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Why some carbonate fillers cause rapid increases of viscosity in dispersed cement-based materials

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Abstract

Fine carbonate fillers complement the deficiency in fine particles of the cement's particle size distribution, which can enhance both the flowability and stability of fresh concrete. They also fill in between the relatively coarser cement grains, reducing the room available for water and consequently the water demand. In conventional concrete mixtures, slight reductions in the setting time have been often reported when carbonate fillers were used, without significant effects on the workability. However, as the use of high-performance concrete (HPC) continues to rise, carbonate fillers are being added in low water/cement (w/c) ratio superplasticized-mixtures. Increasingly finer fillers are being specified because they enhance the packing density of the particulate system. In such conditions, rapid losses of workability have been reported. Yet, this did not seem to occur with all carbonate fillers. This paper investigates the potential causes of this phenomenon using a model system. Chemical oxide analysis was conducted on various carbonate fillers, which were then ground to sub-micron particle sizes in the presence of polyacrylate dispersants using an agitated ball mill-grinding machine. A rotational co-axial cylinders viscometer was used to study the rheology of the slurries thus obtained. Laser diffraction was employed to establish the particle size distribution of the input and output slurries. It was discovered that the magnesium (MgO) content of the carbonate filler can hinder the effect of the dispersant, which may combine with the acceleration of C_3S hydration due to calcite and possibly the formation of carboaluminates in Portland cement-based mixtures to cause rapid losses of workability. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Generally, limestone fillers complement the deficiency in fine particles of the particle size distribution of cement (mean particle sizes of 5 [1,2] and 3 μm [3] have been used), which can enhance the stability and flow of fresh concrete and mortar. In addition, the carbonate grains can fill in between the relatively coarser cement grains. Beyond the lubricating role they can play, the filler particles can reduce the room available for water, decreasing the water demand and obstructing the capillary pores at later ages [1,2,4]. It was noticed that the lubricating effect of limestone filler was more significant the lower the w/c ratio [1,5].

Bombled [1] argued that when the effect of limestone filler on the rheology of fresh concrete is significant, it is usually in the sense of a higher cohesion, better plasticity and in some instances a pseudo-acceleration of the setting. Neto and Campitelli [6] used a two-point test to characterize the rheology of limestone filler cements. They observed a reduction in the yield stress as the limestone addition increased, and an increase in the plastic viscosity beyond a certain fineness/limestone relationship. Brookbanks [7] presented the results of a comprehensive study on the effect of 5% to 28% limestone powder additions to cement on the properties of fresh concrete. It was observed that the setting times were marginally reduced as the limestone addition rate increased. For the materials used, there was no discernible difference in the water demand at 5% replacement, while a marginal reduction was observed at higher filler levels. The limestone fillers greatly reduced the bleed water and seemed to have no effect on the air entraining properties.

The mechanisms underlying the effect of limestone filler on the rheology of cement paste, mortar and concrete seem to be controlled by the filler particle size distribution. In most of the reported studies, limestone was inter-ground with clinker, which increased the overall fineness of the

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cement due to the lower grinding energy of limestone. Whether the use of blended ultrafine limestone, when dispersed with a superplasticizer, can play a different role, similar to the filler effect of silica fume on the rheological properties of cement paste and concrete, was investigated by Nehdi et al. [8,9]. Ultrafine limestone seemed to reduce the superplasticizer dosage and to enhance the workability of high-performance concrete (HPC). The finer the filler and the higher the replacement rate, the lower were the flow resistance and torque viscosity values measured using a computer-controlled rheometer. This was also applicable for Portland cement–limestone–silica fume ternary cements.

Conversely, Ghezal [10] observed that self-consolidating concrete mixtures containing ordinary Portland cement, silica fume and limestone filler exhibited rapid and severe losses of slump. Although these mixtures initially required less superplasticizer dosage and achieved excellent rheological properties compared to control mixtures, they were rejected because they could not adequately maintain workability in time. On the other hand, Sakara et al. [11] presented a mixture proportioning approach for highly flowable concrete containing limestone powder. They did not report any rapid losses of workability and even highly recommended the use of such a material for the construction of real structures.

