Cement and Concrete Research 53 (2013) 112–118

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Rate of thixotropic rebuilding of cement pastes modified with highly purified attapulgite clays

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ARTICLE INFO

Article history:
Received 26 December 2012
Accepted 28 May 2013
Available online xxxx

Keywords:
Clay (D)
Rheology (A)
Thixotropy (C)
Formwork pressure (E)
Oscillatory shear (B)

ABSTRACT

This study investigates the influence of highly purified, nano-sized attapulgite clays on the rate of structural rebuilding of cement pastes. A shear rheological protocol is implemented that measures the rate of rebuilding of pastes after being broken down under shear and maintained under stress corresponding to the weight of the material. This simulates a real casting situation during which the concrete is initially in motion, then cast in place and measures how quickly it gains green strength immediately after placement. The rate of recovery for different resting times and preshear conditions are considered. The strain rate decay curves are fitted with a compressed exponential model to obtain relaxation time. The results show that the purified attapulgite clays significantly accelerate rate of recovery of pastes, especially at early ages. However, this accelerating effect diminishes at longer resting times as hydration mechanisms begin to dominate.

1. Introduction

Self-consolidating concrete (SCC) improves constructability through its high flowability and superior segregation resistance. But despite its benefits, major issues include high transfer of lateral pressure to the formwork wall by SCC during casting and overall poor understanding of SCC formwork response, both of which can contribute to the possibility of formwork failure. Due to these reasons American Concrete Institute Committee 347, Formwork for Concrete, recommends that formwork be designed to withstand hydrostatic pressure. This raises the cost of formwork, which makes up a significant portion of the cost of construction. Therefore many studies have explored methods to tie the rheological behavior of SCC to formwork pressure response and strategies to reduce SCC formwork pressure through mix design [1–4].

It has been shown that it is possible to reduce formwork pressure through the use of mineral admixtures [5,6]. In one study by Kim et al., it was found that small additions of highly purified attapulgite clay can reduce the formwork pressure of SCC concrete mixes over time [7]. However, the physical origin of this effect is still not fully understood. A major factor affecting SCC formwork pressure is its level of thixotropy — rate of structural breakdown under shear followed by a recovery upon the removal of shear [8,9]. High rate of structural rebuilding indicates a rapid development of green strength (fresh-state stiffness) and subsequently greater reduction in lateral pressure on the formwork wall. Past studies have shown that clays can increase the flocculation strength and floc size of cementitious materials [10,11], which can explain its effect on the rheological properties. To tie it to formwork pressure, it is necessary to measure the effect of clays on the level and rate of thixotropic rebuilding. Many methods have been implemented to measure the thixotropic structural breakdown and recovery of cementitious materials [9,12–17]. For formwork pressure, it is of interest to determine the rate of rebuilding after shear and under an applied stress, which is the equivalent of casting during construction. Also, it is critical to know the change in the rate of flocculation at different ages of the material, as casting occurs over time.

In the present study, the effect of a highly purified attapulgite clay on the rate of structural rebuilding of cement pastes is investigated. A shear rheological protocol, adopted from a separate study [18], is implemented that measures the rate of structural rebuilding of pastes after being broken down under shear and maintained under stress corresponding to the weight of the material. This simulates a real casting situation during which the concrete is initially in motion, then cast in place and measures how quickly it gains green strength immediately after placement. This allows determination of the influence of clays on rebuilding when the material is essentially at rest but under stress corresponding to the weight of the material above the sample considered. Due to the effects of hydration, cementitious materials are both shear-history (thixotropy) and age dependent,

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0008-8846/$ – see front matter © 2013 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.cemconres.2013.05.019

particularly within the first few minutes. Therefore the effect of clays on the rate of recovery for different resting times and preshear conditions is considered. The strain rate decay curves are fitted with a compressed exponential model to obtain relaxation time, which will describe the influence of the various parameters on rate of structural recovery.

The present study is limited to the paste phase. Although there is a marked difference between paste and concrete rheology due to the presence of larger, inert particles in the latter, the time evolution of the rheological properties due to hydration mechanisms and thixotropic rebuilding are primarily tied to the paste phase. Therefore, how attapulgite clays alter the rheology of pastes will reflect how they will alter the fresh-state properties of concretes. And such results can subsequently help to further elucidate their effect on the formwork pressure response of SCC.

