

HYDRAULIC CEMENT SLURRY

The present invention relates to a hydraulic cement slurry composition suitable for use in the cementation of oil wells.

In the cementation of oil wells, a cement slurry is pumped down into a casing and back up the annular space between the outside of the casing and the wall of the well. The two most important purposes of the cementation process are to prevent transport of gas and liquid between subterranean formations and to tie up and support the casing pipe. In addition to sealing oil, gas and water producing formations, the cement also protects the casing against corrosion, prevents gas and oil blow-outs (as the cement slurry very quickly seals the well), protects the casing against shock-loads, and seals formations against lost-circulation.

In order to obtain successful cementation, the hydraulic cement slurry has to satisfy a number of specific requirements. The rheology of the cement slurry has to be adjusted in order that the slurry may easily be pumped into the well. The cement slurry must displace drilling mud effectively in the annular space between the casing and the well. The cement slurry must also have a low fluid loss in order to avoid loss of liquid from the cement slurry into the formation, as loss of liquid will increase the viscosity of the cement slurry. Finally, the cement slurry must have as small as possible a tendency to water separation.

The setting time of the cement slurry must be adjusted to ensure that the cement slurry does not set before the slurry reaches the right location when

pumped into the well. The setting time which is needed will amongst other things depend upon the depth of cementation and on the temperature in the well.

The density of the cement slurry is of great importance for the cementation process and for the results which are achieved.

For oil wells which are drilled through high pressure formations, cement slurries having a high density are used in order to avoid uncontrolled blow-out. For oil wells which are drilled through low pressure formations where it is not advisable to expose the formations to high hydrostatic pressure, cement slurries having a low density have to be used, as a cement slurry having too high a density, and thereby a high hydrostatic pressure, may result in breakdown of the formations and loss of the cement slurry into the formations (lost circulation).

Another important property of the cement slurry is its early strength. The early strength is critical to how quickly the drilling procedure can be restarted after the cementation process is finished.

Cements which have a compressive strength after 24 hours of at least 1.5 MPa are usually satisfactory. The development of the early strength of the cement slurry is very dependent on the temperature in the well.

For cement slurries which are used for cementation of high temperature wells, it is also important that the cement slurries do not lose their strength over a period of time. It is known that at temperatures above about 110°C, ordinary Portland cement slurries over a period of time will lose their strength as the normal binding phase, calcium hydroxide, is transformed to

alpha-dicalcium silicate. This phenomenon is well known and is called cement strength retrogression.

It is known that cement strength retrogression can be overcome by the addition of silicon dioxide materials to the cement slurry. The most frequently used silicon dioxide materials for this purpose are silica flour and silica sand. At high temperatures, these silicon dioxide materials react with calcium hydroxide to form new binding phases, mainly tobermorite. Tobermorite is a binding phase which is stronger than the normal binding phases which form during the hardening of cement slurries. However, addition of silica flour has the disadvantage that the water requirement increases and it becomes difficult to produce a cement slurry having an acceptable low viscosity. On the other hand, by addition of silica sand, settling of the sand and the high-density filler material increases at high temperatures.

For some oil wells, the zones adjacent the cement containing annulus, contain gas under substantial pressure. This gas can cause serious problems during cementation of oil wells as the gas may penetrate through the cement slurry whereby an undesirable phenomenon referred to in the art as gas migration may occur.

Gas migration may start during setting of the cement slurry. When the cement sets the cement slurry will change from a hydrostatic fluid to a solid state body. If the cement slurry in this critical phase is not able to resist the gas pressure, channels will be formed in the partially cured cement slurry. Gas under pressure will then flow through the column during the setting of the cement slurry and/or at the boundary

between the cement slurry and the wall of the well. This may result in channels which can reach the top of the well.