The possible acceleration of C_3S hydration due to the presence of calcite and the formation of carboaluminates due to the reaction between calcite and C_3A alone may not explain the discrepancy between the above results. In these apparently conflicting studies, comparable w/c ratios and cements containing comparable C_3A contents and limestone fillers of comparable fineness were used and could have equally accelerated C_3S hydration and/or formed comparable amounts of carboaluminates. The present author used a much finer limestone filler (average particle size = 0.7 μm) at addition rates of 20% in superplasticized concrete and in the presence of silica fume without rapid losses of workability [12].

This paper investigates the hypothesis that the nature of the limestone filler may be partly responsible for the rapid loss of workability. It is possible that when a limestone filler has certain physical or chemical properties, a certain reaction may occur inhibiting the beneficial effects of dispersants and causing rapid losses of workability.

2. Experimental

Various calcium carbonate fillers having average particle sizes of 3 μm were obtained and their particle size distributions were established using laser diffraction. The fillers were obtained from the same industrial grinding circuit; therefore, their particle size distributions were similar. Carbonate slurry samples with 63% solid content by weight in water were made using a mechanical helical-mixer. In addition, slurries with 76% solid content and containing various dosages of polyacrylate dispersants were prepared using the same mixer. The rheological properties of all slurries were assessed using a rotational co-axial cylinders viscometer.

Furthermore, various samples of carbonate fillers with 15 μm average particle sizes (also having comparable particle size distributions) were acquired. Slurries with 76% solid contents by weight (in water) and containing various dosages of polyacrylate dispersants were prepared for each sample. Mixing was carried out using the helical mixer mentioned above. The slurries were ground using an agitated ball mill-grinding machine. The average particle sizes of the input and output slurries were measured using laser diffraction particle size analysis. All slurries were ground to average particle sizes below 1 μm. Rheological measurements were conducted on the output slurries 5 min after the grinding operation.

Generally, it was found [13] that the most effective dispersants for calcium carbonate are inorganic polyphosphate compounds. Other inorganic compounds such as silicates are much less effective. If the slurry is to be held for a prolonged period or at elevated temperatures, use of a polyacrylate dispersant, alone or in combination with a polyphosphate, is recommended. Because this investigation involves agitated ball mill-grinding that usually increases the temperature of the slurry, polyacrylate dispersants were selected. In the rest of the text, the dispersant dosage is expressed as the ratio of the weight of the liquid dispersant (solid content typically = 40%) to the weight of the dry calcium carbonate, in percent.

Care was taken to use water at a constant temperature of 17°C, a uniform feeding rate, and constant mixing time and mixer paddle speed for the preparation of the slurries. The controlling parameters for the grinding machine were also maintained constant for all slurries.

3. Apparatus

The viscometer used for rheological measurements on the slurries is a VT-550 HAAKE rotational viscometer (Fig. 1). It is capable of rotational speeds from 0.5 to 800 rpm. The resulting torque is measured via a non-contact, low displacement sensor. The operating temperature is measured using probes located in the sensor. The viscometer is connected to a data acquisition system. A customized software controls the device, enables the user to set testing parameters, and displays the results on-line. In this study, viscosity versus shear rate flow-curves were obtained and used to compare the behavior of the different slurries.

The wet grinding of calcium carbonate fillers was conducted using a laboratory-size agitated ball mill-grinding machine (Fig. 2). The feed slurry was introduced in the grinding chamber of the mill via a pumping system at a controlled rate of about 6.62 l/h (1.75 g/h). The mill speed was maintained at around 2200 rpm while the