2. Materials and experimental methods

2.1. Materials

Tap water and type I Portland cement with a Blaine fineness of 385 m^2/kg are used in all mixes. A commercially available, highly purified form of the mineral attapulgite, or palygorskite, is the clay chosen for the study. They are chemically exfoliated from bulk attapulgite to remove impurities such as smectite, bentonite and other swelling clays, making them effective rheology-modifiers for various materials, including concretes. It is a rod-like nanoclay — 1.75 μm in average length and 3 nm in average diameter [19]. Given its high aspect ratio, it can form a gel even at small solid concentrations. Herein, the purified attapulgite clay will simply be referred to as "clay" or "nanoclay," but the results are for this specific type of clay and not necessarily representative of other types.

Cement paste mixes with a water-to-cement ratio of 0.43 by mass are tested. They are each prepared by hand-stirring for 60 s, then loaded in the rheometer and tested immediately after. Pastes with 0 and 0.5% nanoclay addition by mass of cement (labeled 0NC and 0.5NC, respectively) are tested. For the clay-modified pastes, the nanoclays are introduced as an aqueous suspension — the nanoclay is blended with the mixing water in a blender for 5 min to disperse.

2.2. Experimental methods

All rheological tests are performed on a Paar Physica MCR rheometer with a parallel-plate geometry. The top plate has a diameter of 50 mm and the bottom plate is temperature-controlled with a circulating water bath set to 20 °C. The surfaces of the plates are covered with 150-grit adhesive sandpaper to prevent slip. The measuring gap is 1 mm. All the measurements are performed at least three times in order to ensure the reproducibility of the results. Details on the experimental procedures can be found elsewhere [20].

2.2.1. Rate of structural recovery

To measure the effect of clays on rate of structural rebuilding, a rheological protocol is applied where the sample is initially sheared at a constant shear rate to break down its structure and then a fixed shear stress lower than its yield stress is applied. The strain rate decay provides a measure of the rate at which the material regains enough structure to resist the applied stress. The faster the rate of decay, the higher the rate of rebuilding and vice versa. The protocol is shown in Fig. 1. It is initially strain rate controlled, where a preshear is applied for 60 s. Then it switches to shear stress control and the strain rate decay is measured. The shear stress is applied until the strain rate reaches zero. A break criterion is defined in this step: when the shear rate becomes less than 0.01 s^{-1} (essentially zero) it skips to the next step or to the end of the test.

During the creep step, constant shear stresses of 20 and 30 Pa are applied, both of which are lower than the yield stress of the mixes tested. Due to hydration mechanisms, the rate of recovery will vary depending on the age of the sample and the shear condition. Therefore resting times of 0, 120, and 1800 s and shear rates of 50 and 300 s^{-1} are considered. For the cases of 120 and 1800 s resting time, the preshear at the beginning of the test is always set to 50 s^{-1} (to ensure all mixes start with the same shear history before the rest period) and only the preshear in the step prior to the creep step is varied.

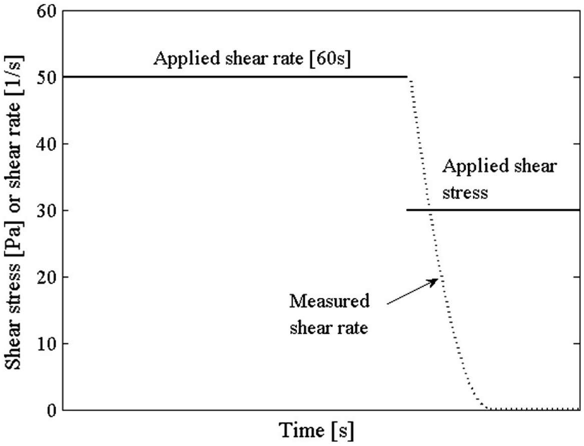

Fig. 1. Shear rheological protocol to measure strain rate decay during creep.

2.2.2. Yield stress

In the shear rheological protocol for obtaining relaxation time, the applied shear stress must be less than the yield stress. Therefore it is necessary to determine the yield stress of the paste samples. This is done through the protocol shown in Fig. 2. The applied shear stress is incrementally increased (by 10 Pa) until the shear rate no longer reaches zero (the material cannot rebuild enough structure to resist the applied stress). When shear rate diverges away from zero, the yield stress has been exceeded.

2.2.3. Low-amplitude oscillatory shear rheometry

The structural evolution of the pastes is obtained through low-amplitude oscillatory shear rheometry, a method that provides a measure of the viscoelastic properties of suspensions. It has been demonstrated to be applicable to fresh cement paste and the details of the test can be found elsewhere [21].

