

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
25 November 2004 (25.11.2004)

PCT

(10) International Publication Number
WO 2004/101463 A2

- (51) International Patent Classification⁷: **C04B 28/02**
- (21) International Application Number:
PCT/EP2004/005124
- (22) International Filing Date: 12 May 2004 (12.05.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/470,341 14 May 2003 (14.05.2003) US
- (71) Applicant (for FR only): **SERVICES PETROLIERS SCHLUMBERGER** [FR/FR]; 42, rue Saint Dominique, F-75007 Paris (FR).
- (71) Applicant (for AT, AZ, DE, DK, IT, KP, KR, KZ, NO, NZ, PL, RO, RU, TM, UA, ZA only): **SCHLUMBERGER TECHNOLOGY B.V.** [GB/GB]; Parkstraat 83-89, NL-2514 JG The Hague (GB).
- (71) Applicant (for GB, JP, NL only): **SCHLUMBERGER HOLDINGS LIMITED**; P.O. Box 71, Craigmuir Chambers, Road Town, Tortola (VG).
- (71) Applicant (for CA only): **SCHLUMBERGER CANADA LIMITED** [CA/CA]; 525 - 3rd Avenue S.W., Calgary, Alberta T2P 0G4 (CA).
- (71) Applicant (for all designated States except AT, AZ, CA, DE, DK, FR, GB, IT, JP, KP, KR, KZ, NL, NO, NZ, PL, RO, RU, TM, UA, ZA): **SOFITECH N.V.** [BE/BE]; 140, rue des Stalle, B-1180 Brussels (BE).
- (72) Inventors; and
(75) Inventors/Applicants (for US only): **ZUSATZ, Benedicte** [FR/FR]; 63, voie de la Vallée aux Loups, F-92290 Châtenay Malabry (FR). **NILSSON, Frederik** [SE/FR]; 1, place Alfred Sauvy, F-75015 Paris (FR).
- (74) Agent: **MENES, Catherine**; Etudes et Productions Schlumberger, 1, rue Henri Becquerel, Boîte postale 202, F-92142 Clamart (FR).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: COMPOSITIONS AND METHODS FOR TREATING LOST CIRCULATION

(57) Abstract: A cement system for use in treating lost circulation includes a slurry of cement, water and a super-absorbent polymer which absorbs free water in the slurry to form a gel - ore preferably a solid-like structure - when placed in the well, and which releases the absorbed water to the cement hydration reaction as the cement sets. The absorption of water causes the slurry to develop a solid-like structure. In one embodiment, the superabsorbent is polyacrylamide or modified crosslinked poly(meth)acrylate. Also presented is a method of treating lost circulation by pumping the above-mentioned cement system.

WO 2004/101463 A2

Compositions and Methods for Treating Lost Circulation

Technical Field of the Invention

[0001] The present invention relates to treatment of lost circulation during the drilling of
5 a well and in particular, to methods involving the use of cement slurries for curing lost
circulation issues.

Background of the Invention

[0002] During the construction of underground wells, it is common, during and after
drilling, to place a liner or casing, secured by cement pumped into the annulus around the
10 outside of the liner. The cement serves to support the liner and to provide isolation of the
various fluid-producing zones through which the well passes. This later function is
important since it prevents fluids from different layers contaminating each other. For
example, the cement prevents formation fluids from entering the water table and
polluting drinking water, or prevents water from passing into the well instead of oil or
15 gas.

[0003] A problem which is encountered in the placement of cement in wells is the
development of gel strength in situations in which materials are easily lost from the
cement slurry before it is set in the correct position. One example of this is in the
placement of cement for lost circulation problems. In normal cement systems, the cement
20 is pumped into the well in a slurry that is very fluid and gel strength develops during the
early part of the setting reaction. However, this can take a significant time during which
some or all of the components of the cement slurry can be lost to the formation. It has
been proposed to add fibers to cement slurries to help build a filter cake and retain the
cement in position. However, the lack of a gel structure still makes loss of materials to
25 the formation a problem.

