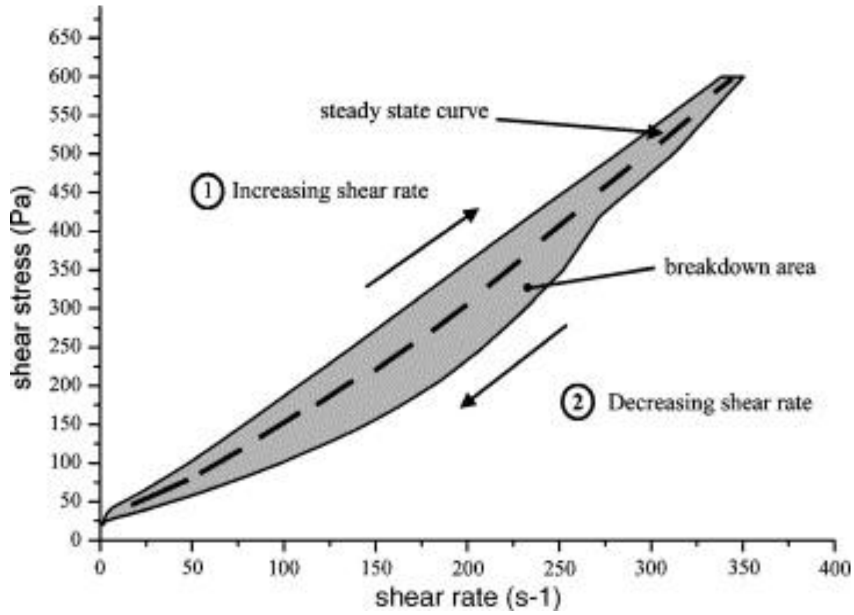



**Figure 2 - 10.Typical hysteresis loop for measuring thixotropy**

Normally, the area between the up curve and down curve can be used for the measurement of thixotropy and used as an indication of energy needed to breakdown the microstructure. The reason for the different positions of up and down curve can be explained as the following: when the shear stress is over a certain value, the flow will occur and the microstructure will be separated. However, it is true that the cement paste particles have a tendency to reconnect and coagulate with each other and the flocculation will not be quick enough to get back to the initial state. The differences between a shear thinning and shear thickening material are shown in the Figure 2-11.

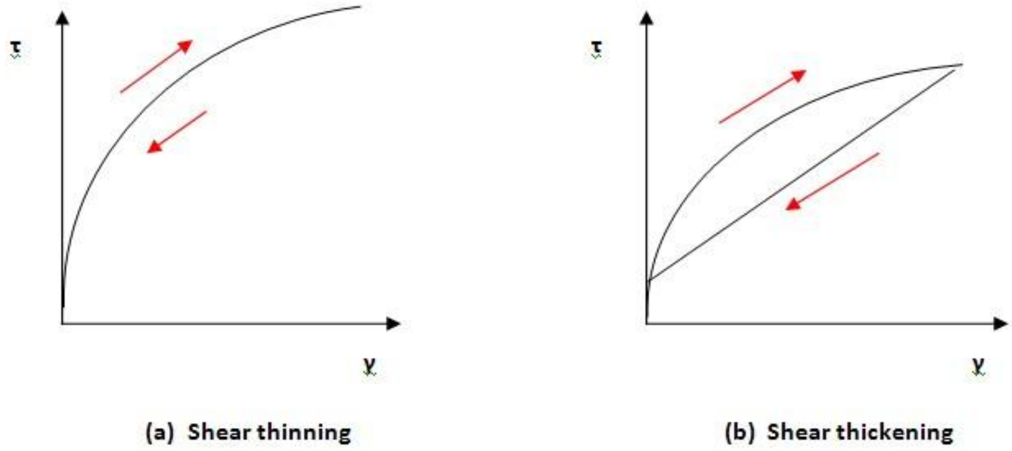



**Figure 2- 11.Differences between the shear thinning and shear thickening materials**

Tattersall took advantage of the different shear rate methods to measure the structural breakdown and thxiotropic properties of Portland cement [54]. The cycles of increasing and decreasing shear rate were repeated several times after mixing, by which these hysteresis loops can give information about the structure breakdown and rebuilding.

Chemical admixtures can dramatically influence the thixotropy of cementitious materials. Many researches about the effect of superplastisizers on thixotropy of cement paste were conducted. Ur'ev et al [55] performed the hysteresis loop for each cement mixture with addition of different types of superplasticizers. He concluded that superplastisizers can decrease the area between the up and down curve. However, compared to superplasiticizers, the information of Viscosity Modifying Agent on the thixotropy is limited. T.H. Phan compared the influences of High Range Water Reducer and VMA on the thixotropy of cement paste. He indicated that the VMA has function to stabilize concrete by increasing the viscosity and thixotropy [56].

Mineral admixtures also have an important effect on the thixotropy of cement-based materials. V. Petkova [57] substituted some amount of cement with slag and applied the hysteresis loop to study the effect of slag on the thixotropy of cement paste. The obtained results demonstrated that slag will increase the area of hysteresis loop, which is due to the increase of surface contacting. Salem [58] studied the effect of silica fume replacement on thixotropy of cement paste. She revealed that the hysteresis loop area increase as silica fume amount increases, which is due to the interaction of free $Ca(OH)_2$ and silica fume and more quick rate of transformation of ettringite-monosuflate. Besides, more water content will decrease the area between hysteresis loop. Janotka [59] studied the rheological properties of metakaolin blended cement paste. He investigated the hysteresis loop area for mixtures with varied amount of metakaolin. He confirmed that the metakaolin blended cement paste has a thixotropic behavior and demonstrated that the hysteresis loop area increases with the increasing amount of metakaolin content. Such pozzolanic material will also increase the yield stress of cement paste due to the higher specific surface.

Although the shape of hysteresis loop is a very useful measurement for quantifying thixotropy, the hysteresis loop is very sensitive to the shearing protocol. Thus, it is very important to determine an appropriate shear history. For the constant shear rate method, the shear stress will be measured as a function of time with a constant shear rate. There are two parameters describing this method, one is called the initial stress ($\tau_i$) and the other one is named the equilibrium stress ($\tau_{eq}$). It is proved that $\tau_i$ depends on the initial structural condition of the mixture and $\tau_{eq}$ indicates a balance between the structural breakdown and rebuilding [60]. A typical flow curve of constant shear rate method used for measuring thixotropy is shown as Figure 2-12.

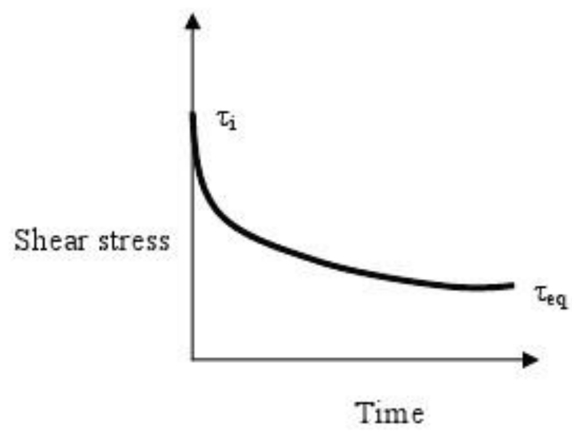



**Figure 2 - 12.Flow curve of constant shear method [60]**

## 2.7 Flocculation

Flocculation results from the process by which fine particles can combine together into floc. In the earth sciences, flocculation can be explained as a condition where clays, polymers or other small charged particles become attached and thus a fragile structure is formed. In dispersed suspensions, flocculation occurs when there is no external shearing and the dispersed particles spontaneously form flocs because of attraction resulting from opposing charged particles. The explanations of flocculation mechanism include two aspects: the first one is attractive forces and the second one is repulsive forces. This section will discuss them in terms of Portland cement paste in details.

## 2.7.1 Attractive Forces

Although the cement paste cannot be totally defined as a colloid, it is true that the cement paste consists of colloid particles. The particles of cement paste have charged particles surface. These charges are intrinsic and come from interactions during dissolution, adsorption and ionization of particles [61, 62]. When outer orbital electrons are switched or shared by the other atoms, ionic and metallic bond, which are considered as strong primary bonds, will form. Besides, the Van der Waals force can be characterized as a secondary bond. It exists between molecules and is much weaker than the primary bonds. If the molecules are contacting close to each other, the secondary forces will be very effective.

Secondary bonds can also be defined as physical bonds. It is possible that these weaker secondary forces are the most contributive factors to the thixotropic properties of cement paste. In another words, they are the main reasons why cement paste has the reversible flocculation and deflocculation when it is placed. There are three types of weaker secondary forces which can be defined as follow: London dispersion forces, dipole-dipole and hydrogen bonding. During the following pages, more detail information about these three types of secondary forces will be given in details.

London dispersion forces are caused by instantaneous changes in the dipole of atoms due to the location of the electrons in the orbital of atoms. Schrödinger equation describes the probability of an electron in an atom. When an electron is on one side of the nucleus, this side will be slightly negative charged (δ-). It will repel electrons of other atoms around, which makes these regions positive charged (δ+). The electrostatic attraction will be broken if the electron moves to another point. What's more, the London dispersion forces are also affected by the shapes of molecules. London dispersion forces are the weakest secondary force because of small charges involved and the attractions are so quickly and easily broken. As shown in the Figure 2-13, a temporary dipole can be developed by an atom or molecule when the distribution of electrons are unsymmetrical, which is due to the constant motion of electrons. A second atom or molecule will be distorted by the dipole formed from the first atom or molecule because of the electrons, repulsive forces. Thus, this tends to lead to electrostatic attraction between these two atoms or molecules. London dispersion forces exist between any two molecules when they are contacting very closely. If the molecules are larger and heavier, the London dispersion forces will be stronger.

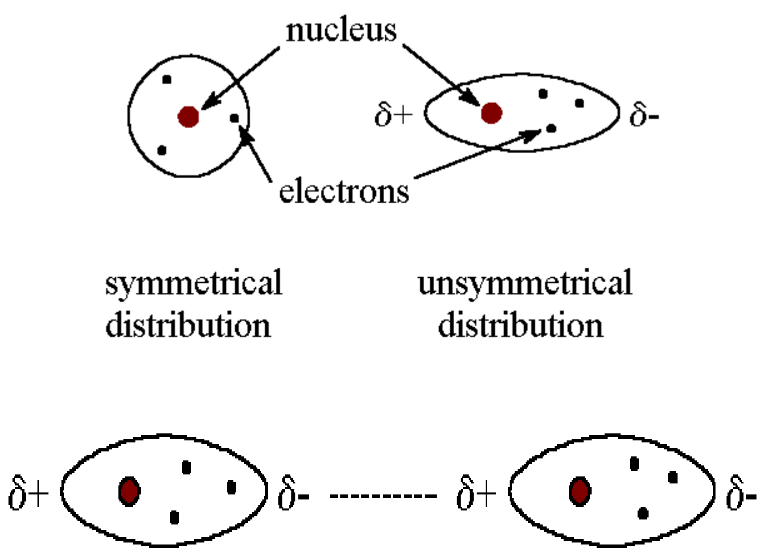



**Figure 2 - 13.Description of London Dispersion Forcecs**

Besides, electrons in a larger atom or molecule are farther from the nucleus than in a smaller atom or molecule. Thus, they are loosely held and more easily form temporary dipoles. London dispersion forces have a close relationship with the degree of polarity of atoms and molecules. If the molecules are hard to polarize, weaker London dispersion forces will form. However, if molecules can be easily polarized, stronger disperswion forces will be expected. In cement paste which is a colloidal material, London dispersion forces have a very significant role to play in the flocculation.

Dipole-Dipole interactions are caused from permanent dipoles of molecules. When one atom is combined with another because of electronegative differences, the electronegative atom draws the electrons in the bond closely to itself and become slightly negative. At the same time, the other atom becomes slightly positive. The opposing charges generate electrostatic forces and the molecules tend to align themselves in order to improve the attraction and the potential energy reduces. However, due to atoms hardly having a permanent dipole, the dipole-dipole interaction between two atoms is almost zero.

Hydrogen bonds result from by highly electronegative atoms and they are stronger form of dipole-dipole interaction. They are the strongest intermolecular force and only exist between hydrogen and oxygen, fluorine or nitrogen. High polar bonds with hydrogen can be created by high electronegativities of F, O and N and strong bonding between them can be expected.

The relative strength of the listed three types of bonds can be seen in the Table2-3.

**Table 2 - 3. Strength of secondary bonds**

| Bond type | Energy of Dissociation energy (kcal) |
|---|---|
| Hydrogen bonds | 12~16 |
| Dipole-dipole interactions | 0.5~2 |
| London dispersion forces (Van der Waals) | Smaller than 1 |

As we can see in such table, the London dispersion force is the most important factor to determine the flocculation of cement paste. The cement paste is made of heterogeneous materials and it has different phases because of hydration, therefore, more electrostatic attraction will also be created between particles [63]. Plassard applied atomic force microscopy in order to study if some other forces, except of Van der Waals forces, can be responsible for flocculation of cement paste [64]. He pointed out that calcium hydroxide concentration also affects the attractive forces. Higher the concentration of calcium hydroxide is, the stronger attractive forces can be expected. He assumed that the attraction results from ion-ion forces and interaction and some other types of forces also have an important effect on the flocculation of cement paste.

## 2.7.2 Repulsive Forces

The repulsive force mechanism includes two aspects: electrostatic repulsion and steric repulsion.

### 2.7.2.1 Electrostatic repulsion

The electrostatic field due to charged particles is described by the double layer model [65,66] which is shown in Figure2-14.

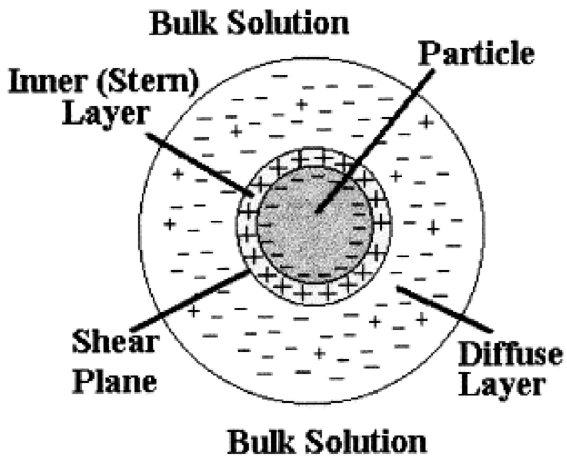



**Figure 2 - 14.Double charged layer model of particles**

The cement particles are positively charged. They will attract the ions with negative charges to their surfaces. The layer just outside particle surface with positive charge is defined as stern layer. The so called diffuse layer lies outside of the stern layer and it is made of negative ions. The concentration of these negative ions is very high near the surface of the Stern layer. However, the concentration of the negative ions will reduce linearly and exponentially with the increase of distance between the diffuse and the Stern layer. However, the positive charged cement particles will also attract some other negatively charged ions and these ions tend to be repelled by each other. A dynamic balance of these competitive ions with negative charge will be built up, by which the diffuse layer forms. If the particles are with the same chemical nature and their surface charges and potentials are the same, the repulsive forces between particles will always be expected [67].

The pore solution has an important role to play to determine the electrostatic repulsion force. The Debye-Huckel length (1/k) represents the thickness of the double layer model.

The Debye-Huckel length ranges from 1 – 100 nm in the colloidal dispersions [68]. The following equation indicates the electrostatic repulsion force:

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon\varepsilon_0 RT}{F^2 \Sigma c_i {z_i}^2}}$$

**Equation 2-3 [67]**

Where

**$\varepsilon_0$**----- Permittivity of the vacuum

**ε**------Dielectric constant of the dispersion medium

**R**----- Gas constant

**T**----- Absolute temperature

**F**----- Faraday constant

**$C_i$**-----Ionic concentration of the ions in the whole medium

**$Z_i$**-----Charge number of the ions

In addition, the electrostatic repulsion curve is widely used to describe energy required to resist the flocculation of particles. A typical electrostatic repulsion curve is shown in Figure 2-15. From this figure, maximum energy will be obtained when the particles are very close to each other. Once the distance reduces up to outside of double layer, the energy will reduce to zero.

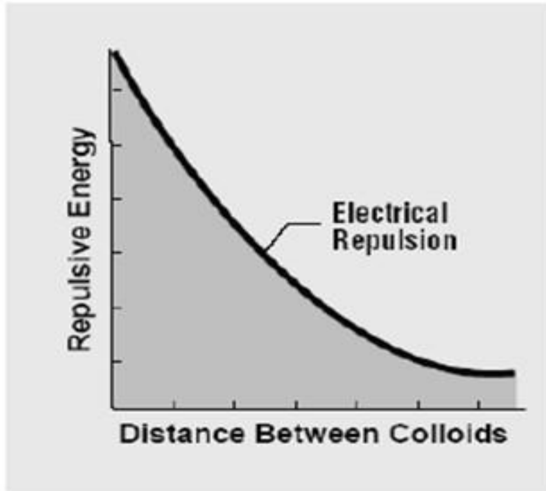



**Figure 2- 15. Repulsive energy as a function of distance between particles [69]**

Considering the cement paste will experience different states due to hydration, the surface of particles is not stable. A shear plane exists between the Stern and the diffuse layer. It can be defined as a layer at which the diffuse and the Stern layers meet with each other.

### 2.7.2.2 Steric Repulsion

Actually, there will be some amount of spaces in each atom of a molecule. An increase of free energy due to overlap of adsorbed layers can be expected if two atoms are very close to each other [70]. The increasing of free energy will also affect the preferred shape and reactivity of molecules. It is noted that surface-active agents in water will dissolve into water and attach on the interfaces of particles, which will change the properties and shapes of cement particles. Therefore, the flocculation of cement particles will be inhibited by large molecules of surface-active agents. However, this inhibition will not happen if the main length of particles attached on interfaces is smaller than distance between particles. Based on this mechanism, new chemicals with better dispersing ability are developed, for example, superplasticizers with high water reducing ability used in self consolidating concrete (SCC). This development is very meaningful for civil engineering construction. The polymers of superplasticizers are negatively charged and have ability to attach on the cement particles. Thus, as shown in Figure 2-16, the steric repulsion of protective layer of attached polymers on the cement paste tends to inhibit the flocculation of cement particles.

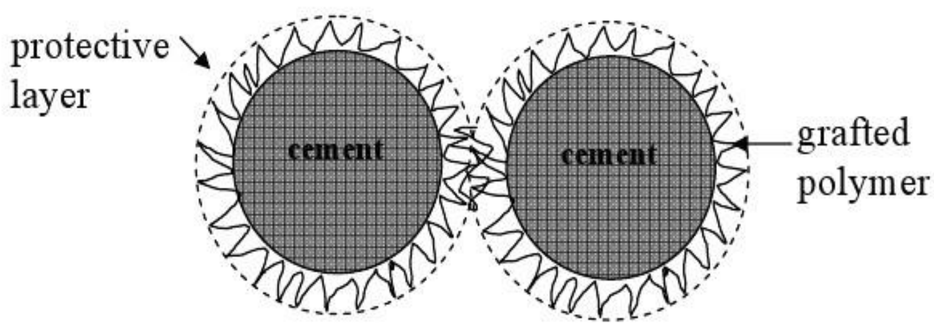



**Figure 2- 16.Schematic of steric repulsion mechanism of superplasticizers**

## 2.7.3 The Effect of Hydration on Flocculation Mechanism

The major factors affecting the flocculation of cement paste involve distribution of particle size, volume fraction of particles, interparticle forces and cement hydration. However, information about the effect of hydration of cement paste on the flocculation mechanism is not enough. Since concrete will experience different states and physical phases due to cement hydration, it has to be placed before setting. Powers pointed out that Van der Waals forces, electrostatic forces and hydration forces cause the rheological behavior of cement paste [71]. Some other research also confirmed that agglomeration and flocculation of cement particles are caused from these forces [72, 73]. Recently, et al. [74] and Kauppi et al. [75] developed a model in order to measure these forces, by which they predicted rheological properties of fresh concrete. Uchikawa [76] and Banfill [77] indicated that the interparticle interaction will be increased by the formation of ettringite and the flocculation of cement paste is accelerated. Rößler, Eberhardt, Kučerová and Möser [78] qualitatively and quantitatively characterized cement hydration. They tried to advance the basic understanding on how the formation of hydration products influence the cement paste flowability and evaluated the influence of hydration products (syngenite and AFm) on the fluidity of cement pastes. A model used for describing the fluidity of cement paste had been developed by understanding the properties of flocculation of cement paste under application of shear energy. During cement hydration, formation of long prismatic crystals like syngenite or gypsum will make a preferred crystal orientation with application of shear energy and increase the flowability of cement paste.

The fluidity and rheological properties will be improved when there is external shearing, which can be explained as follow: Firstly, network structure of AFm formation connects the particles of cement paste. Such connection will be broken by shear and mixing. What's more, ettringite transformed from AFm because of anhydrite elements will slowly dissolve and reduces the amount of composition available for formation of ettringite such as calcium and sulphate. Since separated ettringite cannot connect cement particles with the same rate as AFm, a better dispersion and weaker flocculation can be expected, which will lead to improvement of cement flowability. In addition, insufficient $C_3A$ retardation is represented by longer crystals and shorter crystals indicate a sufficient $C_3A$ retardation. It was proved that longer prismatic crystals are correlated with an increasing flocculation.

# Chapter 3 Experiment Program

## 3.1 Material Characterization and Mix Composition

There are two major parts for the whole experiment. The first part aims to study the effect of different clay addition/replacement on the structural rebuilding of cement paste while the second part aims to investigate how different cement compositions will affect the structural rebuilding rate of cement paste.

For different cement composition, the cements used for the experiment included Ashgrove Type I cement, Lafarge Type I/II cement, High alkali cement(Type I) and Type IV cement from Korea. The chemical composition and physical properties of these four types of cement are listed in Table3-1.

**Table 3 - 1. Chemical and physical properties of different types of cement**

| | **Ashgrove Type I** | **Type IV** | **Lafarge Type I/II** | **High Alkali** |
|---|---|---|---|---|
| **CaO** (%) | 62.8 | 63.03 | 63.37 | 62.50 |
| **$SiO_2$** (%) | 20.6 | 25.13 | 20.54 | 20.19 |
| **Al2$O_3$** (%) | 4.13 | 2.51 | 4.39 | 5.57 |
| **$Fe_2O_3$** (%) | 2.99 | 3.48 | 3.17 | 2.33 |
| **$SO_3$** (%) | 2.56 | 2.05 | 3.46 | 4.40 |
| **MgO** (%) | 2.99 | 1.66 | 3.48 | 2.40 |
| **$K_2O$** (%) | 0.64 | 0.64 | 0.67 | 1.15 |
| **$Na_2O$** (%) | 0.1 | 0.04 | 0.09 | 0.23 |
| **L.O.I** (%) | 2.53 | 1.25 | 1.16 | 0.69 |
| **Specific gravity** | 3.14 | 3.14 | 3.14 | 3.15 |
| **Specific surface area** | 452.7 $m^2/kg$ | 347 $m^2/kg$ | 386 $m^2/kg$ | 418 $m^2/kg$ |
| **Compound** | | | | |
| **$C_3S$** (%) | 60 | 38 | 58 | 48 |
| **$C_2S$** (%) | 14 | 43 | 15 | 22 |
| **$C_3A$** (%) | 6 | 1 | 6 | 11 |
| **$C_4AF$** (%) | 9 | 11 | 9 | 7 |

**Table 3 - 2. Chemical and physical properties of different types of clay**

| Oxide Analysis | Actigel | High Reactivity Metakaolin | Ground Clay Brick |
|---|---|---|---|
| **$SiO_2$** (%) | 49.57 | 51-53 | 69.9 |
| **$Al_2O_3$** (%) | 9.44 | 42-44 | 15.4 |
| **$Fe_2O_3$** (%) | 3.31 | <2.20 | 6.8 |
| **MgO** (%) | 8.81 | <0.10 | 1.6 |
| **CaO** (%) | 1.88 | <0.20 | 0.8 |
| **$Na_2O$** (%) | 0.59 | <0.05 | <2.8 |
| **$K_2O$** (%) | 0.66 | <0.40 | |
| **$TiO_2$** (%) | 0.42 | <3.0 | - |
| **$P_2O_5$** (%) | 0.68 | <0.2 | - |
| **MnO** (%) | 0.02 | - | - |
| **$CrO_3$** (%) | 0.02 | - | - |
| **$SO_4$** (%) | - | <0.5 | - |
| **$SO_3$** (%) | - | - | 0.1 |
| **L.O.I** (%) | <0.50 | 19.50 | 0.2 |
| **Specific surface area** | 150$m^2$/g | 15$m^2$/g | 0.370$m^2$/g |
| **Specific gravity** | 2.62 | 2.6 | 2.65 |
| **Mean particle size** | 2 um | 4.5um | 80um |

For clay addition/replacement part, this thesis used three different kinds of clay, Actigel, High Reactivity Metakaolin (HRM) and Ground Clay Brick (GCB). The chemical composition and physical properties of the three types of clay used for the whole experiment are shown in the Table 3-2.

Tap water (70±3 ℉) was used for all mixing of the cement paste.

## 3.2 Mix Proportions

In order to study how clay addition/replacement will affect the structural rebuilding rate, the mixing proportions are shown in Table 3-3. w/c of 0.4 was selected for all the mixtures. Ashgrove Type I cement was used for all mixtures. All pastes were mixed by a Hobart mixer according to the mixing procedure described in Section 3.3. The factors studied included different types of cement and different amount of clay addition/replacement. The amount of clay addition/replacement was all by percent weight of cement.

**Table 3 - 3. Pastes with clay addition/replacement mix proportions**

| Clay | w/c | Amount of clay addition/replacement |
|---|---|---|
| **Actigel** | 0.4 | 0.5%, 1%, 2%, 3% |
| **High Reactivity Metakaolin** | 0.4 | 5%, 10%, 15% |
| **Ground Clay Brick** | 0.4 | 15%, 25%, 35% |

For the study of how different types of cement will affect the structural rebuilding rate, the mix proportions are shown in Table 3-4. The w/c of 0.4 was fixed for all mixtures.

Four different types of cement were studied and the w/c can ensure suitable flowability of cement pastes. All pastes were also mixed by a Hobart mixer according to the mixing procedure shown in Section 3.3.

**Table 3 - 4. Different types of cement mix proportion**

| Type of cement | w/c |
|---|---|
| **Ashgrove Type I** | 0.4 |
| **Lafarge Type I/II** | 0.4 |
| **High Alkali** | 0.4 |
| **Type IV** | 0.4 |

## 3.3 Mixing Procedure

One mixer and one mixing procedure were used to study the effect of clay addition/replacement and different cement types on structural rebuilding of cement paste. The Hobart model N50 mixer which is shown in Figure 3-1 was used for mixing based on the mixing procedures described as following:

1. Add the cement and clay into the mixing bowl of the mixer,

2. Mix the dry cement and clay on low speed ($140 \pm 5 r/min$) for 60 seconds,

3. Put the water into the mixing bowl and keep mixing on low speed ($140 \pm 5 r/min$) for 120 seconds,

4. Stop the mixer for 60 seconds, during this time scrape down any paste or dry ingredients that collected on the edges of the Hobart mixer,

5. Start mixing again on medium speed ($285 \pm 10 r/min$) for 150 seconds,

6. Stop the mixer for another 60 seconds, during this time scrape down the paste on the edges of Hobart Mixer,

7. Start mixing again on medium speed ($285 \pm 10 r/min$) for another 150 seconds.

**Figure 3 - 1.Hobart mixer**

## 3.4 Test Methods

### 3.4.1 Paste Rheology Measurement

Typically, the rheometer is applied to evaluate the rheological parameters of cement-based materials. For this thesis, the Brookfield R/S SST2000 rheometer which is shown in Figure 3-2 was used to measure the rheological parameters of cement paste. It is a constant shear stress rheometer controlled by a computer program. The calculation of shear stress and shear rate are based on readings in the load cell and the rotating vane size.


**Figure 3 - 2.Brookfield R/S SST2000 rheometer**

Vane size may have a significant effect on rheology measurement of cement-based material, only one size of rotating vane was used according to the rheological parameters of different materials under test. Table 3-5 lists the physical parameters of rotating vane. Figure 3-3 shows the vane and cylinder for rheology test.

