

The influence of hormitic clay on the time dependent properties of formulated gypsum plaster pastes

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When a new product is in development or an existing product is being improved, unforeseen complications may arise in terms its rheological performance. The objective of the work was to determine the cause of an unwanted rheological phenomenon that will be referred to as 'viscosity drift.' The work involved experimental design, viscosity as a function of time at a constant shear rate, and pH as a function of time. Organically modified hormitic clay was the sole influence on the viscosity drift exhibited by the plaster pastes. It was determined that setting was not the mechanism by which the clay caused the viscosity to drift. It was, however, established that a structure was being developed within the plaster paste, specifically a clay network. © 2003 Kluwer Academic Publishers

1. Introduction

Manufacturers of gypsum plaster products are often overwhelmed with the effects of numerous additives on the rheological properties of their plasters. This is common when a new product is being developed or an existing product is being improved.

A typical commercial gypsum plaster formulation can contain several classes of additives, such as clays, cellulose ethers, and polymeric binders, to name a few. Some of these additives introduce various undesirable rheological effects to a plaster paste with relatively small variations to their concentrations.

Unwanted thixotropic and anti-thixotropic behaviour was observed in some gypsum plaster paste samples, the cause of which was initially unknown. Rheological behaviour is one of the most important aspects of plaster manufacturing and an unknown variation in rheological behaviour can reduce product performance.

Time dependent effects such as thixotropy have been examined extensively [1, 2] in various fluids. Some work has been done on the thixotropic nature of gypsum in non-formulated plaster pastes [3], along with work covering the physical properties of gypsum plaster with the addition of clay materials [4]. However, a void exists in the study of the relationship between industry relevant additives and their effects on the time dependent rheology of formulated gypsum plaster pastes.

The objective of the work was to determine the cause of an unwanted, time dependent rheological phenomenon that will be referred to as 'viscosity drift.' The work involved experimental design, viscosity as a function of time (at a constant shear rate), and pH as a function of time. An overall objective of the

work was to link rheological behaviour with molecular interactivity, since work in this particular field is limited in the area of formulated gypsum plaster pastes.

2. Experimental

2.1. Materials

The materials used in this investigation consisted of gypsum plaster (calcium sulphate hemihydrate, $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) that was modified using six different additives; two cellulose ether thickeners, two polymeric binders, a hormitic clay, and hydrated lime. The formulated plaster also contained setting retardants, calcium carbonate and several other additives that were not examined in this paper. To avoid batch variation in the gypsum plaster the one batch was used for all of the laboratory work. Distilled water was used throughout the laboratory work.

The type of clay used was an organically modified, needle or fibrous-like clay [5], also known as an organoclay. Organoclays consist of a mineral component, or substrate, and an ionically bonded organic component. In the raw state the agglomerated mineral component is hydrophilic and will deagglomerate upon the addition of water [5]. The organic component is typically a quaternary amine compound which when reacted with the clay converts it from hydrophilic to a hydrophobic material [5]. A typical example of quaternary amine compound can be seen in Fig. 1. It should be pointed out that the fatty acid radical (long hydrocarbon chain) in Fig. 1 is the hydrophobic end that extends from and covers the surface of the clay, thus making it hydrophobic.

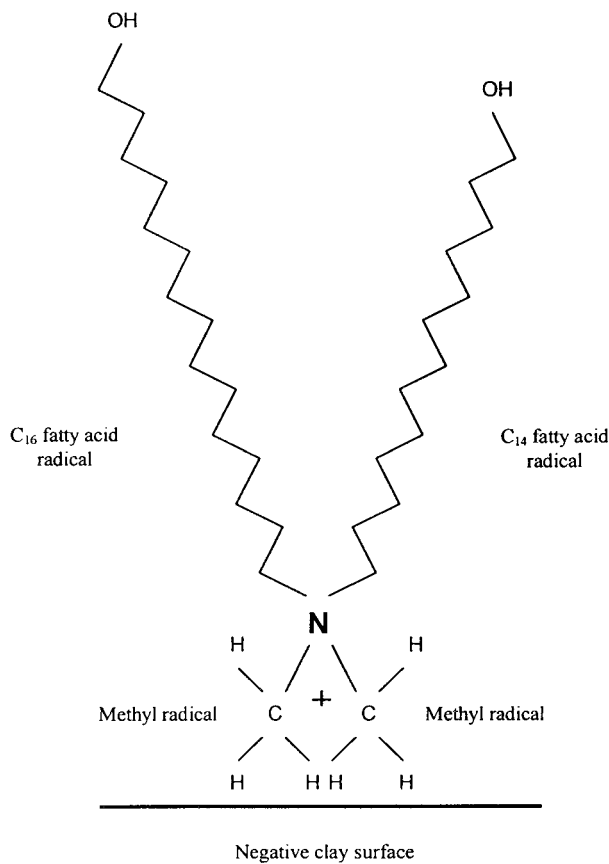


Figure 1 A quaternary amine compound attached to hormitic clay surface [adapted from Newman and Brown, 1987].