[0004] It is an objective of the present invention to provide well cementing systems that
can be placed by pumping in the normal manner, and which contain materials that favor
the development of the gel strength for curing lost circulation.

Summary of the Invention

[0005] In accordance with the invention, there is provided a system which adapts downhole to allow lost circulation problem to be addressed. By using super-absorbent copolymers, liquid water is quickly removed from the slurry, which is transformed into a solid-like material with certain gel strength and with little or no flow. In many cases when lost circulation problems are faced, the importance of changing a pumpable lost circulation treatment material into a non-pumpable one and with solid-like properties, as soon as the target zone is reached, cannot be underestimated. This is particularly true when cross-flow is present down-hole and which, may "wash away" any lost circulation treatment, unless the treatment "set" and block the cross-flow instantly when applied.

[0006] The term "solid-like structure" is used here to indicate that the water in the slurry that makes it pumpable and flowable has been removed (by the super-absorbent polymer) such that what is left has more of the characteristic of a solid than a liquid slurry.

[0007] Super-absorbent copolymers can rapidly transform a cement slurry, having the necessary rheological properties to be pumpable, into something that is solid-like and with high extrusion strength. This does not mean that cement has "set" at this stage but has merely lost its flowing properties. The water content remains the same in the slurry but the super-absorbent material has immobilized it.

Detailed Description

[0008] Due to the nature of super-absorbent copolymers they will, as soon as in contact with water, start absorbing it forming a solid-like structure. As a consequence, to avoid any change in the cement slurry rheology during placement, the super-absorbent copolymers need to be protected from water contact until the lost circulation target zone has been reached. The preferred way of protecting the super-absorbent copolymer is encapsulation. There are different types of encapsulation and with different related release mechanisms. Two common types of encapsulation are resins and mineral oxides of e. g. silica or aluminum.

[0009] Resin encapsulation can use temperature as the release mechanism. Above a certain temperature the resin will melt and the copolymer is released. There are different

types of resins with a range of melting points and the must be taken into account for well cementing applications with large temperature variations.

[0010] Using different types of mineral oxides, forming a "hard cover" round the copolymer is another solution. The release mechanism in this case is pressure. The pressure resistance of the "hard cover" will depend upon the chemical composition as well as the thickness of the covering layer.

[0011] A further solution to protect the super-absorbent copolymer from water contact is an inverse emulsion where the copolymer is dispersed in the oil-continuous phase. There are several different ways of triggering emulsion inversion down-hole and transforming the water-in-oil emulsion into an oil-in-water emulsion. A good example of emulsion inversion has been described in WO94280855 and PCT-NO94-00163 where a pressure drop through the bit nozzles is used to trigger the inversion of a water-in-oil emulsion into an oil-in-water emulsion.

[0012] A further approach is to use a down-hole release tool. In such a case, the copolymer system is protected "mechanically" until the target zone has been reached and where it is released.

[0013] Two types of super-absorbent copolymers are considered as particularly useful. The first is a copolymer of poly(2-propenamide-co-2-propenoic acid, sodium salt). The second super-absorbent copolymer is a sodium polyacrylate and presented as a comparison to demonstrate the particular properties of the first. Other SAP such as polyacrylamide or modified crosslinked poly(meth)acrylate are also interested for self healing applications.

[0014] These types of copolymers are made up of cross-linked polymers, which swell into a gel when in contact with water. The swelling is a consequence of electrostatic repulsion between charge sites on the copolymers in the presence of water. The addition of highly concentrated salt solution will make the gel collapse instantly due to the screening of the charged site on the copolymer. The sensitivity towards high salinity has at least one drawback but also advantages.

[0015] The major drawback is that in the presence of ions in the water, the copolymer will swell less as well as lose some of its gel strength compared with fresh water. This is the case when used in e. g. cement where high concentrations of calcium ions are present.