**Table 3 - 5. The physical parameters for vane of Brookfield Rheometer**

| Vane type | Diameter (m) | Height (m) | Torque range (Pa) | Size of container |
|---|---|---|---|---|
| V30-15 | 0.015 | 0.030 | 121-4040 | 2’’×4’’ Cylinder |

**Figure 3 - 3.Vane and cylinder for rheometer**

The shearing procedure of rheology measurement is shown in Figure 3-4. This procedure was used for all paste rheology measurements. Once the mixing of paste was finished, the mixture was placed into 6 cylinders at the same time for rheology measurement. Then one of the paste specimens was placed into the rheometer. There was no pre-shear step due to the fact that the experiment aims to evaluate how clay addition/replacement and different types of cement will affect the structural rebuilding rate and flocculation of cement paste. Although the pre-shear has the ability to protect the sedimentation of cement paste during the experiment, the pre-shear will break the structural connection and flocculation, which will negatively affect the evaluation of structural rebuilding and flocculation. At the very beginning, the specimen was subjected to perform a hysteresis loop. The shear rate increased from 0 to $100s^{-1}$ over 60 seconds and then ramped down from 100 to $0s^{-1}$ over another 60 seconds. This procedure was repeated 6 times for each mixing proportion (The second specimen was allowed to rest for 15 minutes from the end of mixing, the third specimen was allowed to rest for 30 minutes from the end of mixing, etc. ), and each specimen was performed a hysteresis loop. Similarly, the hysteresis loop for the sixth specimen was performed 75 minutes from the end of mixing. It is expected that an increasing shear stress can be seen with the change of time. Since the rheology measurement is very sensitive, three repetitions were performed for each mixing proportion.

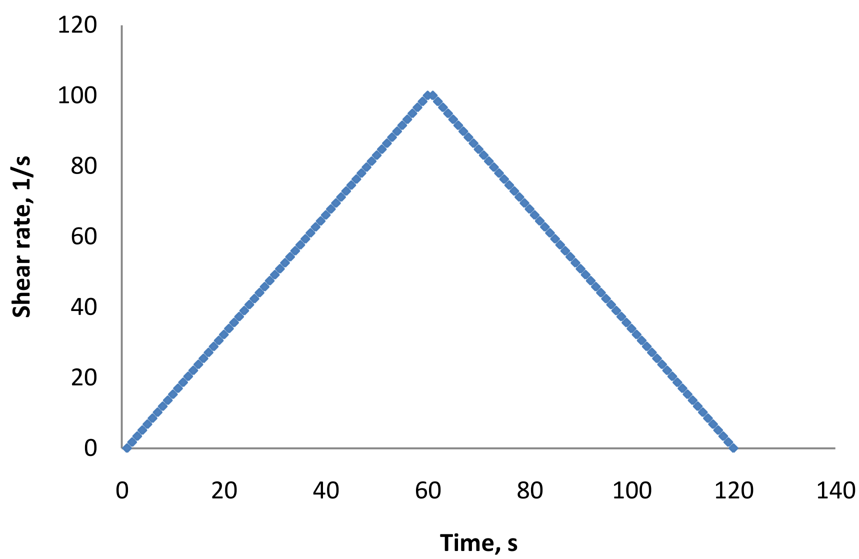



**Figure 3 - 4.Shear history for paste rheology measurement**

The thxiotropic value (area within the up and down curve of each hysteresis loop), was calculated for each specimen and the average values were plotted versus time. The slope of the line can be used to indicate the structural rebuilding rate. If the thixotropic values for different mixtures can be plotted together it can give information about comparisons among the rates of structural rebuilding for different paste with different clay addition/replacement or pastes made with different types of cement. For example, as we can see in Figure 3-5, the structural rebuilding rate of material 1 is highest followed by material 2 and material 3 while the slope of the plane for material 4 is lower than the other three.

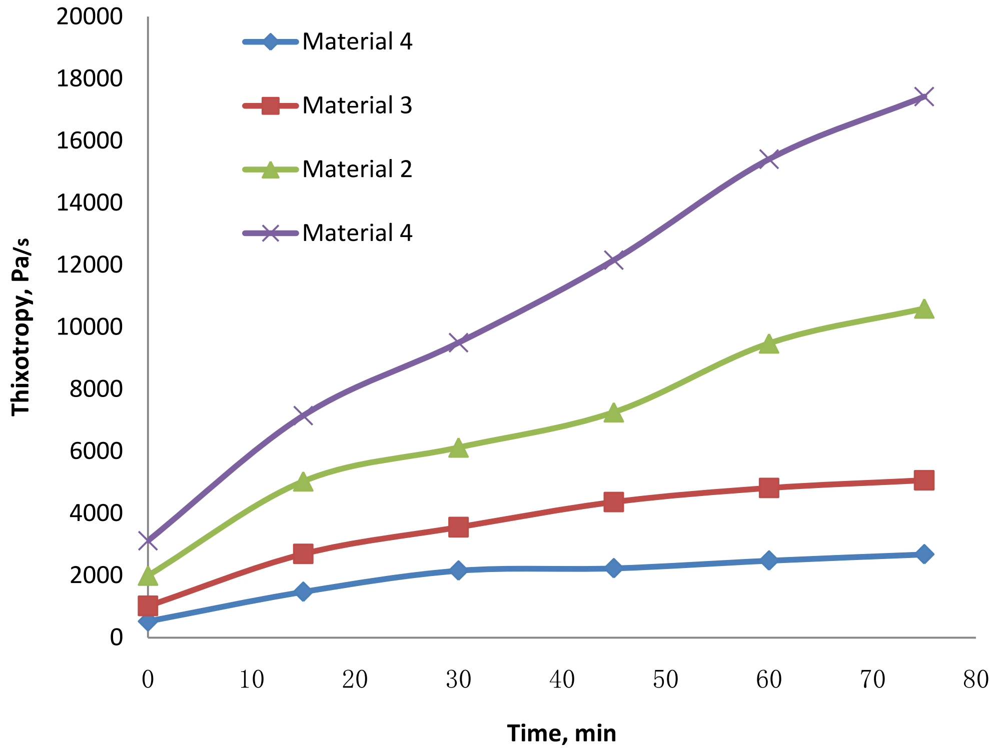



**Figure 3 - 5. Application of experimental procedure to compare the structural rebuilding rate of different mixtures**

In addition, the other two rheological parameters (yield stress and viscosity) for each specimen were also plotted versus time because both the yield stress and viscosity are informative parameters which can be related to the structural rebuilding and flocculation of cement paste. Therefore, the plots provide valuable information about the study focus. Since the rheological test is very sensitive, in order to protect errors from experiment, the rheological test for each mix proportion was repeated for three times and the average values for each parameter were plotted versus time.

In addition to the rheology test for paste mixtures, a flow table test was used to evaluate the flowability of cement-based materials, so that the rheological parameters can be compared with the standard tests in order to correlate the rheology test results to better evaluate the structural rebuilding and flocculation of cement paste. The flow table test were done according to the ASTM C230 and estimated the flowability of mortar based on the spread of a mortar specimen subjected to 25 drops of the flow table which is shown in Figure 3-6. The flow percentage of the mortar was calculated by measuring the diameter of spread of mortar. It is known that the higher flow percentage indicates better flowability of mortar. This thesis applied this test method to cement paste. The ASTM C1437 describes the test procedure and mixing procedure described in Section 3.3 was used for the flow table test. For the paste specimens with very high flowability, they might lead to a spread larger than the measurable range at 25 drops. Thus, a modified flow percentage measuring equation was developed based on the spread diameter on a logarithm scale. The modified equation can be described as following [91]:

$$F_{25} = F_t + 46.779\ (\ln 25 - \ln t)$$

**Equation 3-1**

Where $F_{25}$ is the flow percent of paste at 25 drops and $F_t$ is the flow percent of paste sample at $t$ drops. Similar with the rheology measurement of cement paste, six specimens for each mixing proportion were prepared right after mixing, the first one was tested right after mixing and the sixth specimen was tested 75 minutes after mixing. The flow percentage of each specimen was plotted versus time.

**Figure 3 - 6. Flow table equipment**

## 3.4.2 Heat of Hydration

Another part of this thesis is to investigate how cement hydration will influence the structural rebuilding rate of cement based materials. Therefore, paste specimens were prepared for isothermal calorimeter testing. The paste samples were prepared based on the mixing procedure previously described in section 3.3. The isothermal calorimeter is manufactured by Thermometric. It can be used for measuring the rate of heat of hydration of cement paste. There are eight individual sample channels and all of them can be tested at the same time. The picture of isothermal calorimeter is shown in Figure 3-7.


**Figure 3 - 7. The unit of isothermal calorimeter**

Right after mixing, the pastes (approximately 100 grams) were placed into the chamber which has two heat flow senors, one is an inert sensor and the other is an output sensor. The heat generated from hydration of cement paste will be measured by these two sensors. Once the heat generated from physical and chemical reaction spread to the surrounding, it will be detected by the two sensors. The differences between inert and output sensor will generate a voltage based on the proportion of heat flow. The measurement will be conducted every 30 seconds and last for 48 hours. By a calibrating procedure, the detected voltage signal will be converted to rate of heat of hydration. In this thesis, the total heat of hydration generated by all cement paste mixtures at 20 degree C was measured.

### 3.4.3 Compressive Strength

The compressive strength of cubic specimens of cement paste with different clay addition/replacement or different types of cement were also studied in this thesis. The test procedure followed the ASTM C150. The equipment is shown in Figure 3-8. Concerning the High Reactivity Metakaolin and Ground Clay Brick are pozzolanic materials which have slow/rapid rate of hydration, for each mix proportion with clay addition/replacement described in Section 3.2, 3, 7, 28 and 56 days compressive strength were tested. However, for another experimental step studying the effect of different types of cement on structural rebuilding and flocculation, 3, 7 and 28 days compressive strength were tested for each mix proportion described in Section 3.2. Three specimens for each test were prepared and the average compressive strength was plotted together.


**Figure 3 - 8. Test Mark compressive strength testing equipment**

# Chapter 4 Evaluation of Structural Rebuilding Rate

## 4.1 Introduction

The objective for this chapter is to investigate how different clay addition and types of cement will affect the structural rebuilding rate of cement based materials. The rheology test method and flow table test described in Chapter 3 were used for measuring the rate of structural rebuilding. The rheology measurements were analyzed and a regression model was developed to describe the structural rebuilding rate of cement paste. Because the different clays will not be used at the same time in construction field, therefore only pastes with individual clay addition/replacement were studied.

## 4.2 Rheology Test Results

Figure 4-1, Figure 4-2 and Figure 4-3 show the plot of thixotropy, yield stress and viscosity versus time for cement paste specimens with addition of Actigel, respectively. It can be seen that the rate of structural rebuilding rate was obviously affected by the addition of Actigel. The plot indicates that the Actigel addition increased the energy required to breakdown the structure of paste since that thixtropic value for each time point increased with the increasing amount of Actigel addition. Besides, the thixotropic values were highest for 3% amount of Actigel addition and lowest for the pure cement paste. Similar results can be seen in the plots of yield stress and viscosity. However, the rate of structural rebuilding varied a lot for pastes with different amounts of Actigel addition. Small amount of Actigel addition increased structural rebuilding rate. The highest structural rebuilding rate was obtained by paste with 1% Actigel addition and with continuing addition of Actigel, rate of structural rebuilding started to decrease gradually and the lowest rate of structural rebuilding was seen in paste samples with 3% addition of Actigel.

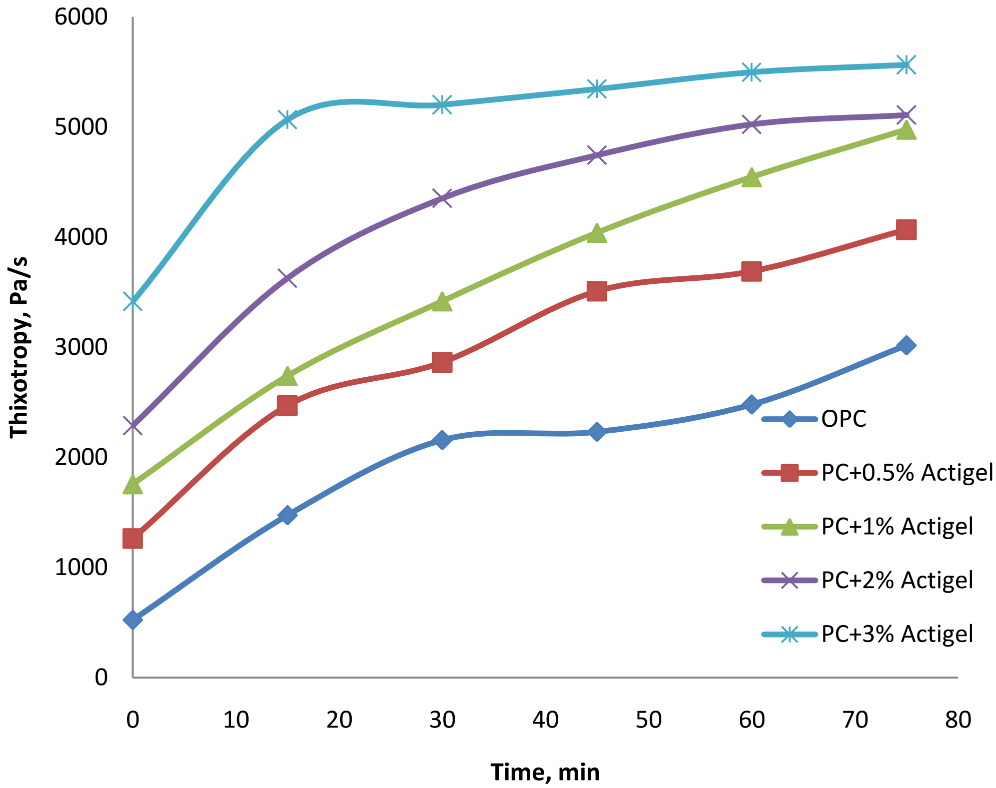



**Figure 4 - 1. Thixotropy versus time for pastes with different amount of Actigel**

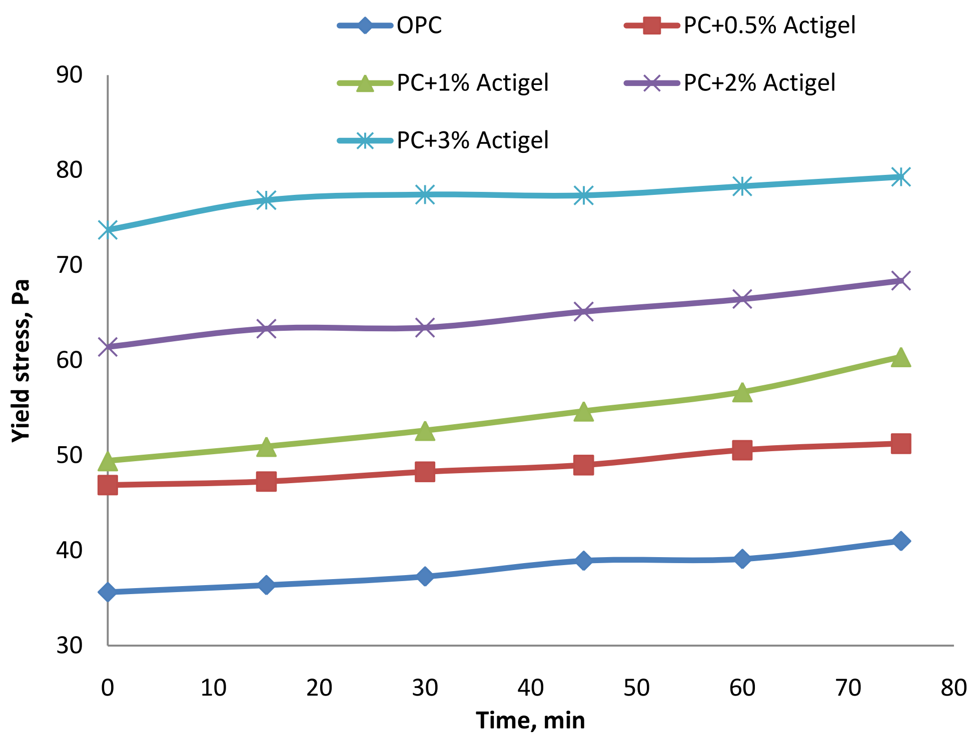



**Figure 4 - 2. Yield stress versus time for pastes with different amount of Actigel**

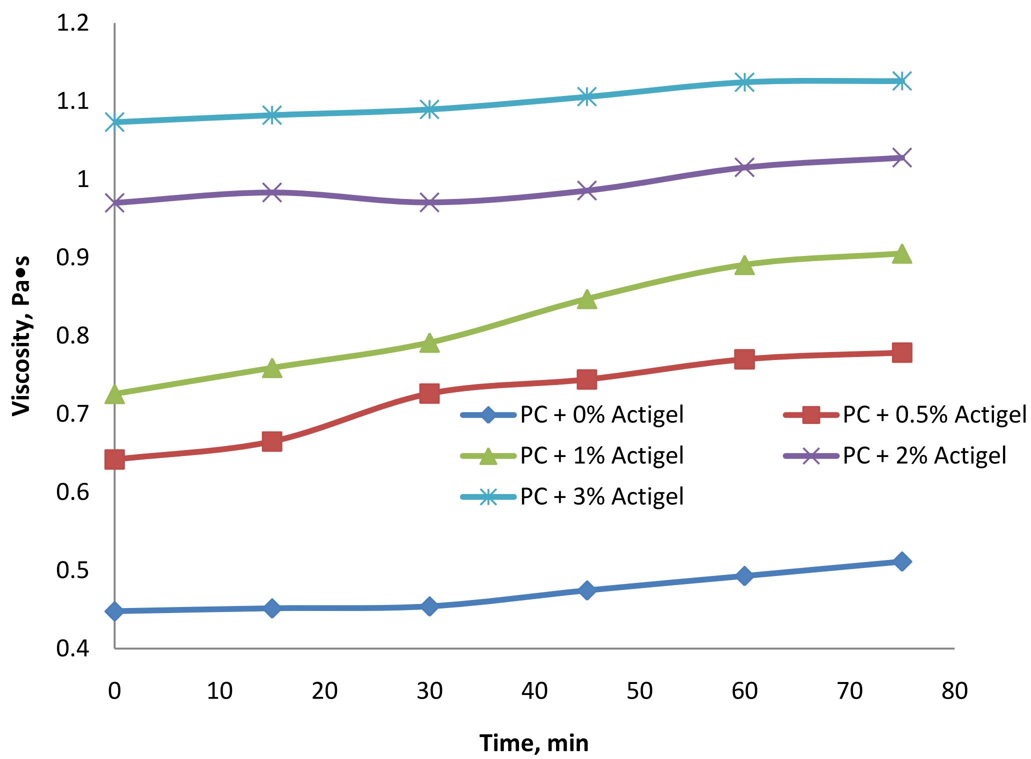



**Figure 4 - 3. Viscosity versus time for pastes with different amount of Actigel**

Figure 4-4, Figure 4-5 and Figure 4-6 show the plot of thixotropy, yield stress and viscosity versus time for cement paste specimens with replacement of High Reactivity Metakaolin (HRM) clay respectively. Similarly, the pastes with HRM replacement were shown to have improved thixotropic behavior due to the fact that higher thixotropic values with increased amounts of HRM replacement were seen at each time point. It seems that there is an increase in yield stress with increasing HRM, but yield stress is not significantly affected by time when the HRM amount is low. However, the yield stress increase with the time when HRM amount is larger than 10%. The same trend can be seen for viscosity. As expected, the rate of structural rebuilding rate increased with the amount of HRM replacement. The highest rebuilding rate was obtained when the amount of replacement is 15% while pure cement paste had the lowest structural rebuilding rate.

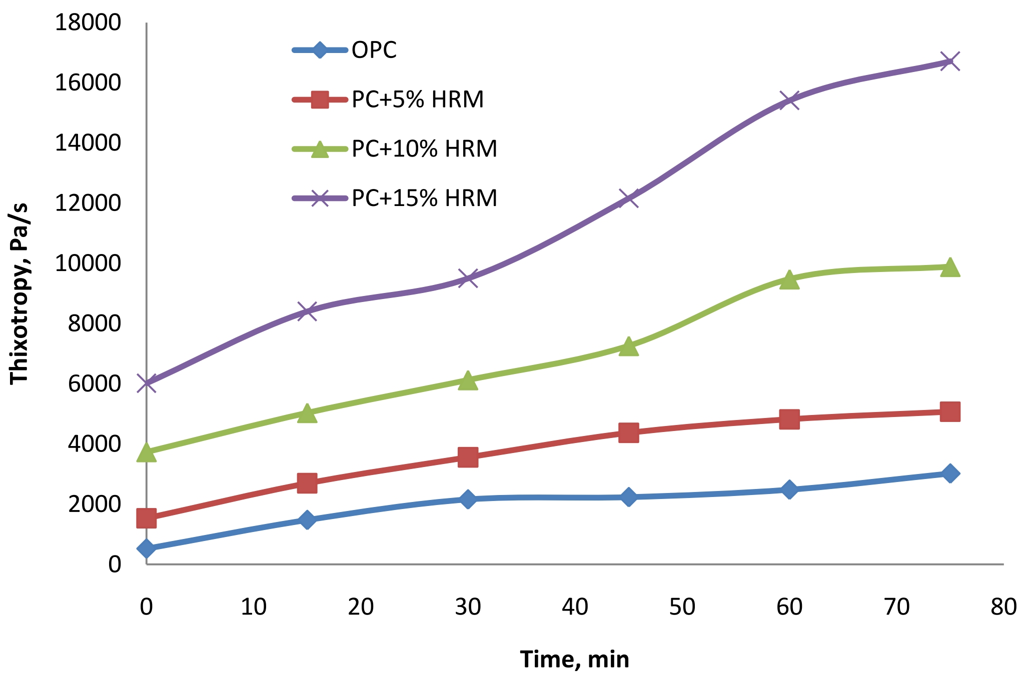



**Figure 4 - 4. Thixotropy versus time for pastes with different amount of High Reactivity Metakaolin replacement**

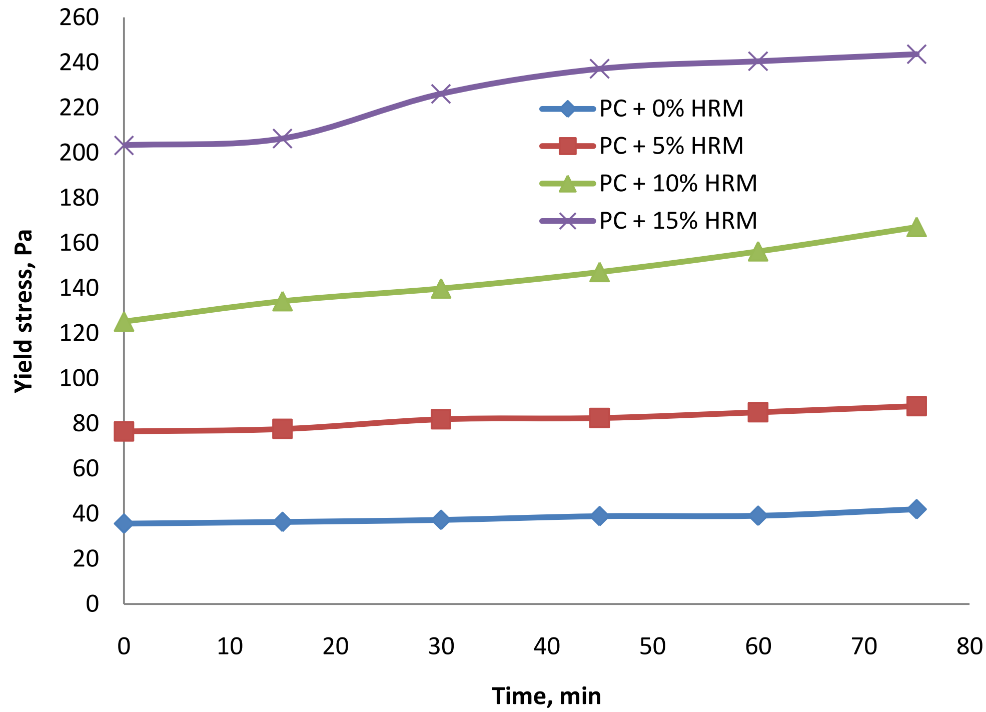



**Figure 4 - 5. Yield stress versus time for pastes with different amount of High Reactivity Metakaolin replacment**

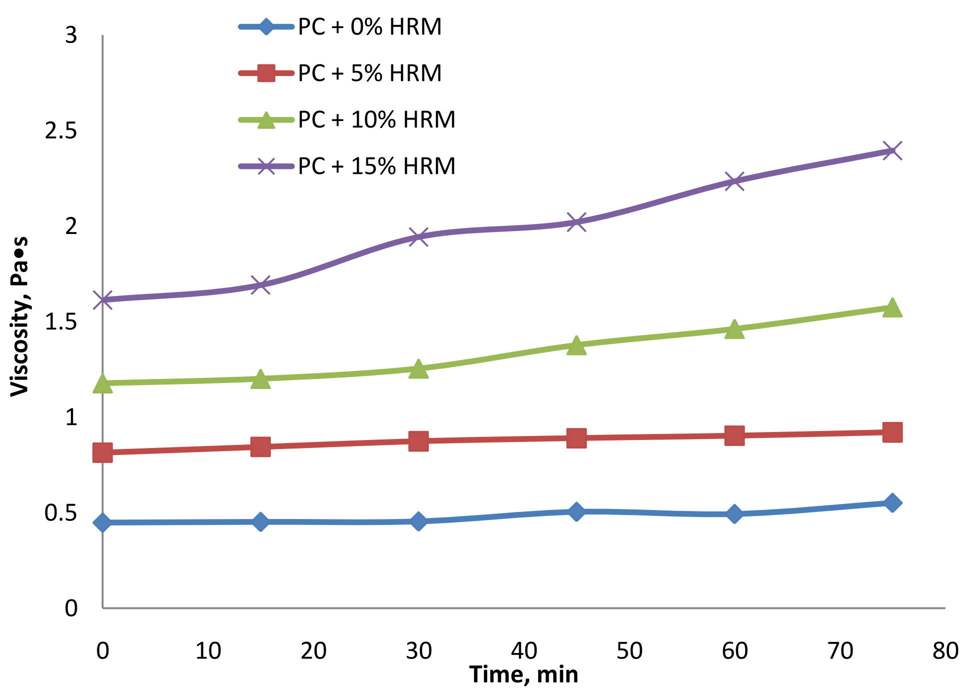



**Figure 4 - 6. Viscosity versus time for pastes with different amount of High Reactivity Metakaolin replacment**

For the replacement of Ground Clay Brick (GCB), Figure 4-7, Figure 4-8 and Figure 4-9 show the plot of thixotropy, yield stress and viscosity versus time for cement paste specimens with different amount of Ground Clay Brick replacement respectively. It is shown that cement pastes with replacement of GCB had thixotropic behavior and the higher thixotropy, yield stress and viscosity value with increasing amount of GCB replacement can be seen at each time point. For the structural rebuilding rate, it seems that the replacement of GCB increased the structural rebuilding rate of cement paste slightly. Higher structural rebuilding rate was seen in the paste specimens with 25% and 35% GCB replacement. However, no pronounced differences between them were found. The pure cement paste and paste with 15% GCB replacement had similar rate of structural rebuilding and both of them were lower than pastes with 25% or 35% GCB replacement.

