

## Rheological Properties of the Silica phases in Clinker slurries.

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### ABSTRACT

The setting time of cement slurries is controlled by the addition of gypsum to the clinker during the grinding process. This addition has a different influence on the various constituents of the clinker. We have studied the rheological properties of triclinic and monoclinic  $C_3S$ , the main constituents of the clinker phase, and compared their behaviour with that of a Class G clinker.

### INTRODUCTION

The first stage in the manufacture of cement is the production of the clinker. The raw materials consist of various rock minerals rich in calcium and silica. The minerals are fed into a roller oven where they are heated to approximately 1500 °C, at such a high temperature the minerals are partly melted. Thereafter follows a section where the minerals are cooled at a controlled rapid rate. Because of rapid cooling these minerals are unstable and re-crystallize when water is added. The product that comes out of the oven is called clinker and it consists of a balanced mixture of amorphous and crystalline compounds. The particle size of the clinker varies from powder to pebbles of centimetre size.

The production of cement from the clinker comprises the grinding of clinker together with minerals mainly containing gypsum. The gypsum in cement affects the setting time, the strength development and the volume stability<sup>1</sup>.

Alite or  $C_3S$  as written in the abbreviated form used in cement chemistry is the most important constituent of all normal Portland cement clinkers, of which it constitutes 50-70%. It is  $Ca_3SiO_5$  or tricalcium silicate. In pure compounds, when cooled to room temperature only the triclinic structure is present. In production clinkers, due to the incorporation of foreign ions, the form present at room temperature is normally the monoclinic structure. However, the triclinic structure is also present. Thus, the pure monoclinic  $C_3S$  we used was  $Al_2O_3+MgO$  stabilized. In this study we also used a Portland cement for comparison. This was an API-specified<sup>2</sup> Class G cement.

### EXPERIMENTAL CONDITIONS

#### Sample preparation

The clinker, the gypsum and the anhydrite used were all delivered by Norcem AS. They are used as the basic constituents in the production of Class G cement, as specified by API<sup>2</sup>. Before measurement they were all ground separately by the use of a Tecon, 400VL ball mill. The particle size used in our experiments, if otherwise not stated, were the fraction that during dry sieving passed through a sieve with a mesh of 75 micron.

The Class G cement used was also delivered by Norcem AS. The Class G cement has a Blaine surface area of 320 m<sup>2</sup>/kg. Before measurement it was also dry sieved through a mesh of 75 micron.

The monoclinic and triclinic  $C_3S$  used were laboratory minerals delivered by Construction Technology Laboratories, Inc. in Skokie, Illinois. The samples were delivered as pure compounds having a measured specific Blaine surface area of 299 and 313  $m^2/kg$  for the monoclinic and the triclinic  $C_3S$  respectively. The monoclinic  $C_3S$  had been stabilized by  $Al_2O_3$  and  $MgO$ .

Before use the samples were dry sieved through a mesh of 45 micron.

For the rheological testing, samples of 10 ml were made. They were first vigorously stirred by hand in the measuring cup for 30 seconds giving a homogenous test sample. Only the monoclinic  $C_3S$  had to be hand stirred for 60 seconds before it resulted in a homogenous test sample. After hand mixing the samples were placed in the rheometer and sheared for 60 seconds at a shear rate of 1020  $s^{-1}$ . The samples were then measured at a constant shear rate of 51  $s^{-1}$ .

The solid phase volume fraction of all the samples was 0.419. The specific density used was 3.12  $kg/m^3$  for the triclinic  $C_3S$  and 3.15  $kg/m^3$  for all the other cement materials.

For all samples distilled water was used and all experiments were carried out at a temperature of 25°C.

#### Viscosity measurements

The rheological properties of the slurries were measured using a Physica UDS 200 rheometer (Physica Meßtechnik GmbH, Stuttgart) fitted with a concentric cylinder configuration named Z3 DIN. All tests were done within  $\pm 0.5^\circ C$  of the set temperature.

#### Zeta potential measurements

The zeta potential was measured by use of an AcoustoSizer from Colloidal Dynamics, Warwick, RI, USA. All tests were done within  $\pm 1.0^\circ C$  of the set temperature. The samples were mixed in accordance with API<sup>2</sup>.