Oscillatory strain is applied as a sine function:

$$\gamma = \gamma_0 \sin \omega t \quad (1)$$

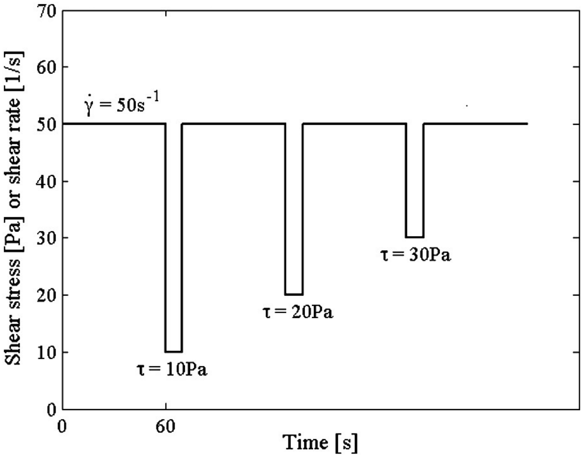

Fig. 2. Shear rheological protocol to measure yield stress.

where γ_0 is maximum strain amplitude, t is time, and ω is frequency. If the strain is sufficiently low, the material will recover elastically. The measured response in terms of stress is as follows:

$$\tau(t) = \gamma_0\left(G' \sin \omega t + G'' \cos\omega t\right) \tag{2}$$

where τ is shear stress, G' is storage modulus, and G'' is loss modulus. G' is the elastic component while G'' is the viscous component. A strain amplitude of 0.0001 and a frequency of 1 Hz are found to be within the linear viscoelastic region and are applied to find the evolution of G' and G'' of the pastes.

3. Results and discussion

3.1. Yield stress

The yield stress of each mix is determined by incrementally increasing shear stress between shearing steps. The results for cement paste mixes with 0 and 0.5% nanoclay addition subjected to a shear rate of 50 s^{-1} are shown in Fig. 3A and B, respectively. The figures show the evolution of shear rate decay for each applied shear stress. (Note: For the 0.5% nanoclay cement paste, only the curves for select shear stresses are plotted, although shear stress was incrementally increased by 10 Pa.) For the plain cement paste, the shear rate begins to diverge from zero at 40 Pa. Therefore the yield stress is considered to be between 30 and 40 Pa. For 0.5% nanoclay cement paste, the yield stress is between 140 and 150 Pa. In the rheological protocol to measure structural recovery, the applied shear stress must be the same for all mixes and less than the yield stress of each mix. Since the plain cement paste has the lower yield stress, it governs — for the shear condition of 50 s^{-1} the applied shear stresses are 20 and 30 Pa. Similar steps are taken for 300 s^{-1} shear and the applied shear stresses are selected to be 20 and 30 Pa, as well.

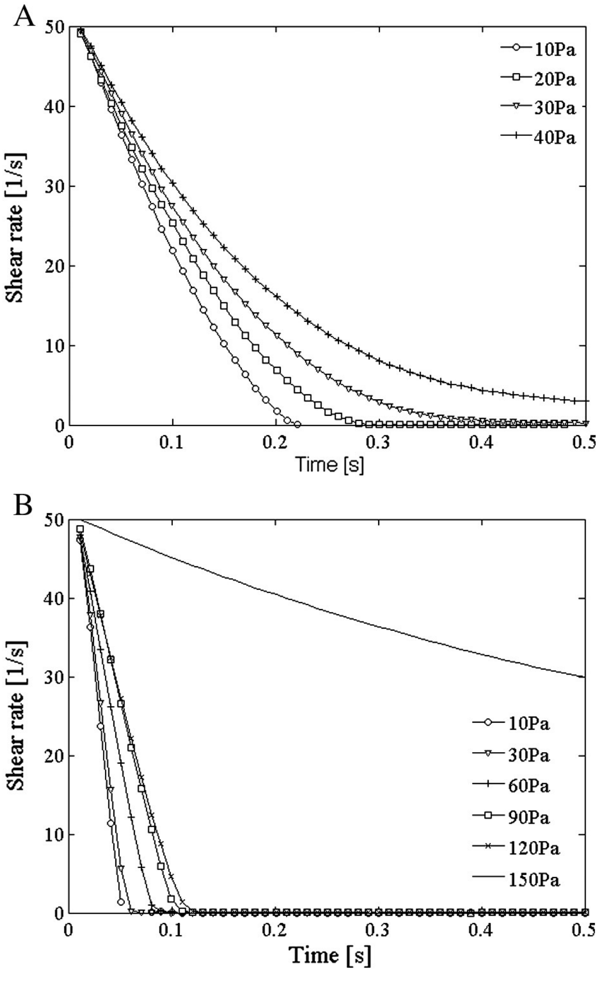

Fig. 3. Results of shear rheological protocol to determine yield stress for cement pastes with A) 0% and B) 0.5% nanoclay addition subjected to 50s^{-1} shear [20].

