Pergamon

Cement and Concrete Research, Vol. 26, No. 5, pp. 707-715, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00059-2

THE EFFECT OF ILMENITE PLANT DUSTS ON RHEOLOGICAL PROPERTIES OF CLASS G OIL WELL CEMENT SLURRIES

Arild Saasen and Per Arne Log
Høgskolen i Stavanger, Department of Petroleum Technology,
P.O.Box 2557, Ullandhaug, N-4004 Stavanger, Norway

(Refereed)
(Received September 1, 1995; in final form March 22, 1996)

ABSTRACT

A series of experiments was conducted to evaluate two ilmenite plant dusts as an alternative to barite as weight material for oil well cement slurries. These dusts had a similar particle size distribution to ground barite. Rheological investigations show that one of the dusts could be applied if it was properly dispersed. However, a change in consistency with time resulting from chemical reactions within the slurry was observed before the initial set. Such changes in consistency was not observed for a similar slurry weighted with barite. This makes the use of ilmenite plant dusts less favourable than the use of barite as a weight material for well cements.

Introduction

In a primary cementing operation in deep oil wells the water cement ratio (w/c) is seldom less than 0.44. At this w/c ratio the cement slurry has a density of approximately 1.90 S.G. Occasionally, cement slurries with larger densities are needed. These slurries are typically designed with a w/c ratio near 0.44 and the needed slurry weight is obtained by the addition of weighting agents. The most common weighting agents for cement slurries are barite, ilmenite or hematite (1). Barite is ground to a typical particle size distribution not very different from that of the class G cement itself. Ground ilmenite is typically coarser than the ground barite, while the hematite is normally delivered as a finer material. Both barite and hematite require an additional amount of water not to allocate less water for the cement hydration. Typical properties of these weighting agents is shown in Table 1.

Another frequently used weighting agent is manganese tetraoxide (2). This material originates from metalurgical melting plants. The manganese tetra oxide powder is dust from the plant smoke withdrawn to reduce air pollution. These particles have a surface are of approximately 3000 m^3/kg. With this fineness it is possible to disperse the particles completely in the cement mixing water prior to the addition of cement.

In ilmenite plants there are produced different kinds of particles and dusts collected from different filter systems. These particles have a high content of titanium. This implies that the density is fairly large; being approximately equal to that of ilmenite. At the same time the particle sizes are finer than the particle sizes of ground ilmenite. In the present study, dust from

TABLE 1

Typical Propeties of Common Weight Materials
Used in Well Cementing

Material	Density (S.G.)	Additional water requirement (L/kg)	Typical maximum slurry density (S.G.)
Barite	4.33	0.20	2.28
Hematite	4.95	0.019	2.64
Ilmenite	4.45	0.00	>2.4
Manganese tetraoxide	4.90	?	>2.55

two different filters is collected and evaluated as a weighting agent for well cements. The annual volumes produced from each filter make these dusts potentially favourable for use as a cementing additive. In the following sections the effect of replacement of barite with these two different types of dusts on rheological performance of the cement slurries is shown.

Materials

The applied cement used in the testes was a commercial Norwell class G oil well cement. The typical chemical composition of the Norwell class G oil well cement, is given in Table 2. The Blaine fineness of the cement was 318 m^2/kg.

The ilmenite plant dusts were collected from different filter systems at the Ilmenitt-smelteverket A.S. in Tyssedal, Norway. Two types of ilmenite plant dusts were evaluated: a

TABLE 2

Chemical Composition of Norwell
Class G Well Cement

Chemical compound	%
C_3S	58.9
C_2S	15.2
C_3A	2.3
C_4AF+2C_3A	19.2
SO_3	1.83
M	1.45
Loss on ignition	0.39

Filter dust (Dust F) and a Multicyclon dust (Dust M). As barite is the most frequently used weight material, it was used to develop a baseline for the evaluation of the ilmenite plant dusts.

The particle size distribution of the different weight materials is shown in Figure 1. The particle size distribution was determined using the Andreason pipette method (3). Note that the small particle fraction of Dusts F and M might have been slightly underestimated as the density of these dust materials is slightly larger than the density of barite.