## RESULTS

### Viscosity measurements

In Fig. 1 the viscosity development of the clinker as a function of time is plotted at a constant shear rate of 51  $s^{-1}$ . The measurements start approximately 200 seconds after the clinker and water was initially mixed. Three different samples of the same composition were measured at various durations of time. All three series indicate the same time dependant development of the viscosity.

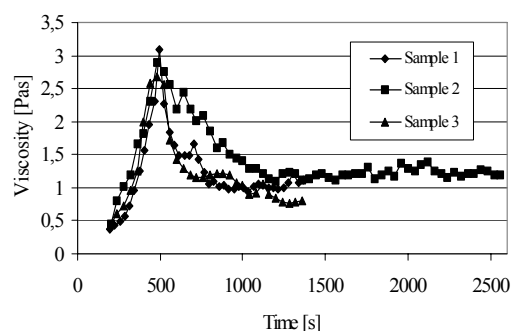


Figure 1. Viscosity development as a function of time for a Class G clinker measured at a constant shear rate of 51  $s^{-1}$ .

During the first approximately 300 seconds of measurement there is a marked increase in the viscosity followed by a decrease and a stabilisation at a slightly higher value than the initial. In this period the viscosity increases from an initial value slightly below 0.5 Pas to a maximum in the range of 2.7 to 3.1 Pas followed by a decrease and apparent stabilisation around 0.8 to 1.3 Pas.

In Fig. 2 the effect of adding gypsum and anhydrite to the clinker is shown. The clinker has been added 4 and 3.2% by weight of gypsum and anhydrite respectively the latter being reduced thus adding a comparable amount of calcium to the clinker. Also a sample of Class G cement from Norcem AS was measured for comparison. The Class G cement consists of clinker that has been added gypsum. All

three curves represent the average values of two different measurements.

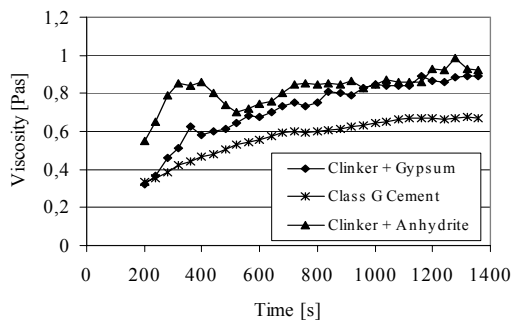


Figure 2. Viscosity development at a shear rate of  $51 \text{ s}^{-1}$  as a function of time for a Class G clinker added gypsum and anhydrite, and for a Class G cement.

The effect of adding gypsum and anhydrite to the clinker is profound as can be seen when comparing the measured values in Fig. 2 with those in Fig. 1. The initial measured viscosity at 200 seconds and the measured viscosity after 1360 seconds are within the same range, but the rapid increase to a maximum value followed by a decrease can no longer be found.

When comparing the effect of adding gypsum to the clinker with that of adding anhydrite we see that adding gypsum gives initially a larger reduction in the viscosity but the difference is somewhat reduced towards the end of the measuring period. When comparing the effect of adding gypsum and anhydrite to clinker with the measured values of the Class G cement we see that the Class G cement viscosity is the lowest.

In Fig. 3 the viscosity development of both the triclinic and the monoclinic  $\text{C}_3\text{S}$  phases as a function of time has been measured. All four curves represent the average values of two different measurements. Both the monoclinic and the triclinic  $\text{C}_3\text{S}$  show an increase in viscosity during the measured interval, monoclinic  $\text{C}_3\text{S}$  showing the highest viscosity. The effect of adding

gypsum is also shown. For the monoclinic  $\text{C}_3\text{S}$  the adding of gypsum results in a marked drop in viscosity while for triclinic  $\text{C}_3\text{S}$  the adding of gypsum results in lower viscosity in the beginning of the measuring period and a higher viscosity towards the end of the period.

