

The Effect of Gypsum and Anhydrite on Rheological Properties of Cement Slurries

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ABSTRACT

The addition of gypsum and anhydrite to the clinker phase of an API Class G oilwell cement affects the rheological properties of cement slurries. Experiments indicate that precipitation of ettringite crystals on tricalcium-aluminate particles resulting from this addition will effect rheological properties of cement slurries.

INTRODUCTION

Portland cement

The primary constituents of a Portland cement clinker are tricalcium-silicate (C_3S), dicalcium-silicate (C_2S), tricalcium-aluminate (C_3A) and tetracalciumaluminoferrite (C_4AF). Here cement chemistry terminology is used where C=CaO, S=SiO₂, A=Al₂O₃, F=Fe₂O₃ and, to be used later, H=H₂O. In order to understand the influence of gypsum and anhydrite on rheological properties of cement slurries it is important to give a brief explanation of the early hydration of cement. The hydration of C_2S and C_4AF is similar, however much slower than the hydration of C_3S and C_3A , respectively. Therefore only the hydration of C_3S and C_3A will be outlined in some detail¹.

Hydration of C_3S

In the hydration of C_3S there is a initial period immediately after blending water with cement powder where there is considerable heat development. In this period which is called the pre-induction period, water reacts with the surface of the C_3S . Due to impurities in the mineral content, there is not a complete hydration product at this stage. The hydration

product is a thin amorphous surface on the C_3S grains known as C-S-H gel.

In the following period, called the induction period, there is no further rapid hydration of the C_3S grains. The C-S-H gel prevent contact between water and C_3S grains. Thus, there is a period with little change in slurry properties. At room temperature this period may last a few hours. All cement slurry pumping and placement must be performed while the cement slurry is in this induction period. When this period is terminated the cement slurry starts to set rapidly. Different types of chemical additives are added to control the length of this period for the needed temperature and pressure conditions. Termination of the induction period occurs when the fluid phase is supersaturated with respect to calcium ions. However, the mechanisms involved in this termination is beyond the scope of this paper.

Hydration of C_3A

The hydration of C_3A is different than that of C_3S . The calcium aluminate hydrates are present as hexagonal crystals. Thus, these hydrate products are not amorphous and no protective layers are formed on the C_3A surfaces that prevent further rapid hydration. There is therefore no natural induction period and an induction period must then be formed by chemical reactions with additives.

Most frequently 3-5% of gypsum, $CaSO_4 \cdot 2H_2O$, is added to the clinker to create an artificial induction period. Some producers use anhydrite, $CaSO_4$, in stead of gypsum to create this induction period.

Upon contact with water part of the

gypsum or anhydrite dissolves. The released calcium and sulphate ions in solution react with the aluminate and hydroxyl ions of the calcium aluminate to form a calcium trisulfoaluminate hydrate. This is known as the mineral ettringite which occurs as needle-shaped crystals. The ettringite crystals precipitate onto the C₃A surfaces and hinder further rapid hydration of the C₃A. The rapid hydration of C₃A resumes when the supply of gypsum or anhydrite is exhausted.

Dissolution of gypsum and anhydrite

Gypsum dissolves more rapidly than anhydrite in water. This solubility affects the growth rate of ettringite crystals. Thus, the hydration of a Portland cement with anhydrite is retarded compared to a Portland cement with gypsum. The knowledge of the effects of substituting gypsum with anhydrite on other properties of well cements is limited.

In oil well cementing the control of rheological properties is crucial for obtaining a proper job performance. Therefore, it is important to know what effect a possible change in the gypsum/anhydrite content may have on rheological properties. Such effects are the main objective in this paper.

EXPERIMENTAL PROCEDURES AND CONDITIONS

Materials preparation

The investigated cements were all based on an API sulphate resistant class G oil well cement clinker. Roughly 1000 tons of clinker was produced for preparing each of the anhydrite containing cements to ensure a commercial quality cement. From each of these two volumes approximately 500 kg of cement was collected for further investigation.

Sample A is a commercial class G oil well cement where the hydration of tricalcium aluminates is retarded by gypsum only. In the experimental cements B and C, 25% and 50% of the gypsum content has been replaced by anhydrite, respectively.

Each slurry sample consisted of 792 g cement and 349 g distilled water. The samples were all blended and conditioned in accordance with API procedures².

Rheology measurements

The rheology measurements were done using a Chan 35 viscometer. Each sample was sheared for 1 minute at a shear rate of 511 s⁻¹.

Thereafter the shear rate was reduced every 20 s at the following shear rates: 341, 170, 102, 51.1, 34.1, 17, 10.22, 5.11, 3.41 and 1.7 s⁻¹. At the end of each interval the shear stress was recorded.