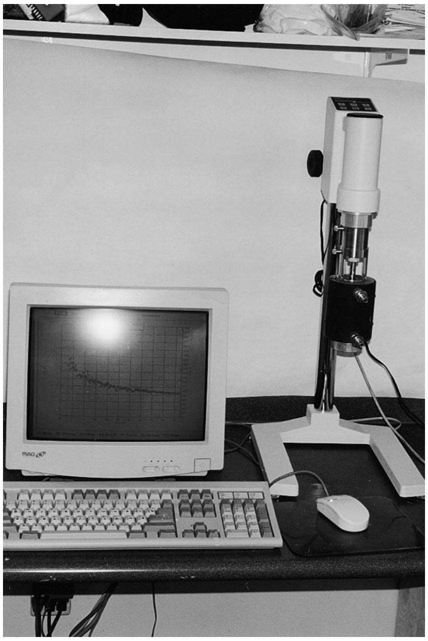

Fig. 1. Illustration of the co-axial cylinders viscometer.

temperature and pressure inside the grinding chamber were at around 29°C and 42 kPa, respectively. These values were sometimes difficult to maintain constant because some slurries had higher viscosity, therefore demanding more work for grinding. This caused higher pressure and temperature rises inside the chamber. Manual control was needed to limit fluctuations of temperature and pressure inside the grinding chamber. The grinding media was spherical zirconium oxide balls with particle sizes ranging between 0.6 and 0.8 mm. Preliminary tests showed that either coarser or finer grinding media was less efficient and that optimal grinding was achieved when the grinding media occupied 85% of the total volume of the grinding chamber. Thus, the volume of the grinding media was kept constant at 85%.

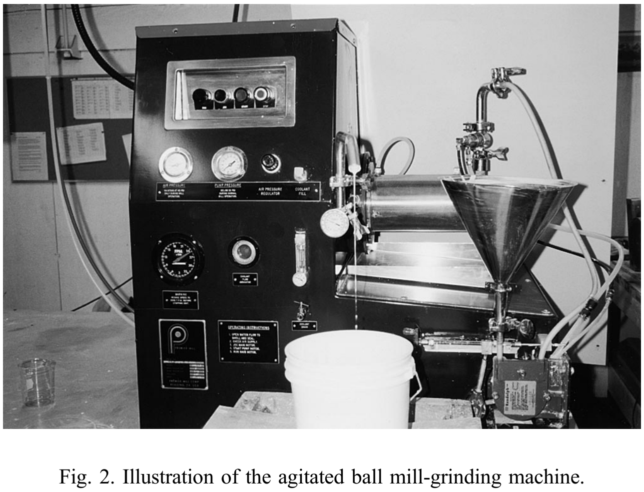

Fig. 2. Illustration of the agitated ball mill-grinding machine.

4. Results and discussion

4.1. *Effect of MgO content*

Fig. 3 shows the viscosity versus shear rate flow curves for three calcium carbonate slurries with 63% solid content, average particle sizes around 3 μm and no dispersant. At very low shear rates, the relationship between shear rate and shear viscosity was not stable. Therefore, the initial part of the curve was discarded. There was no clear indication that the viscosity of the slurries depended on the MgO content of the filler (in this study limestone fillers having various MgO contents were used, no MgO was added). A slurry made with a filler having 1.75% MgO had slightly higher viscosity than a slurry made with a filler having 2.30% MgO. The slurry made with a filler having 2.86% MgO generally had higher viscosity, but this could be related to the slightly lower average particle size of the filler (2.95 versus 3.0 μm for the two other fillers).

Fig. 4 illustrates the viscosity versus shear rate flow curves for slurries made from the same calcium carbonate fillers above with 76% solid content and 0.7% of a polyacrylate dispersant. It was observed that the polyacrylate dispersant was very efficient in decreasing the viscosity of the slurries, even though a higher solid content was used. Clearly, the higher the MgO content of the calcium carbonate filler, the higher the viscosity of the slurry. For the 63% solid content filler suspensions, the slurries generally behaved like shear-thinning fluids (Fig. 3). Conversely, for the 76% solid content suspensions containing 0.7% dispersant, after the initial breakdown of the flocculated structure, the behavior of the 2.30% and 2.86% MgO slurries was rather comparable to that of shear thickening fluids, with the higher MgO filler exhibiting a higher shear thickening tendency (Fig. 4). The 1.75% MgO slurry did not exhibit a shear thickening behavior. If shear thickening was due to particle interactions, it would have occurred to the same extent for the three slurries because they have similar solid and dispersant contents. The fact that this effect was more