3.2. Rate of structural recovery

The decay in strain rate of cement pastes with and without a 0.5% nanoclay addition after being subjected to two different preshear rates (50 and 300 s^{-1}) for various resting times are determined for applied shear stresses of 20 and 30 Pa. The decay in shear rate is due to the structural rebuilding of the material over time. Once sufficient structural recovery is achieved to resist the applied stress, the shear rate goes to zero. It is shown that the strain rate decay during the creep step can be fitted fairly well with the following exponential model:

$$\dot{\gamma}(t) = \dot{\gamma}_0{}^* \exp\left[-(t/\tau)^r\right] \tag{3}$$

where t is time, τ is an average relaxation time, and r is a dimensionless exponent. In many cases the stretched exponential, where $0 < r < 1$, has been used to model stress relaxation of suspensions, including viscoelastic and thixotropic materials [22–27]. For a system with a single relaxation time, which would characterize an aqueous monodisperse suspension, $r = 1$. However, in systems with a distribution of particle or floc sizes, as in the case for colloidal or granular suspensions, there will be a distribution of relaxation times. And the width of the relaxation time distribution can be described by r. Small values of r indicate that the relaxation rate becomes increasingly small (compared to a simple exponential) while the property of interest (shear-rate or shear-stress) goes to zero. To illustrate such behavior, the evolution of the shear-stress versus time during the preshear period of the protocol, as represented in Fig. 2, for cement pastes with and without nanoclay are presented in Fig. 4.

Fig. 4A represents the stress transient behavior in the case of preshear at 50 s^{-1} and Fig. 4B represents the case of preshear at 300 s^{-1}. The transient curves can be fitted fairly well with a stretched exponential. The fitting parameters including the relaxation time τ and the stretching exponent r are reported in Table 1. For a flocculated suspension such as cement paste, stretched exponential-like breakdown kinetics is expected. Indeed, for a given shear-rate it becomes increasingly difficult to break the flocs as they become increasingly small since the experienced hydrodynamic torque scales with the size of the floc [28]. Table 1 shows that both the stretching exponents and the relaxation times are small, indicating that the breakdown kinetics is much slower than an exponential. Previously published breakdown experiments on flocculated dispersions reported significantly higher stretching exponents [29]. The particularly slow kinetics of the stress decay is probably due to the interference of the hydration phenomenon, as discussed below when considering the rebuilding phase.

The rebuilding kinetics under an applied stress following preshear (i.e. creep step) is qualitatively different from the breakdown kinetics during the preshear phase. Indeed in this case, the strain rate decay rather follows a compressed exponential, where $r > 1$. The kinetics in this case are faster than an exponential. Compressed exponential behavior is much less frequent than stretched exponential behavior. Although it has been experimentally found in a few cases in glasses and jammed granular materials, including clay suspensions [30–33], to the best of the authors' knowledge it has never been reported for cementitious materials. The behavior of the cement pastes during the rebuilding process after shear can actually be considered to be akin to a jammed system since the relaxation is towards a yield stress state. The more the system approaches the yield stress state, the faster the shear rate goes to zero. The shear rate decay is then expected