In order to control or prevent gas migration through cement slurries, it has been proposed to add fluid loss control additives or a latex such as a styrene/butadiene copolymer to the cement slurries. For normal and low density cement slurries it is also known that the addition of microsilica, which is a product obtained from the off-gases of furnaces used in the production of silicon or ferrosilicon, strongly improves the gas-tightness of cement slurries.

High density cement slurries are produced by adding an inert high density filler material such as barite to an ordinary oil well cement slurry, based on Portland cement, water and additives, for controlling the rheological properties of the cement slurry. The density range for so-called high density oil well cement slurries is from about 2.0 to 2.3 g/cm³.

As set out above, high density cement slurries for oil well cements which are either gas tight or have a low tendency to strength retrogression at high temperatures are known. However, high density cement slurries which are both gas tight and have a very low tendency to strength retrogression are not known.

A further disadvantage of the known high density cement slurries for cementing of oil wells, is that the high density filler material shows a tendency to settle as the temperature increases. The settling of the high density filler material will result in a varying density in the column of cement slurry with a higher density at the bottom of the column and a lower density at the top of the column. This difference in

density can result in problems for the operators in controlling the pressure in the well and may in the worst cases cause an uncontrolled blow-out.

It is an object of the present invention to provide a high density hydraulic cement slurry for cementing oil wells which is gas tight, has a very low strength retrogression at high temperatures and which shows substantially no tendency of settling or segregation.

Accordingly the present invention provides a high density, gastight hydraulic cement slurry for use in the cementation of oil wells, which comprises a hydraulic cement, 5 - 85% microsilica based on the weight of the cement, 5 - 250% of a high density filler material based on the weight of cement, 0 - 5% of a retarder based on the weight of cement, 0 - 12% of a thinner (dry weight) based on the weight of the cement, 0 - 8% fluid loss additive (dry weight) based on the weight of cement, 0 - 45% silica flour and/or silica sand based on the weight of the cement, and water in such an amount that the cement slurry has a density between 1.95 and 2.40g/cm³ and the ratio of the water content to the content of the cement plus the microsilica in the slurry is equal to or greater than 0.49.

Any ordinary hydraulic cement can be used, such as for example Portland cement, but preferably cements for oil well cementation specified by API are used.

The microsilica used in the hydraulic cement slurry is preferably amorphous silica dust collected from the off-gases from electrothermal smelting furnaces used in the production of silicon or ferrosilicon containing at least 75% by weight of

silicon, but silica dust from furnaces producing 50% ferrosilicon may also be used.

By adjusting the operation parameters, it is also possible to produce amorphous silica dust as the main product from the above mentioned furnaces. Amorphous silica of this kind can also be produced synthetically without reduction and reoxidation. Alternatively a silica generator can be used for producing finely divided silica or silica can be produced by precipitation.

The amorphous silica dusts which may be used in the hydraulic cement slurry of the present invention consist to a very high extent of submicron, spherical particles.

The silica dust particles may contain 60 to 100% by weight of SiO_2 , may have a real particle density between 2.00 and 2.40 g/cm^3 and may have a specific area of 15 to 30 m^2/g . The individual particles are mainly spherical and have a diameter below 1 μm . Variation of these values are of course possible. The silica dust may for example have a lower SiO_2 content and the particle size distribution may be adjusted by removing coarse particles.

In order to obtain the most gas-tight cement slurry, the hydraulic cement slurry preferably contains 10 to 60% microsilica based on the weight of cement. Cement slurries containing 20 to 50% microsilica based on the weight of the cement are especially preferred.

The hydraulic cement slurry according to the present invention preferably contains 25 to 110% of the high density filler material. As the high density filler material, any conventional high density filler material for high density oil well cement slurries can

be used. Such high density filler material may therefore comprise barite, haematite and ilmenite and others.

The hydraulic cement slurry according to the present invention also preferably contains a retarder in an amount of 0.1 to 3% (dry weight) based on the weight of cement. The chemical composition of retarders are known in the art. They may be based on lignosulphonates, modified lignosulphonates, polyhydroxy carboxylic acids, carbohydrates, cellulose derivatives or borates.