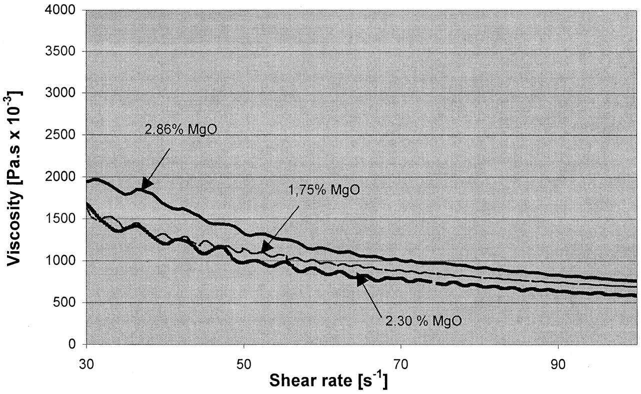

Fig. 3. Effect of MgO content on the viscosity of calcium carbonate slurries (no dispersant, solid content = 63%, particle size = 3 μm).

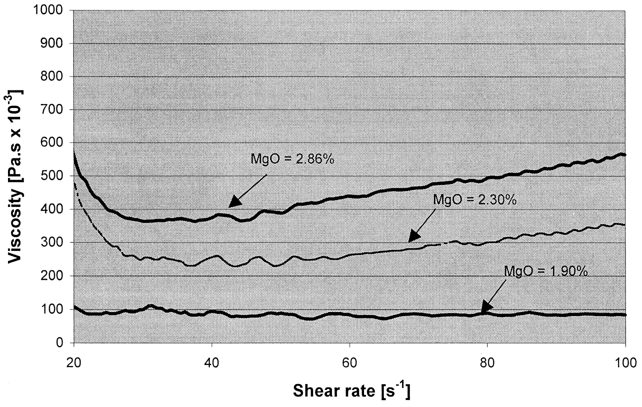

Fig. 4. Effect of MgO content on viscosity of calcium carbonate slurries (0.7% polyacrylate dispersant-1, solid content = 76%, average particle size = 3 μm).

pronounced for high MgO content fillers indicated that perhaps a certain reaction between MgO and the dispersant took place and was enhanced by the higher energy imparted via the shearing action of the viscometer.

Fig. 5 shows the effect of temperature on the viscosity versus shear rate flow curve of a carbonate filler suspension in water (MgO = 2.65%, solid content = 76%, average particle size = 3 μm, dispersant = 0.7%). The viscosity of the slurry increased when the temperature increased from 25°C to 60°C. When the slurry was cooled down back to 25°C, its viscosity increased even further. It is believed that this was due to the fact that the cooling was not instantaneous so that the slurry had more residency time at higher temperatures, which further decreased the efficiency of the dispersant, combined with the fact that the viscosity of water increases from 60°C to 25°C.

For all flow curves discussed above, it was observed that the viscosity reached peak values at low shear rates, and then decreased substantially. It is believed that this was due to the fact that the stagnant slurries had a flocculated structure. As the torque increased, they offered increased resistance to flow until a shear rate level beyond which the flocculated structure was broken down. A drastic reduction of the apparent viscosity was observed thereafter.

Fig. 6 illustrates the viscosity at a constant shear rate of 100 s^{-1} for slurries of ground fillers with initial average particle size of 15 μm, solid content of 76% and dispersant content of 2%. These slurries were selected because their average particle size after grinding was around 0.75 μm and their particle size distributions were comparable. Therefore, the effect of the surface area on their viscosity should be limited. It can be observed that the increased MgO content of the fillers increased the viscosity of the ground slurries. This increase seemed to be slight below 2% MgO, then it became substantial beyond this value. However, tests conducted on a slurry with MgO content of 6% showed that the viscosity curves flattened beyond 3% to 4% MgO at which level a pessimum value was reached (Fig. 6). Apparently, very high MgO contents in the filler would not significantly increase the viscosity of ground slurries beyond the maximum value reached around 3% to 4% MgO.