[0016] One advantages is that in the event that a cement-copolymer system becomes solid-like in the wrong location, for example inside a drillpipe or a casing, a concentrated salt solution can be pumped to make the gel collapse with a regained low rheology. Saturated sodium chloride water solution has proven to be highly efficient to make the gel collapse. A solid-like cement obtained with a cement-copolymer system based on a 15.8 ppg cement slurry with 1.00 %BWOW (percent by weight of water) of a copolymer (copolymer A, see explanation below) can be rapidly transformed back into a slurry by treatment with a saturated NaCl water solution. The rheology directly after the adding 33% (by volume of the solid-like cement-copolymer) of the salt solution gave a PV of 22.3 cP and a τ_y of 6.0 lbf/ft². This rheology is similar to any standard and pumpable cement slurry.

[0017] Another advantage is that this cement-copolymer slurry can be used when drilling faulted reservoirs. Placing a solid-like cement-copolymer system would assure "safe" and easy drilling in this type of reservoirs. When drilling is finished, a saturated salt solution could be used to remove the solid-like cement-copolymer and the initial reservoir properties would be regained.

[0018] In Table 1, some physical properties of the copolymers, A, B and C are presented. The copolymers A and B are of the poly(2-propenamide-co-2-propenoic acid, sodium salt) type whereas C is based on sodium acrylate. From here and on, the super-absorbent copolymers described in this patent memo will be referred to as copolymers A, B and C.

Copolymer	Appearance	Granular dimension	Density
A	Light tan granular powder	98%<850 μm	1.473 g/cm ³
B	Light tan granular powder	98%<850 μm 20%<75 μm	1.187 g/cm ³
C	White granular powder	33% 500-850 μm	1.617 g/cm ³

Copolymer	Appearance	Granular dimension	Density
		66% 106-500 μm	

Table 1. *Physical properties of the copolymers A, B and C.*

[0019] In Table 2, the water absorbency of copolymers A, B and C are presented. Copolymers A and B have a significantly better capacity of absorbing distilled water than copolymer C although C is also considered as a super-absorbent copolymer. Table 2, also demonstrates that super-absorbent copolymers are sensitive to the presence of salt in the water. In this particular case 1 %BWOW of NaCl was used which reduces the absorbing capacity by a factor of 10.

Copolymer	Water absorbency (tap water)	NaCl (1 wt%) in distilled water
A	270 g/g	75 g/g
B	270 g/g	90 g/g
C	220 g/g	-

Table 2. *Water absorbency of copolymers A, B and C. The water absorbency is expressed as gram (g) of water absorbed per gram (g) of dry copolymer.*

[0020] In Table 3, the obtained results from measuring the gel strength using a HAAKE Rotovisc RV12 are presented. For this particular measurement, samples of copolymers A, B and C were prepared in a beaker using 1.5 gram of each respectively, mixed with 150 g distilled water giving a final concentration of 1%BWOW. The measurements were performed at ambient temperature and pressure.

Copolymer	Gel Strength (lbf/100 ft ²)	Gel strength (Pa)
A	266	127
B	183	88

Copolymer	Gel Strength (lbf/100 ft ²)	Gel strength (Pa)
C	699	335

Table 3. The measured gel strength of a 1.00-%BWOW solution of copolymers A, B and C respectively. The tests were performed under ambient temperature and pressure conditions.

[0021] The gel strength and the solid-like nature of a lost circulation treatment once at its target zone is important. A low gel strength value will most likely result in low extrusion strength once the copolymer is placed in a lost circulation zone e.g. fractured or cavernous formation. However, a low water (fluid) absorbency will enhance the risk that the copolymer will be “washed away” before any gel strength has been built up. To overcome this problem, a small amount of copolymer can be dry blended with cement to form a slurry.