A gelation test was performed after recording the viscosity curve following oilfield practices. The sample was sheared for 1 minute at a shear rate of 1022 s⁻¹. Then the sample remained static for 10 s. A shear rate of 5.11 s⁻¹ was applied to the sample and the peak shear stress was recorded. This value is referred to as the 10 s gel strength. Thereafter, the sample was once again sheared for 1 minute at 1022 s⁻¹, followed by a 10 minutes static period. Then the peak shear stress was recorded again at a shear rate of 5.11 s⁻¹. This value is referred to as the 10 minute gel strength. A constant shear rate of 5.11 s⁻¹ was applied to the sample after obtaining the 10 minute gel to investigate the break up, or the fragility, of the gel. In studying the gel fragility, this shear stress was recorded 0.5, 1 and 2 minutes after obtaining the 10 minutes gel strength.

RESULTS AND DISCUSSION

The shear stress measured as function of the shear rate for the different cement slurry samples is shown in Fig. 1. In this figure it is seen that at 22°C the viscosity is slightly reduced if 25% of the gypsum is replaced with anhydrite. This is believed to be as a result of having smaller ettringite crystals on the tricalcium aluminate particles. This should reduce the effect of particle entanglements as well as reducing the total surface area of the cement particles.

As the anhydrite concentration is increased to 50% the slurry viscosity exceeds the viscosity of the commercial G-cement significantly. This is shown by the curve for slurry C measured at 22°C in Fig. 1. The reason why this slurry viscosity is higher than that of the commercial cement is not known. A possible explanation is that the anhydrite particles have not been totally dissolved. Thus, there is an increase in particle concentration. This contributes to a significant increase in surface area. An increase in particle concentration, especially in the small particle range, yields an increase in viscosity. This may be the reason for the observed high viscosity of slurry C.

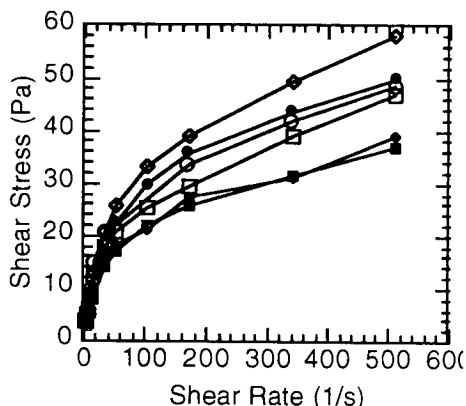


Figure 1. Shear stress versus shear rate for sample A (O), B (□) and C (◇) at 22°C (open symbols) and at 52°C (filled symbols).

If this hypothesis is correct, there are two conflicting mechanisms affecting the viscosity of cement slurries with different content of gypsum and anhydrite. A lower dissolution rate of sulphate ions leads to a reduction in viscosity with increasing anhydrite/gypsum ratio as ettringite formation is delayed, while the increased content of fine undissolved solids leads to an increase in slurry viscosity.

The viscosity measurements performed at 52°C partly support this theory. The viscosity of the gypsum based cement is slightly increased. This is probably a result of having slightly larger or more ettringite crystals. The cement hydration process is enhanced due to the increased temperature.

The viscosity of the two anhydrite modified cement slurries is reduced significantly. Less or smaller ettringite crystals have been precipitated on the tricalcium aluminate particles of these slurries than what experienced with the gypsum retarded cement. The large reduction in viscosity with the temperature increase is probably the result of having most of the gypsum or anhydrite solid particles dissolved.

A significant increase was measured in the viscosity at 52°C when the measurements were repeated after the gel tests were performed. In the measurements performed at lower temperatures, the original viscosity curve was obtained when repeating the viscosity measurements after the gel tests.

The gel tests are shown in Fig. 2. It is evident that some type of structure forms

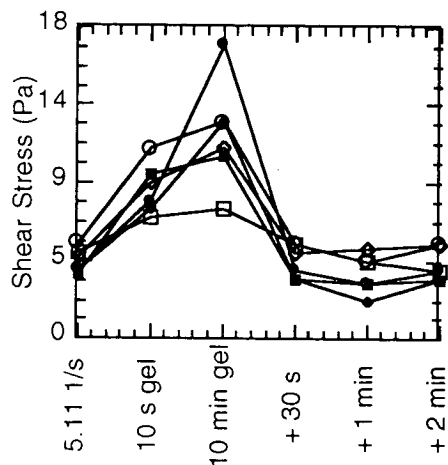


Figure 2. Gel formation and fragility properties of sample A (O), B (□) and C (◇) at 22°C (open symbols) and at 52°C (filled symbols).

when the slurries are static for some time. Likewise, it seems that at continuous rotation, the measurements resumes the value measured in the viscosity curve measurements. There is some scatter in these results. The final viscosity has been observed to be higher than the original viscosity measured at 5.11 s⁻¹ when tap water has been used instead of distilled water. However, in this case chloride ions have enhanced hydration. This gives an effect somewhat similar to increasing the temperature.

CONCLUSION

A series of experiments have shown that substitution of gypsum with anhydrite affects the rheological properties of cement slurries. Furthermore, the temperature dependence of these properties are different for cements with different gypsum/anhydrite ratios.

REFERENCES

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