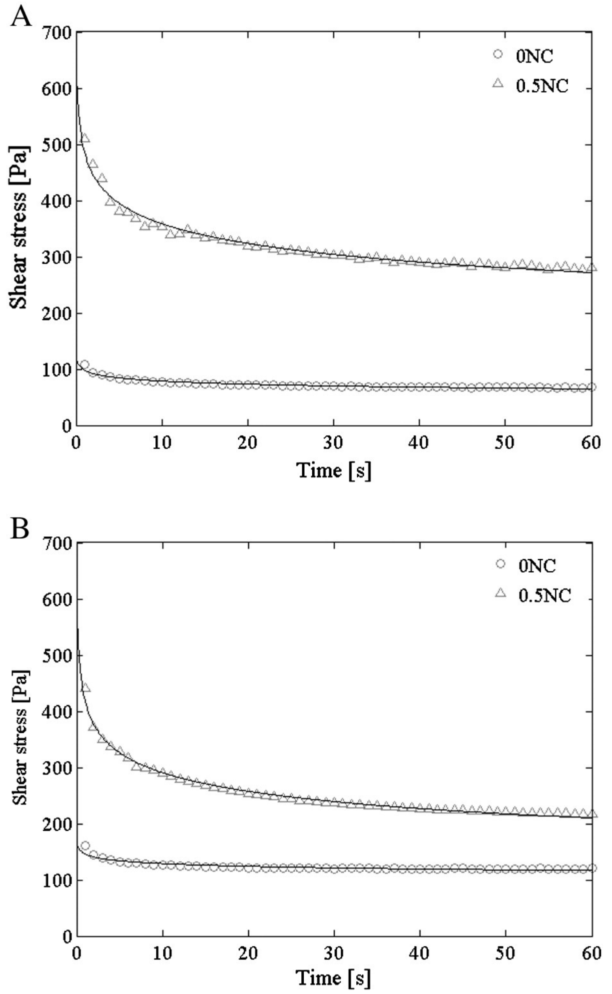

Fig. 4. Shear-stress decrease kinetics under a constant applied shear-rate [20]: (A) 50s^{-1}; (B) 300 s^{-1}.

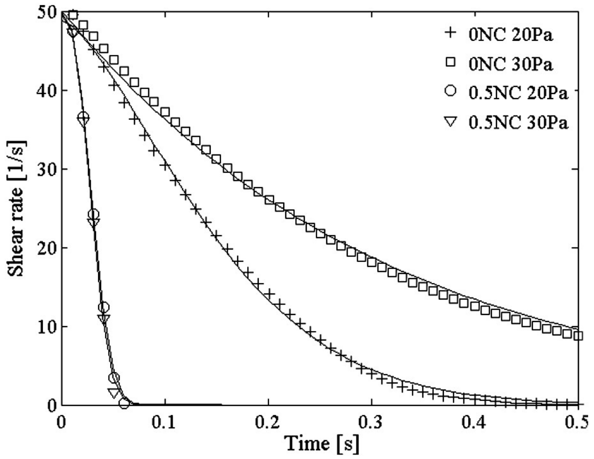

Fig. 5. Strain rate decay of cement pastes after 50 s^{-1} preshear with fitted compressed exponential [20].

to relax faster than a simple exponential, that is compressed exponential-like.

The strain rate decays during the creep step with the fitted compressed exponential are shown in Fig. 5 and the corresponding parameters are given in Table 2. It is apparent that the clay-modified pastes exhibit smaller τ and higher r than the plain cement pastes. This indicates that the clays are in a more jammed state and thereby can exhibit higher rate of rebuilding immediately after shear. The exact mechanisms underlying this behavior are unclear. It may be tied to the flocculation behavior of the clays. Immediately after cement makes contact with water, the tricalcium silicate (C_3S) phase rapidly releases calcium and hydroxide ions. As a result, the ionic strength and pH of the pore solution will increase. This will heavily influence the flocculation behavior of clays given that they are highly charged particles. They possess negatively charged faces and positively charged edges, which make them prone to form "house of cards" or scaffolding structures in aqueous suspensions. In a study on the effect of pH and ionic concentration on the stability of attapulgite aqueous suspensions, Chang et al. found that high ionic concentration, at low and high pH, led to high viscosity [34]. This was attributed to the shrinkage of the electrical double layer around the clay particle surfaces. Subsequently, the electrical double layer repulsion decreases and flocculation will occur due to van der Waals attractions [35]. Therefore clays can expect to flocculate in pore solution, which has been confirmed by previous studies [10,11]. However, given that the clays in this study are highly purified attapulgite, their behavior may be different from those reported in other studies. It is possible for them to exhibit high colloidal stability and form a gel in the pore solution, which can effectively increase the apparent rate of rebuilding of the system. To better understand the mechanisms underlying the effect of purified attapulgite on the thixotropy of cementitious systems, more investigation is needed.