The residency time of the slurries in the grinding chamber was increased to achieve more grinding and to observe the effect on viscosity. A very low MgO content (0.6%) calcium carbonate was obtained from a different mineralogical source and was ground to a very low average particle size. The rheological behavior of the slurry was compared to that of 2.5% and 3% MgO slurries with similar average particle sizes and containing equal amounts of dispersant. For an increased residency time in the grinding machine, the viscosity of the 3% MgO slurry reached extremely high values so that the grinding machine was clogged and the grinding test was halted. The two slurries with 0.6% and 2.5% MgO were ground to average particle sizes of 0.62 and 0.64 μm, respectively (92–90% passing 2 μm and 68–66% passing 1 μm). The flow curves of the two slurries are illustrated in Fig. 7. Clearly, for the same solid and dis-

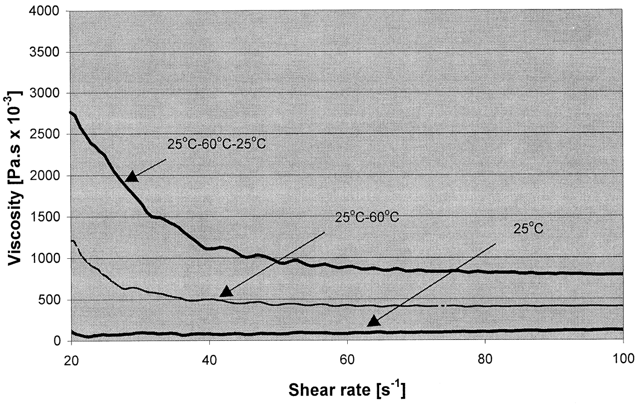

Fig. 5. Effect of temperature on viscosity of calcium carbonate slurries (MgO = 2.6%, dispersant = 0.7%, solid content = 76%, average particle size = 3 μm). Note that the initial viscosity at 25°C is lower than that of a filler with MgO = 2.3% in Fig. 4 because the dispersant-4 used herein is more efficient than the dispersant-1 used for data in Fig. 4.

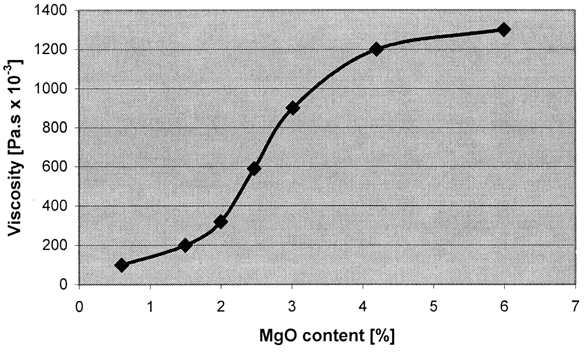

Fig. 6. Effect of MgO content on viscosity of calcium carbonate slurries (shear rate = 100 s^{-1}, average particle size = 0.75 μm, solid content = 76%, dispersant = 2%).

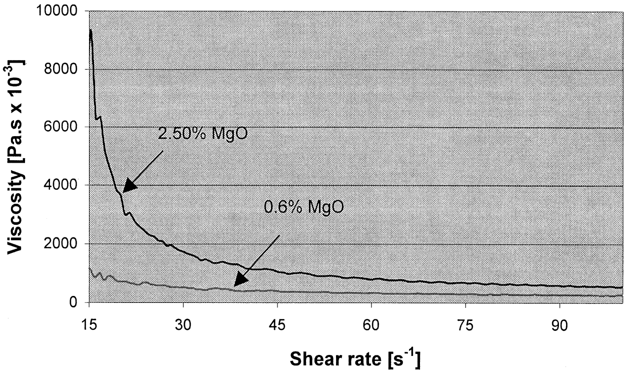

Fig. 7. Effect of MgO content on the viscosity of very fine calcium carbonate slurries (average particle size ≈0.63 μm, solid content = 76%, dispersant = 2%).

persant contents, and similar average particle sizes, the slurry with the higher MgO content had a much higher viscosity, especially at low shear rates. This suggests that the dispersant was much less efficient in the slurry containing a higher MgO content.