2.2. Sample preparation and equipment

The gypsum plaster and additives were individually weighed in a vessel to make up a 100 g sample. The constituents were weighed in a certain order as specified by the manufacturer. Before water was added to the dry powders the vessel was sealed and agitated for 1 min. Distilled water was then added to the dry plaster powder and allowed to soak into it for a further minute, this allowed for easier and lump-free mixing. The mixture was then mixed at 100 rpm for 1 min using a U-shaped paddle stirrer attached to an overhead, torque controlled laboratory mixer. It should be pointed out that prior to mixing, the contents of the vessel were not transferred to another vessel, and this ensured that none of the sample was lost during preparation. The speed and duration of mixing was pre-determined through preliminary tests on the basis that the paste should not be exposed to unnecessarily high shear rates, but still being sufficiently high enough to provide adequate mixing. Previous papers on gypsum plaster were also in agreement with this mixer speed [3, 6]. The mixing speed was held at a constant 100 rpm throughout all experiments since any variation in the mixing rate could lead to experimental error [4, 7].

Rheological measurements were carried out using a Contraves Rheomat 115 controlled shear rate rheometer. Viscosity as a function of time was measured using couette geometry, with a profiled bob to minimise the effects of slip. It was determined in preliminary work that slip was effectively eliminated, in most cases, using a profiled edge bob. Slip analysis involved using

a two-geometry couette system with the same concentric cylinder ratio [8]. The viscosity as a function of time measurements was carried out at a constant and arbitrary shear rate of 0.75 s^{-1} .

Shear stress as a function of time at constant shear rate was also measured using the same equipment, geometry and shear rate as used for the viscosity measurements.

Finally, the pH was measured using an Orion 290A pH meter exactly 2 min after the plaster pastes were mixed and subsequently measured every minute for 35 min which is the approximate plaster setting time (in this case).

2.3. Experimental design

Experimental design is a branch of statistics that is very useful to research involving multivariable experiments [9]. A fractional factorial design was developed to quantitatively investigate the effects of 6 factors (variables), in this case additive concentrations, on the properties of gypsum plaster pastes. Specifically the factorial design provided all of the possible combinations of 6 different factors, held at two levels-low and high concentrations. Furthermore, experimental design quantifies interactive effects of additives, however the type of interaction measured depends on the type of design that is selected [9].

The factors were clay, thickener B, thickener C, binder D, binder E, and lime concentrations. All other factors such as temperature, water/plaster ratio and mixing speed were held constant (20°C , 60, and 100 rpm respectively).

A resolution VI (high resolution) design was selected for this investigation. This provided clear main effects, i.e., non-interactive, and also two-factor interactions. However three factor interactions were undeterminable, from one other three-factor interaction. In other words the effect of one three-factor interaction was the same as that of another three-factor interaction and therefore indistinguishable.

The factorial design was fractioned by one half, meaning that only half of the 64 required number of runs (not including replicates) were needed to be completed to obtain the necessary results for analysis. The fractional factorial design can also be written as Equation 1.

$$2_{\text{VI}}^{6-1} = 32 \text{ runs} \quad (1)$$

Furthermore, all results were randomised to prevent systematic bias [10] and results were repeated up to 4 times to ensure repeatability and hence valid results. Analysis of the results was performed using a Minitab statistical software package.

3. Results and discussion

Several batches of the same formulation of a commercial plaster powder were examined to determine whether there was any rheological variability from batch-to-batch. The purpose of this exercise was to

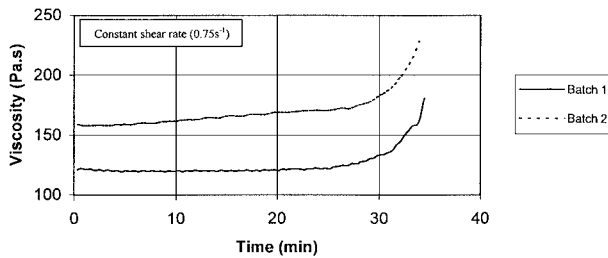


Figure 2 Two distinct trends between batches of the same formulated plasters at a constant shear rate of 0.75 s^{-1} .

eliminate a possible source of error when conducting rheological tests. As expected there was wide variation in viscosity data between individual batches of the same formulation. Four separate batches were received over almost one-year, all of which displayed one of two distinct trends that became apparent in all of the samples that were tested as shown in Fig. 2.