The chemical composition of the two dusts is different. The differences in crystalline content of the two dusts is shown in Table 3. In both dusts there is a large fraction of amorphous material. According to the ilmenite plant, the total content of TiO_2 is approximately 41% in both dusts. The content of Al_2O_3 is 1.1% in Dust F and 1.8% in Dust M. The content of magnesium oxide is 4.5% in Dust F and 5.1% in Dust M. The content of magnesium oxide may lead to unsoundness of the cement (4). However, the total magnesium oxide will still be fairly low in the slurry. Furthermore, the material is planned for use under high pressure conditions where the surroundings may accept an expansion. Therefore, the magnesium oxide content is not expected to give any serious disadvantages for the slurry.

It is observed from electron microscopy analysis that the particle shape is different for the different dusts. Barite and Dust F has a similar particle shape which is irregular. In Dust M roughly half of the particles are spherical and the remaining particles have irregular shapes.

Experimental Methods

Each slurry sample consisted of 600 ml slurry. Prior to the addition of weight material, the cement slurry had a density of 1900 kg/m^3 and a w/c ratio of 0.44. The cement slurry formulations are shown in Table 4. The sample preparation procedure was as follows: The water was filled into a Waring blender. At a blender rotation rate equal to 4000 rpm, the dry material was added during a 20s period. Thereafter, the rotation rate of the Waring blender was set to 12000 rpm for 35s. When the blending was finnished, the samples were transferred to a

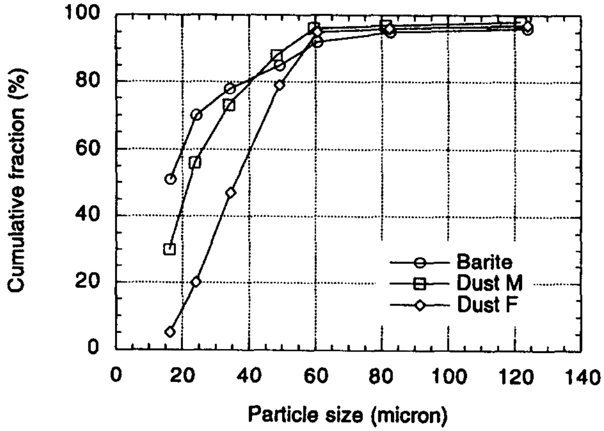

FIG. 1.
Particle size distribution of the evaluated weight materials.

TABLE 3

Major Crystaline Contents in Dusts F and M
Determined by X-ray Analysis

Mineral	Chemical formula	Dust F (%)	Dust M (%)
Ilmenite	$FeTiO_3$	50	20
Pseudo Brookite	Fe_2TiO_5	30	50
Magnetite	Fe_3O_4	18	10
Hematite	Fe_2O_3	2	15

Chandler Atmospheric Consistometer. The samples were then conditioned in accordance with API procedures (5) at a temperature of 50°C for 20 minute.

The rheology measurements were performed using a Chan 35 viscometer. A heating cup was applied to maintain the temperature during testing. 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 slurry gel formation 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.

The consistency development of cement slurries with different weight material compositions was investigated using the atmospheric consistometer (5). The slurry consistency was measured continuously from mixing cement with water to the initial set of the cement paste. The initial set is in this study defined as the point when the consistency reading reached 30 Bearden units of consistency (Bc) (5). At a consistency of 30 Bc the cement slurry is no longer pumpable.

TABLE 4

Cement Slurry Formulations

Density (S.G.)	1.90	2.06	2.10	2.15
Water (g)	349	324	317.5	311
Cement (g)	792	735.7	723.1	706.3
Weighting material (g)		177.5	217.9	273.3

Whenever desired, 2–3 ml of cement slurry was collected and immidiately dispersed in 80–100 ml of normal propanol. The added propanol terminates further cement hydration. Furthermore, the water phase is now dissolved in the propanol. The liquid phase containing the original water was removed by vacuum evaporation and a powder consisting of hydrated cement was collected. The powder was used for microscopy analysis or X-ray difraction.