An attempt was made to verify whether different polyacrylate dispersants might be more efficient in dispersing fillers with high MgO contents. Fig. 8 illustrates the viscosity versus shear rate flow curves for a calcium carbonate slurry made with various dispersants (average particle size = 3 μm, MgO = 2.86%, dispersant = 0.7%). It is shown that some of the dispersants were more efficient than others in dispersing the filler and achieving lower viscosity. There is need, however, for more research to investigate whether similar effects can be observed with dispersants and superplasticizers having different chemical nature.

4.2. Effect of nucleation of hydration products on calcite particles

It is conceivable that rapid losses of workability in limestone filler concrete are related to the acceleration of the hydration reaction due to the presence of calcite particles. Jiang et al. [14] observed that limestone, titanium dioxide and barium carbonate fillers accelerated the cement hydration, while quartz and alumina retarded the hydration. They suggested that the filler acceleration effect depends on the number and nature of inter-particle contacts achieved in a cement-filler system. Only fillers with an acceleration effect would have coagulation contacts on which nuclei of hydration products will initiate. However, rheological results [8,9] and Zeta-potential measurements by Kjellsen and Lagerblad [15] provide no evidence for such coagulation. On the contrary, the rheology of cement suspensions was improved when ultrafine limestone particles were added to the mixture, which contradicts any extra coagulation of the system due to calcite.

Likewise, Beedle et al. [16] observed that graphite and α-alumina did not affect the rate of hydration of cement, while clays and γ-alumina had a significant acceleratory effect. It is believed that early hydration proceeds through a nucleation and growth mechanism and that hydration products may preferentially nucleate on calcite particles. Being a surface mechanism, the nucleation will depend on the surface characteristics of the filler, namely: its chemical composition, atomic structure and surface morphology. However, calcite does not have a strong ionic nature, and would thus not precipitate ions through particularly high inter-atomic forces. Rather, it would constitute a preferential substrate for the germination and growth of hydration products, thus accelerating the hydration process.

Although there is abundant literature suggesting the nucleation mechanism as the primary cause for the microfiller acceleration of the early age hydration, there is a certain confusion as to what is nucleating: C–S–H or portlandite or both, and in what sequence? For instance, Ramachandran and Zhang [17] suggested that calcite not only accelerates the hydration of C_3S, but that a certain percentage of calcite is consumed before 1d in this process. They explained the increased hydration rate by the nucleation of C–S–H around calcite particles, which would incorporate a part of the calcite in some kind of a composite. They supported this idea by 1d SEM micrographs illustrating the growth of C–S–H around calcite grains. Kjellsen and Lagerblad [15] argued that the acceleration of the hydration is initiated during the induction period, before any notable long-range nucleation of C–S–H can be expected. Therefore they questioned the above explanation.

Nehdi and Mindess [18] argued that in the presence of calcite removal of calcium ions from the cement–water solution would start earlier, and would enhance further dissolution of calcium ions. By the same token, there will be a stronger concentration gradient for the migration of calcium ions through the hydration membrane that engulfs cement particles. The continued germination of CH on calcite implies an increased dissolution of C_3S since the system will tend to restore the equilibrium between the surrounding solution and the hydration membrane. Further-

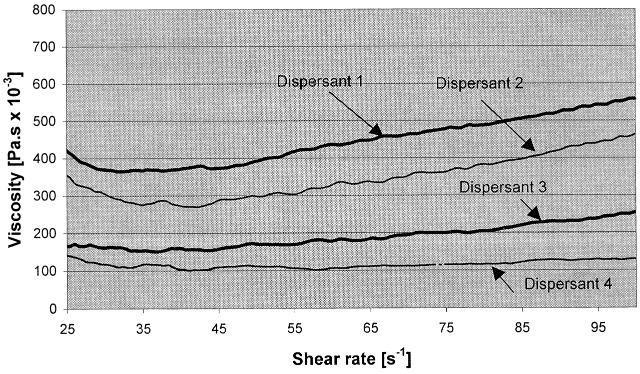

Fig. 8. Effect of various polyacrylate dispersants on the viscosity of calcium carbonate slurries (solid content = 76%, average particle size = 3 μm, MgO = 2.86%, dispersant = 0.7%).

more, more osmotic pressure would have built up since more silicate ions are now trapped inside the hydration shell. This promotes the conditions for rupture of this shell, and thus, an earlier end of the induction period. Likewise, this would stimulate the appropriate thermodynamic conditions for a re-crystallization of the hydration shell around the C_3S particles into a more permeable structure. This also signals an earlier end of the induction period.