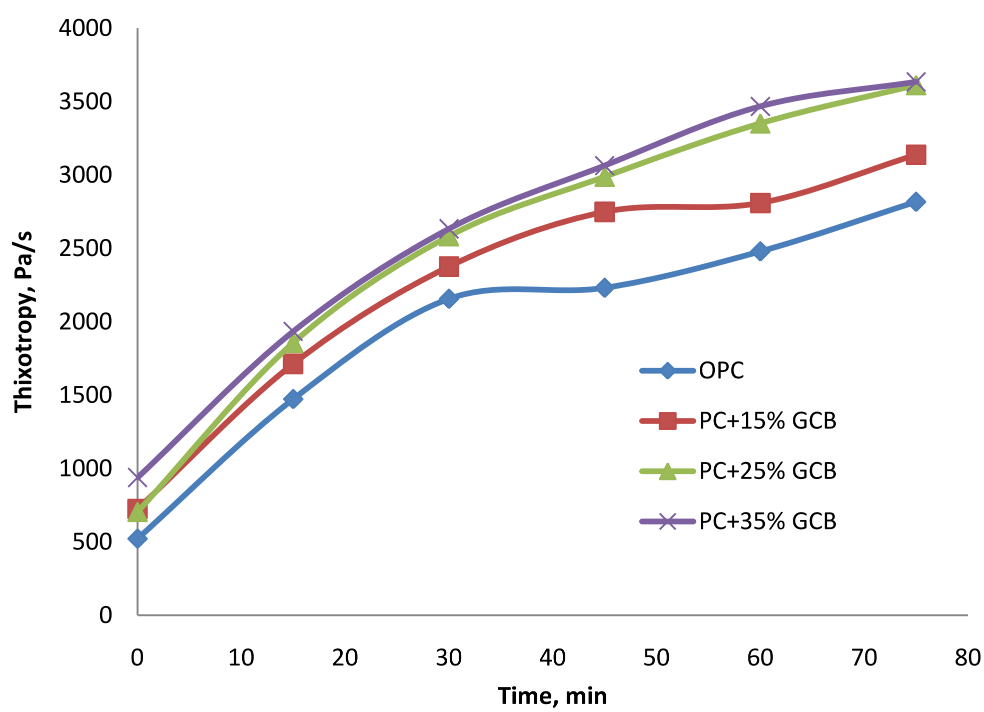



**Figure 4 - 7. Thixotropy versus time for pastes with different amount of Ground Clay Brick replacement**

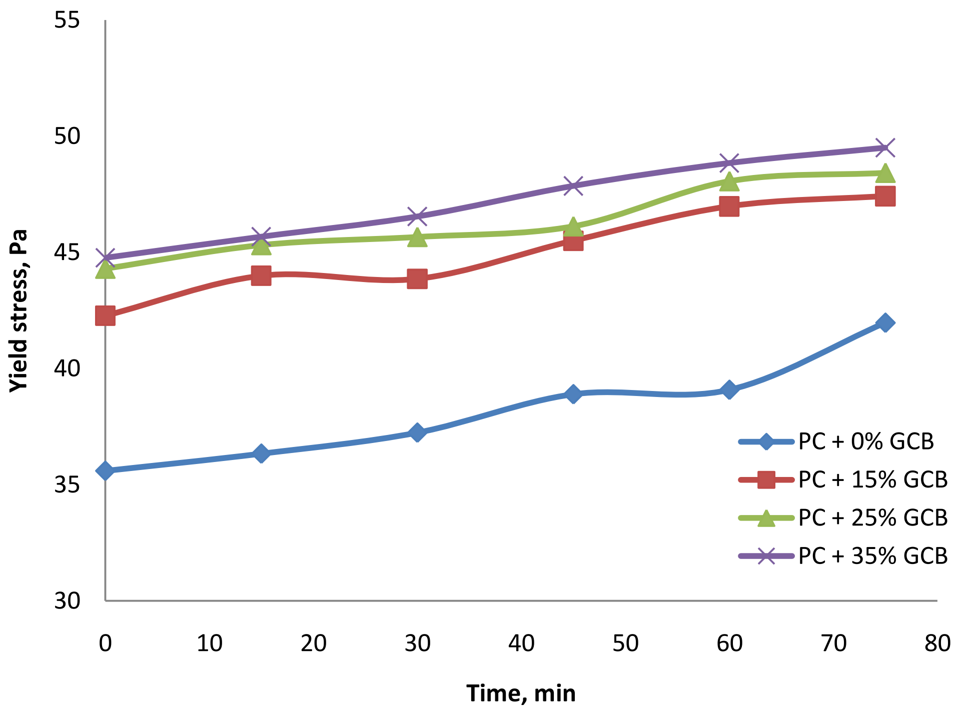



**Figure 4 - 8. Yield stress versus time for pastes with different amount of Ground Clay Brick replacement**

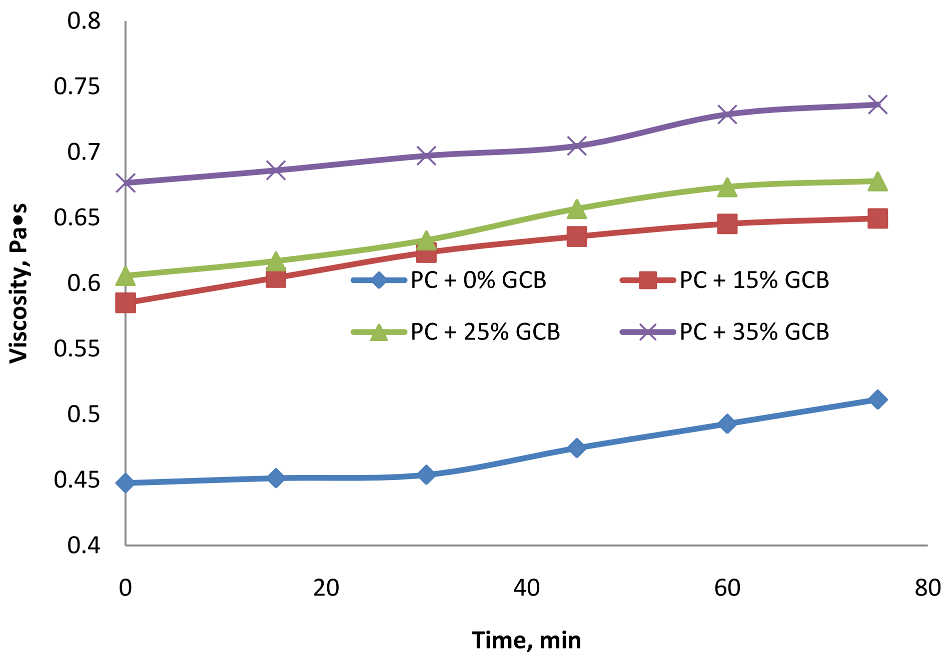



**Figure 4 - 9. Viscosity versus time for pastes with different amount of Ground Clay Brick replacement**

Figure 4-10, Figure 4-11 and Figure 4-12 show the plot of thixotropy, yield stress and viscosity versus time for pastes made with different types of cement. From these figures, high alkali cement gained the highest thixotropy, viscosity and yield stress with time, followed by Lafarge Type I/II and Type IV cement. The Ashgrove Type I cement obtained the lowest thixotropy, yield stress and viscosity. We can also observe that the higher structural rebuilding rate was obtained by High Alkali cement and Lafarge Type I/II cement. At the same time, lower structural rebuilding rate was seen for pastes made with Type IV cement and Ashgrove Type I cement and rates for them were similar with each other.

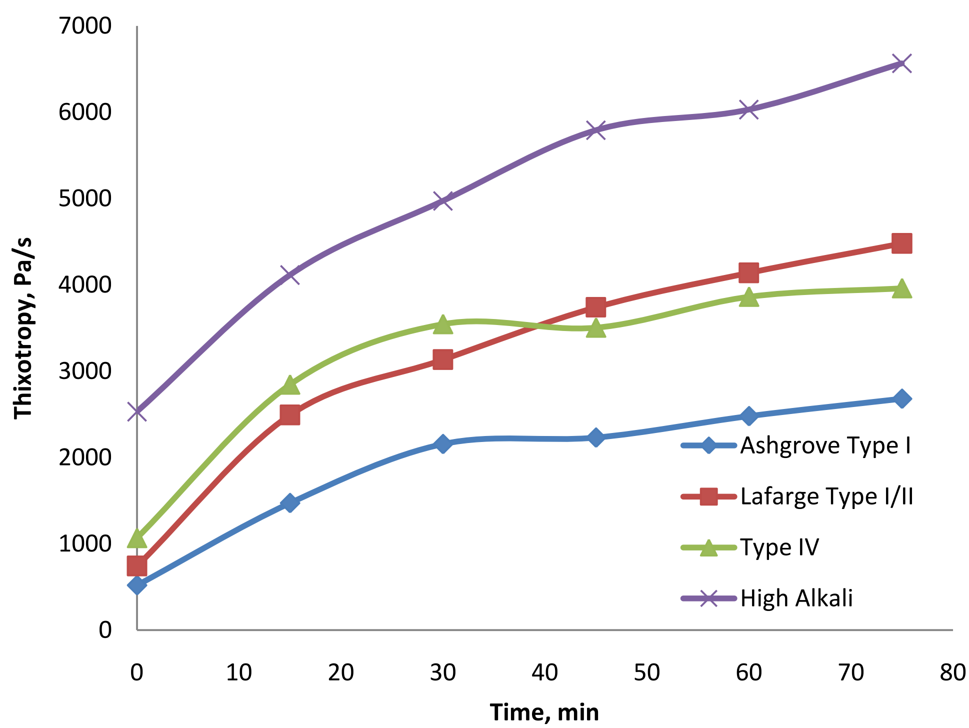



**Figure 4 - 10. Thixotropy versus time for pastes made with different types of cement**

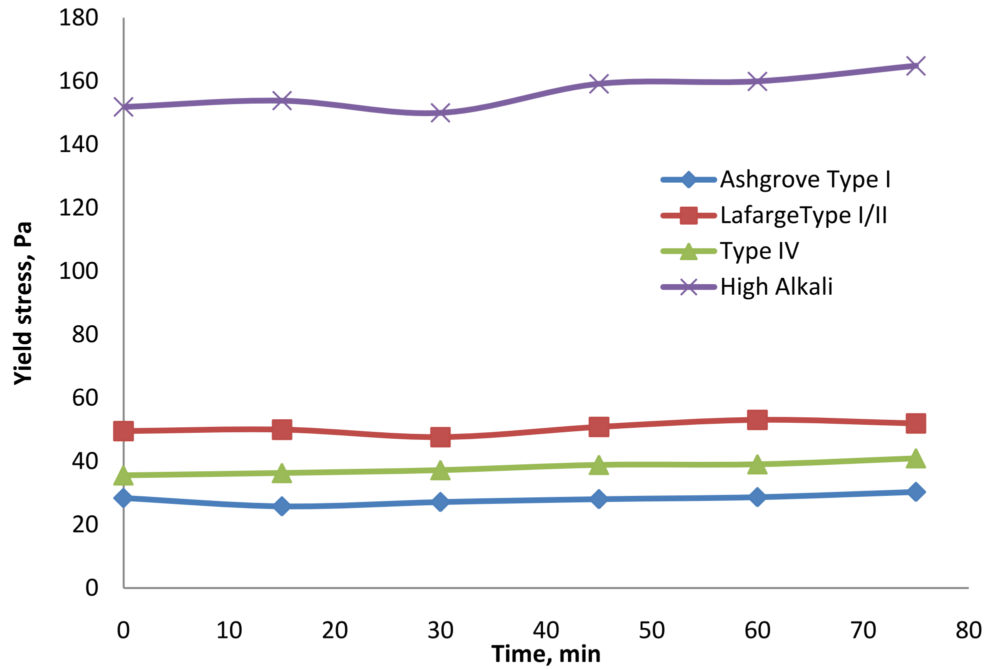



**Figure 4 - 11. Yield stress versus time for pastes made with different types of cement**

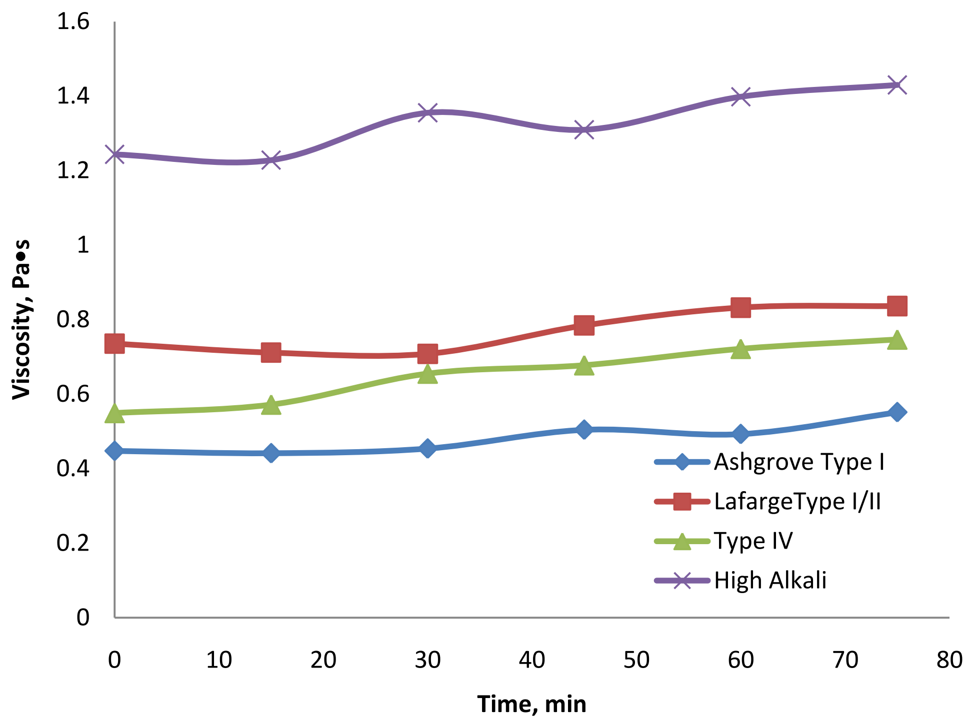



**Figure 4 - 12. Viscosity versus time for pastes made with different types of cement**

## 4.3 Understanding Rheology Results Based on Statistical Analysis

### 4.3.1 How to Understand Analysis of JMP

The Thixotropy values for each mixtures used for analyzing structural rebuilding rate were analyzed by a statistical software program (JMP 8.0). From the previous descriptions about plots of thixotropy versus time, we can see that the structural rebuilding trend cannot always be linearly described. Thus, for those that cannot be described as a linear relationship, bivariate fit was transformed to a model as a function of square root of time. The regression models were used for analyzing structural rebuilding rate. The table of Parameter Estimates indicated whether the changing of structural rebuilding rate is statistically significant. If P-value in such a table is less than 0.05, it indicated that the changing of structural rebuilding rate is statistically significant.

### 4.3.2 Actigel

Table 4-1 shows the thixotropy values for paste mixtures with different amount of Actigel addition at each time point.

**Table 4 - 1. Thixotropy of each repetition for paste mixtures with Actigel addition**

| Time | | 0min | 15min | 30min | 45min | 60min | 75min |
|---|---|---|---|---|---|---|---|
| **OPC** | rep1 | 558.49 | 1430.89 | 2257.29 | 2124.46 | 3000.62 | 3127.68 |
| | rep2 | 483.98 | 1909.28 | 2169.72 | 2723.94 | 2580.00 | 3106.03 |
| | rep3 | 520.33 | 1077.27 | 2040.26 | 1843.59 | 1856.06 | 2816.85 |
| | **Aveage** | 520.93 | 1472.48 | 2155.75 | 2230.66 | 2478.89 | 3016.85 |
| **PC+0.5% Actigel** | rep1 | 1108.75 | 2033.59 | 2643.92 | 3478.13 | 3985.57 | 4256.92 |
| | rep2 | 1391.48 | 2480.09 | 3202.38 | 3379.57 | 3647.71 | 4246.66 |
| | rep3 | 1285.03 | 2893.58 | 2739.84 | 3664.50 | 3430.31 | 3698.13 |
| | **Average** | 1261.75 | 2469.09 | 2862.05 | 3507.40 | 3687.87 | 4067.24 |
| **PC+1% Actigel** | rep1 | 1612.27 | 2542.44 | 3673.83 | 4058.34 | 4897.36 | 5128.37 |
| | rep2 | 1708.73 | 2498.78 | 3587.06 | 3877.17 | 4579.26 | 4924.70 |
| | rep3 | 1945.28 | 3172.46 | 2989.44 | 4182.35 | 4158.51 | 4876.39 |
| | **Average** | 1755.43 | 2737.90 | 3416.78 | 4039.29 | 4545.04 | 4976.49 |
| **PC+2% Actigel** | rep1 | 2424.46 | 3852.88 | 4108.87 | 4425.00 | 4904.65 | 5369.28 |
| | rep2 | 2207.99 | 3438.84 | 4796.39 | 5267.18 | 5684.22 | 4937.68 |
| | rep3 | 2231.83 | 3588.93 | 4151.91 | 4542.10 | 4485.96 | 5021.74 |
| | **Average** | 2288.09 | 3626.88 | 4352.39 | 4744.76 | 5024.94 | 5109.57 |
| **PC+3% Actigel** | rep1 | 3423.98 | 5119.93 | 5388.33 | 5160.38 | 6124.39 | 5813.67 |
| | rep2 | 3309.30 | 5390.35 | 5498.74 | 5872.82 | 5203.49 | 6203.27 |
| | rep3 | 3515.63 | 4692.39 | 4722.02 | 5005.48 | 5168.15 | 4680.28 |
| | **Average** | 3416.30 | 5067.56 | 5203.03 | 5346.23 | 5498.67 | 5565.74 |

The data was analyzed by JMP and Figure 4-13 shows the bivariate (Actigel amount and Time) fit of Thixotropy by time. Five curves with different colors can be seen from this figure and each curve represents a specific amount of Actigel addition.

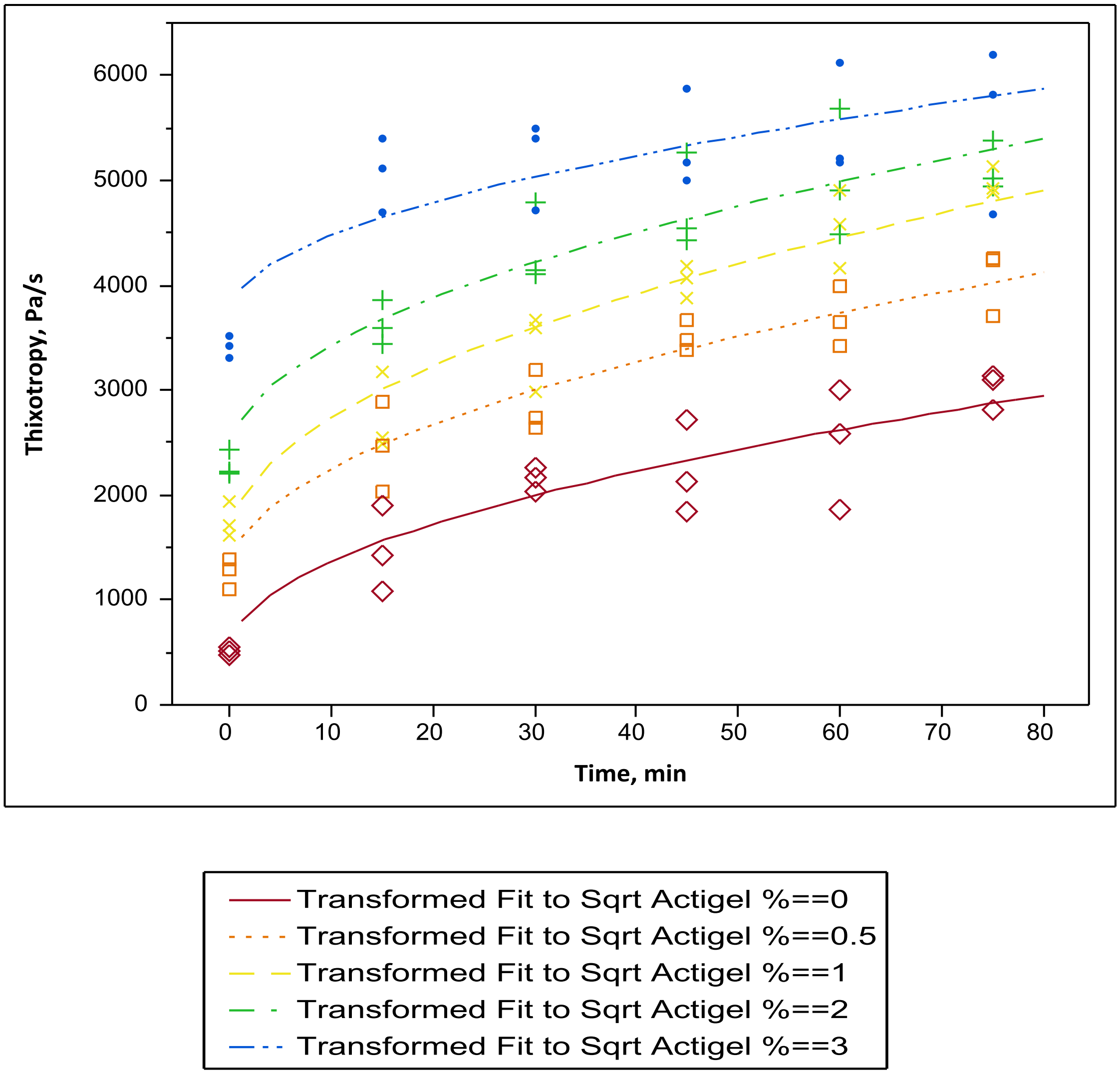



**Figure 4 - 13. Bivariate Fit of Thixotropy by Time for Actigel Addition**

Considering the two variables of Actigel amount and time, the regression model is:

$$\textbf{\textit{Thixotropy}} = 493.77529 + 733.57977\, \mathbf{A_{0.5}} + 1051.1934\, \mathbf{A_1} + 1852.2802\, \mathbf{A_2} + 3214.1573\, \mathbf{A_3} + 284.5427\, \sqrt{\mathbf{t}} + 48.616844 * \mathbf{A_{0.5}} * \sqrt{\mathbf{t}} + 101.28476\, \mathbf{A_1} * \sqrt{\mathbf{t}} + 66.453103\, \mathbf{A_2} * \sqrt{\mathbf{t}} - 32.74304\, \mathbf{A_3} * \sqrt{\mathbf{t}}$$

$\mathbf{R^2 = 0.943032}$

**Equation 4-1**

Where 493.77529 is the average of response and the code variables are amount of Actigel addition and time. In this equation, if Actigel amount is 0.5%, $\boldsymbol{A_{0.5}}$ =1, and $\boldsymbol{A_1}$, $\boldsymbol{A_2}$ and $\boldsymbol{A_3}$ all equal to zero. Similarly, if the Actigel amount is 3%, $\boldsymbol{A_3}$ =1 and $\boldsymbol{A_{0.5}}$, $\boldsymbol{A_1}$, $\boldsymbol{A_2}$ all equal to zero. Therefore, the equation above can be transformed as following:

when Actigel amount = 0%, $\textbf{\textit{Thixotropy}} = 493.77529 + 274.5427\sqrt{\boldsymbol{t}}$;

when Actigel amount = 0.5%, $\textbf{\textit{Thixotropy}} = 1227.3551 + 323.15955\sqrt{\boldsymbol{t}}$;

when Actigel amount = 1%, $\textbf{\textit{Thixotropy}} = 1544.9687 + 375.82747\sqrt{\boldsymbol{t}}$;

when Actigel amount = 2%, $\textbf{\textit{Thixotropy}} = 2346.0555 + 340.99581\sqrt{\boldsymbol{t}}$;

when Actigel amount = 3%, $\textbf{\textit{Thixotropy}} = 3707.9326 + 241.79966\sqrt{\boldsymbol{t}}$.

The coefficient of $\sqrt{\boldsymbol{t}}$ indicates the structural rebuilding rate of pastes with different amount of Actigel addition. The plot of coefficient of $\sqrt{\boldsymbol{t}}$ is plotted versus Actigel amount which is shown in Figure 4 - 14. It is not difficult to see that the structural rebuilding rate will increase as the increasing amount of Actigel addition from 0% to 1% while the rebuilding rate will decrease if the amount of Actigel is over 1%.

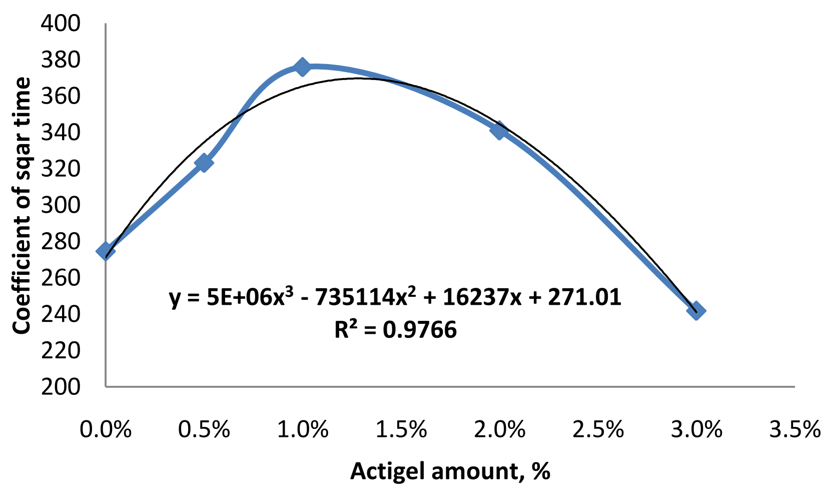



**Figure 4 - 14. The plot of coefficient of square time vs. Actigel amount**

**Table 4 - 2. Parameters Estimates for paste with Actigel addition**

| Term | Estimate | Std Error | t Ratio | Prob>\|t\| |
|---|---|---|---|---|
| Intercept | 493.77529 | 180.2522 | 2.74 | 0.0076* |
| Actigel_0.5 | 733.57977 | 254.9151 | 2.88 | 0.0051* |
| Actigel_1.0 | 1051.1934 | 254.9151 | 4.12 | <.0001* |
| Actigel_2.0 | 1852.2802 | 254.9151 | 7.27 | <.0001* |
| Actigel_3.0 | 3214.1573 | 254.9151 | 12.61 | <.0001* |
| **SQRT(Time)** | **274.5427** | **29.43506** | **9.33** | **<.0001*** |
| **SQRT(Time)*Actigel_0.5** | **48.616844** | **41.62746** | **1.17** | **0.2463** |
| **SQRT(Time)*Actigel_1.0** | **101.28476** | **41.62746** | **2.43** | **0.0172*** |
| **SQRT(Time)*Actigel_2.0** | **66.453103** | **41.62746** | **1.60** | **0.1143** |
| **SQRT(Time)*Actigel_3.0** | **-32.74304** | **41.62746** | **-0.79** | **0.4339** |

Table 4-2 gives the Parameters Estimates of this regression model. From this table, the highlighted part can be used for estimating if the increasing of structural rebuilding rate compared with paste with 0% Actigel is statistically significant in terms of unit square time. Based on the p-value of each part, we can see that only increase of structural rebuilding rate of paste with 1% Actigel (**p-value=0.0172<0.05**) is statistically significant.

### 4.3.3 High Reactivity Metakaolin

Table 4-2 shows the thixotropy values for paste mixtures with different amount of HRM replacement at each time point.

**Table 4 - 3. Thixotropy of each repetition for paste mixtures with HRM replacement**

| Time | | 0min | 15min | 30min | 45min | 60min | 75min |
|---|---|---|---|---|---|---|---|
| **OPC** | rep1 | 558.49 | 1430.89 | 2257.29 | 2124.46 | 3000.62 | 3127.68 |
| | rep2 | 483.98 | 1909.28 | 2169.72 | 2723.94 | 2580.00 | 3106.03 |
| | rep3 | 520.33 | 1077.27 | 2040.26 | 1843.59 | 1856.06 | 2816.85 |
| | **Average** | 520.93 | 1472.48 | 2155.75 | 2230.66 | 2478.89 | 3016.85 |
| **PC+5% HRM** | rep1 | 1587.74 | 2721.23 | 3678.70 | 4361.65 | 4484.08 | 4958.47 |
| | rep2 | 1331.19 | 2677.02 | 3424.86 | 4485.52 | 4919.28 | 4881.78 |
| | rep3 | 1692.33 | 2689.36 | 3569.37 | 4258.97 | 5056.52 | 5368.46 |
| | **Average** | 1537.08 | 2695.87 | 3557.64 | 4368.71 | 4819.96 | 5069.57 |
| **PC+10% HRM** | rep1 | 3466.33 | 4367.66 | 5916.81 | 6747.58 | 8842.22 | 9526.10 |
| | rep2 | 3853.66 | 5828.83 | 6521.79 | 7774.27 | 9951.08 | 9887.36 |
| | rep3 | 3879.64 | 4908.66 | 5936.53 | 7258.64 | 9636.72 | 10258.14 |
| | **Average** | 3733.21 | 5035.05 | 6125.04 | 7260.17 | 9476.67 | 9890.53 |
| **PC+15% HRM** | rep1 | 5352.01 | 8822.05 | 9888.81 | 12850.38 | 15127.21 | 15643.95 |
| | rep2 | 6445.75 | 8306.24 | 9379.03 | 10053.29 | 16105.56 | 15868.64 |
| | rep3 | 6258.94 | 8081.63 | 9237.62 | 13582.41 | 15008.35 | 18631.99 |
| | **Average** | 6018.90 | 8403.31 | 9501.82 | 12162.03 | 15413.71 | 16714.86 |

The data was analyzed by JMP and Figure 4 - 15 shows the bivariate (HRM replacement amount and Time) fit of Thixotropy by time. Four curves with different color can be seen from this figure and each curve represents a specific amount of HRM replacement.