In Fig. 2 the plaster pastes can be seen to set shortly after 25 min, as expected. However, between 0 and 25 min the viscosity of batch 2 increases constantly or 'drifts' whereas the viscosity of batch 1 (between the same time interval) remains constant with time. This constantly increasing viscosity at a constant shear rate (of 0.75 s^{-1}) seen in batch 2 is an undesirable characteristic of a plaster paste. It was later discovered that some plaster formulations decreased constantly in viscosity with constant shear rate. Results such as in Fig. 2 prompted further work to determine the cause of this effect.

Due to the large number of additives that the formulated plaster contained it was necessary to develop a fractional factorial design. The statistically designed experiment could monitor 6 different variables (factors), in this case the concentrations of clay, thickener B, thickener C, binder D, binder E and lime. The experimental design measured the response of altering the concentrations of these factors on the viscosity of the plaster pastes as a function of time.

Statistical analysis such as this required data in the form of a single datum point, in this case the gradient of a viscosity as function of time graph was used as a measure of the effect that a particular additive may exert. Fig. 3 is an example of such a graph that depicts the viscosity as having a positive gradient with respect to time and a constant shear rate of 0.75 s^{-1} . Gradients were usually taken between 10 and

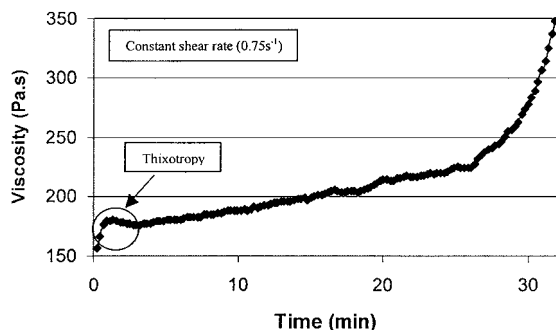


Figure 3 One of thirty-two graphs from which the gradient was obtained between the time interval of 10 and 20 min.

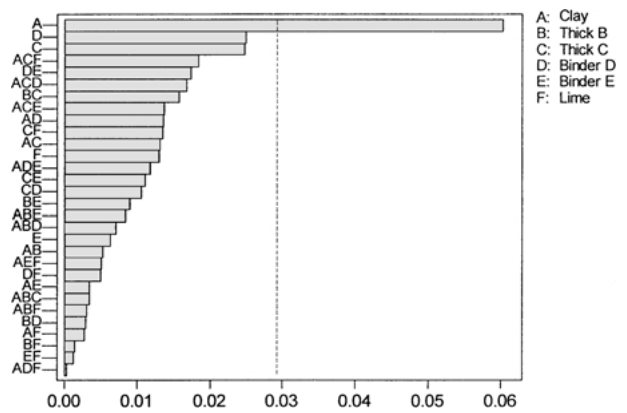


Figure 4 Pareto chart showing the effects of the additives on the degree of viscosity drift. Effect A is positive.

20 min from 32 different graphs, each a result of an individual plaster formulation set out by the factorial design.

The gradient values were then collated and statistically analysed to provide a Pareto chart (Fig. 4). It should be noted that the Pareto chart does not indicate whether the effect was positive or negative (increase or decrease in gradient, respectively), however the specifics of the results will be discussed later. Despite this ambiguity of the Pareto chart, it is the user-friendliest interpretation of simultaneously depicting over 60 individual sets of data.

The y-axis of Fig. 4 represents the effect that an individual or group of additives has on the viscosity drift. A single letter represents a single additive, either A, B, C, D or E whereas two or three letters represent a two- or three-factor interactive effect on the viscosity drift. The x-axis represents the change in gradient value or the extent of viscosity drift.

The vertical dotted line (Fig. 4) represents the 95% confidence interval, therefore any result falling to the left of this line can be deemed statistically insignificant. Hence there is one statistically significant result in Fig. 4 that should be looked into further—clay (A). In other words the results indicate that a 95% assurance can be made that the clay additive is responsible for the viscosity drift. Although other additives and their interactions are present, it can be safely asserted that they have no influence on the observed phenomenon. In Fig. 4 the clay (A) alters the gradient by approximately 0.06 in a positive direction and shall be considered as the sole influence on the viscosity drift.