Experimental Results And Discussion

The particle concentration and shape has an impact on the rheological properties of a slurry. An increased particle concentration yields an increased slurry viscosity (6). This is clearly illustrated in Figure 2, where the viscosity as function of shear rate is shown for three cement slurries with different concentrations of barite. In Figure 3, the viscosity curves for similar slurries weighted with Dust F and Dust M are shown. Little difference exists between the curves for the slurries weighted with barite and the slurries weighted with Dust M. The behaviour of the slurries weighted with Dust F is different. It is evident from Figure 3 that the low shear viscosity of the 2.06 SG slurry with Dust F is significantly higher than the viscosity of the slurries with Dust M and with barite. It was not possible with the used equipment to measure rheological properties of cement slurries weighted with Dust F at densities of 2.10 SG or higher.

From particle size analysis it is expected that the viscosity of slurries weighted with barite should be larger than the viscosity of the other slurries as there are more particles to affect the slurry viscosity. It is possible however, since barite bounds a fairly large amount of water as shown in Table 1, that electrical double layer forces are effective on barite particles surfaces and thus disperse these particles to some degree. These forces may be less effective on the Dust F and M surfaces. Thus, the barite weighted slurry should have a reduced viscosity compared to the other two slurries. Furthermore, if such colloidal forces are active, a more Newtonian viscosity profile is expected for the viscosity curve of the barite weighted slurry compared to the other two slurries.

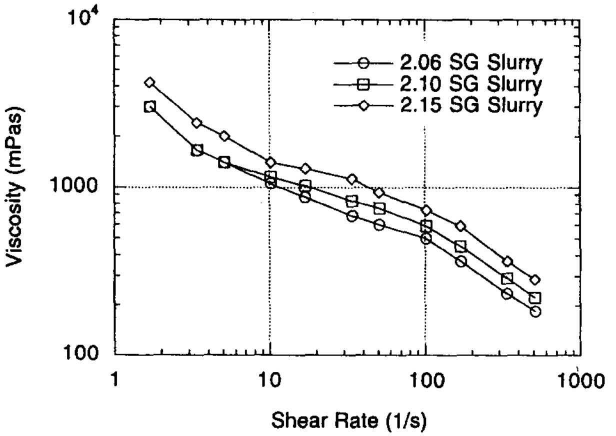

FIG. 2.
Viscosity versus shear rate for slurries weighted with barite.

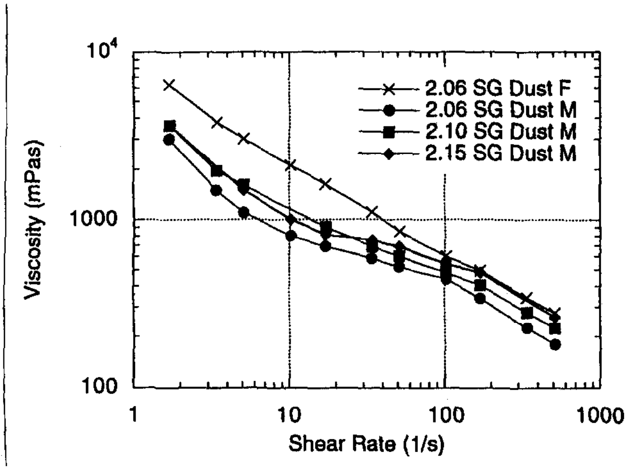

FIG. 3.
Viscosity versus shear rate for slurries weighted with Dust F and Dust M.

A slightly more Newtonian viscosity profile is observed for the barite weighted slurry compared to the viscosity profile of the slurry containing Dust F when the density was 2.06 SG. The viscosity curve for the slurry weighted with Dust M is equal to curve for the slurry weighted with barite. However, it has been observed from electron microscopy analysis that roughly half of the Dust M particles are spherical. The particle shape has a large impact on the viscosity curve. The slurry weighted with a large fraction spherical particles should have a lower viscosity than a similar slurry weighted with irregular shaped particles. With these differences between the weighting agents in mind, it seems reasonable that colloidal forces may play an important part in dispersion of the barite particles. A similar dispersion of the ilmenite