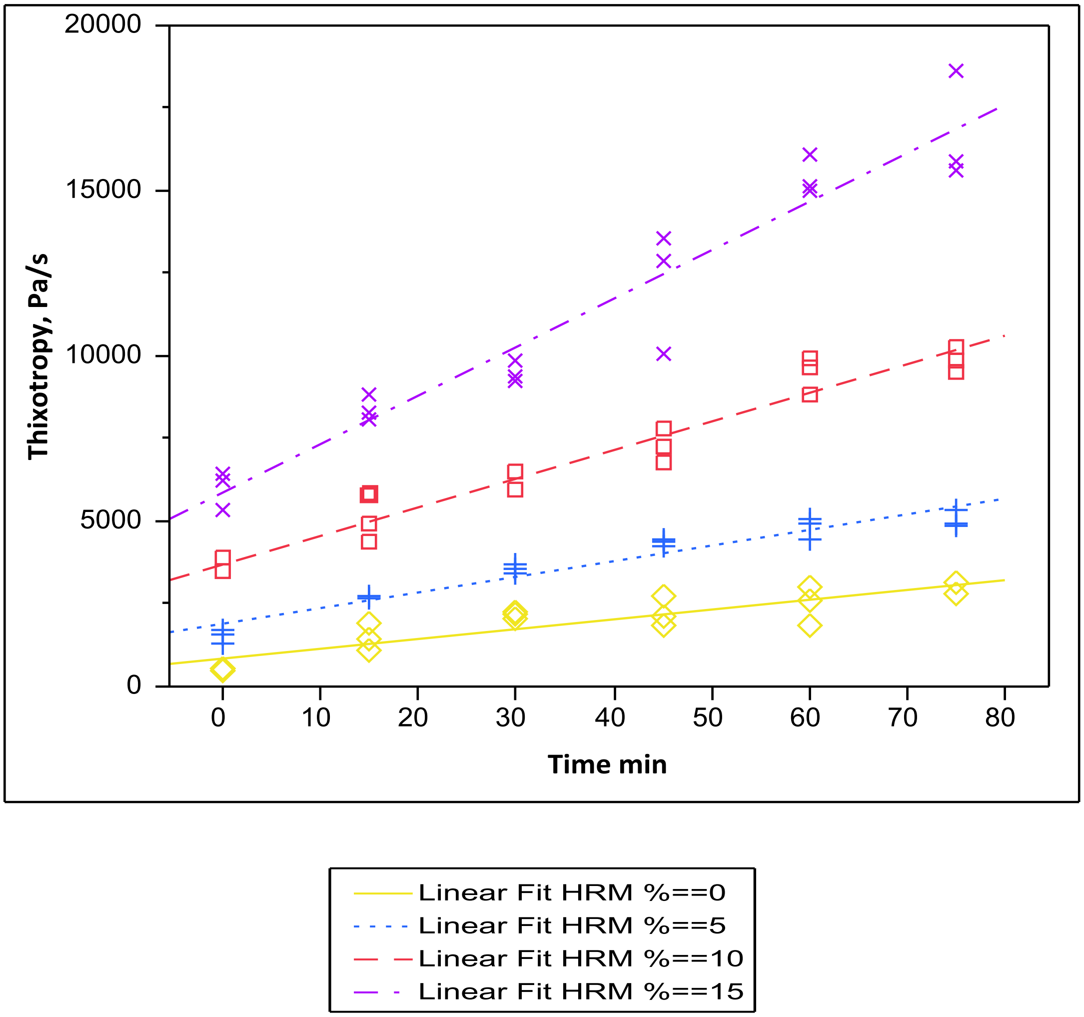



**Figure 4 - 15. Bivariate Fit of Thixotropy by Time for HRM replacement**

From this figure, the curves are fitted as a linear function. Considering the two variables of HRM replacement amount and time, the regression model is:

$$\textbf{\textit{Thixotropy}} = 866.85286 + 1033.2575\ \boldsymbol{H_5} + 2821.3589\ \boldsymbol{H_{10}} + 4990.0214\ \boldsymbol{H_{15}} + 29.664279\ \boldsymbol{t} + 17.660971\ \boldsymbol{*t*H_5} + 56.519733\boldsymbol{*\ t*\ H_{10}} + 117.3285\boldsymbol{*\ t*\ H_{15}}$$

$$\boldsymbol{R^2 = 0.979287}$$

**Equation 4-2**

Similarly with analysis of Actigel,

when HRM amount is 0%, $\mathbf{H_5}$, $\mathbf{H_{10}}$, $\mathbf{H_{15}}$ = 0, ***Thixotropy = ****866.85286 + 29.664279*****t;***

when HRM amount is 5%, $\mathbf{H_5}$=1, $\mathbf{H_{10}}$, $\mathbf{H_{15}}$=0, ***Thixotropy = ****1900.1103 + 47.325251*****t;***

when HRM amount is 10%, $\mathbf{H_{10}}$=1, $\mathbf{H_5}$, $\mathbf{H_{15}}$=0, ***Thixotropy = ****3688.2117 + 86.184013*****t;***

when HRM amount is 15%, $\mathbf{H_{15}}$=1, $\mathbf{H_5}$, $\mathbf{H_{10}}$=0, ***Thixotropy = ****5856.8743 + 146.99277*****t.***

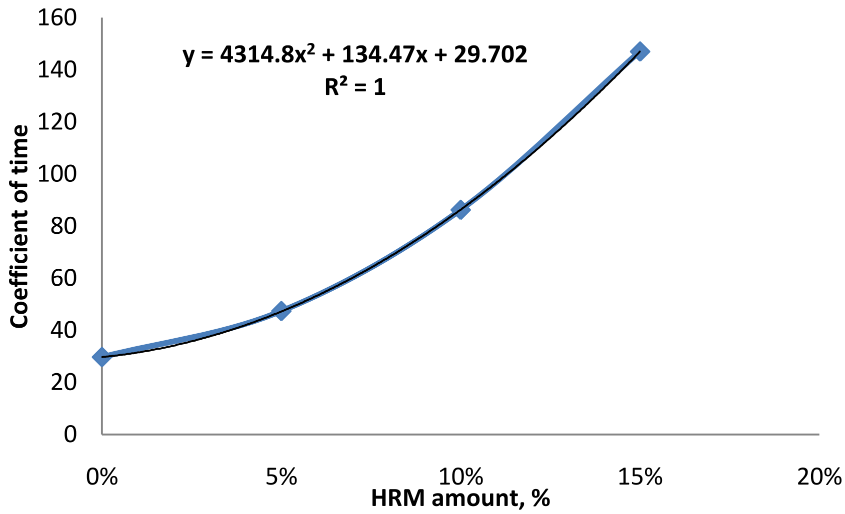



**Figure 4 - 16. Plot of coefficient of time vs. HRM amount**

The coefficient of ***t*** are plotted versus HRM amount (Figure 4 - 16)and can be used for indicating structural rebuilding rate of cement paste with HRM replacement. With increasing amount of HRM replacement (from 0%~15%), a sustained increasing rate of structural rebuilding was obtained.

**Table 4 - 4. Parameters Estimates for paste with HRM replacement**

| Term | Estimate | Std Error | t Ratio | Prob>\|t\| |
|---|---|---|---|---|
| Intercept | 866.85286 | 274.1282 | 3.16 | 0.0024* |
| Time | 29.664279 | 6.036104 | 4.91 | <.0001* |
| HRM_5% | 1033.2575 | 387.6758 | 2.67 | 0.0097* |
| HRM_10% | 2821.3589 | 387.6758 | 7.28 | <.0001* |
| HRM_15% | 4990.0214 | 387.6758 | 12.87 | <.0001* |
| **Time*HRM_5%** | **17.660971** | **8.53634** | **2.07** | **0.0426*** |
| **Time*HRM_10%** | **56.519733** | **8.53634** | **6.62** | **<.0001*** |
| **Time*HRM_15%** | **117.3285** | **8.53634** | **13.74** | **<.0001*** |

Table 4-4 gives the Parameters Estimates of regression model of cement paste with HRM replacement. From the highlighted part of this table, the p-values of cement paste with 5%, 10% and 15% are 0.0426, <.0001 and <.0001 respectively. All of them are less than 0.05, which indicated that structural rebuilding rate of paste with different amount of HRM replacement are statistically significant compared with pure cement paste in terms of unit time.

### 4.3.4 Ground Clay Brick

**Table 4 - 5. Thixotropy of each repetition for paste mixtures with GCB replacement**

| **Time** | | **0min** | **15min** | **30min** | **45min** | **60min** | **75min** |
|---|---|---|---|---|---|---|---|
| **OPC** | rep1 | 558.49 | 1430.89 | 2257.29 | 2124.46 | 3000.62 | 3127.68 |
| | rep2 | 483.98 | 1909.28 | 2169.72 | 2723.94 | 2580.00 | 2406.03 |
| | rep3 | 520.33 | 1077.27 | 2040.26 | 1843.59 | 1856.06 | 2916.85 |
| | **Average** | 520.93 | 1472.48 | 2155.75 | 2230.66 | 2478.89 | 2816.85 |
| **PC+15% GCB** | rep1 | 760.11 | 1956.73 | 2716.70 | 3143.17 | 3078.81 | 3144.32 |
| | rep2 | 623.33 | 1698.36 | 2543.80 | 2672.70 | 2797.60 | 3562.49 |
| | rep3 | 787.74 | 1482.80 | 1865.56 | 2429.30 | 2550.73 | 2704.61 |
| | **Average** | 723.72 | 1712.63 | 2375.35 | 2748.39 | 2809.04 | 3137.14 |
| **PC+25% GCB** | rep1 | 647.27 | 1829.65 | 2850.40 | 3267.46 | 3183.19 | 3430.23 |
| | rep2 | 857.36 | 2009.66 | 2796.45 | 2646.59 | 3625.56 | 3409.09 |
| | rep3 | 606.55 | 1729.64 | 2102.04 | 3050.69 | 3246.92 | 4000.62 |
| | **Average** | 703.73 | 1856.31 | 2582.96 | 2988.25 | 3351.89 | 3613.31 |
| **PC+35% GCB** | rep1 | 982.52 | 1966.85 | 2626.36 | 3863.77 | 4209.62 | 3531.00 |
| | rep2 | 1025.76 | 2036.47 | 2947.55 | 3059.10 | 2933.47 | 3496.07 |
| | rep3 | 807.75 | 1798.85 | 2324.64 | 2268.43 | 3258.41 | 3874.65 |
| | **Average** | 938.68 | 1934.06 | 2632.85 | 3063.77 | 3467.16 | 3633.91 |

Table 4-5 shows the thixotropy values for paste mixtures with different amount of GCB replacement at each time point. Figure 4 - 17 shows the bivariate (GCB replacement amount and Time) fit of Thixotropy by time. Four curves with different color can be seen from this figure and each curve represents a specific amount of GCB replacement.

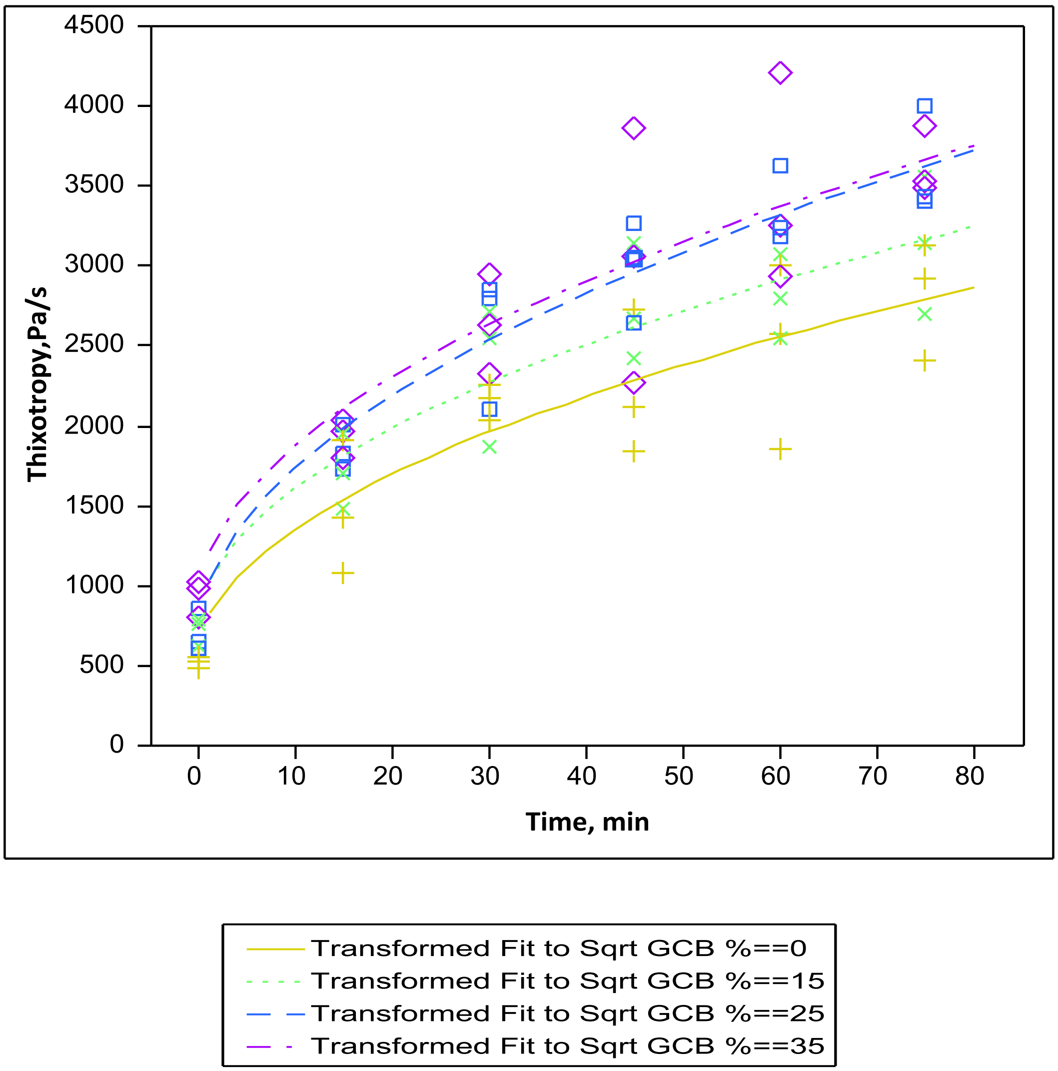



**Figure 4 - 17. Bivariate Fit of Thixotropy by Time for paste with GCB replacement**

Concerning the two variables (Cement types and time), the regression model is given as:

$\textit{Thixotropy} = 531.70972 + 192.00578\, G_{15} + 125.06957\, G_{25} + 325.28075\, G_{35} + 261.37124\sqrt{t} + 20.904963*G_{15}*\sqrt{t} + 82.257489*G_{25}*\sqrt{t} + 62.934911*G_{35}*\sqrt{t}$

$R^2 = 0.895022$

**Equation 4-3**

Where:

When GCB amount is 0%, $G_{15}$, $G_{25}$, $G_{35}$=0, $\textit{Thixotropy} = 531.70972 + 261.3712*\sqrt{t}$;

When GCB amount is 15%, $G_{15}$=1, $G_{25}$, $G_{35}$=0, $\textit{Thixotropy} = 723.7155 + 282.27621*\sqrt{t}$;

When GCB amount is 25%, $G_{25}$=1, $G_{15}$, $G_{35}$=0, $\textit{Thixotropy} = 656.7792 + 343.62873*\sqrt{t}$;

When GCB amount is 35%, $G_{35}$=1, $G_{15}$, $G_{25}$=0, $\textit{Thixotropy} = 856.9904 + 324.30616*\sqrt{t}$.

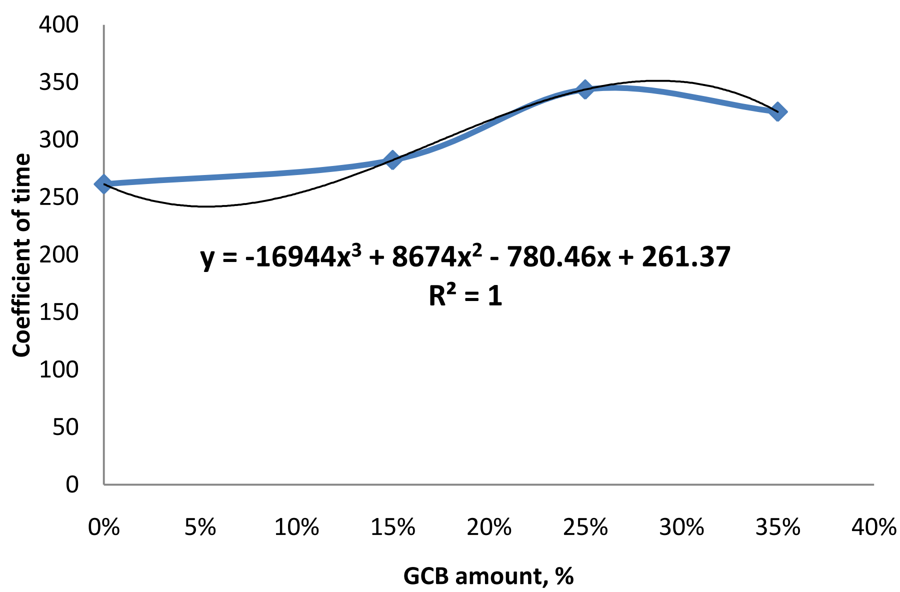



**Figure 4 - 18. Plot of coefficient of square time vs. GCB amount**

From Figure 4 - 18, it is found that the highest coefficient of $\sqrt{t}$ was obtained by cement paste with 25% GCB followed by paste with 35% GCB. Lower coefficients were gained by pure cement paste and paste with 15% GCB. This indicated that paste specimens with 25% and 35% tended to have higher structural rebuilding rate.

**Table 4 - 6. Parameters Estimates for paste with GCB replacement**

| Term | Estimate | Std Error | t Ratio | Prob>\|t\| |
|---|---|---|---|---|
| Intercept | 531.70972 | 166.5888 | 3.19 | 0.0022* |
| GCB_15% | 192.00578 | 235.5921 | 0.81 | 0.4181 |
| GCB_25% | 125.06957 | 235.5921 | 0.53 | 0.5973 |
| GCB_35% | 325.28075 | 235.5921 | 1.38 | 0.1722 |
| SQRT(Time) | 261.37124 | 27.20384 | 9.61 | <.0001* |
| **SQRT(Time)*GCB_15%** | **20.904963** | **38.47204** | **0.54** | **0.5888** |
| **SQRT(Time)*GCB_25%** | **82.257489** | **38.47204** | **2.14** | **0.0363*** |
| **SQRT(Time)*GCB_35%** | **62.934911** | **38.47204** | **1.64** | **0.1068** |

Table 4-6 gives the parameter estimates for paste with different amount of GCB replacement, from which, the only p-value of paste with 25% GCB (p-values=0.0363<0.05) indicates that the increasing of thixotropy within unit of square time is statistically significant compared with OPC.

### 4.3.5 Different Types of Cement

**Table 4 - 7. Thixotropy of each repetition for paste mixtures made with different types of cement**

| | Time | 0min | 15min | 30min | 45min | 60min | 75min |
|---|---|---|---|---|---|---|---|
| **Ashgrove Type I** | rep1 | 658.49 | 1430.89 | 2257.29 | 2124.46 | 3000.62 | 3127.68 |
| | rep2 | 883.64 | 1909.28 | 2169.72 | 2723.94 | 2580.00 | 3106.03 |
| | rep3 | 20.67 | 1077.27 | 2040.26 | 1843.59 | 1856.06 | 2816.85 |
| | **Average** | 520.93 | 1472.48 | 2155.75 | 2230.66 | 2478.89 | 3016.85 |
| **Type IV** | rep1 | 805.17 | 2339.43 | 3057.19 | 4059.37 | 3330.08 | 4219.87 |
| | rep2 | 1116.76 | 2887.47 | 3712.59 | 3163.27 | 4226.05 | 3638.58 |
| | rep3 | 1283.28 | 3309.40 | 3867.47 | 3292.84 | 4032.43 | 4025.94 |
| | **Average** | 1068.40 | 2845.43 | 3545.75 | 3505.16 | 3862.85 | 3961.46 |
| **Lafarge Type I/II** | rep1 | 847.33 | 2556.47 | 3065.99 | 4039.79 | 4159.40 | 4223.77 |
| | rep2 | 681.10 | 2337.19 | 3092.68 | 3732.35 | 4319.45 | 4673.27 |
| | rep3 | 702.37 | 2587.13 | 3245.12 | 3451.39 | 3941.37 | 4544.99 |
| | **Average** | 743.60 | 2493.59 | 3134.59 | 3741.17 | 4140.07 | 4480.68 |
| **High Alkali** | rep1 | 2007.40 | 4188.01 | 5060.56 | 5897.32 | 5664.06 | 6015.86 |
| | rep2 | 2457.10 | 4293.61 | 4504.06 | 5605.70 | 5954.27 | 6895.09 |
| | rep3 | 3128.31 | 3858.54 | 5352.05 | 5869.14 | 6472.37 | 6784.16 |
| | **Average** | 2530.94 | 4113.39 | 4972.22 | 5790.72 | 6030.23 | 6565.03 |

Table 4-7 lists the thixotropy values for paste mixture made with different types of cement and Figure 4-16 shows the bivariate (Type of cement and Time) fit of Thixotropy by time. The code of cement types can be described as:

**Cement Type = 0** : Ashgrove Type I cement

**Cement Type = 1** : Lafarge Type I/II cement;

**Cement Type = 2** : Type IV cement;

**Cement Type = 3** : High Alkali cement.

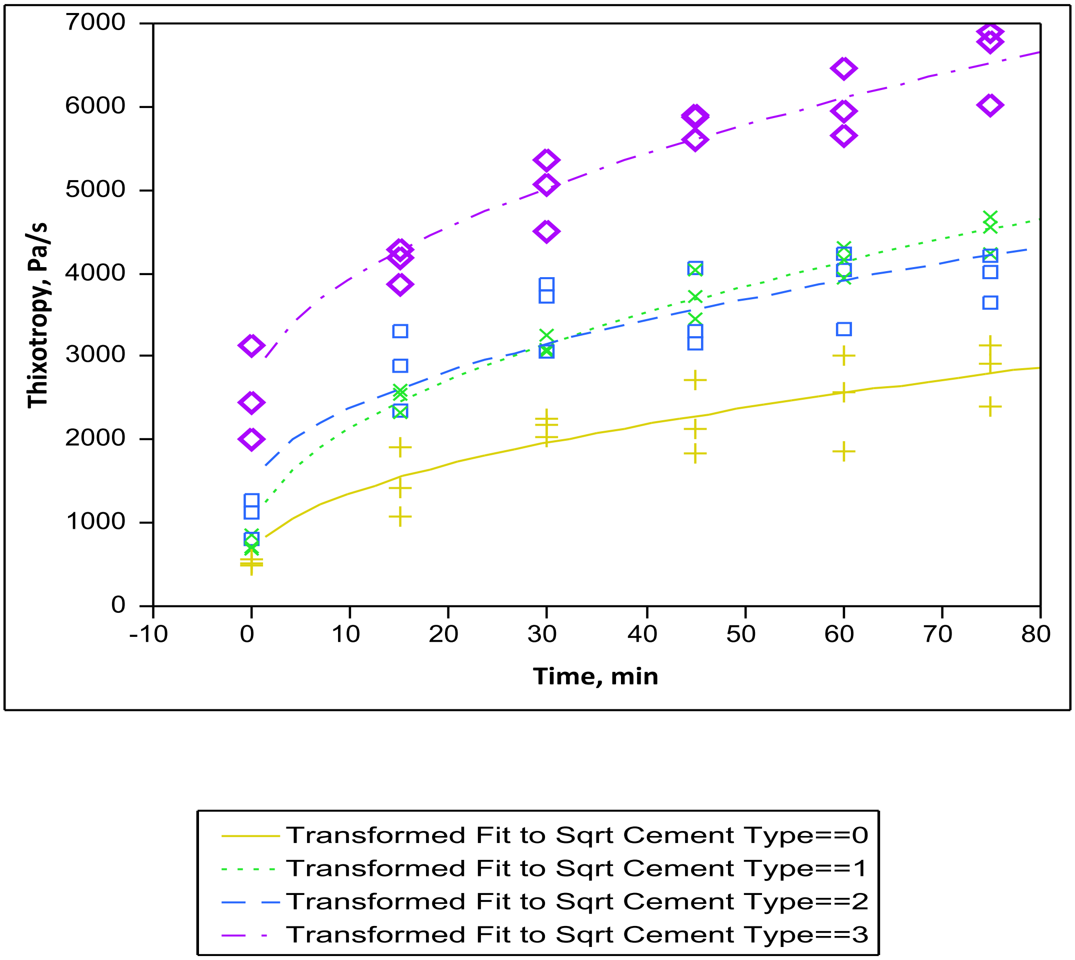



**Figure 4 - 19. Bivariate Fit of Thixotropy by Time for different types of cement**

Considering the two variables (Cement type and time), the regression model is given as:

$$\textit{\textbf{Thixotropy}} = 531.70972 + 240.35029\,\mathbf{C_1} + 788.21598\,\mathbf{C_2} + 1920.3882\,\mathbf{C_3} + 261.37124\sqrt{\mathbf{t}} + 172.98942 * C_1 * \sqrt{\mathbf{t}} + 73.439532 * C_2 * \sqrt{\mathbf{t}} + 209.60124 * C_3 * \sqrt{\mathbf{t}}$$

$R^2 = 0.958128$

**Equation 4-4**

Where:

When Ashgrove Type I cement is used, $\mathbf{C_1}$, $\mathbf{C_2}$, $\mathbf{C_3} = 0$:

$$\textit{\textbf{Thixotropy}} = 531.70972 + 261.37124 * \sqrt{\mathbf{t}};$$

When Lafarge Type I/II cement is used, $\mathbf{C_1}$=1, $\mathbf{C_2}$, $\mathbf{C_3}$=0:

$$\textbf{\textit{Thixotropy}} = 772.06 + 434.36067 * \sqrt{t};$$

When Type IV cement is used, $\mathbf{C_2}$=1, $\mathbf{C_1}$, $\mathbf{C_3}$=0:

$$\textbf{\textit{Thixotropy}} = 1319.9257 + 334.81078 * \sqrt{t};$$

When High Alkali cement is used, $\mathbf{C_3}$=1, $\mathbf{C_1}$, $\mathbf{C_2}$=0:

$$\textbf{\textit{Thixotropy}} = 2452.0979 + 470.97248 * \sqrt{t}.$$

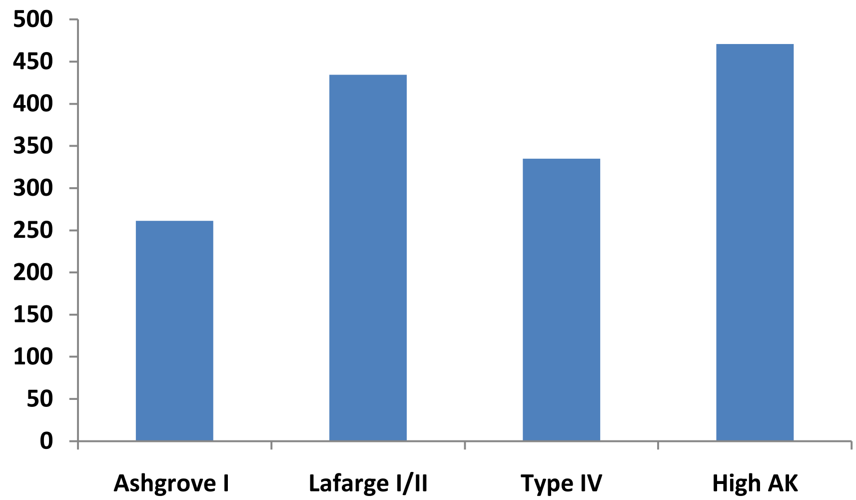



**Figure 4 - 20. The plot of coefficient of square time vs. cement types**

From Figure 4 - 20, cement paste made with High Alkali cement had highest coefficient of $\sqrt{t}$ (470.97248) followed by Lafarge Type I/II cement (434.36067). However, lower coefficient of $\sqrt{t}$ was obtained by Type IV (334.81078) and Ashgrove Type I cement (261.37124). This indicates that structural rebuilding rate is highest for High Alkali cement and lowest for Ashgrove Type I cement.