To ensure that the clay was responsible for the viscosity drift a simple means to check the data provided by the Pareto chart (Fig. 4) was to take one plaster formulation and alter the clay concentration while maintaining all of the other factors constant. This indeed provided further evidence of the clay's responsibility for the viscosity drift (Fig. 5).

Fig. 5 shows that the viscosity gradient increases sharply as the amount of clay increases above 2.5 wt%, below 2.5 wt% there is little change to the gradient. Therefore a clay weight percent of 2.5 and above will cause the viscosity to drift significantly.

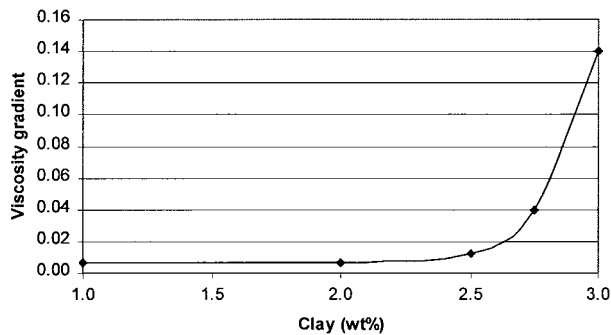
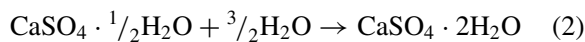


Figure 5 Relationship between viscosity drift and clay concentration.

3.1. Setting

After confirming that the clay was actually responsible it was necessary to determine how the clay caused the viscosity to drift. It was initially suggested that the clay caused the plaster paste to prematurely set via the well-documented means of forming a dihydrate crystalline structure after the addition of water to the hemihydrate powder via a hydration reaction [11] as in Equation 2.



Looking back at Figs 2 and 3, the commencement of setting of the plaster pastes was taking place at around 1500 s, since there was a rapid increase in viscosity after this particular time. Furthermore this was the desired setting time that was controlled by the addition of specific amounts of setting inhibitors. Since setting is a chemical reaction [11], an associated change in pH should accompany any setting that occurred.

Figs 6–8 show three graphs depicting viscosity and pH as a function of time. These graphs are examples of the viscosity drift, each having a different combination of additive concentrations. They show a distinct trend in viscosity (until 25 min) that increases, decreases or is constant in this region as shown in Figs 6–8. The pH curves, however, in Figs 6–8 are identical in trend

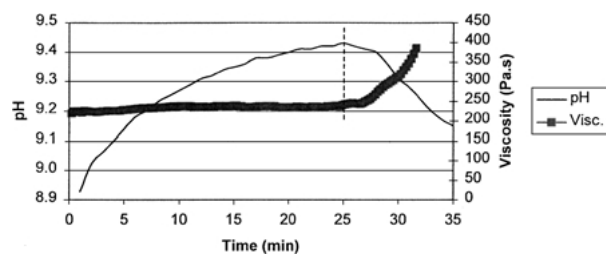


Figure 6 Constant viscosity, no drift.

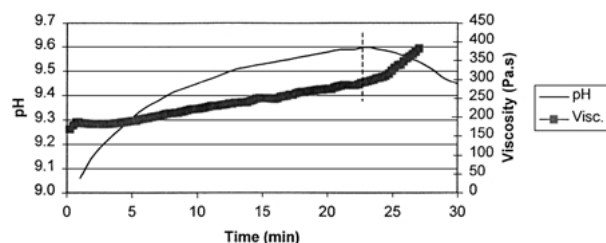


Figure 7 Increasing viscosity, positive drift.

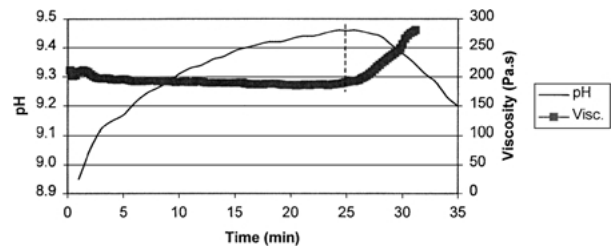


Figure 8 Decreasing viscosity, negative drift.

and very similar in value to each other, suggesting that pH and the viscosity drift are independent. The vertical dotted lines in Figs 6–8 represent the point at which setting (due to the chemical reaction) commenced. Beyond this point the viscosities increase sharply, corresponding to a notable decrease in pH due to the presence of a chemical reaction.

This implies that if the viscosity drift were due to setting then the pH would also follow a distinct trend with each of the three viscosity trends, however, it did not and instead followed the same trend in all three graphs.