Some of the retarders may also act as thinners in the hydraulic cement slurry and when such retarders are used, the dosage of thinners may be reduced.

The hydraulic cement slurry according to the present invention preferably contains a thinner or dispersant in an amount of 0.1 to 6% (dry weight) based on the weight of the cement. As thinners, additives which are known as plasticisers or superplasticisers in cement based systems can be used. These are well-known additives which may be based on lignosulphonate, sulphonated naphthaleneformaldehyde or sulphonated melamineformaldehyde products.

The hydraulic cement slurry according to the present invention preferably contains 0.1 to 4% (dry weight) of a fluid loss additive based on the weight of the cement. As the fluid loss additive, known additives such as additives based on starch or derivatives of starch, derivatives of cellulose such as carboxymethylcellulose, methylcellulose or ethylcellulose or synthetic polymers such as polyacrylonitrile or polyacrylamide may be used.

Cement slurries which are used at high well

temperatures preferably contain 10 to 35% silica flour and/or silica sand based on the weight of the cement.

Both fresh water and sea water may be used in the hydraulic cement slurry of the present invention. If necessary, accelerators may be incorporated into the cement slurry in order to adjust the setting time.

It has been found, surprisingly, that the high density hydraulic cement slurry of the present invention is gas tight, shows very little tendency towards segregation and settling and has a very small tendency towards strength retrogression. Thus, the content of high density filler material and the content of silica sand or silica flour can be increased above conventional levels without affecting the plasticity of the cement slurries while the tendency of settling is strongly reduced.

The present invention may be carried into practice in various ways and will now be further illustrated by the following non-limiting examples:

EXAMPLE 1

Four cement slurries A, B, C, D were produced. Cement slurries A, B and C have compositions according to the present invention, while cement slurry D has a composition according to the state of the art.

The compositions of cement slurries A-D are shown in Table I.

TABLE I

Cement Slurry	A	B	C	D
	kg	kg	kg	kg
G-cement	100	100	100	100
EMSAC 465T	10	30	40	-
Thinner (D-31)	-	2.4	2.4	-
Retarder (R-12)	2.4	2.4	2.4	3.6
Haematite	-	103.7	-	34.3
Barite	35.1	-	200.5	-
Water	54.3	76.2	109.0	41.8

The theoretical density for slurry A is 2.00 kg/dm³ and for slurries B - D 2.16 kg/dm³.

- G-cement is a Portland cement delivered by Norcem A/S, Norway.
- EMSAC* 465T is a high quality microsilica product in dry form which is produced and sold by Elkem a/s, Chemicals, Norway.

* EMSAC is a Registered Trade Mark

- D-31 is a thinner and R-12 a retarder, both supplied by B.J. Hughes, USA.

Cement slurries A to D were mixed and tested according to API Specification 10. The results are shown in Table II.

TABLE II

5	Cement Slurry	A	B	C	D

	Rheology (20°C)				
	Apparent viscosity, cp	29.5	26.5	31	65.5
	Plastic viscosity, cp	36	29	28	68
10	Yield point, lb/100ft ²	(-13)	(-5)	6	(-5)
	[kg/m ²]	[-6347]	[-2441]	[2929]	[-2441]

	Rheology (93°C)				
	Apparent viscosity, cp	20	21	20	34.5
15	Plastic viscosity, cp	21	23	15	35
	Yield point, lb/100ft ²	(-2)	(-4)	10	(-1)
	[kg/m ²]	[-976]	[-1953]	[4882]	[-488]

	Compressive strength,				
20	MPa (after 5 days at				
	50°C and 1 day at				
	93°C)	36	50.6	41.4	35

25 From Table II it can be seen that slurries A to C according to the present invention, are easy to pump into the well-bore and have a good compressive strength compared to the conventional slurry D. Slurries A to C thus fulfil the requirements which are set to the

30 rheological properties for high density oil well cement slurries.