**Table 4 - 8. Parameters Estimates for pastes made with different types of cement**

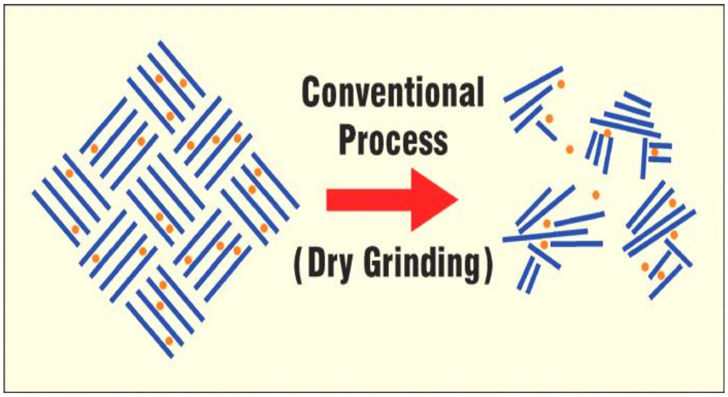
| Term | **Estimate** | **Std Error** | **t Ratio** | **Prob>\|t\|** |
|---|---|---|---|---|
| Intercept | 531.70972 | 173.2911 | 3.07 | 0.0032* |
| Lafarge Type I | 240.35029 | 245.0707 | 0.98 | 0.3304 |
| Type IV | 788.21598 | 245.0707 | 3.22 | 0.0020* |
| High Alkali | 1920.3882 | 245.0707 | 7.84 | <.0001* |
| **SQRT(Time)** | **261.37124** | **28.29832** | **9.24** | **<.0001*** |
| **SQRT(Time)*Lafarge Type I** | **172.98942** | **40.01987** | **4.32** | **<.0001*** |
| **SQRT(Time)*Type IV** | **73.439532** | **40.01987** | **1.84** | **0.0711** |
| **SQRT(Time)*High Alkali** | **209.60124** | **40.01987** | **5.24** | **<.0001*** |

Figure 4-8 gives parameters estimates for pastes made with different cement types. From the highlighted part, we can see that both Lafarge Type I/II and High Alkali cement have p-values smaller than 0.05, this indicates that, compared with Ashgrove Type I cement, their increasing of structural rebuilding rate is statistically significant. Never the less, although the structural rebuilding rate is higher for Type IV cement, its difference with Ashgrove Type I cement is not statistically significant since its p-value is 0.0711 and larger than 0.05.

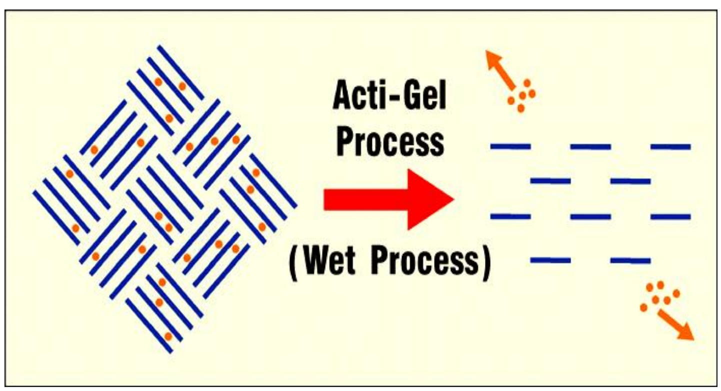
## 4.4 Discussion

Actigel is nano clay characterized as a highly purified Magnesiun Alumino Silicate which can be applied for improving the performance of concrete. Unlike most industrial and commercially available Magnesium Alumino Silicates which are made by a dry method (as shown in Figure 4 - 21. a), it is made from a wet process (as shown in Figure 4 - 21. b). The dry process will lead to impurities that cannot be removed because the bristles are not exfoliated (as shown in Figure 4 - 22. a). By contrast, wet processing significantly removes most of grit ($SiO_2$, $CaCO_3$) and impurities (Smectite) mechanically. However, the pure, uniform size and shaped particles are kept. Besides, it is made without grinding.

Actually, the Magnesium Alumino Silicate Bristles of Actigel are chemically exfoliated (as shown in Figure 4 - 22. b).



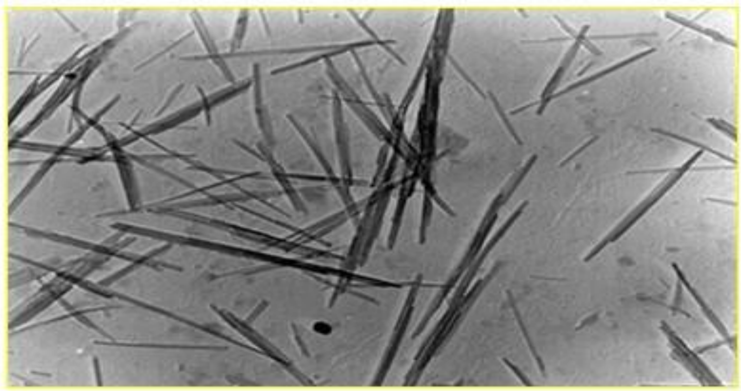

**(a)**




**(b)**

**Figure 4 - 21. (a) Traditional dry process, (b) Wet process ( Actigel process) of Actigel**

**(a)**



**(b)**

**Figure 4 - 22. (a) Bristles of commercially available Magnesium Alumino Silicates, (b) Bristles of Actigel**

Figure 4 - 23 shows the particle morphology of Actigel. It has an average particle size of 1.5 to 2 microns in length and an average diameter of 30 Angstroms. The bristles of Actigel are positively charged on the ends and negatively charged along the axis, which is the significant factor affecting gel formation to connect the microstructure of cement based materials.

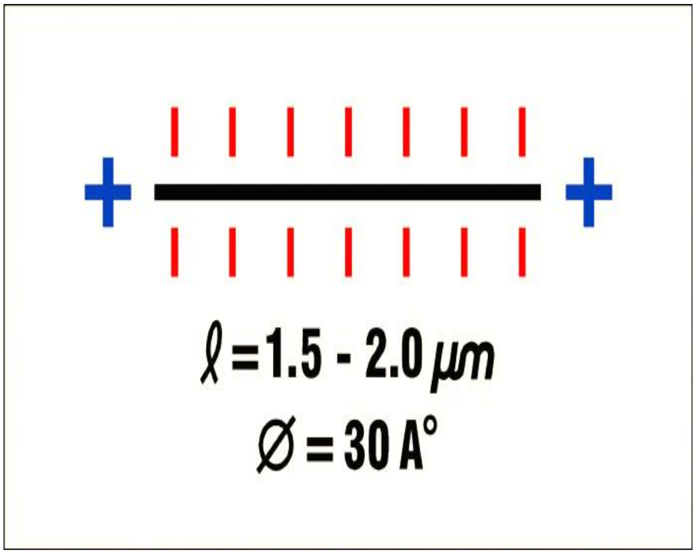



**Figure 4 - 23. Particle Morphology of Actigel**

The cement paste with clay addition of Actigel has been proved to be thixotropic and the thixotropic value increases with the amount of Actigel addition, which can be explained by Figure 4 - 24. When the cement paste is at rest ( No shear applied ), the positively charged particle ends tend to be attached on the particle axis with negative charge, which will result in a formation of a card-house network microstructure. However, when the shear is applied to the paste, the particles will be rearranged into the preferred direction and the new orientation of Actigel particles will offset the structural connection between particles. Therefore, the addition of Actigel has the ability to improve the structural connection of cement paste and more energy is required to break down the microstructural network. It also explains the increasing yield stress and viscosity of paste specimens.

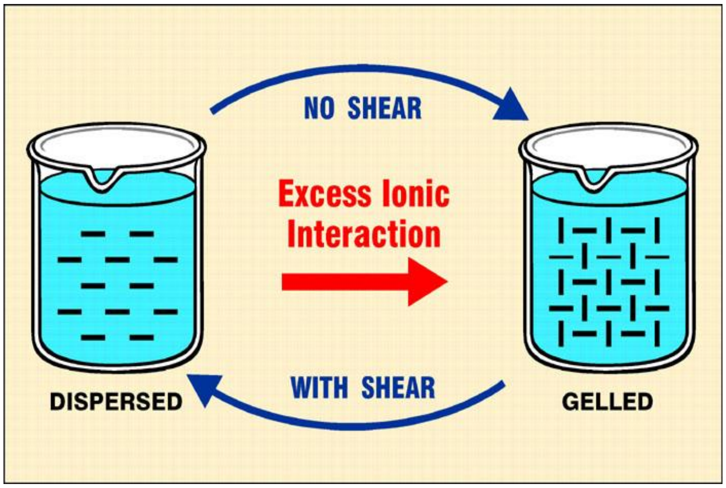



**Figure 4 - 24. The mechanism of increasing thixotropy for paste with Actigel addition**

The increasing structural rebuilding rate of cement paste with small amount of Actigel addition (0.5% and 1%) is possibly due to the ultra high fineness of the Actigel particles. Thus the Actigel particles are characterized as micro/nano-fillers and connectivity of the networking structure will be improved. The smaller particles of Actigel will fill the interstices of larger cement particles. Thus, the number of physical contacting points will increase significantly. As mentioned in the literature review, the strength of the force of particle attraction from London dispersion force is significantly affected by the particle size. Actigel is composed of ultra fine particles and its specific surface is very high. The smaller particle sizes result in more effective London dispersion forces between particles and the particles are easier to flocculate together. Besides, the higher surface area makes the particles easily contact with each other and the particles are prone to aggregate. Water has a function to lubricate the microstructure and disperse the particles, which makes the particles of cement paste easily slide past each other. However, the Actigel has high water absorption of 200% by weight and it is surface absorption. Without the lubricating water, the suspension tends to have a higher yield stress and also a stronger microstructural network connection. Thus, it is expected that higher floc strength and higher rate of structural rebuilding of cement paste can be obtained. In addition, due to the addition of Actigel, the solid volume content will increase and the distance between flocs will reduce. Therefore, it is also possible that the increasing solid volume content is responsible to the increasing structural rebuilding rate.

As described previously, the charged Actigel particles will attract with each other and a strong interlocking connection will form when the mixture is placed without shear. However, the structural rebuilding rate will decrease if the addition amount is more than 1%. This is possibly due to too much Actigel particles existing in the interstices of cement particles and there is not enough room for Actigel particles to be rearranged to form an interlocking microstructure. Thus, the structural rebuilding rate of cement paste with large amount of Actigel is inhibited.

High Reactivity Metakaolin (HRM) is a manufactured pozzolanic mineral admixture, which significantly enhances performance and many characteristics of cement-based materials. It is derived from purified kaolin clay and it is an amorphous alumino-silicate with white color. It is shown that the replacement of HRM has the ability to improve the cohesiveness of cement based material even at very low dosage [84]. HRM can aggressively react with calcium hydroxide to form compounds with cementitious value. The application of HRM will contribute to increased strength, reduced permeability, greater durability, effective control of efflorescence and the better control of degradation.

The sustained increasing rate of structural rebuilding as the increasing amount of substitution of HRM was seen in the previous description of test results. It indicated that the replacement of HRM had a very significant role to play to affect the structural rebuilding rate of cement paste. Firstly, it is possible that the finer particle size will contribute to stronger attractive forces between particles, which can possibly result in faster formation of flocs and aggregation of particles. Secondly, the high reactivity metakaolin clay has a spiny needle-like microstructure (as shown in Figure 4 - 25) with a very high surface area. It is expected that the water demand will increase significantly because the high specific surface area and irregular particle shape tends to interweave and bridge solid particles by which flocculation efficiency will significantly increase. In another word, the bond strength of particles will significantly increase. This is consistent with research which shows that the modification of some natural clay can be used to net and bridge solid particles and increase the flocculation efficiency of solid particles in a freshwater system [86]. Thirdly, it is noted that the cement substitution is a mass basis process. Due to the different specific gravity of cement and HRM, more solid particles volume will be obtained, which may also contribute to the increasing structural rebuilding rate because of the decreasing distance between particles. In addition, the high reactivity of HRM combined with more chemically contacting points (due to smaller particle size), the replacement will aggressively and quickly react with the cement hydration products and generate more stable and stronger paste interlocking network, which might be another explanation of sustained increasing rate of structural rebuilding for pastes with different amount of HRM replacement.

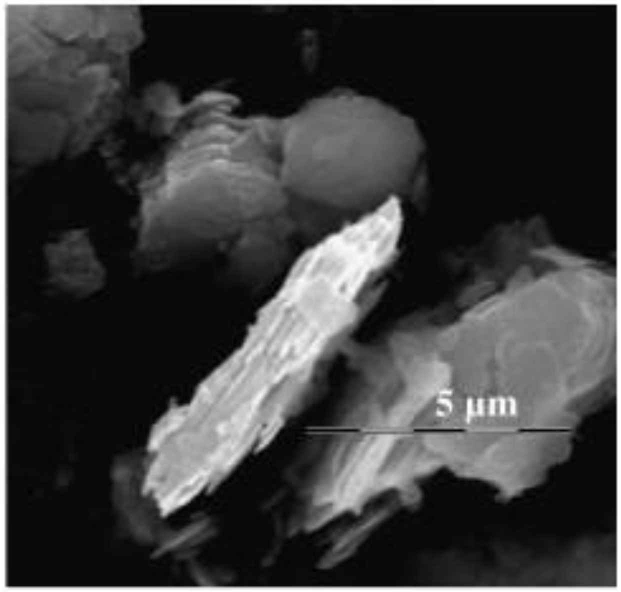



**Figure 4 - 25. SEM (Scanning electron microcopy) micrograph of metakaolin [85]**

Ground clay brick (GCB), is defined as a calcined natural pozzolanic material and is generated from finely grinding of waste brick. The clay brick manufacturing process can be defined as a pozzolanic procedure. Thus, the ground clay brick can be used as a supplementary cementitious material to improve the durability of concrete. It has a relatively regular particle shape, which can be seen in Figure 4 - 26. It was shown that the replacement tended to slightly increase the rate of structural rebuilding and no obvious differences were found among structural rebuilding rates of paste with 25% and 35% ground clay brick replacement. However, compared with Actigel addition and HRM replacement, the ability of increasing rebuilding rate is much less effective. Considering that the fineness of ground clay brick is approximately identical to the fineness of cement, its much higher particle size compared to that of Actigel and HRM and its regular microstructural shape, the slightly increasing structural rebuilding rate possibly results from the higher solid volume content contributed by lower specific gravity of GCB. This will reduce the distance between particles and result in stronger attractive forces between particles. Besides, the higher absorption of water of GCB reduces the water available for lubricating the microstructure and dispersing the matrix of cement paste, therefore the particles are prone to floc together, which might also contribute to the slightly increasing structural rebuilding rate.

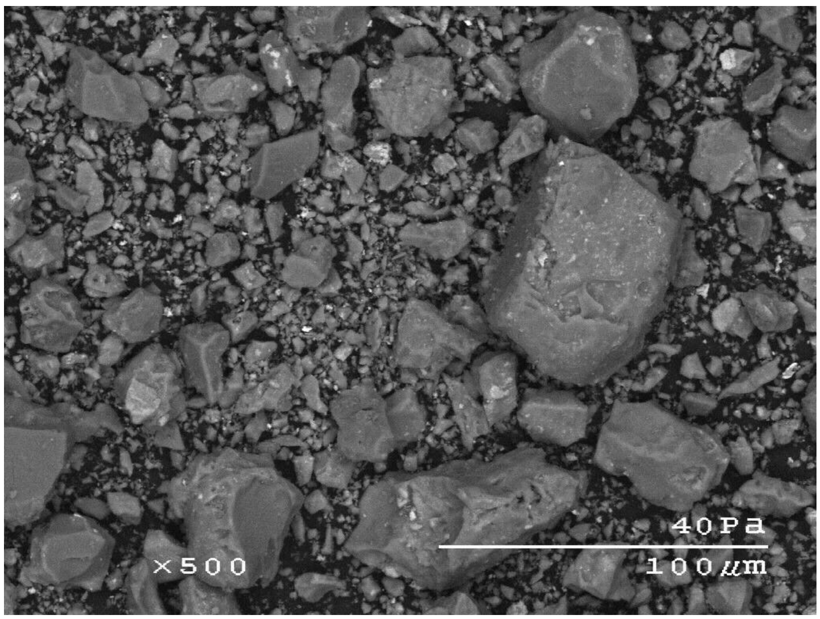



**Figure 4 - 26. SEM (Scanning electron microcopy) micrograph of ground clay brick [87]**

Considering the investigation of the effects of different types of cement on the structural rebuilding rate of cement paste, test results from Figures 4-10, 4-11 and 4-12 indicated that cement paste with high alkali amount was expected to have higher rate of structural rebuilding. The high alkali cement (alkali content is 1.38%) used for this thesis obtained a higher rate of structural rebuilding than others. Due to the fact that alkali content for Type IV cement and Ashgrove Type I cement is similar, the rebuilding rates for these cements are approximately equal. The testing result was consistent with the research from Lyon and Talor [88,89]. They revealed that the structural build up of cement paste during early ages depends on the amount of $C_3A$ (this will be discussed in Chapter 5) and alkali. The higher the amount, the faster rate of structural rebuilding can be expected. The explanation they provided was that the alkali formed from sodium and potassium will dissolve in the pore solution very quickly. When the cement reacts with water, the dissolution of alkali will quickly combine with the released $Ca^{+2}$ and $OH^-$ ions, which will result in stronger attractive forces and more cohesive paste. It is proved that ionic strength of aqueous phase of cement paste will increase significantly with the addition of alkali, especially with the addition of sodium addition. This is due to the fact that the potassium and sulphate ions will be consumed by syngenite formation [90]. The ionic strength of pore fluid is a determinative factor to the double-layer thickness of ions around cement particles. Normally, with the higher ionic strength, the thickness of double-layer decreases very quickly, by which the particles will be prone to contact closely. Therefore, the cement particles are easy and fast to floc and aggregate together to form a 3-dimensional network structure.

In addition, the ESEM investigation of microstructure of cement paste with high content of potassium proved that the increasing amount of potassium sulphate leaded to an increasing amount of long prismatic crystals formation [90].The prismatic crystals were found right after the contacting of cement particles with mixing water and the detection lasted up to 2 hours. Actually, the microanalysis (EDX) and its morphology indicated that these crystals were syngentie. Figure 4 - 27 [7] shows the ESEM-FEG image during

2 hours hydration of cement paste with high/low alkali content. These prismatic crystals serve as an agent to rapidly build an interlocking microstructure and lead to higher rate of structural rebuilding. Figure 4 - 27 (A and B) describes cement with high amount of Alkali sulphate, from (A) we can see that large amount of prismatic crystals randomly orientate in order to interlock the paste matrix without applying shear energy while (B) indicates that the prismatic crystals obtain preferred orientation with shearing. Figure 4 - 27 (C) describes the microstructure of paste with small amount of Alkali sulphate and we can see that much less prismatic crystals (Syngenite) are formed.

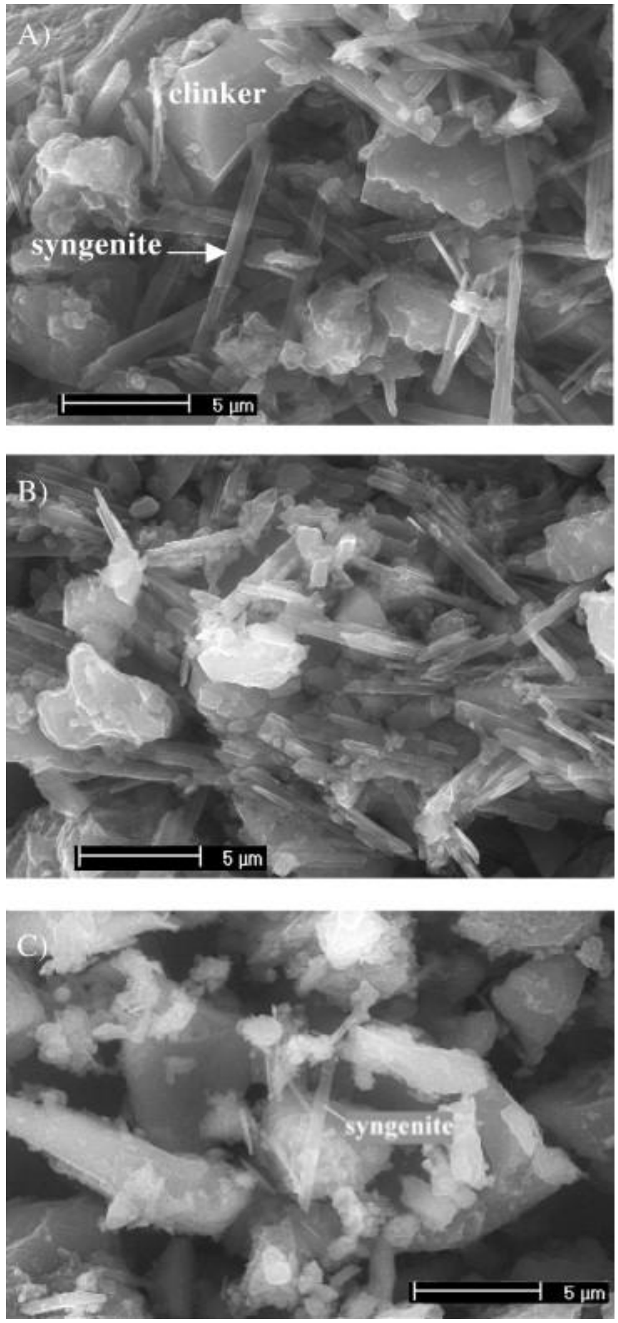



**Figure 4 - 27.“A, B: Syngenite formation imaged by ESEM-FEG 2 h of hydration of cement A with 4.49 wt.% potassium sulphate. A) Cement hydrated without agitation; random orientation of syngenite, B) cement paste after shearing in the viscometer; preferred orientation of syngenite crystals. C: Cement paste A with 1.56% $K_2SO_4$ content: minor amount of syngenite.” [90]**

## 4.5 Correlation between Flow Table Test and Structural Rebuilding Rate

The flow table test was performed to try to verify the rate of structural rebuilding obtained from rheology test. The plot of flow percent change versus time for pastes with Actigel addition, high reactivity metakaolin clay, ground clay brick replacement and pastes made with different type of cement are shown in Figure 4 - 28, Figure 4 - 31, Figure 4 - 34 and Figure 4 - 37 respectively. Each curve for different clay or cement types are fitted in to a liner regression equation, the coefficients of time are plotted versus clay amount or cement types, which are shown in Figure 4 - 29, Figure 4 - 32, Figure 4 - 35 and Figure 4 - 38. The correlation plot of flow percent and thixotropy can be used for see whether there is correlation between them, which are shown in Figure 4 - 30, Figure 4 - 33, Figure 4 - 36 and Figure 4 - 39.

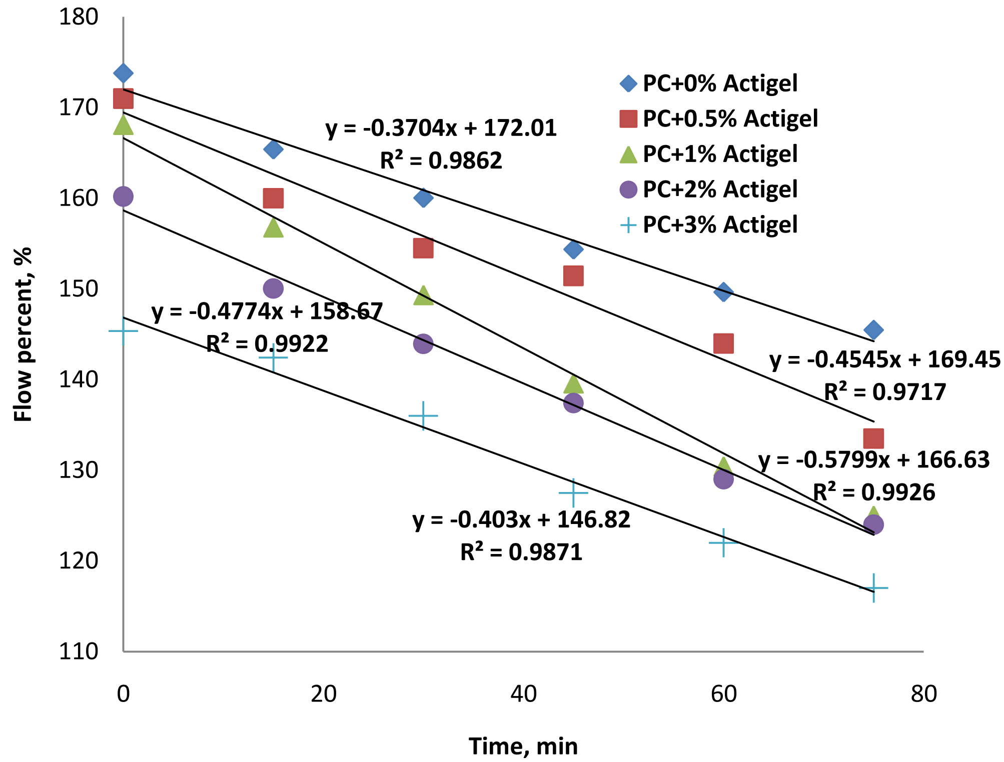



**Figure 4 - 28. Flow percent change with time for pastes with different amount of Actigel addition**

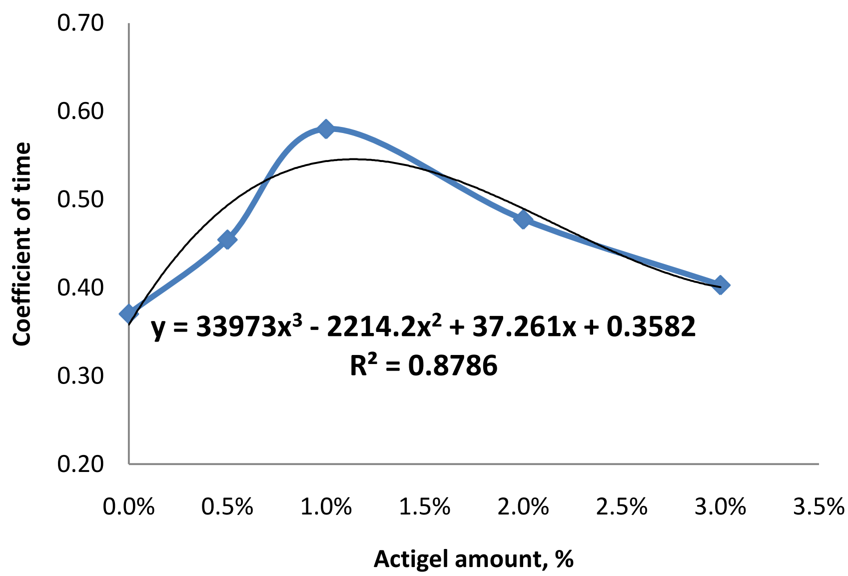



**Figure 4 - 29. The coefficient of time vs. Actigel amount**

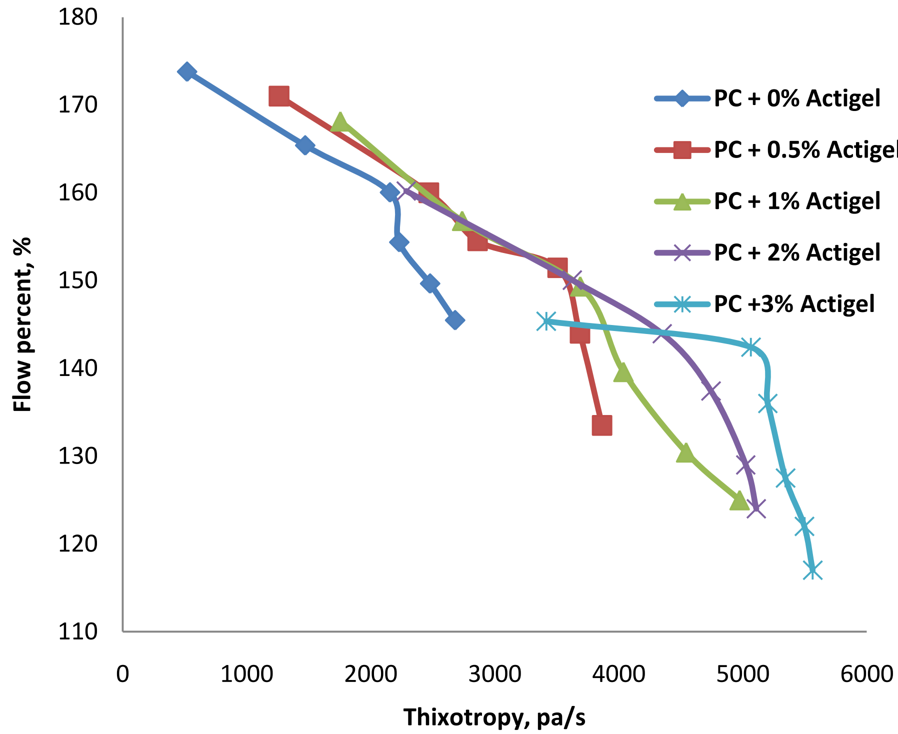



**Figure 4 - 30. Correlation plot of thixotropy vs. flow percent for PC+Actigel**

In Figure 4 - 28, the coefficient of time indicates the rate of flow percent decreasing. From, we can see that small amount (0.5%-1%) of Actigel accelerates the decreasing of flow percent while over dosage (2%-3%) decreases such rate. Figure 4 - 30 indicates the flow percent decreases as the increasing thixotropy.