Another important observation was that the viscosity drift in Fig. 8 is negative, that is, it is decreasing. Setting in this case would not be a plausible explanation for the drift in viscosity. The negative drift observed in Fig. 8 was a thixotropic effect caused by the distribution of substituents in the two cellulose ether thickeners. Association among polymer chains (of the cellulose ethers) via electrostatic, hydrogen bonding, or hydrophobic effects can lead to thixotropy [12].

3.2. The cause of viscosity drift and the time dependent effects of clay

It was established earlier in this section that the clay was responsible for the drift in the viscosity of the plaster pastes and its mechanism was not that of setting. A more likely scenario was that a structure was being established within the plaster paste.

It has been previously shown [3, 13] that simple gypsum-plaster and water pastes exhibit thixotropic behaviour, as did the plaster pastes examined in this work. Fig. 3 is a good example of the thixotropic behaviour of gypsum plaster pastes. A peak existed at the beginning of the graph between zero time and 10 min. To the right of the peak the viscosity drops, indicating a structure breakdown at constant shear rate known as thixotropy [1]. However, this breakdown soon ended with the beginning of a structure being built, as can be seen by the continuously increasing viscosity (until 25 min) with constant shear rate in Fig. 3.

The reason that the thixotropic structure breakdown could be observed was due to a delay in the building of another similar structure. The type of clays that were discussed in the 'Materials' section, that are used as rheological additives do not form networks (activate) immediately, instead they require time to commence the formation of a gel network structure [5]. The initial state of the clay was in an agglomerated form, that is, dry clay molecules in large groups. Upon the addition of water

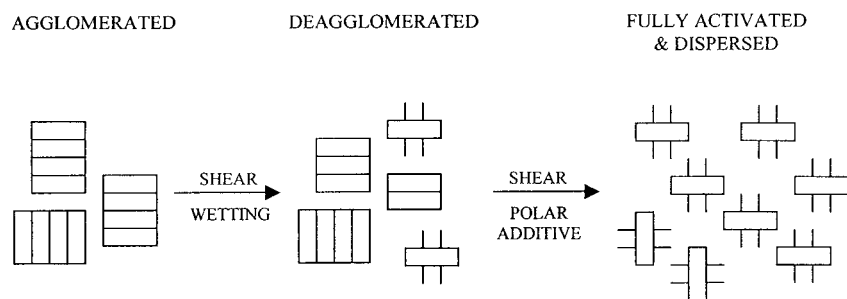


Figure 9 The sequence of events prior to the generation of a gel structure of organically modified clay molecules [adapted from Newman and Brown, 1987].

and applying shear the agglomerates began to break up into individual clay molecules, thus deagglomerating. With further shear and in the presence polar substances such as lime and water the clay became polar activated [5], thereby exposing long hydrophobic tails extending from the surface of each clay molecule (see section titled *Materials*). With further shear the clay became fully activated and fully dispersed and hence ready to develop the structure seen in Fig. 3 after the observed thixotropic breakdown. A simplified diagram showing this series of events can be seen in Fig. 9.

The edges of these activated clay molecules then interact via hydrogen bonds in the presence of water, to form a three-dimensional structure or gel [5]. Obviously the sequence in Fig. 9 takes a specific amount of time to achieve and it is this time delay that can be seen in Fig. 3 before the viscosity begins to increase after the thixotropic breakdown occurs. In this case the activation of the clay took approximately 2 min and once activated the clay network continued to develop (increasing viscosity in Fig. 3) until the plaster paste began to set via a hydration reaction of the hemi-hydrate gypsum [11] at approximately 25 min.

Looking back at Fig. 5, which shows the relationship between the extent of viscosity drift (in terms of the gradients of viscosity-time graphs) and the wt% of clay it was apparent that a critical amount of clay (around 2.50 wt%) was required to cause the viscosity of the plaster pastes to drift upwards. It was theorized that 2.50 wt% was very close to the critical value of clay required to form a minimal clay network within the plaster paste. Anything below this value would result in a partially networked structure that in turn offers little or no increases in viscosity. This is also in agreement with the rapid increase in viscosity gradient between 2.75 and 3.00 wt% clay (Fig. 5) that suggests a significantly developed network of clay is already established and the addition of more clay has a minimal effect on the viscosity.

4. Conclusions

The time dependent variation in viscosity or 'viscosity drift' that was observed in certain formulated gypsum plaster pastes, was caused by the organically modified clay. Furthermore, a 2.50 wt% of clay was very close to the critical value of clay required to form a minimal clay network within the plaster paste.

It was determined that setting was not the mechanism by which the clay caused the viscosity to drift. It was, however, established that a more likely scenario was that a clay network was being established within the plaster paste.

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