In order to examine the settling of the cement slurries A to D, the fresh slurries were heated in an

atmospheric consistometer to 93°C after which each slurry was poured into a 250 ml graduated cylinder. The cylinders containing the cement slurries were put into water having a temperature of 93°C and the cement slurries were allowed to cure at this temperature for 24 hours.

Thereafter, the cylinders were removed from the water and test specimens with a height of 3cm were cut from the top and the bottom of each cylinder and density of the test specimens were measured. The results are shown in Table III.

TABLE III

Cement slurry	A	B	C	D
Density, top, kg/dm ³	2.04	2.15	2.16	2.09
Density, bottom, kg/dm ³	2.04	2.19	2.14	2.41

Table III shows that practically no settling or segregation occurred in the cement slurries A-C. In contrast the conventional cement slurry D showed a very significant settling. The very low tendency to settling for the cement slurries according to the present invention is very surprising as the viscosities especially of slurries A and B are much lower than for the conventional slurry D and the content of high density material is much higher for cement slurries A, B and C than for the conventional slurry D.

EXAMPLE II

Eight cement slurries E, F, G, H, I, J, K, L were produced. Cement slurries E to J have compositions according to the present invention while cement slurries K and L have compositions according to the state of the art.

The compositions of cement slurries E - L are shown in Table IV.

TABLE IV

Cement Slurry	E	F	G	H	I	J	K	L
kg	kg	kg	kg	kg	kg	kg	kg	kg
G-cement	100	100	100	100	100	100	100	100
EMSAC 460 S	60	-	-	-	-	-	-	-
EMSAC 465 T	-	30	20	50	70	15	-	-
Silica flour	-	-	-	-	-	30	35	-
Thinner (D-31)	4.2	4.2	-	4.8	9.6	4.2	7.2	-
Retarder (R-12)	0.96	0.96	0.96	-	-	0.96	-	-
Fluid loss additive (D-19)	0.7	0.7	-	-	-	-	0.5	0.5
Haematite	104.9	104	-	-	-	-	-	-
Barite	-	-	81.1	98.5	110.3	98.1	71.4	20.6
Water	47.6	75.7	75.0	83.2	87.3	86.7	71.9	43.8

The theoretical density of slurries E and F is 2.16

g/cm^3 and the theoretical density of slurries G - L is 2.04 g/cm^3 .

EMSAC 460 S is a high quality microsilica product in the form of a liquid suspension which is produced and sold by Elkem/as, Chemicals Norway.

Cement slurries E - L were mixed and tested according to API specification 10. The results are shown in Table V.

TABLE V

Cement	E	F	G	H	I	J	K	L
Slurry	kg	kg	kg	kg	kg	kg	kg	kg
Rheology								
(20°C)								
Plastic								
visco-								
sity, cp	44	57	29	33	34	40	53	27
Yield point,								
lb/100ft^2	16	4	18	14	12	9	29	5
$[\text{kg/m}^2]$	[7812]	[1953]	[8788]	[6835]	[5859]	[4394]	[14,159]	[2441]
Rheology								
(93°C)								
Plastic								
Visco-								
sity, cp	36	30	25	27	29	35	48	25
Yield point,								
lb/100ft^2	1	(-4)	8	6	4	6	22	3
$[\text{kg/m}^2]$	[488]	[-1953]	[3906]	[2929]	[1953]	[2929]	[10,741]	[1465]

In order to examine the tendency of strength retrogression, the compressive strength of test specimens of cement slurries E - L were measured after 7, 14, 21 and 28 days. The test specimens were stored at a temperature of 140°C.

The results are shown in Table VI.