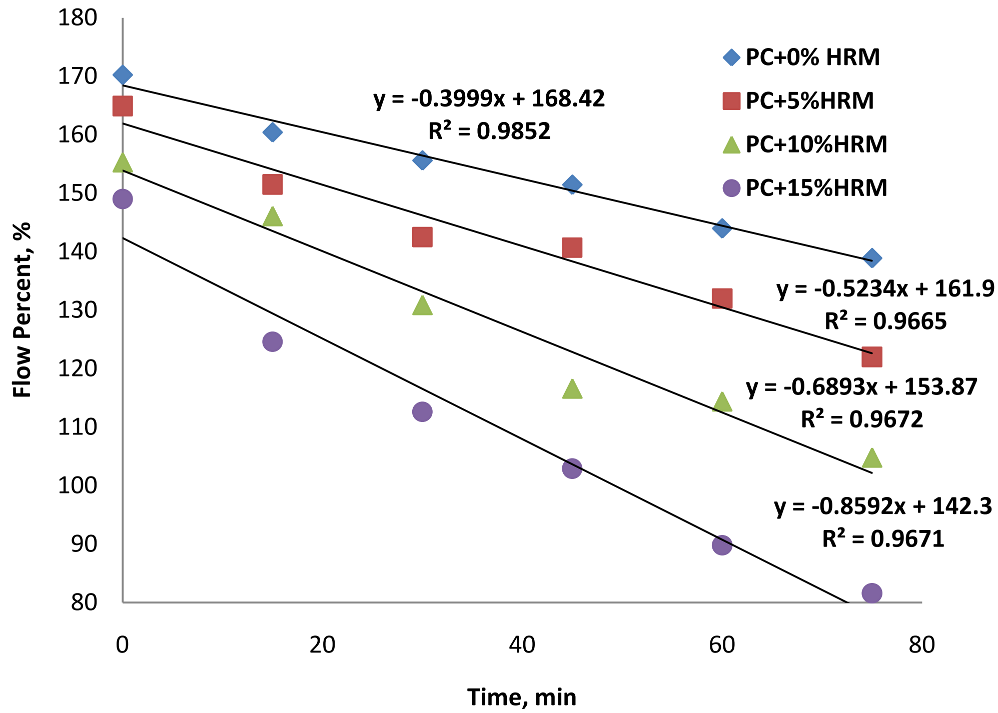



**Figure 4 - 31. Flow percent change with time for pastes with HRM replacement**

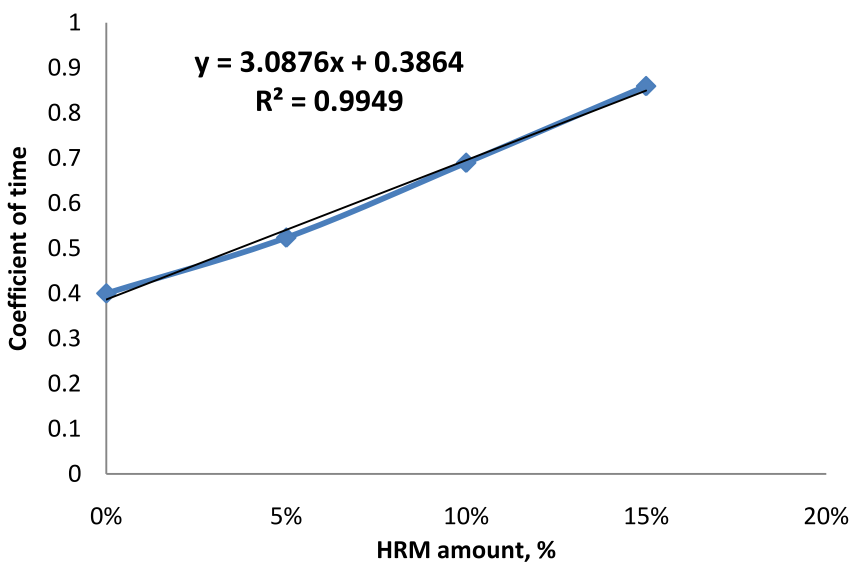



**Figure 4 - 32. The coefficient of time vs. HRM amount**

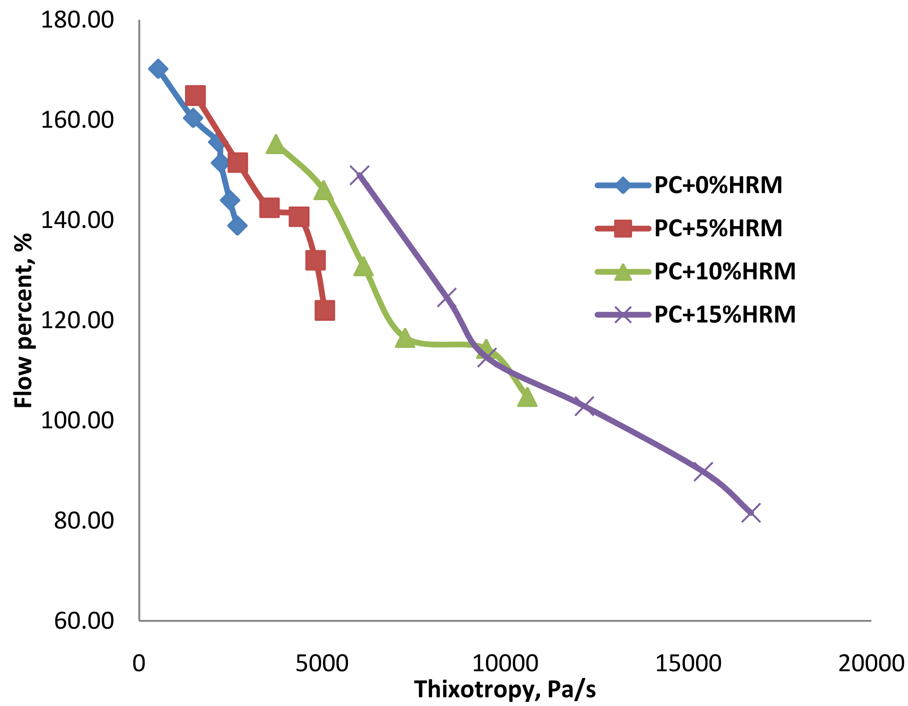



**Figure 4 - 33. Correlation plot of flow percent vs. thixotropy for PC+HRM**

Figure 4 - 31 indicates the changing rate of flow percent. It is not difficult to see that the rate of flow percent decreasing increases with the increasing amount of HRM. From Figure 4 - 32, we can see that the flow percent decreases with the increasing of HRM.

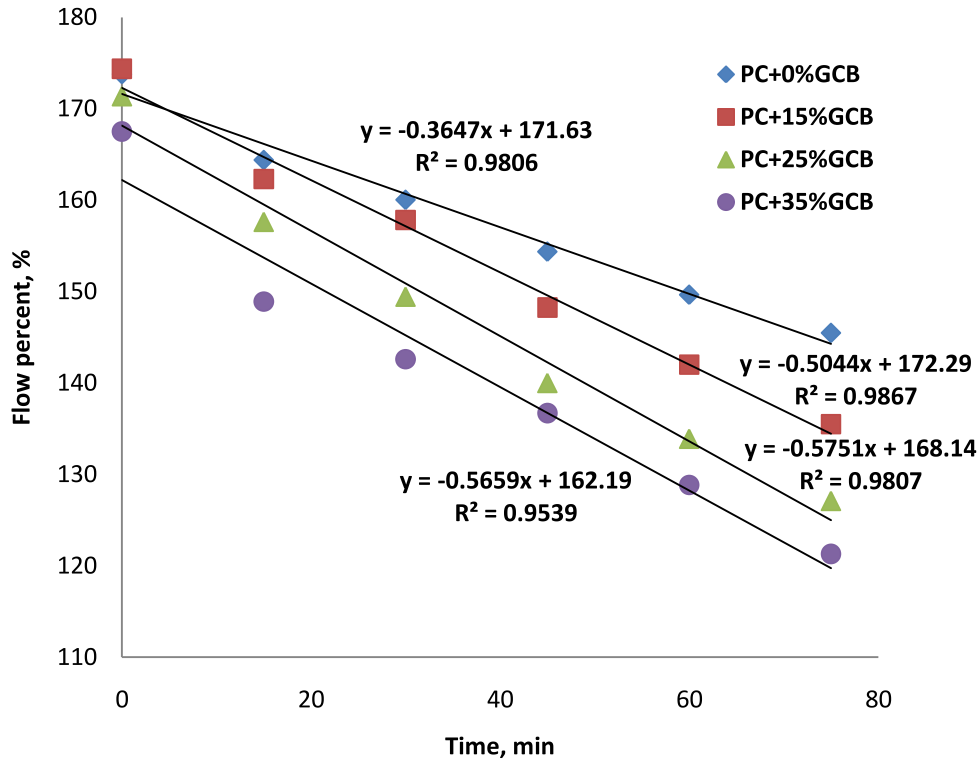



**Figure 4 - 34. Flow percent change with time for pastes with GCB replacement**

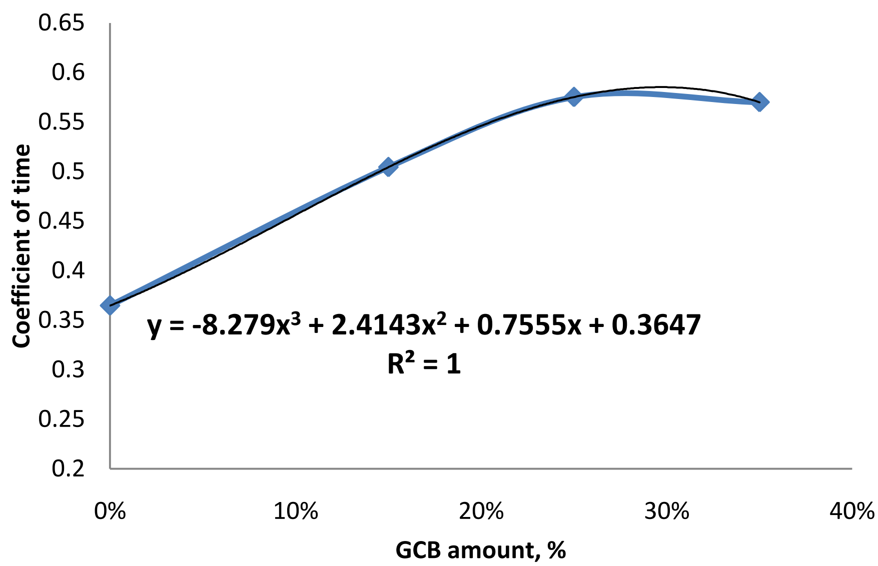



**Figure 4 - 35. The coefficient of time vs. GCB amount**

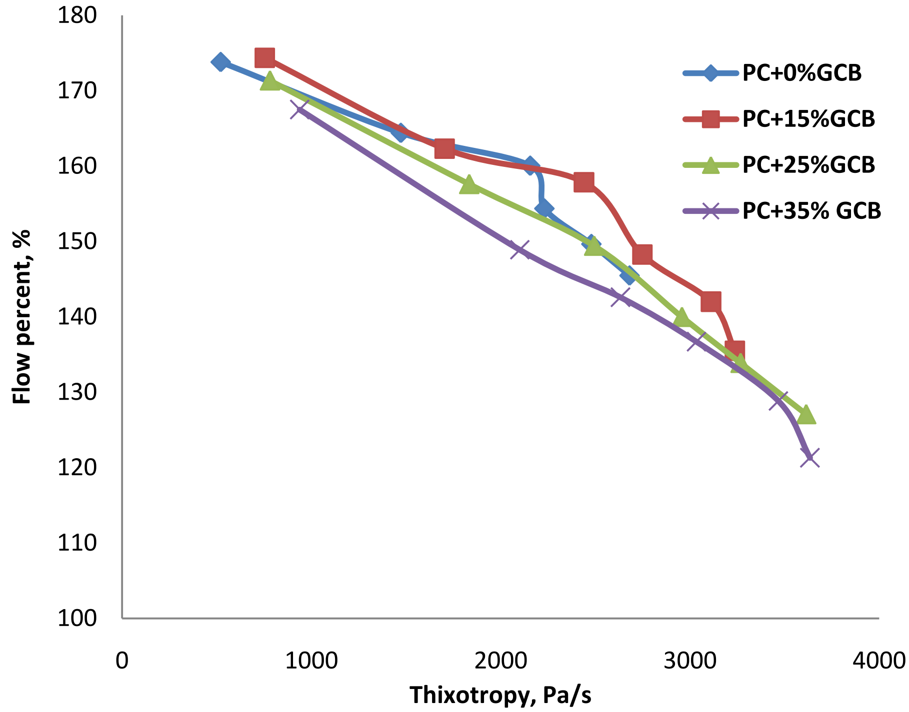



**Figure 4 - 36. Correlation plot of flow percent vs. thixotropy for PC+GCB**

From Figure 4 - 35, we can see that, from 0% to 25% percent GCB replacement, the decreasing rate of flow percent increases. However, when the amount of GCB is more than 25%, such rate starts to slightly slow down. Figure 4 - 36 indicates that the flow percent will decrease as the increasing thixotropy.

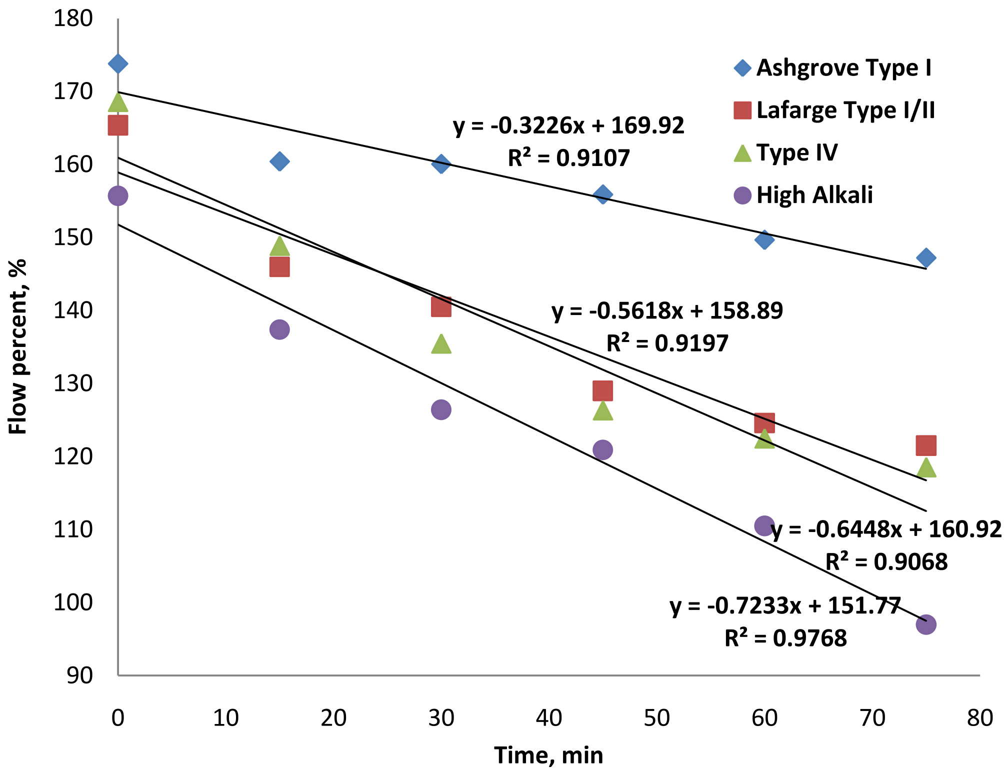



**Figure 4 - 37. Flow table test results for pastes made with different types of cement**

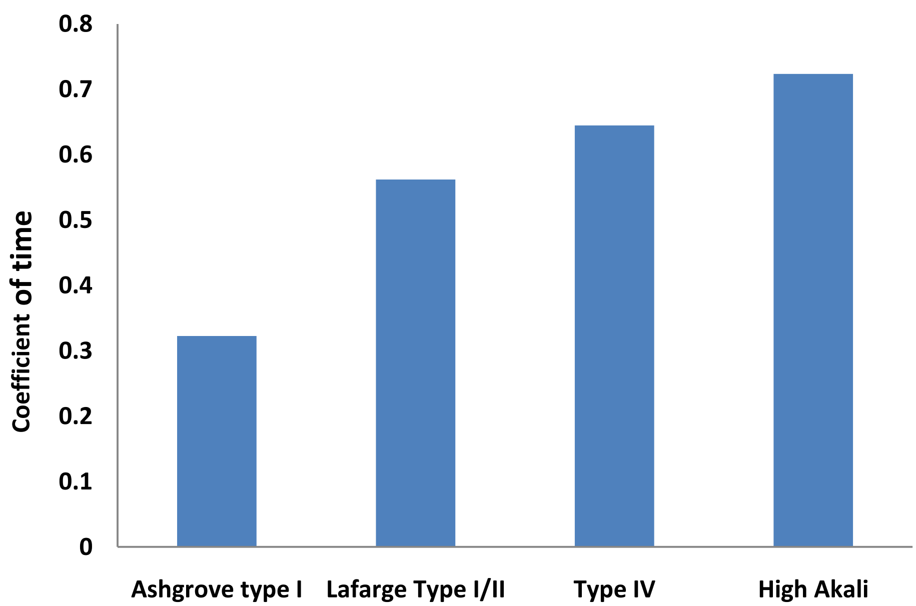



**Figure 4 - 38. The coefficient of time vs. cement types**

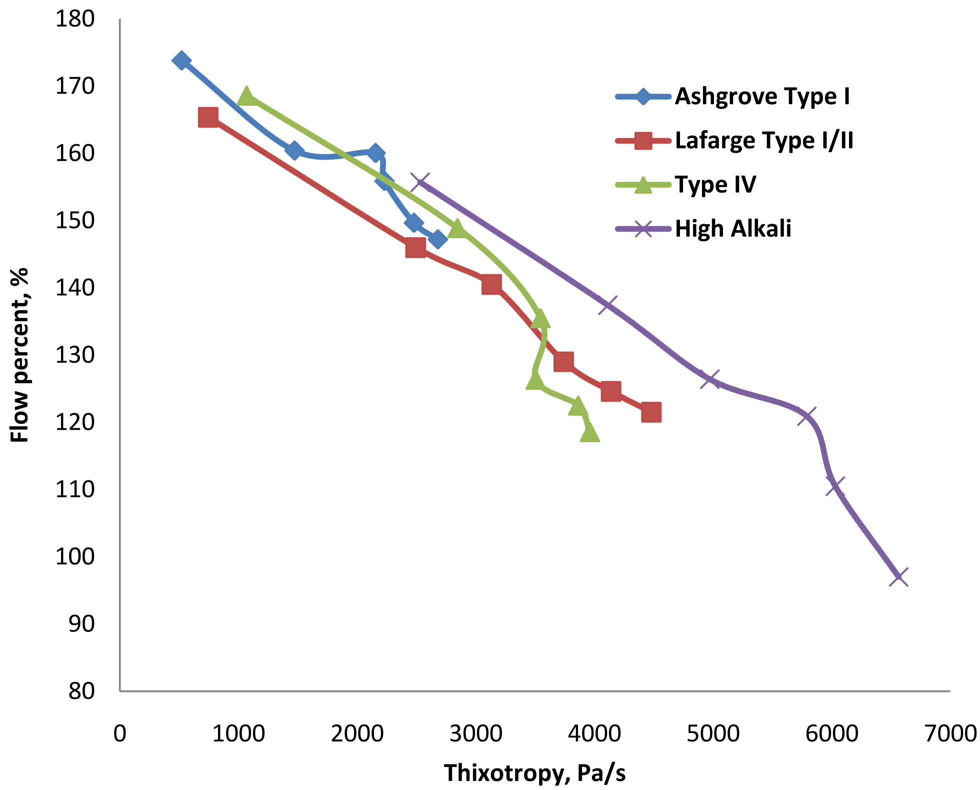



**Figure 4 - 39. Correlation of flow percent vs. thixotropy for different cement types**

It is believed that the flow table test results have a close relationship with rheological parameters of yield stress and viscosity at a very low amount of aggregate [91]. However, the experimental method used for this thesis measured the flow percent of paste over a 75mins time scale and a curve fitted for flow percent of pastes at different time point. The rate of decreasing of flow percent might be an indication of structural rebuilding rate. From the flow table test results, it seems that a relatively strong correlation between structural rebuilding rate and the flow percent decreasing with time exists for different mixtures.

For clay addition of Actigel, the flow percent decreasing rate increased from 0% to 1%, then with more addition, the decreasing of flow percent started to slow down. Concerning the replacement of HRM, the rate of flow percent decreasing increased as the increasing amount of HRM replacement. In addition, the substitution of GCB slightly accelerated the reduction of flow percent but no significant differences were found for paste specimens with different amount of GCB replacement. For different types of cement, the faster rate of decreasing flow percent was obtained by high alkali cement while the lowest rate of decreasing flow percent was obtained by Ashgrove type I cement. The flow percent decreasing rate of Type IV and Lafarge Type I/II cement were similar, which was not totally agree with the rheology test since rheology tests showed that Lafarge Type I/II cement and High Alkali cement gained higher structural rebuilding rate while lower and similar structural rebuilding rate was found by Type IV and Ashgrove Type I cement. Although some small discrepancies between flow table test and rheology test were shown, it seems that a strong relationship between them still exists.

## 4.6 Comparison among Different Clays

From previous discussions, based on thixotropic changing rate analysis, the optimum amount of clay addition or replacement is 1% Actigel, 10% HRM or 25% GCB. Figure 4 - 40 plot the thixotropy change for each of them.

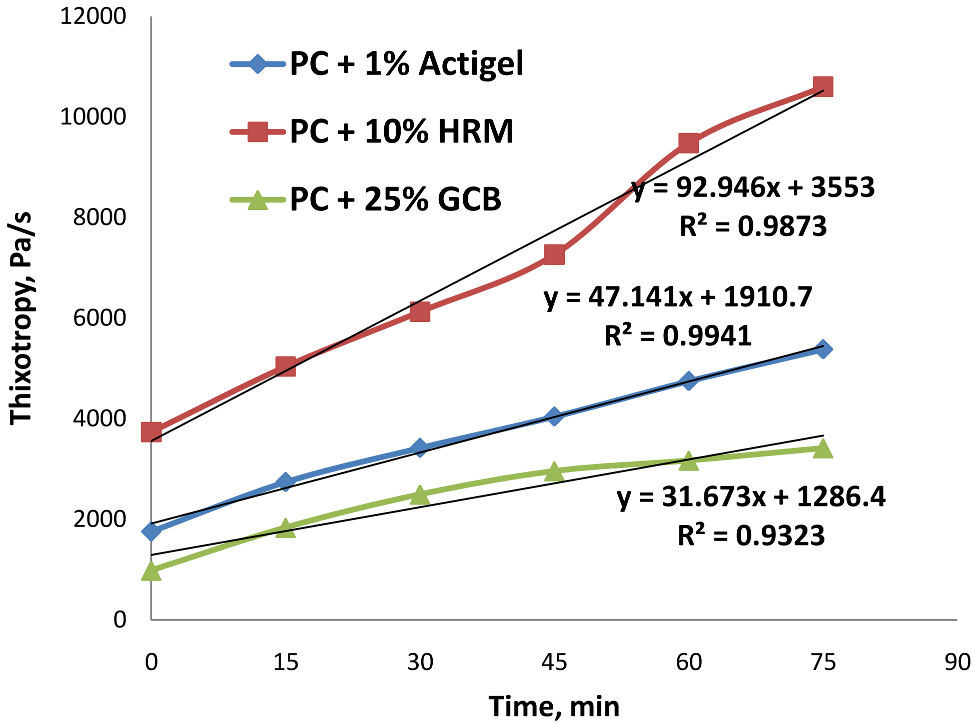



**Figure 4 - 40. Comparison amoung different clay addition/ replacement**

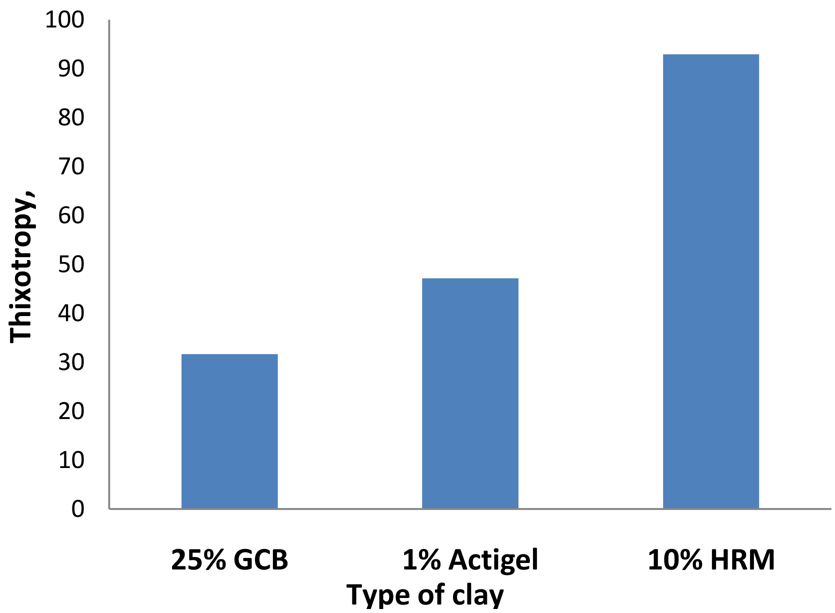



**Figure 4 - 41. The plot of coefficient of time versus clay types**

The plot of coefficient of time versus types of clays is shown in Figure 4 - 41. It indicates that, 10% HRM can be used for obtaining the highest structural rebuilding rate, which is followed by 1% Actigel and 25% GCB.

## 4.7 Chapter Summary

The main aim of this chapter was to investigate the effects clay addition/replacement and different cement types have on the structural rebuilding rate of cement based materials. A systematic experimental program was applied to determine the influence of Actigel addition, High Reactivity Metakaolin and Ground Clay Brick replacement and different cement types. Based on the descriptions of test results in this chapter, the conclusions can be made as follows:

- The addition of Actigel, replacement of HRM and GCB were shown to advance the thixotropic behavior of cement paste, also the yield stress and viscosity. However, comparing with GCB, Actigel and HRM were more effective in this function.
- Structural rebuilding rate of cement paste was strongly influenced by clay addition/replacement and cement composition.
- Due to the ultra fine particle size, charged particle morphology and high water absorption, the addition of Actigel had the ability to efficiently build up an interlocking and networking microstructure, increased the opportunities for solid particles to floc together and thus increased the structural rebuilding rate. Cement paste with small amount of addition of Actigel (1%) gained the highest structural rebuilding rate. However, over-dosage of Actigel might lead to a reducing

structural rebuilding rate. It is possible that not enough room for them to rearrange the particles orientation to form a card-house like microstructure.

- The replacement of High Reactivity Metakaolin (HRM) strongly increased the rate of structural rebuilding of cement paste and the rate increased with the amount of HRM replacement. The finer particle size and spiny needle-like microstructure with high specific surface area of HRM might contribute to the increasing rebuilding rate. Besides, because the paste was mixed depending on a mass-based theory, solid volume significantly increased, which lead to closer distance between particles. More chemical contacting points and stronger attractive forces tended to rapidly increase the interparticle-bond and structure degree.
- The Ground Clay Brick replacement (GCB) slightly increased the structural rebuilding rate of cement paste, which is possibly contributed by the small specific gravity and high water absorbing ability. However, the differences of structural rebuilding rate among pastes with different amount of replacement were not obvious.
- Fixing the w/c ratio, the cement composition obviously affected the structural rebuilding rate. The cement pastes with high alkali content had faster rate of structural rebuilding, which is possibly contributed by the pore solution chemistry which tended to increase the bond strength of particles. Besides, its higher alkali sulphate content leaded to increasing amount of prismatic crystals formation. These crystals effectively bridged and netted the microstructure of cement paste and acceleration of structural rebuilding was expected. Type IV and Ashgrove

Type I cement gained lower and similar structural rebuilding rate, which possibly resulted from their lower alkali content.

- Flow table test was used to correlate the flow percent reduction with structural rebuilding of cement paste. Based on flow percent change with time, it was proved that a strong relationship existed between them. The higher rate of decreasing flow percent indicated a faster structural rebuilding rate.
- The 10% HRM can be used for concrete mixing in order to obtain the highest structural rebuilding rate.