In addition, there may be a particle size (and shape) effect. In a study by Kaci et al., the influence of bentonite clays on the rate of structural rebuilding of cement mortars was investigated [18]. Bentonite clays were found to decrease relaxation time, as well, but the effect was not as significant as the one observed here. The nanoclays can reduce relaxation time by nearly a factor of 10 (see Table 2 for applied shear stress of 30 Pa) while the bentonite clays reduced it only by about a factor of 2. The clays in the present study are very fine and have a rod-like shape, which give them a high aspect ratio. The bentonite clays considered in the study of Kaci et al., on the other hand, were likely microsized since there was no specific consideration of the dispersion issue. The high specific surface area of attapulgite in combination with their fine size will lead to higher surface forces between particles. Also, they can provide more contact points within the material and make its structure more interconnected.

It can be noticed (in Table 2) that the relaxation time of the cement pastes without nanoclay increases with applied stress (slowdown of recovery kinetics). In addition, the rebuilding kinetics becomes exponential-like when the applied stress is increased. This can be attributed to the fact that the applied stress becomes close to the material yield stress and the system is then less jammed. We do not observe this trend in the case of clay-modified paste since the applied stress is still far from the material's yield stress.

Table 1
Fitting parameters in stretched exponential model for shear-stress decay of pastes subjected to a fixed shear-rate [20].

	0NC		0.5NC	
Applied shear rate. s^{-1}	tau, s	r	tau, s	r
50	9.3e−06	0.051	9.1e-03	0.081
300	1.7e−06	0.033	3.3e-03	0.086

Table 2
Fitting parameters in compressed exponential model for strain rate decay of pastes after 50 s^{-1} preshear [20].

	0NC		0.5NC	
Applied shear stress, Pa	tau, s	r	tau, s	r
20	0.169	1.51	0.0351	2.43
30	0.306	1.02	0.0341	2.52

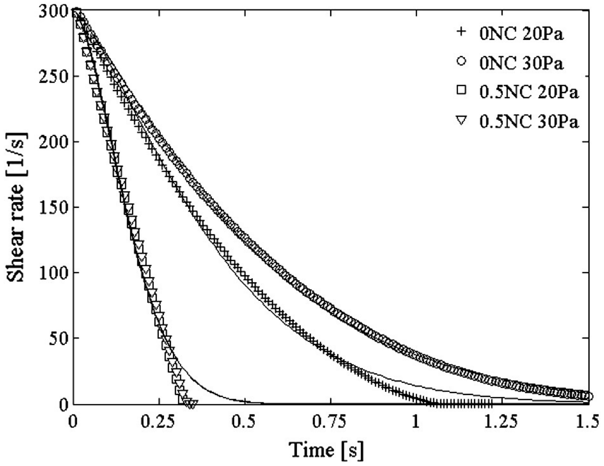

Fig. 6. Strain rate decay of cement pastes after 300 s^{-1} preshear with fitted compressed exponential [20].

3.2.1. Influence of applied rate of preshear

In the results presented thus far, the pastes are subjected to 50 s^{-1} shear leading up to the creep step. To determine the influence of shear condition, the above results are compared against pastes that are subjected to a higher shear of 300 s^{-1}. The strain rate decay is shown in Fig. 6 and the corresponding fitting parameters are shown in Table 3. For the results of pastes subjected to 300 s^{-1}, the fit starts to diverge at the tail, between 50 and 0 s^{-1}, especially in the case of clay-modified pastes. It is apparent that there is a change in the dynamics of the rebuilding process. This is likely due to the different average relaxation times of the two main constituents, i.e. clay and cement. Other studies have found this, as well [32,36]. The same is not observed in the decay from 50 s^{-1}, even in the case for clay-modified pastes, because the relaxation time of the cement was not in the order of the relaxation time of the entire paste system.

Two curves are necessary to fit the complete decay from 300 s^{-1} and the results for the branch from 50 to 0 s^{-1} are shown in Table 4. For both mixes with and without clays, the characteristic times are longer for pastes sheared at 300 s^{-1} (Table 4) compared to those sheared at 50 s^{-1} (Table 2). The pastes subjected to a higher preshear will undergo a higher degree of deflocculation. As a result, during the creep step the pastes must recover more structure in order to resist the applied shear stress.

3.2.2. Influence of resting time

In the previous section, the difference in rate of recovery at 0 s is compared between cement pastes with and without clays. Since the material is time dependent due to cement hydration, it is worth considering the thixotropic properties at different paste ages. Here, the evolution of rate of recovery over cement paste ages up to 1800 s is discussed. For all the ages considered, the rebuilding kinetics can be well described by a compressed exponential, as previously. The evolution of relaxation time after a 50 s^{-1} shear for pastes with and without clay under two different applied stresses is shown in Fig. 7. In plain cement pastes, the relaxation time consistently decreases for both stress conditions. This indicates that the material is approaching an increasingly jammed state during aging. The evolution of relaxation time versus age is qualitatively different for the clay-modified pastes. In this case a slight increase in relaxation time is obtained, indicating reduced rate of recovery. The evolution of relaxation time versus age can be explained by discussing the progression of hydration.