TABLE VI

Cement Slurry	Compressive strength, MPa							
	E	F	G	H	I	J	K	L
7 days	47.6	41.4	38.2	48.1	48.0	46.5	40.2	33.7
14 days	48.0	43.0	39.5	52.4	55.2	46.2	38.7	31.1
21 days	46.7	47.3	38.0	53.0	53.0	48.7	39.8	27.5
28 days	47.2	46.8	37.0	52.1	52.3	45.3	38.3	21.7

From Table VI it can be seen that the cement slurries E - J according to the present invention showed no tendency of strength retrogression. The conventional cement slurry L shows a very significant strength retrogression, and this cement slurry can not be used for cementing oil wells having high temperatures. Cement slurry K shows a low tendency of strength retrogression due to the content of silica flour. However, this cement slurry suffers from a very high tendency of settling in spite of the high viscosity shown in Table V and will cause problems for this reason.

EXAMPLE 3

Cement slurries E and L of Example 2 were tested in a gas migration apparatus . The test was run in the apparatus shown schematically in Figure 1. The apparatus comprises an acrylic pipe 1. The pipe is 2.0 m high and has an inner diameter of 80 mm and a wall thickness of 5mm. In the bottom of the pipe 1, a bottom plate 2 is secured into which an air supply pipe 3 is inserted. Just above the bottom plate 2 there is a permeable sand filter 4 made from a mix of sand of uniform particle size and epoxy. Air is supplied to the bottom of the pipe 1 by a compressor 5 and the air pressure is controlled by a regulator 6. A transducer 7 for measuring the hydrostatic pressure is inserted into the pipe 1. A cover plate 8 is secured to the top of the pipe 1. The cover plate 8 has an opening for the insertion of a pipe 9 which is connected to a gas flowmeter unit 10. A temperature measuring device 11 is also connected to the pipe 1.

The cement slurries were filled into the pipe 1 and the gas pressure was fixed at 0.25 bar which corresponds to 125% of the water gradient.

If no gas flows through the cement slurries at this gas pressure during the setting of the cement slurries, the cement slurries will be gas tight at all practical gas pressures in oil well formations.

When the cement slurries E and L were tested in the gas migration apparatus described above, cement slurry E according to the present invention withstood the applied gas pressure, while a substantial flow of gas was measured through the column of the conventional cement slurry L.

CLAIMS

1. A hydraulic cement slurry for use in the cementation of oil-wells, consisting of a hydraulic cement, 5 - 85% microsilica based on weight of the cement, 5 - 250% of a high density filler material based on the weight of the cement, 0 - 5% of a retarder (dry weight) based on the weight of the cement, 0 - 12% of a thinner (dry weight) based on the weight of the weight of the cement, 0 - 8 % of a fluid loss additive (dry weight) based on the weight of the cement, 0 - 45% silica flour and/or silica sand based on the weight of the cement, and water in such an amount that the cement slurry has a density between 1.95 and 2.40g/cm³ and the ratio of the water content to the content of the cement plus the microsilica in the slurry is equal to or greater than 0.49.

2. A hydraulic cement slurry as claimed in Claim 1 in which the cement slurry contains 20 - 50 % microsilica based on the weight of the cement.

3. A hydraulic cement slurry as claimed in Claim 1 or Claim 2, in which the cement slurry contains 25 - 110% of high density filler material based on weight of cement.

4. A hydraulic cement slurry as claimed in any preceding claim in which the cement slurry contains 0.1 - 3% of a retarder (dry weight) based on the weight of cement.

5. A hydraulic cement slurry as claimed in any



preceding claim in which the cement slurry contains 0.1 - 6% of a thinner (dry weight) based on the weight of the cement.

6. A hydraulic cement slurry as claimed in any preceding claim in which the cement slurry contains 0.1 - 4% of a fluid loss additive (dry weight) based on the weight of the cement.

7. A hydraulic cement slurry as claimed in any preceding claim in which that the cement slurry contains 10 - 35% silica flour and/or silica sand based on the weight of the cement.

8. A hydraulic cement slurry as herein specifically described in the examples under any one of the designations A to C or E to J.