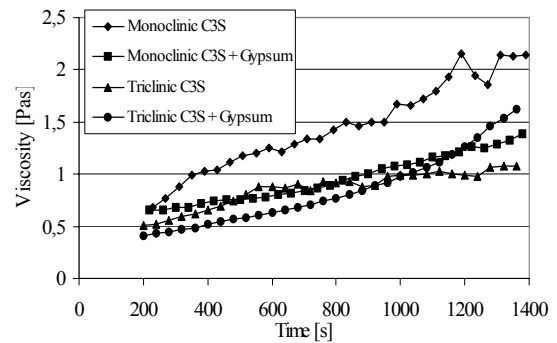


Figure 3. Viscosity development at a shear rate of  $51 \text{ s}^{-1}$  as a function of time for a monoclinic and a triclinic  $\text{C}_3\text{S}$ , with and without gypsum added.

When comparing the measured viscosity of the silica phases in Fig. 3 with that of the clinker shown in Fig. 1 we see that neither the triclinic nor the monoclinic  $\text{C}_3\text{S}$  show the same marked increase followed by a decrease of the viscosity as that of the clinker during the measured interval.

The zeta potential of a 1% by volume clinker slurry was also measured. This clinker was dry sieved through a sieve with a mesh of 20 micron before measurement and only one sample was measured. The time period of measurement was from approximately 225 seconds after initial mixing till 4100 seconds. Only one sample was measured. The zeta potentials were measured subsequently 19 times during this period and were measured to approximately +4 mV. During this period they showed no marked development as a function of time.

## DISCUSSION

The behaviour of the Class G clinker as illustrated in Fig. 1, with the rapid increase

followed by a decrease in the viscosity is expected to be due to a flocculation of the clinker particles followed by a partial deflocculation. This is in accordance with Yang et al<sup>4</sup> who found that normal neat cement suspensions are either flocculated or coagulated and that the degree of flocculation or coagulation is not sensitive to the variation of the zeta potential, for zeta potentials between -20 mV and +20 mV. Our measurement of the zeta potential lying well within this range further confirms this assumption.

The adding of gypsum and anhydrite to the clinker, as shown in Fig. 2 is thus, expected to hinder the rapid onset of a reversible flocculation.

The lower initial viscosity of the gypsum added clinker slurry in Fig. 2 compared with the anhydrite added slurry is expected to be due to the more rapid dissolution of gypsum in water at this temperature. Saasen et al<sup>3</sup> observed the same tendency at 22°C but at a temperature of 52°C they observed a different behaviour. This behaviour is not thoroughly understood.

The Class G slurry in Fig. 2 developed viscosity following a similar trend. However, the viscosity is lower; possibly due to a different particle size distribution.

The triclinic  $C_3S$  is the stable end product of the calcium silicate phase from the oven. It has a perfect  $C_3S$  composition and should not react with gypsum. With the same solid fraction we see no significant difference in viscosity for the pure triclinic  $C_3S$  curve with and without added gypsum.

The reduction in reaction of the monoclinic  $C_3S$  in Fig.3 on the addition of gypsum is more profound. This  $C_3S$  phase is stabilized using impurities and is thus more similar to clinker than triclinic  $C_3S$  is. However, we have no evidence whether the gypsum phase reacts with the impurities or the structure itself.

## CONCLUSION

We have shown that the rheological behaviour to the clinker phase depends on the sulphate source. This was found not to be due to sulphate reaction with the triclinic  $C_3S$

We have found an initial flocculation of the clinker phase that is diminished by the addition of a sulphate source.

## REFERENCES

1. Taylor, H.F.W., (1990) "Cement Chemistry", Academic Press Ltd., London, p. 234.
2. American Petroleum Institute, (1990), *Specifications for Materials and Testing for Well Cements*, API Spec. 10, Fifth ed., Washington DC, July 1.
3. Saasen, A, Haugom, J.O. and Johansen, E. (1994), "The Effect of Gypsum and Anhydrite on Rheological Properties of Cement Slurries", *Ann. Trans. Nordic Rheology Society*, **2**, 85-87.
4. Yang, M., Neubauer, C.M. and Jennings, H.M., (1997), "Interparticle Potential and Sedimentation Behavior of Cement Suspensions", *Elsevier, Advn. Chem. Bas. Mat.*, **5**, 1-7