Table 3
Fitting parameters in compressed exponential model for strain rate decay of pastes after 300 s^{-1} preshear [20].

	0NC		0.5NC	
Applied shear stress, Pa	tau, s	r	tau, s	r
20	0.44	1.36	0.189	1.66
30	0.551	1.23	0.191	1.7

Table 4
Fitting parameters in compressed exponential model for strain rate decay of pastes after 300 s^{-1} preshear [20]: fitting from 50 to 0 s^{-1}.

	0NC		0.5NC	
Applied shear stress, Pa	tau, s	r	tau, s	r
20	0.189	1.62	0.0495	2.35
30	0.319	1.08	0.0463	2.24

To obtain a measure of fresh-state stiffening due to early hydration, low-amplitude oscillatory shear rheometry tests are performed on the pastes. Monitoring the storage modulus can provide a measure of the development of the fresh-state connected structure of pastes over time. The same preshear is applied as that for the rate of recovery protocol (50 s^{-1} for 60 s) and oscillatory shear measurements are taken immediately after. The evolution of storage modulus and loss modulus for the pastes over 1800 s (the duration of the rate of rebuilding test) is shown in Fig. 8. The results indicate that very early on the clay-modified paste exhibits higher storage modulus than the plain cement paste, at least up to 600 s. This agrees well with the relaxation curves, where clays lead to faster relaxation times at 0 and 120 s. By 1800 s, the plain cement paste exhibits a slightly higher storage modulus. Similarly, it experiences a faster rate of recovery, as indicated by the shorter relaxation time observed at this age, as shown in Fig. 7.

Clay-modified pastes exhibit high rate of recovery and higher storage modulus from the beginning (0 s) because the clays have an immediate effect during initial hydrolysis, as discussed previously. In the case of plain cement paste, its degree of flocculation (and subsequently rate of recovery) is highly dependent on the formation of early hydrates. During the dormant period, hydrates such as ettringite will precipitate and early C-S-H gels will start to form around cement grains [37–39]. Both will contribute to the formation of a gel-like network within the pore solution and lead to a higher flocculation rate. Other studies have shown that at later ages the effects of hydration begin to dominate [13,14]. This may be why after longer resting times (1800 s) the plain cement pastes go on to exhibit comparable or faster rate of rebuilding compared to the clay-modified pastes. Another possible explanation is that the clays are having a detrimental effect on hydration during this period. This may be attributed to its high water adsorption capacity, which can be hindering the development of the early hydrates. Also, it is possible that the nanoclays are

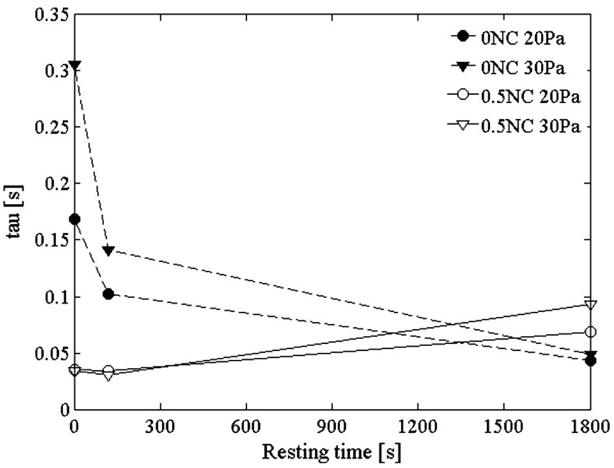

Fig. 7. Evolution of relaxation time versus age for cement pastes subjected to 50 s^{-1} shear [20].