# Chapter 5 Evaluation of Effect of Heat Generation Rate on Structural Rebuilding Rate

## 5.1 Introduction

Due to the fact that cement will hydrate with water after mixing and generate hydration products to build up the structure of cement paste, this chapter aims to investigate if the rate of heat generation from cement hydration will influence the structural rebuilding rate of cement based materials. The rate of heat generation for pastes with different clay addition/replacement and pastes made with different types of cement during the first 1.5 hours after mixing was analyzed.

## 5.2 Effect of Heat generation Rate on Structural Rebuilding Rate

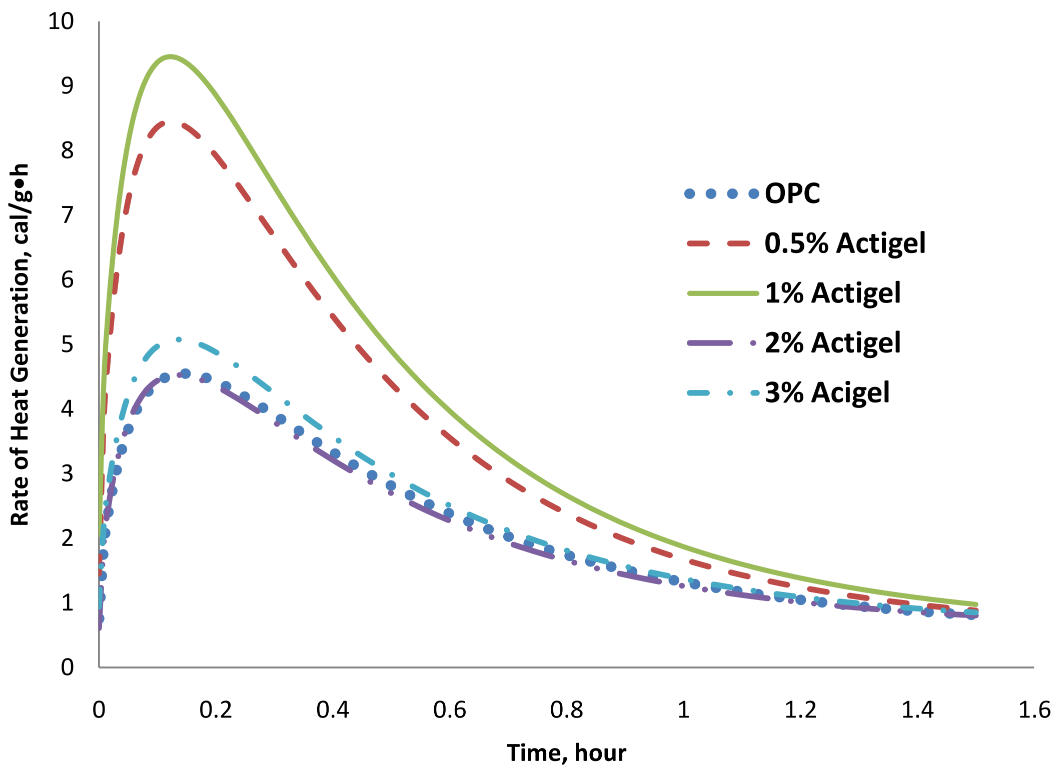



**Figure 5 - 1. Rate of heat generation for pates with Actigel addition**

Figure 5-1 shows the rate of heat generation for paste samples with different amount of Actigel addition during 1.5 hours after mixing. From this figure, we can see that the paste with 1% Actigel had the highest rate of heat generation followed by cement paste with 0.5% Actigel. The rate of heat generation for paste with 0%, 2% and 3% were lower and no pronounced differences were found. This result indicates that, during the first 1.5 hour, the rate of heat generation increased with small amounts of Actigel addition while large amounts of Actigel addition tended to slow down the heat generation rate. Compared with the rheology measurement, the rate of heat generation and structural rebuilding rate are verywell correlated. As shown in table 3-2, the potassium content of

Actigel is very high. Based on the discussion in section 4.4, higher potassium content will increase the amount of formation of syngenite with long prismatic crystals which increases the structural interlock efficiently during the first 2 hours of hydration. It is possible that the increasing rate of heat generation resulted from the increasing amount of syngenite formation. However, Actigel has water absorption of 200% and very high specific surface area. Over-addition of Actigel might lead to high contacting with water and reduce the water available used for $C_3A$ hydration. Thus, the heat generation rate reduced and slowed down the structural build up.

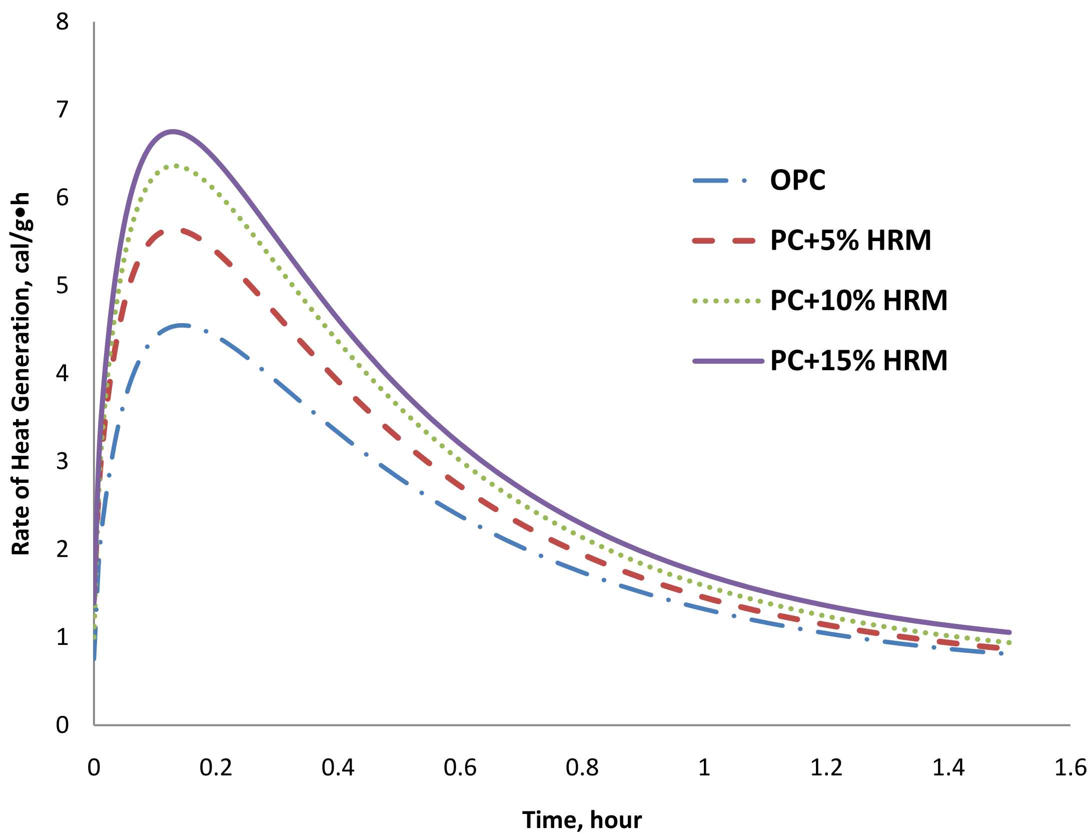



**Figure 5 - 2. Rate of heat generation for pates with replacement of High Reactivity Metakaolin**

Figure 5-2 shows the rate of heat generation for pastes with different amount of HRM replacement. From this figure, we can see that the rate of heat generation increased with the increasing amount of HRM replacement. Since the results from rheology test indicated that the rate of structural rebuilding also increased with the increasing amount of HRM replacement, this supports an association between the rate of heat generation and the structural rebuilding rate of paste with HRM replacement. The increasing rate of heat generation is possible due to the reactivity of Metakaolin will increase with amount of HRM. The reaction between $AS_2$ and CH from cement hydration will form additional cementitious aluminium containing CSH gel and crystalline products. Thus, the higher the reactivity of Metakaolin will lead to a higher rate of heat generation and thus a higher and faster structure degree.

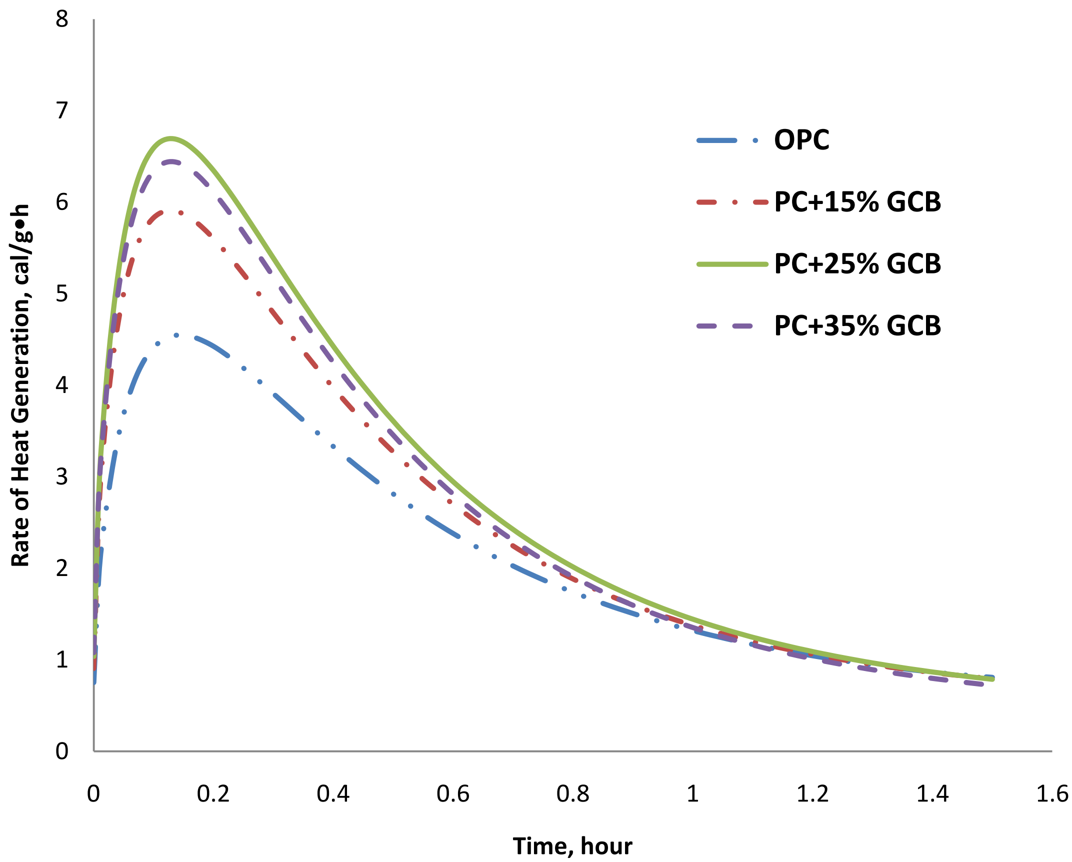



**Figure 5 - 3. Rate of heat generation for pates with replacement of Ground Clay Brick**

Figure 5-3 indicates the rate of heat generation for pastes with different amounts of GCB replacement. It can be seen that higher rates of heat generation were obtained by pastes with 25% and 35% GCB replacement during the first 1.5 hours, while pure cement paste had lowest rate of heat generation. Comparing with rheology measurement, cement paste with 25% and 35% GCB also gained higher structural rebuilding rate while pure cement paste obtained the lowest rate. Similarly, this indicates the existence of a good correlation between the structural rebuilding rate and the rate of heat generation. The increasing rate of heat generation is possibly due to the pozzolanic reactivity of GCB.

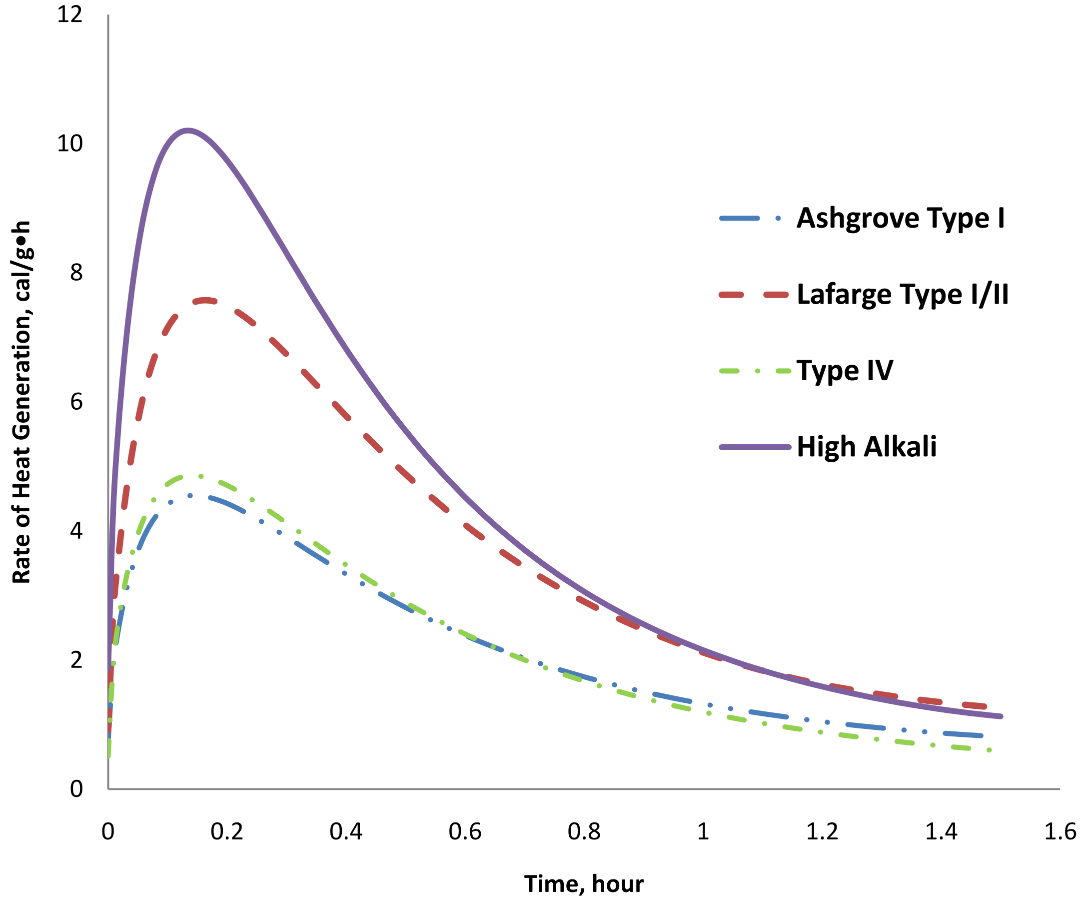



**Figure 5 - 4. Rate of heat generation for pates made with different types of cement**

Figure 5-4 indicates the rate of heat generation for pastes made with different types of cement during the first 1.5 hours. It is easy to see that the highest rate of heat generation was obtained by High Alkali cement which was followed by Lafarge Type I/II cement. At the same time, the rates of heat generation of Type IV and Ashgrove Type I cement were lowest and no big differences between them were found. Again, considering rheology measurement, there is a good correlation between the rate of heat generation and structural rebuilding. The initial structural degree depends a lot on the $C_3A$ content.

As shown in table 3-1, the $C_3A$ content of High Alkali cement is 11% which is much higher than the others and its alkali content is also higher. It is expected that these two factors might contribute the higher heat generation rate and thus a higher structural rebuilding rate. The $C_3A$ content for Ashgrove Type I (6%) is higher than Type IV (1%) and the alkali content for them are similar. However, neither a higher heat generation rate nor higher structural rebuilding rate was found for Ashgrove Type I cement. Actually, concerning microstructure of $C_3A$, there are two types of $C_3A$: cubic and orthorhombic. It is known that the increasing amount of orthorhombic $C_3A$ tends to result in a lower reactivity of $C_3A$. Therefore, it is possible that the reactivities of $C_3A$ for these two different types of cement are not the same. It is likely that the $C_3A$ existing in Ashgrove Type I cement is dominated by orthorhombic $C_3A$ with low reactivity, which leads to a lower rate of heat generation and slower structural rebuilding rate.

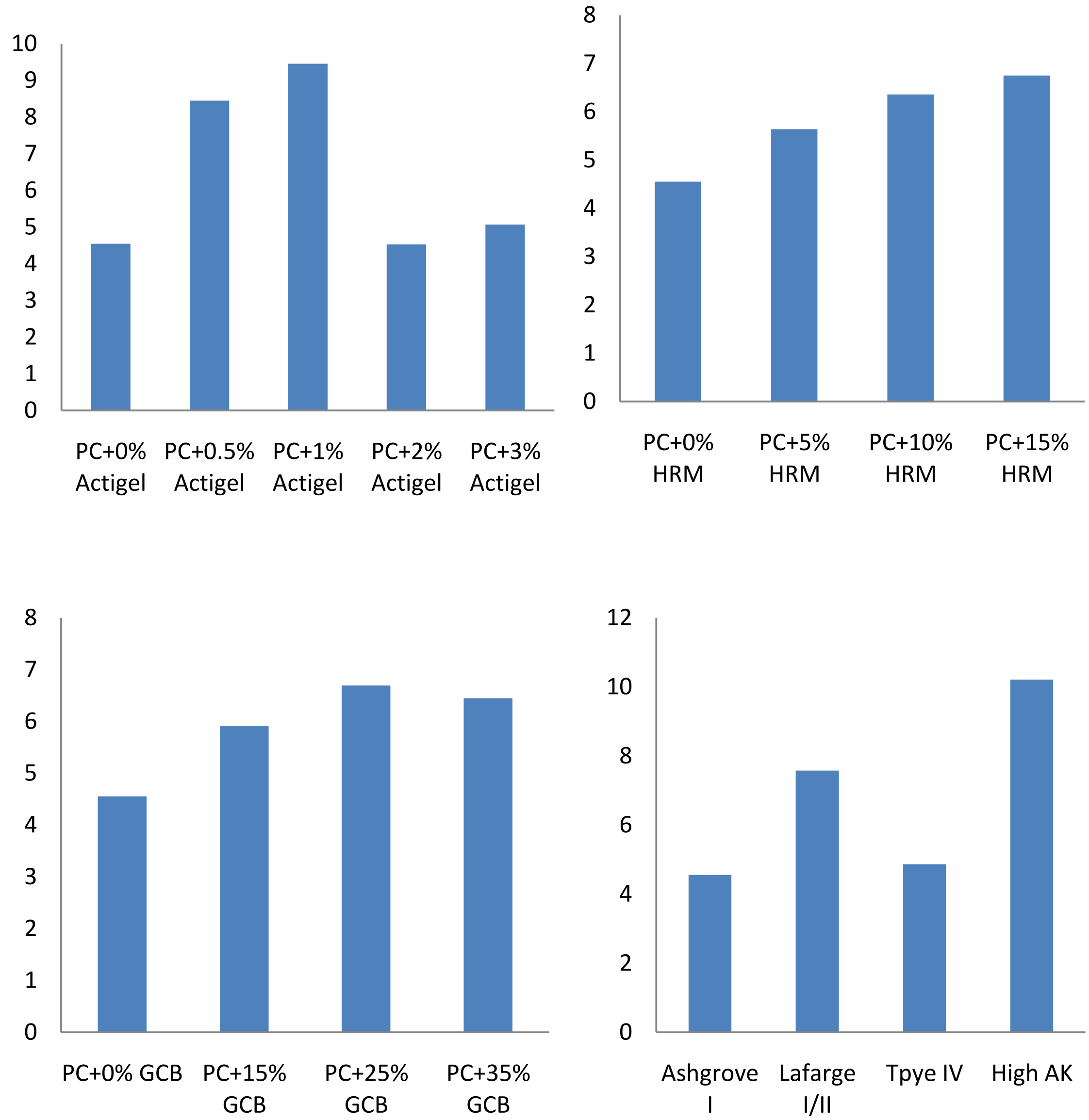



**Figure 5 - 5. The peak rate of heat generation vs. clay and cement types**

Figure 5-5 plots the peak rate of heat generation versus different clay amount and cement types, by which we can see the higher the peak of heat generating rate, higher the thixotropy changing rate we can obtained.

## 5.3 Chapter summary

The isothermal calorimeter was used to investigate if the rate of heat generation from cement hydration during the first 1.5 hours has correlation with structural rebuilding rate. Based on the test results shown in this chapter, the following conclusions can be made:

- A strong correlation between the rate of heat generation and structural rebuilding was found for pastes with different clay addition/replacement and pastes made with different types of cement. A higher rate of heat generation related with a faster structural rebuilding rate.
- Small amount of Actigel addition (up to 1%) increased the rate of heat generation and structural degree, thus a higher structural rebuilding rate can be obtained. It is possibly due to the high content of Alkali in Actigel. However, over-dosage of Actigel addition decreased the rate of heat generation. It seems that the high water absorption of Actigel prohibited the reaction between cement and water.
- The rate of heat generation increased as the amount of High Reactivity Metakaolin replacement, which is contributed by its high pozzolanic reactivity.
- For the Ground Clay Brick, the 35% and 25% amount of replacement had higher heat generation rate and lowest rate of heat generation was obtained by pastes without GCB replacement. However, significant differences among pastes with different amount of GCB were no found.
- The $C_3A$ predominately determines the rate of heat generation of pure cement paste during the first 1.5 hours hydration. For study about different types of cement, high alkali cement with relatively higher alkali and $C_3A$ content gained

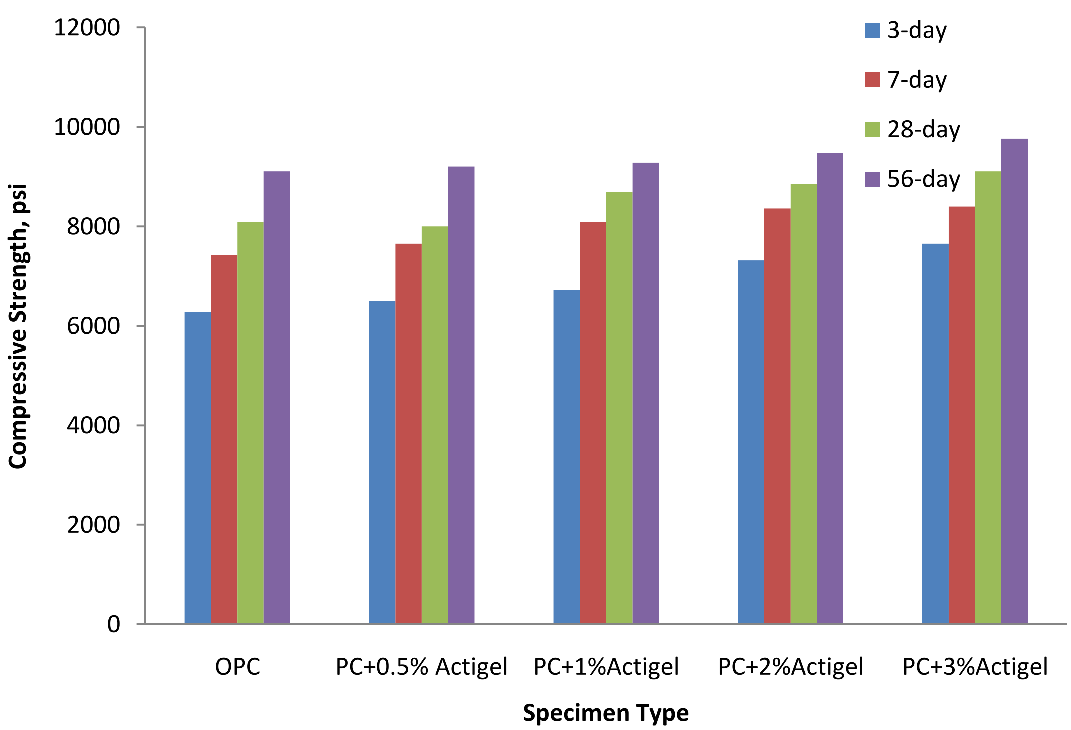
the fastest heat generation rate, which was followed by Lafarge Type I/II cement. The rate for Type IV and Ashgrove Type I cement were similar and both of them were lower than the others, it is possible that the amount of orthorhombic $C_3A$ with low reactivity in Ashgrove Type I cement is higher.

# Chapter 6 Compressive Strength Test

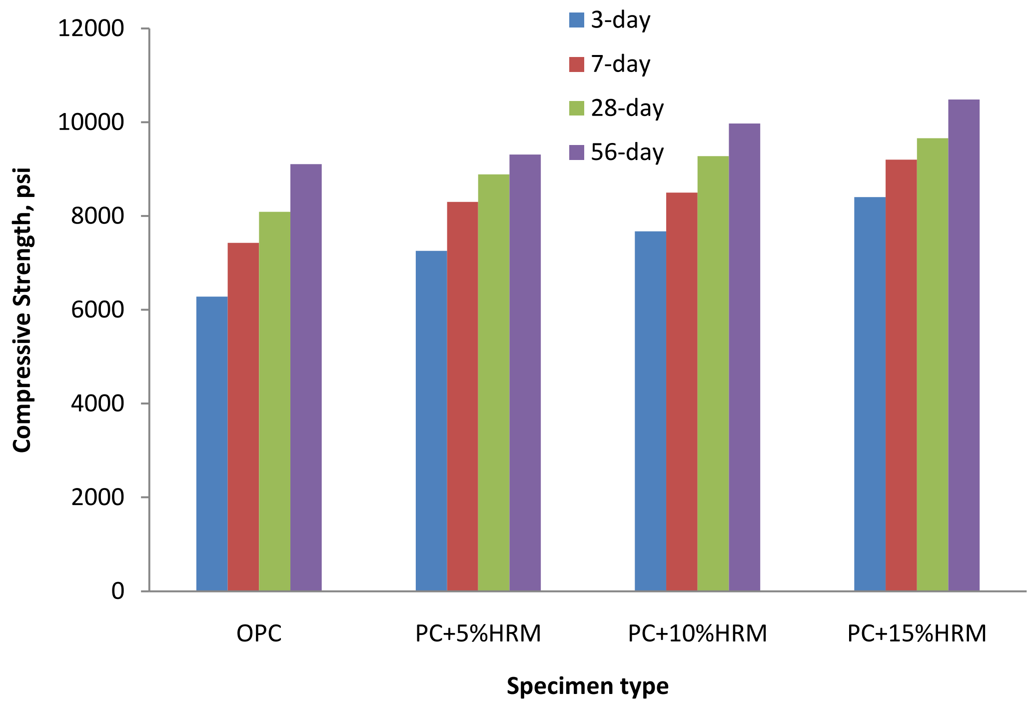
## 6.1 Introduction

This chapter investigated the influence of Clay addition/replacement and different types of cement on the mechanical performance of cement paste. For the study of clay addition or replacement, because the High Reactivity Metakaolin and Ground Clay Birck are characterized as pozzolanic materials, 3, 7, 28 and 56 day strength were studied. However, for investigation of influence of different cement types, just 3, 7 and 28 day strengths were considered.