[0022] In Table 4, 5 and 6, the results from mixing copolymers A, B and C with class G cement at densities of 15.8 ppg (pounds per gallon), 14 ppg and 12 ppg respectively are presented. For each different case, the slurry rheology has been measured using a Chan 35 rheometer (unless other stated) and compared with neat class G cement. In some cases, when the rheology was too high to measure using the Chan 35, a HAAKE Rotovisc RV12 was used to obtain the gel strength instead. The cement slurry is based on cement, water (corresponding to the density for each particular case), a dispersing agent at a constant concentration of 0.04 gps (gallons per sack cement) and an anti-foam agent at a concentration of 0.02 gps. API mixing procedure has been applied.

System	Copolymer (%BWOW)	Plastic viscosity (PV)	Yield Strength (τ_y)
Neat class G slurry	0.00	6.1 cP	23.2 lbf/100 ft ²
Copolymer A + class G	0.50	13.2 cP	40.5 lbf/100 ft ²
Copolymer A + class G	0.75	too viscous	too viscous
Copolymer A + class G	1.00	too viscous	~1500 lbf/100 ft ² *
Copolymer B + class G	0.50	too viscous	too viscous

System	Copolymer (%BWOW)	Plastic viscosity (PV)	Yield Strength (τ_y)
Copolymer B + class G	0.75	too viscous	too viscous
Copolymer B + class G	1.00	too viscous	>3000 lbf/100 ft ² *
Copolymer C + class G	1.00	30.1 cP	8.6 lbf/100 ft ²

Table 4. Copolymers A, B and C have been dry blended with Class G cement, water corresponding to a 15.8 ppg slurry, a dispersing agent (0.04 gps) and an anti-foam agent (0.02 gps). The rheology results are compared with a neat Class G cement, that is without any copolymer. The rheology where measured with a Chan 35 Rheometer unless otherwise stated.

*Value obtained using a HAAKE Rotovisc RV12.

In Table 4, the results from a 15.8 ppg slurry are presented. The results clearly show that the addition of copolymer A or B have a significant influence upon the cement slurry rheology resulting in an instant solid-like formation with a non-measurable rheology. For copolymer A, a reasonable low slurry rheology is obtained at a concentration of 0.50 %BWOW but at a concentration of 0.75 BWOW and above a solid-like cement-polymer structure is obtained. In the case of copolymer B, the three concentrations tested viz. 0.50, 0.75 and 1.00- % BWOW all give rise to the formation of an instant gel. Copolymer C has some effect upon the slurry rheology at a concentration of 1.00- %BWOW but the slurry remains pumpable.

System	Copolymer conc. %BWOW	Plastic viscosity (PV)	Yield Strength (τ_y)
Neat class G slurry	0.00	6.5 cP	1.6 lbf/100 ft ²
Copolymer A + class G	0.50	3.0 cP	14.4 lbf/100 ft ²
Copolymer A + class G	0.75	25.6 cP	8.7 lbf/100 ft ²
Copolymer A + class G	1.00	40.4 cP	10.9 lbf/100 ft ²
Copolymer B + class G	1.00	too viscous	~285 lbf/100 ft ² *

Copolymer C + class G	0.50	7.2 cP	1.9 lbf/100 ft ²
Copolymer C + class G	0.75	7.9 cP	1.4 lbf/100 ft ²
Copolymer C + class G	1.00	7.1 cP	1.7 lbf/100 ft ²

Table 5. Copolymers A, B and C have been dry blended with Class G cement, water corresponding to a 14.0 ppg slurry, a dispersing agent (0.04 gps) and an anti-foam agent (0.02 gps). The rheology results are compared with a neat Class G cement, that is without any copolymer. The rheology where measured with a Chan 35 Rheometer unless
5 otherwise stated.

*Value obtained using a HAAKE Rotovisc RV12.

[0024] In Table 5, the results from the 14 ppg cement slurries are presented. A 14 ppg cement slurry has a higher water-cement ratio and this is clearly reflected in the results
10 for copolymer A. In Table 5, results from different concentrations of copolymers A, B and C are presented. Copolymer A shows the expected behavior: increased polymer concentration resulting in increased rheology. Although the increased rheology when increasing the concentration of polymer A from 0.50 %BWOW, to 0.75 %BWOW and finally 1.00 %BWOW the slurry rheology remains reasonable and pumpable. To obtain
15 the desired "instant" solid-like state the concentration needs to be further increased and above 1.00 %BWOW. In the case of copolymer B, an instant solid-like structure is formed similar as in the 15.8 ppg case.