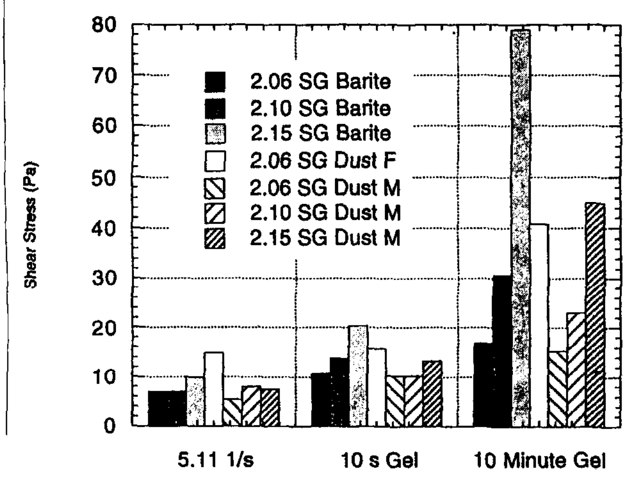

FIG. 4.
Gel tests for weighted cement slurries.

plant dusts is more unlikely to occur. However, the data are not sufficient to verify this hypothesis. Analysis of the zeta potential for the different materials is needed to verify the hypothesis. If the hypothesis is correct, barite is more suitable as a weight material than the ilmenite plant dusts.

All slurries form a particle structure when the slurries have been allowed to remain static for a period. These structures lead to a gel formation in the cement slurries. A gel formation is measurable even if the static period is as short as 10 s. This is illustrated in Figure 4. None of the measurements shown in Figure 4 for the slurries weighted with barite or Dust M show any unexpected characteristics. The measured values of the 10 minute gel strengths for the 2.10 and 2.15 SG slurries weighted with barite are very high. These high values reflect the high solid fraction in these slurries along with the water bonding properties of barite as shown in Table 1.

The measured values of the gel strengths for slurry weighted with Dust F are very high even though the density was only the 2.06 SG. Furthermore, it is a question if the gel structure that was formed during the static period could be broken completely if the slurry is sheared continously after the 10 minutes gel test.

The consistency development of the different cement slurries is different. An illustration of this difference is shown in Figure 5 for the slurries with density equal to 2.10 SG. At a consistency of 30 Bc a slurry is too viscous to be pumped. It is possible, if the slurry is not set, to disperse the particles and hence reduce the viscosity to an acceptable level. For a workable slurry this acceptable level is a consistency less than 30 Bc. The time where the consistency of an oil well cement slurry reach 30 Bc is normally well correlated to the time of initial set of the cement. This would be the case for the barite weighted slurry. The consistency is constant for a long period. Then the consistency value increase progressively. The time to reach 100 Bc is expected to be only slightly larger than the time to reach 30 Bc, which was the maximum attainable consistency of the utilized equipment. The time to reach 100 Bc is referred to as the thickening time of a cement slurry (5).

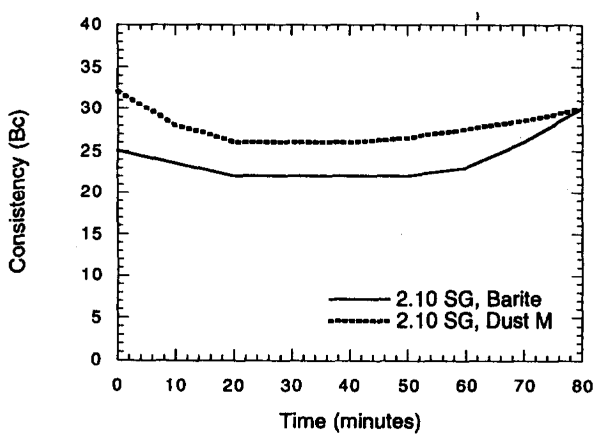

FIG. 5.
The consistency of cement slurries weighted with barite and Dust M to a density of 2.10 SG.