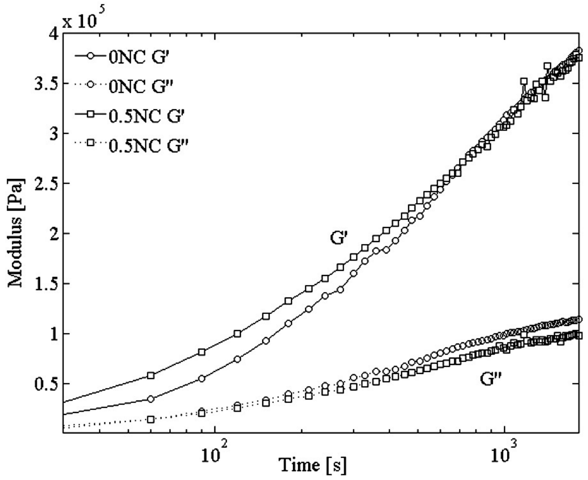

Fig. 8. Evolution of storage modulus (G′) and loss modulus (G″) for cement pastes subjected to 50 s^{-1} shear [20].

interacting with ettringite and/or other early hydrates. Ettringite carries a positive charge while the nanoclays have negatively charged sides. Therefore it may be possible for the two particles to be flocculating. This results in less nanoclays to be available in the rest of the system to continue to contribute to structural rebuilding over time. Looking at the oscillatory shear results, the storage modulus of the plain cement paste starts to exceed that of the clay-modified paste around 10 min. This corresponds well with the formation of ettringite, which is known to occur within the first 10 min of initial cement and water contact [38]. This can be further investigated by testing different parameters such as nanoclay dosage and chemical/mineral admixture types on the rate of recovery of pastes over time, which will be pursued in future work.

Looking at the influence of both shear rate and time, Fig. 9 shows the evolution of relaxation time for pastes subjected to 50 and 300 s^{-1} preshear rates. In most cases, the relaxation time is longer after a 300 s^{-1} shear. As discussed prior, this is due to the increased breakdown the pastes experience after a higher shear. Interestingly, this effect is the most pronounced after an 1800 s resting time. This may be explained by the change in the degree of reversible versus irreversible changes within the material [40]. At 0 s, it is reasonable to assume that flocculation behavior is governed by van der Waals attraction and electrostatic repulsion, in which case most of the changes that occur during shearing are reversible. Over time, hydration mechanisms become an increasing factor, where the development of hydrates (e.g. AFt and C-S-H gel) will contribute to flocculation, as well. These are irreversible changes that result in irreversible breakdown under shear. By 1800 s, the pastes develop a more interconnected network and shearing at a higher rate will result in a higher number of permanent link breakages than at a lower rate. It follows that the influence of shear rate will increase over time as the mechanisms of flocculation change, transitioning from reversible to irreversible coagulation and breakdown.

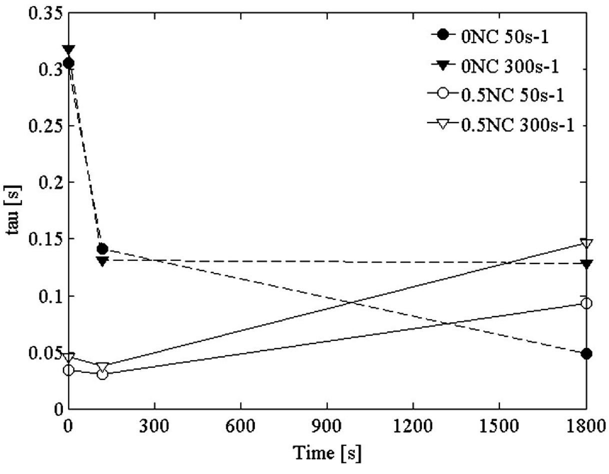

Fig. 9. Influence of preshear on evolution of relaxation time of pastes subjected to 30 Pa stress [20].

4. Conclusions

The influence of clays on the rate of recovery of pastes is evaluated through comparing strain rate decay curves and relaxation time. The results show that the rate of recovery after shear-induced breakdown exhibited by the clay-modified pastes is very rapid compared to the plain cement pastes, especially at early ages (0 and 120 s resting times). However, the accelerating effect of clays on rate of recovery diminishes at longer resting times (1800 s) as hydration mechanisms begin to dominate. This may also be tied to negative effects of clays on hydration due to their high water adsorption, or possible interaction between the clays and ettringite. In all pastes, higher shear leads to longer relaxation times. This is due to the increased degree of structural breakdown the material undergoes and subsequent increase in the recovery necessary. Over time, this effect becomes more pronounced. This may be due to the transition from reversible to irreversible coagulation and breakdown within the material.

Acknowledgments

The authors would like to acknowledge the financial support from the Infrastructure Technology Institute at Northwestern University, Tennessee Valley Authority (TVA) and Oak Ridge Associated Universities (ORAU) (Award 105866); and Active Minerals, WR Grace and Lafarge for providing materials.

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