[0025] It is interesting to note that copolymer C has no influence at all on the slurry rheology when the concentration is increased to levels similar to polymer A, from 0.50
20 %BWOW to 1.00 %BWOW. The slurry rheology obtained using polymer C remains stable and basically the same as the neat 14 ppg class G.

System	Copolymer conc. %BWOW	Plastic viscosity (PV)	Yield Strength (τ_y)
Neat class G slurry	0.00	3.9 cP	0.2 lbf/100 ft ²
Copolymer A + class G	1.00	9.9 cP	0.9 lbf/100 ft ²

Copolymer A + class G	1.50	45.2 cP	13.8 lbf/100 ft ²
Copolymer A + class G	2.00	too viscous	~450 lbf/100 ft ² *
Copolymer A + class G	2.50	too viscous	too viscous

Table 6. Copolymers A has been dry blended with Class G cement, water corresponding to a 12.0 ppg slurry, a dispersing agent (0.04 gps) and an anti-foam agent (0.02 gps). The rheology results are compared with a neat Class G cement, that is without any copolymer. The rheology where measured with a Chan 35 Rheometer unless otherwise stated.

5 *Value obtained using a HAAKE Rotovisc RV12.

10026] In Table 6 copolymer A has been dry blended with class G cement to obtain a 12 ppg slurry and then compared with neat class G cement at various copolymer concentrations in the range from 1.00 to 2.50 %BWOW. At a copolymer concentrations of 1.00 and 1.50-%BWOW the slurry remains fluid with reasonable low rheology for a pumpable slurry. However, at a concentration of 2.00 %BWOW and above the “instant” cement-copolymer solid-like structure is formed similar to those presented in Table 4.

Claims

1. A composition for treating lost circulation comprising a pumpable slurry of cement, water and a super-absorbent polymer which absorbs free water in the slurry when placed in the well, and which releases the absorbed water to the cement hydration reaction as the cement sets.
2. The composition of claim 1, wherein the absorption of water causes the slurry to develop a solid-like structure.
3. The composition of claim 2, wherein the super-absorbent polymer is present in the slurry in an encapsulated form to prevent formation of the solid-like structure before the slurry is placed in the well.
4. The composition of claim 3, wherein the encapsulation is in the form of a resin or other material that releases the polymer in response to exposure to temperature.
5. The composition of claim 3, wherein the encapsulation is in the form of a mineral system that release the encapsulated material in response to pressure.
6. The composition of claim 3, wherein the encapsulation is in the form of an emulsion which can be inverted downhole by shear, pressure drop, or by temperature.
7. The composition of claim 1, wherein the polymer is injected separately into the slurry at a downhole location.
8. The composition according to any of the preceding claims, wherein the copolymer is a super-absorbent copolymer based on poly(2-propenamide-co-2-propenoic acid, sodium salt).
9. The composition according to any of claims 1 to 7, wherein the copolymer is polyacrylamide or modified crosslinked poly(meth)acrylate.

10. The composition according to any of the preceding claims, wherein the dry copolymer has a granular dimension of less than 850 μm .
11. The composition according to any of the preceding claims, wherein the copolymer density lies in the range 0.9 to 1.48 g/cm^3 .
- 5 12. The composition according to any of the preceding claims, wherein the copolymer is formulated in concentration up to 2.50 %BWOW (percentage by weight of water).
13. A method of treating lost circulation comprising pumping a composition according to any of the preceding claims into the region of lost circulation, causing the slurry
10 to form a solid-like structure in that region and allowing the cement to set.
14. The method of claim 13, wherein the cement slurry is pumped through the drill bit and the release of the copolymer is triggered by the pressure drop occurring through the bit nozzles