The consistency values of the slurry weighted with Dust F were too large to be measured with the utilized equipment. No success was obtained in dispersing and/or retarding this slurry to an acceptable consistency. The consistency of the Dust M weighted slurry had better properties. However, as shown in Figure 5, this slurry has a shorter period with constant consistency. Furthermore, there is a continous increase in consistency after conditionning the slurry for 40 minutes. There is no progressive increase in consistency that would have indicated an healthy initial set point for the slurry. There is observed a change in consistency before a real initial set occurs. The consitency is changed most likely as a result of chemical reactions which subtract water from the liquid phase of the cement slurry. This makes the use of Dust M less favourable than barite as weight material for well cements.

Presently, there is little knowledge about why the ilmenite plant dusts have a larger impact on cement hydration than does barite. It was investigated if the amorphous part of the ilmenite plant dusts could be hydraulically reactive. Blast furnace slag from pig iron plants have been utilized in well cementing (7). Blast furnace slag consists of a latent hydraulically reactive glass. The glass may be activated by an pH increase in the water solution. A similar activation was tested on the ilmenite plant dusts. The pH was increased to above 12 in a water dust blend. However, no reactivity was observed.

It is, however, some other indications that the cement hydration is enhanced in the slurries containing Dust M compared to the barite weighted slurry. Slurry samples were collected at the moment when the slurry consistencies reached 30 Bc; being typically 80 minutes after blending with water for both slurries. Thereafter the cement hydration was terminated by the addition of normal propanol to the slurry and the liquid phase was removed under vacuume. The resulting powder was sued in X-ray difraction analysis.

At a consistency of 30 Bc, a larger amount of portlandite was observed in the slurry weighted with Dust M than in the slurry weighted with barite. This indicates that Dust M accelerate the hydration of the cement. No other significant difference between the two slurries was observed during the X-ray difraction analysis.

A similar study of the slurry weighted with Dust F reveiled only traces of portlandite. However, in this case the consistency value was immediately above 30 Bc. This investigated sample was collected after 20 minutes of consistometer time which is significantly shorter than the 80 minutes spent on the other slurries. Therefore, little time had been available for the formation of portlandite.

Conclusion

A series of experiments was conducted to evaluate ilmenite plant dusts as an alternative to barite as weight material for oil well cements. These dusts had a similar particle size distribution as does ground barite. Rheological investigations concluded that one of the dusts may be applied if it was properly dispersed. However, a change in consistency with time was observed before the initial set occurs for the slurries weighted with ilmenite plant dusts. This results from chemical reactions within the slurry. Such a change in consistency was not observed for the slurry weighted with barite. This makes the use of these ilmenite plant dusts less favourable than use of barite as weight material for well cements.

Acknowledgement

The authors would like to thank West-Lab A/S who provided the X-ray analysis and Ørnulf Valla from Tinfos Developments A.S who provided the ilmenite plant dusts.

References

1. Nelson, E.B., Baret, J.-F. and Michaux, M., Cement Additives and Mechanism of Action, in Well Cementing, ed. E.B. Nelson, Elsevier, Amsterdam, 1990. pp. 3-1–3-37.
2. Johnston, N. and Senese, M., New Approach to High-Density Cement Slurries for Cementing High-Pressure, High-Temperature Wells, paper SPE 24976 presented at the European Petroleum Conference, Cannes, 16–18 November, 1992.
3. British Standards Institution, British Standard Methods for Particle Size Distribution, BS 3406: Part 2, 1984.
4. Rehsi, S.S., Magnesium Oxide in Portland Cement, in S.N. Gosh, Advances in Cement Technology, Pergamon Press, Oxford, 1983, pp. 467–483.
5. American Petroleum Institute, API spec. 10, "Specifications for Materials and Testing for Well Cements", Dallas, Texas, 1986.
6. Barnes, H.A., Hutton, J.F. and Walters, K., An Introduction to Rheology, Elsevier, Amsterdam, 1989, pp. 115–139.
7. Saasen, A., Salmelid, B., Blomberg, N., Hansen, K., Young, S.P. and Justnes, H., "The use of Blast Furnace Slag in North Sea Cementing Applications", paper SPE 28821, presented at the European Petroleum Conference, London, 25–27 Oct. 1994, pp. 143–153.