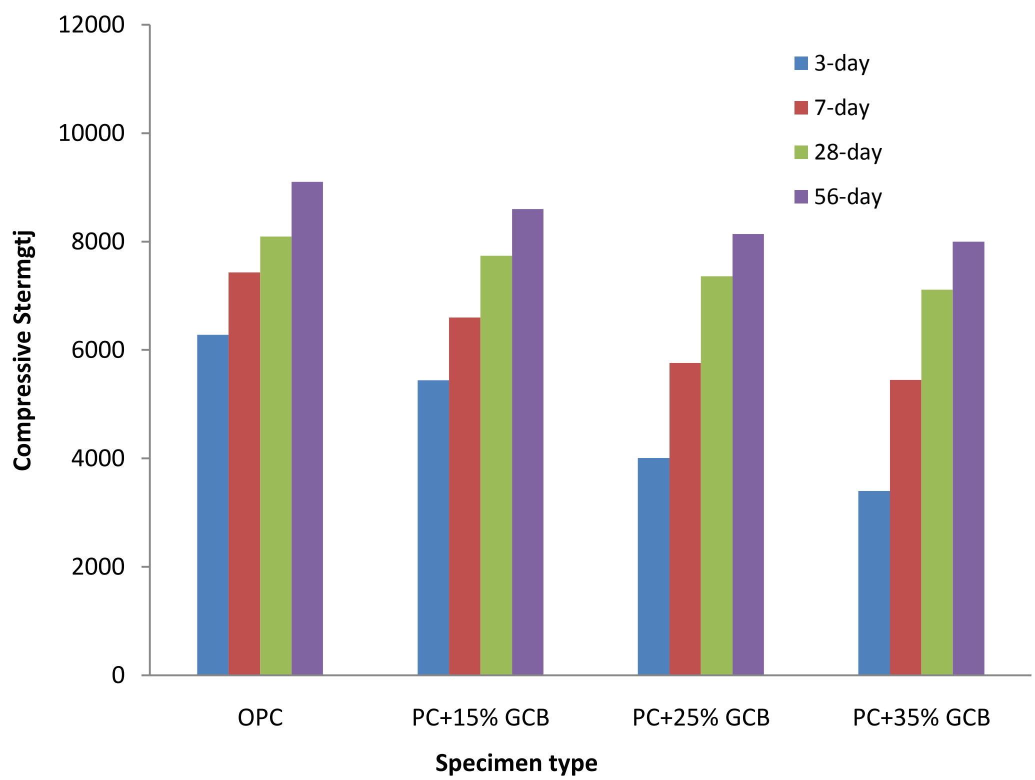
## 6.2 Test Results



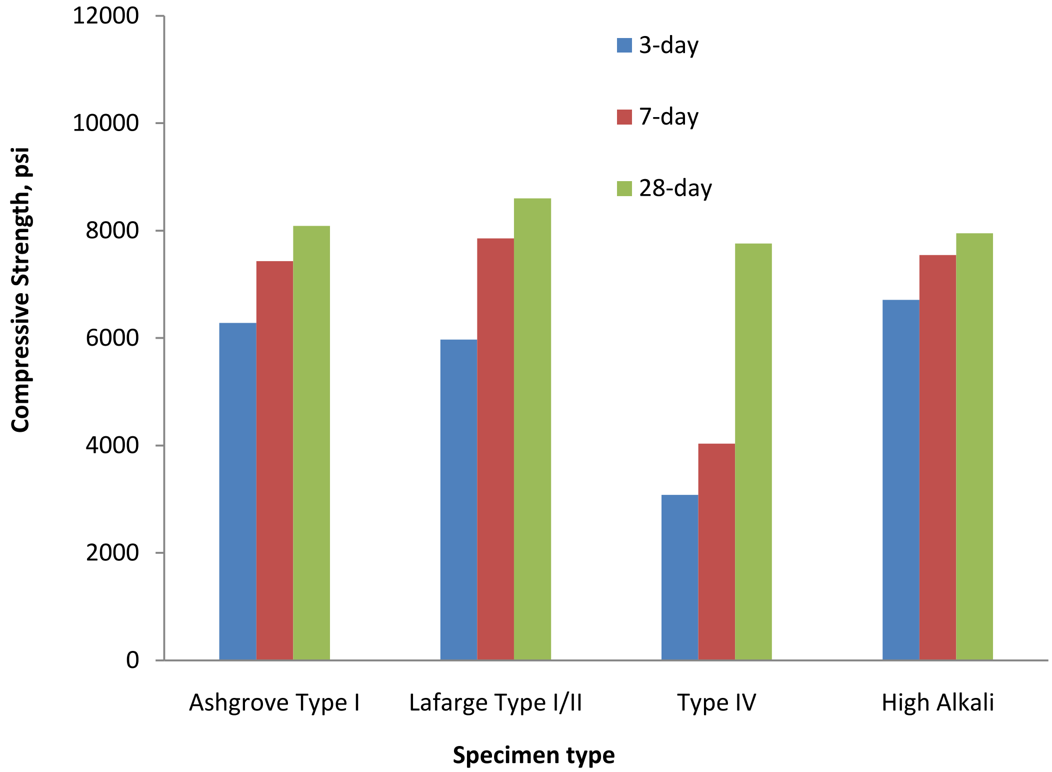

(a)


12000
10000
8000
6000
4000
2000
0
Compressive Strength, psi
3-day
7-day
28-day
56-day
OPC
PC+5%HRM
PC+10%HRM
PC+15%HRM
Specimen type

**(b)**


12000
10000
8000
6000
4000
2000
0
Compressive Stermgtj
3-day
7-day
28-day
56-day
OPC
PC+15% GCB
PC+25% GCB
PC+35% GCB
Specimen type

**(c)**




**(d)**

**Figure 6 - 1. (a) Compressive strength for pastes with Actigel addition; (b) Compressive strength for pastes with HRM replacement; (c) Compressive strength for pastes with GCB replacement; (d) Compressive strength for pastes made with different types of cement**

Figure 6-1 shows the compressive strength test results for paste samples with addition of Actigel, High Reactivity Metakaolin, and Ground Clay Brick replacement and cement paste made with different types of cement. From the test results, we can see that the Actigel addition had ability to increase the compressive strength of paste specimen. This might be due to that the smaller particle size of Actigel can create a more dense paste. Compared with Actigel, the replacement of HRM with high pozzolanic reactivity and finer particle size obviously increased compressive strength of paste specimens. However, concerning the replacement of Ground Clay Brick, although the early strength of specimens were much lower than pure cement pastes, the rate of compressive strength gain increased with curing age. Besides, it is expected that the later strength (91-day or 180-day compressive strength) of paste samples with GCB replacement might be comparable and even equal to the compressive strength of pure cement paste samples. For the pastes made with different types of cement, compressive strength of Ashgrove Type I cement and Lafarge Type I/II were similar with each other. Type IV cement gained much lower compressive strength at early age, however, the rate of strength gain at later age is high. This might be due to that lower $C_3A$ content result in a slow strength development at early stage. High Alkali cement gained more compressive strength than others at early stage, but the rate of strength gain is low. Thus, the 28-day compressive strength is closer to Ashgrove Type I and Lafarge Type I/II cement.

# Chapter 7 Conclusions and Recommendations

## 7.1 Conclusions

The main goal of the thesis is to investigate how clay addition/replacement and different types of cement affect the structural rebuilding of cement based materials. The major conclusions based on test results were made as follows:

(1) Clay addition/replacement and different cement composition had a significant effect on the thixotropic changing rate of cement based materials.

(2) Small amounts (0.5% -1%) of Actigel increased the thixotropic changing rate of cement paste, which is possibly due to the ultra fine particle size, charged particle morphology and high water absorption of Actigel. The particles tended to build up an interlocking and networking microstructure, increased the opportunities for solid particles to floc together and thus accelerated the thixotropic changing rate. However, over-dosage (larger than 1%) of Actigel tended to slow down thixotropic chaning rate. It is possible that not enough room for them to rearrange the particles orientation to form a card-house like microstructure.

(3) The replacement of High Reactivity Metakaolin significantly increased thixotropic changing rate of cement paste. The higher amount of replacement, the faster rate of thixotripic increasing rate can be obtained. The finer particle size and spiny needles-like microstructure with high specific surface area of HRM might contribute to the increasing rebuilding rate. Because paste was mixed depending on a mass-based theory, solid

volume significantly increased, which leads to closer distances between particles. More chemical contacting points and stronger attractive forces tended to rapidly increase the interparticle-bond and structure degree.

(4) Substitution of Ground Clay Brick slightly increased the thixotropic changing rate of cement paste, which is possibly contributed by the small specific gravity and high water absorbing ability.

(5) Compared to 25% GCB replacement, 1% Actigel addition or 10% HRM replacement of HRM can be used for field trial (slipform construction) due to that they have higher increasing rate of thixotropy, which is beneficial to obtain better shaper holding ability after mixing.

(6) Cement with high Alkali and $C_3A$ tended to gain higher thixotropic changing rate. Thus, highest rate of increasing thixotropy was obtained by High Alkali cement, which was followed by Lafarge Type I/II cement. The lowest rate was obtained by Type IV and Ashgrove Type I cement. The pore solution chemistry of cement with high alkali content tended to increase the bond strength of particles. Additionally, its higher alkali sulphate content leaded to increasing amount of prismatic crystals formation. These crystals effectively bridged and netted the microstructure of cement paste and acceleration of structural rebuilding was expected.

(7) Strong relationship exists between flow percent decreasing rate and thixotropic changing rate. It seems that faster flow percent decreasing rate indicated higher

thixotropic increasing rate. Besides, the increasing of thixotroy comes with decreasing flow percent.

(8) A good correlation between rate of heat generation and thixotropic changing rate was found. A higher heat generation rate can be related with faster structural rebuilding rate.

(9) Actigel and High Reactivity Metakaolin improved the compressive strength of cement paste while Ground Clay Brick decreased the early strength. However, as the increase of curing age, the strength gaining rate increased significantly. Ashgrove Type I cement and Lafarge Type I/II cement obtained similar mechanical performance. High Alkali cement gained higher early strength than others while Type IV cement gains much lower early strength. However, the strength gaining rate at later stage of Type IV was much higher.

## 7.2 Recommendations

The results from this thesis provided some information for the cement and concrete industry. The influence of clay addition/replacement and types of cement on structural rebuilding rate was analyzed. At the same time, rate of heat generation and flow percent decreasing of paste were also correlated with rheology tests. The following recommendations are proposed for the future development:

(1) Concrete industry not only focuses on cement paste because it has a complicated composition including aggregates and some other chemical admixtures. Therefore, more study should be developed for mortar and concrete in terms of structural rebuilding rate. This will provide more information in terms of predicting rheological behavior of fresh

concrete. A general model to describe structural rebuilding of concrete should be also considered as future research.

(2) Clay addition/replacement is always combined with different chemical admixtures in the field construction, such as Viscosity Modifying Agent and superplastisizers. Therefore, the interaction between clay and chemical admixtures deserves more emphasis.

(3) In order to verify influence of different clay addition/replacement on structural rebuilding rate, just Ashgrove Type I cement was used for mixing in this thesis. However, different types of cements (High Alkali cement or type IV) will be applied based on different construction purposes. Therefore, the interaction between clay addition/replacement and cement types should be paid more attention in future research.

# References

[1] G. H. Tattersall and P. F. G. Banfill, The Rheology of Fresh Concrete, First ed. Marshfield: Pitman Publishing Inc, 1983.

[2] Jones, T.E. R.; and Taylor, S., (1977), " Mathematical model relating the flow curve of a cement paste to its water/cement ratio", Magazine of Concrete Research, Vol. 29, No. 101, pp. 207-212.

[3] Banfill, P. F. G. (1994). "Rheological methods for assessing the flow properties of mortar and related materials", Construction and Building Materials, Vol. 8, No. 1, pp. 43-50

[4] A.M. Alshami, A.R. Sabouni and A.H. Bushlaibi, Influence of set retarding superplasticizer and microsilica on setting time of pastes at various temperatures, Cem Concr Res 23 (3) (1993), pp. 562–598.

[5] J.Y. Petit, E. Wirquin and B. Duthoit, Influence of temperature on the yield value of highly flowable micromortars made with sulfonate-based superplasticizer, Cem Concr Res 35 (2) (2005), pp. 256–266.

[6] Jolicoeur C, Sharman J, Otis N, Lebel A, Simard MA, Page M. The influence of temperature on the rheological properties of superplasticized cement pastes. In: Malhotra VM, editor. Proceedings 5th CANMET/ACI international conference on superplasticizers and other chemical admixtures in concrete. Rome: American Concrete Institute; 1997. p. 379–415.

[7] J. Golaszewki and J. Szwabowski, Influence of superplasticizer on rheological behavior of fresh cement mortars, Cem Concr Res 34 (2) (2003), pp. 235–248.

[8] Petit JY. Coupled effect of temperature, superplasticizers and mineral additions on rheological variations of cement-based micromortars and self consolidating concretes. Ph.D. Thesis, Béthune, University of Sherbrooke and Université d'Artois; 2005.

[9] Jean-Yves Petit, Eric Wirquin and Kamal H. Khayat, Effect of temperature on the rheology of flowable mortars, Cement and Concrete composites, Vol 32, Issue1, January 2010, Pages 45-53

[10] Chia, K. S.; and Zhang, M. H., (2004). " Effect of chemical admixtures on rheological parameters and stability of fresh lightweight aggregate concrete", Magazine of Concrete Research, Vol. 56, No. 8, pp. 465-473.

[11] Struble, L. J.; and Jiang, Q., (2004). "Effects of air entrainment on rheology", ACI Materials Journal, Vol. 101, No. 6, pp. 448-456

[12] Cry, M.; Legrand, C.; and Mouret, M., (2000). "Study of the shear thickening effect of superplasticizers on the rheological behavior of cement pastes containing or not mineral additives", Cement and Concrete Research, Vol. 30, no. 9, pp.1477-1483

[13] Pettet, S.; Palardy, D.; and Ballivy, G., (2000). " Rheological behavior and setting time of microfine cement-based grouts", ACI Materials Journal, Vol. 97, No.4, pp. 472-478.

[14] Lachemi, M.; Hossain, K. M. A.; Lambros, V. ; Nkinamubanzi, P. C.; and Bouzoubaa, N., (2004a). "Self-consolidating concrete incorporating new viscosity modifying admixtures", Cement and Concrete Research, Vol. 34, No.6, pp.917-926

[15] Assaad, J.; Khayat, K. H.; and Mesbah, H., (2003), "Assesment of thixotropy of flowable and self consolidating concrete", ACI Materials Journal, Vol. 100, No. 2, pp. 99-107

[16] Khayat, K. H.; and Yahia, A., (1997). "Effect of Eelan gem-high-range water reducer combinations on rheology of cement grout:, ACI Materials journal , Vol. 94, No. 5, pp. 365-372

[17] Lachemi, M.; Hossain, K. M. A.; V.; Nkinamubanzi, P. C.; and Bouzounaa, N., (2004b). "Performance of new viscosity modifying admixtures in enhancing the rheological properties of cement paste", Cement and Concrete Research, Vol. 34. No. 2, pp. 185-193

[18] Kamal, H. K., (1998). " Viscosity-enhancing admixtures for cement- based materials- An Overview", Cement and Concrete composites, Vol. 20, No. 2-3, pp.171-188

[19] Ferraris, C. F.; Obla, K. H.; and Hill R., (2001). " The influence of mineral admixtures on the rheology of cement paste and concrete", Cement and Concrete Research, Vol. 31, No. 2, pp. 245-255.

[20] Rudzinski, L., (1984). " Effect of fly ash on the rheological behavior of cement paste", Materiaux et Constructions, Materials and Structures, Vol. 17, No. 101, pp. 369-373

[21] Li, Y.; Zhou, S.; Yin, J.; and Gao, Y., (2004b). "The effect of fly ash on the fluidity of cement paste, Motar, and concrete", In: K. Wang, Ed. International Workshop on Sustainable Development and Concrete Technology, Beijing, China, May 20-21, 2004, CTRE

[22] Nehdi, M.; Mindess, S.; ad Aichin, P. C., (1998). " Rheology of high performance concrete: Effect of ultralfine particles", Cement and Concrete Research, Vol. 28, No. 5, pp, pp. 687-697

[23] R. Ferron, A. Gregori, Z. Sun and S.P. Shah, Rheological method to evaluate structural buildup in self consolidating concrete cement pastes, ACI Materials Journal 104 (3) (2007), pp. 242–250.

[24] P. Jarvis, B. Jefferson, J. Gregory and S.A. Parsons, A review of floc strength and breakage, Water Research 39 (14) (2005), pp. 3121–3137

[25] D.M. Liu, Theoretical determination of floc size in highly-concentrated zirconia-wax suspensions, Acta Materialia 50 (8) (2002), pp. 1927–1935.

[26] D.M. Liu, Particle packing and rheological property of highly-concentrated ceramic suspensions: $\phi_m$ determination and viscosity prediction, Journal of Materials Science 35 (21) (2000), pp. 5503–5507.

[27] S.B. Johnson, G.V. Franks, P.J. Scales, D.V. Boger and T.W. Healy, Surface chemistry–rheology relationships in concentrated mineral suspensions, International Journal of Mineral Processing 58 (1–4) (2000), pp. 267–304.

[28] G.H. Tattersall and P.F.G. Banfill, The Rheology of Fresh Concrete, Pitman Advanced Publishing Program, Boston (1983).

[29] R. Shaughnessy and P.E. Clark, The rheological behavior of fresh cement pastes, Cement and Concrete Research 18 (1988), pp. 327–341.

[30] K. Kuder and S.P. Shah,Rheology of extruded cement-based materials, ACI Materials Journal 104 (3) (2007), pp. 283–290.

[31] T. Voigt, T. Malonn and S.P. Shah, Green and early age compressive strength of extruded cement mortar monitored with compression tests and ultrasonic techniques, Cement and Concrete Research 36 (5) (2006), pp. 858–867.

[32] Nathan A. Tregger, Margaret E. Pakula and Surendra P. Shah, Influence of clays on the rheology of cement pastes, Cement and Concrete Research, Volume 40, Issue 3, March 2010, Pages 384-391

[33] G.H. Tattersall and P.F.G. Banfill. The Rheology of Fresh Concrete Pitman Advanced Publishing, Boston (1983).

[34] K. Sujata and H.M. Jennings, Formation of a protective layer during the hydration of cement. J Am Ceram Soc 75 6 (1992), pp. 1669–1673.

[35] M. Yang and H.M. Jennings, Influence of mixing methods on the microstructure and rheological behavior of cement paste. Advn Cem Bas Mat 2 (1995), pp. 70–78.

[36] J. Orban, P. Parcevaux, D. Guillot, Influence of shear history on the rheological properties of oil well cement slurries, in: Proc 8th Intl Cong Chem Cem, Rio de Janeiro. VI.3, 1986, pp. 243–247

[37] ] K. Asaga and D.M. Roy, Rheological properties of cement mixes V: The effects of time on viscometric properties of mixes containing superplasticizers; conclusions. Cem Con Res 10 (1980), pp. 287–295.

[38] R.A. Helmuth, Structure and rheology of fresh cement paste, in: Proc 7th Intl Cong Chem Cem, Paris, VI.0, 16, 1980, pp. 16–30.

[39] F.J. Tang and S. Bhattacharja. Development of an early stiffening test, Report RP46 Portland Cem Assoc, Skokie, IL (1997).

[40] Yang, M.; and Jennnings, H. M., (1995). " Influence of mixing methods on the microstructure and rheological behavior of cement paste", Advanced Cement Based Materials, Vol. 2 No. 2, pp. 70-78.

[41] Hu, C.; and de Larrard, F., (1996). " the rheology of fresh high performance concrete", Cement and Concrete Research, vol. 26, No. 2, pp. 283-294

[42] De Larrard, F.; Hu. C.; Sedran, T.; T.; Szitkar, J.; Joly, C. M.; Claux, F.; and Derkx, F., (1997). " A new rheometer for soft-to-fluid fresh concrete", ACI Materials Jounrnal, Vol. 94, No. 3, pp. 234-243

[43] Krstulovic, P.; and Juradin, S., (1999). "Modeling of fresh concrete behavior behavior under vibration", International Journal for Engineering Modeling, Vol. 12, No. 1, pp. 43-51

[44] Banfill, P. F. G.; Xu, Y.; and Domone, P. L. J., (1999). " Relationship between the rheology of unvibrated fresh concrete and its flow under vibration in a vertical pipe apparatus", Magazine of Concrete Research, Vol. 51, No. 3, pp. 181-190

[45] J. Mewis, J Non-Newton Fluid Mech 6 (1979), p. 1.

[46] H.A. Barnes, J Non-Newton Fluid Mech 70 (1997), p. 1

[47] E. Schalek and A. Szegvari, Kolloid-Z 32 (1923), p. 318 1923;33:326.

[48] A Saak, "Characterization and Modeling of Rheology of Cement Paste: With Applications toward Seld-Flowing Materials," Ph. D. Dissertation, Northwestern University, Evanston 2000

[49] J. Wallevik, "Rheology of Particle Suspensions," Ph. D. Dissertation, The Norwegian University of Science and Technology, Trondheim, Norway 2003.

[50] L. D. A. Schwartzentruber, R. Le Roy, and J. Cordin, "Rheological Behavior of Fresh Cement Pastes Formulated from a Self Compacting Concrete (SCC)," Cement and Concrete Research, Vol. 36, pp. 1203-1213, 2006

[51] C. H. Pierce, "Thixotropy of Oil Well Cement Slurries," Ph.D. Dissertation, Stanford university, Stanford 1940

[52] K. Khayat, M. Saric-Coric, and F. Liotta, "Influence of Thixotropy on Stability Characteristics of Cement Grout and Concrete," ACI Materials Journal, Vol.99, pp.234-241, 2002

[53] P.F.G. Banfill and D.C. Saunders, On the viscosimetric examination of cement pastes, Cem. Concr. Res. 11 (1981), pp. 363–370

[54] G. H. Tattersall, "Rheology of Portland Cement Paste,"British Journal of Applied Physics L2, vol. 6, pp. 165-167, 1955

[55] N. B. Ur'ev, R. L. Baru, A. P. Izhik, S. V. Choi, and V. V. Saskovets, "Rheology and Thixotropy of Cement-Water Siuspesions in the Presence of Superplasticizers," Colloid Journal of the Russian Academy of Sciences, vol. 59, pp. 773-779, 1997

[56] T.H. Phan, M. Chaouche, and M. Moranville, "Influence of organic admixtures on the rheological behaviour of cement pastes" Cement and Concrete Research, Vol 36, Issue 10, October 2006, Pages 1807-1813

[57] V. Petkova, and V. Samichkov, "Some influences on the thixotropy of composite slag Portland cement suspensions with secondary industrial waste" Construction and Building Materials, Vol. 21, Issue 7, July 2007, Pages 1520-1527

[58] Th. M. Salem, "Electrical conductivity and rheological properties of ordinary Portland cement–silica fume and calcium hydroxide–silica fume pastes" Cement and Concrete Research, Vol 32, Issue 9, September 2002, Pages1473-1481

[59] I. Janotka, F. Puertas, M. Palacios, M. Kuliffayov á and C. Varga, "Metakaolin sand–blended-cement pastes: Rheology, hydration process and mechanical properties" Construction and Building Materials, Volume 24, Issue 5, May 2010, Pages 791-802

[60] J. Assaad, "Formwork Pressure of Self Consolidating Concrete-Influence of Thixotropy," Ph.D. Dissertation, University de Sherbrooke (Quebec), Canada 2004.

[61] W.B. Russell, D.A. Saville and W.R. Schowalter. Colloidal Dispersions Cambridge University, Cambridge (1989).

[62] R.J. Hunter. Foundations of Colloid Science, Volume 1 Oxford University, New York (1987).

[63] L. J. Struble, The Rheology of Fresh Cement Paste, in Advances in Cemenitious Materials, v. 16 ed., S. Mindess, Ed., 1991, pp. 7-29.

[64] C. Plassard, E. Lesniewaska, I Pochard, and A. Nonat, "Nanoscale Experimental Investigattion of Particle Interaction at the Origin of the Cohesion of Cement," Langmuir, vol. 21, pp. 7263-7270, 2005.

[65] W.B. Russell, D.A. Saville and W.R. Schowalter. Colloidal Dispersions Cambridge University, Cambridge (1989).

[66] R.J. Hunter. Foundations of Colloid Science, Volume 1 Oxford University, New York (1987).

[67] J. T. G. Overbeek, "Recent Development in the Understanding of Colloid Stability," Journal of Colloid and Interface Science, Vol. 58 , pp. 408 -422, 1977

[68] M. Yang, C. M. Neubauer, and H. M. Jennings, "Interparticle Potential and Sedimentation Behavior of Cement Suspension: Review and Results from Paste," Advance Cement Based Materials, vol. 5, pp. 1-7, 1997

[69] Zeta –Meter Incorporation, "Zeta Potential: A Complete Course in 5 Minutes." Vol. 2005, Z.-M. Inc., Ed, 1998

[70] I. D. Morrison and S. Ross, Colloidal Dispersions: Suspensions, Emulsions, and Foams. New York: Wiley-Interscience, 2002.

[71] T.C. Powers, "The Properties of Fresh Concrete", Wiley, New York (1968).

[72] P.M. McGuiggan and J.N. Israelachvili, Short-range and adhesion forces between surfaces in aqueous electrolyte solutions: interplay of DLVO and hydration forces. In: A. Nonat and J.C. Mutin, Editors, Hydration and Setting of Cements, Proceedings of the International RILEM Workshop on Hydration and Setting, Dijon 1991, E&FN SPON, London (1992), pp. 205–217.

[73] H. Haidara, Fundamental mechanisms of adhesion: relevance to particle interactions, sticking and aggregation in a fluid medium. In: A. Nonat, Editor, Hydration and Setting — Why Does Cement Set? An Interdisciplinary Approach, Proceedings of the Second International RILEM Workshop, Dijon, 1997, RILEM Publications S.A.R.L., Cachan Cedex (2000), pp. 3–22.

[74] R.J. Flatt, Dispersion forces in cement suspensions, Cem. Concr. Res. 34 (3) (2004), pp. 399–408.

[75] A. Kauppi, P.F.G. Banfill, P. Bowen, L. Galmiche, Y.F. Houst, F. Lafuma, U. Mäder, F. Perche, B.G. Petersen, K. Reknes, I. Schober, A. Siebold and D. Swift,

Improved superplasticizers for high performance concrete, Proc. of the 11th ICCC, Durban, Techbook International, New Delhi, India (2003), pp. 528–537.

[76] H. Uchikawa, K. Ogawa and S. Uchida, Influence of character of clinker on the early hydration process and rheological property of cement paste, Cem. Concr. Res. 15 (4) (1985), pp. 561–572.

[77] P.F.G. Banfill, Simultaneous measurements of hydration rate and rheology on cement pastes. In: A. Nonat and J.C. Mutin, Editors, Hydration and Setting of Cements, Proceedings of the International RILEM Workshop on Hydration and Setting, Dijon 1991, E&FN SPON, London (1992), pp. 267–278.

[78] C. Rößler, A. Eberhardt, H. Kučerová and B. Möser , Influence of hydration on the fluidity of normal Portland cement pastes , Cement and Concrete Research, Volume 38, Issue 7, July 2008, Pages 897-906

[79] H.F.W. Taylor. Cement Chemistry Academic, London (1990).

[80] P.J. Andersen. Cem. Concr. Res. 16 (1986), pp. 931–940.

[81] H. Uchikawa, S. Hanehara and D. Sawaki. Cem. Concr. Res**.** 27 (1997), pp. 37–50.

[82] Christopher M. Neubauer, Ming Yang and Hamlin M. Jennings, Interparticle Potential and Sedimentation Behavior of Cement Suspensions: Effects of Admixtures, Advanced Cement Based Materials, Volume 8, Issue 1, July, Pages 17-27

[84] K. G. Kuder, N. Ozyurt, E.B. Mu, and S.P. Shah. " Rheology of Fiber-Reinforced Cementitious Materials," Cement and Concrete Research, Vol. 37, pp. 191-199 2007

[85] K.L. Konan, C. Peyratout, A. Smith, J.-P. Bonnet, S. Rossignol and S. Oyetola, "Comparison of surface properties between kaolin and metakaolin in concentrated lime solutions" , Jounral of Colloid and Interface Science, Vol. 339, Issue 1, November 2009, Pages 103-109

[86] G.Pan, M.-M. Zhang, H. Chen, H. Zou, and H. Yan, "Removal of Cyanobacterial Blooms in Taihu Lake Using Local Soils. I. Equilibrium and Kinetic Screening on the Flocculation of Microcystis Aeruginosa Using Commercially Available Clays and Minerals," Environmental Pollution, vol. 141, pp. 195-200,2006

[87] Fatih Bektas, "Use of ground clay brick as a supplementary cementitious material in concrete-hydration characteristics, mechanical properties, and ASR durability", Dissertation, Iowa State University, 2007.

[88] M.K. Lyon, D. W. Mead, R. E. Elliott, and L. G. Leal, “Structure Formation in Moderately Concentrated Viscoelastic Suspensions in Simple Shear Flow ,” Journal of Rheology, vol. 45. pp. 881-890,2001

[89] H. F. W. Taylor, Cement Chemistry, San Diego: Academic Press Inc., 1990

[90] C. Rößler, A. Eberhardt, H. Kučerová and B. Möser, “Influence of hydration on the fluidity of normal Portland cement pastes”, Cement and Concrete Research, vol. 38, issure 7, pp. 897-906, 2008

[91] Jiong Hu, “A study of effects of aggregate on concrete rheology”, Ph. D dissertation, Iowa State University, 2005

[92] ASTM C230 / C230M – 98, (2003). “Standard Specification for Flow Table for Use in Tests of Hydraulic Cement,” Annual Book of ASTM Standards, Vol. 04. 01

[93] ASTM C1437-01, (2003), “Standard Test Method for Flow of Hydraulic Cement mortar,” Annual Book of ASTM Standards, Vol. 04. 02

[94] ASTM C150 (2002). “Standard Specification for Portland Cement.” Annual Book of ASTM Standards, Vol. 04. 01

[95] Katherine G. Kuder, Nilufer Ozyurt , Edward B. Mu, Surendra P. Shah, “Rheology of fiber-reinforced cementitious materials”, Cement and Concrete Research, vol. 37 , pp.191–199, 2007