The theories above attempt to explain the acceleration of the C_3S hydration in the presence of carbonate fillers, which contributes to the reduction of the induction period. However, they do not provide clear answers as to why some carbonate fillers cause drastic and rapid losses of workability in superplasticized concrete and others do not.

4.3. Effect of calcium ions dissolved from calcite

It might also be that calcite particles would partially dissolve in the limestone–cement–water system, providing extra Ca^{2+} ions and thus modifying the kinetics of the hydration reactions. Because of the low solubility of calcite in alkaline systems, this theory does not seem to be thermodynamically plausible. To investigate this aspect, Nehdi and Mindess [18] made superplasticized concrete mixtures with 5%, 10%, 15% and 20% limestone filler and hydrated lime powder. The hydrated lime is much more soluble in water than limestone powder and would provide many more Ca^{2+} ions in the solution, thus further increasing the rate of hydration. No severe losses of workability were observed. Therefore, the effect of dissolution of Ca^{2+} ions may not have a major effect on the rheological problems associated with some carbonate fillers.

4.4. Effect of reaction between calcite and C_3A

There is a potential reaction between calcite and calcium aluminate (C_3A) in the presence of water to produce calcium carboaluminates ($C_3A{\cdot}CaCO_3{\cdot}11H_20$). The question is: could this reaction be responsible for the reduction of the induction period and the increase of the rate of the early hydration? The attempt to substitute limestone for gypsum as a set regulator [19–22] rather supports the idea that this reaction would form carboaluminates around the C_3A grains, thus preventing their further hydration. This is analogous to the set control action of gypsum through the formation of sulfo-aluminates. Also, based on the observation that calcite accelerates the hydration of pure C_3S (no potential formation of carboaluminates), the hypothesis that the reaction between calcite and calcium aluminate is responsible for the acceleration of the hydration reactions is unlikely.

Using X-ray diffraction of limestone filler cement pastes, Escadeillas [2] observed that the percentage of calcite started to decrease after the first few hours of hydration. However, carboaluminates were not detected before 7d, either because they were too small to be detected by X-ray diffraction, or because the crystallization of carboaluminates is only possible at high carbonate levels in the solution. It was claimed that the transformation of aluminates to carboaluminates was practically complete at around 9 months. Due to the apparently slow nature of this reaction, its real effect on the rheological behavior of fresh concrete remains an open question.

5. Concluding remarks

There is an ongoing discrepancy between published results regarding the rheological effects of very fine limestone fillers in superplasticized concrete. While some researchers claim that limestone fillers help the production of flowable and self-compacting concrete, conflicting results argue that limestone fillers caused severe and dramatic losses of workability of fresh concrete. This paper investigated this issue based on a model system. Various limestone fillers were ground to sub-micron particle sizes in the presence of polyacrylate dispersants. It was demonstrated that the efficiency of the dispersant depended on the MgO content of the filler. This suggests that when polyacrylate-based dispersants are used in a cementitious mixture, the addition of a fine carbonate filler with a high MgO content will likely inhibit the beneficial effects of the dispersant and cause sharp rises in viscosity. Therefore, it is recommended that an oxide analysis of the limestone filler be included in publications that deal with the effect of fillers on the rheological properties of concrete. While this study was limited to polyacrylate dispersants, it is recommended that further work be conducted to investigate the effect of MgO on other types of dispersants and superplasticizers. Research is also needed to clarify whether the mineralogical nature (degree of crystallinity, impurities, etc.) of the limestone filler could affect the rate of C_3S hydration, which would be another cause of the discrepancy between reported results dealing with the effect of carbonate fillers on the rheology of fresh concrete.

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