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(54) SELF-ADAPTIVE CEMENT SYSTEMS

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(57) ABSTRACT

A self-healing cement system includes cement, water and at least one additive that swells in contact with water from reservoir or from formation in the case of a structural failure in the set cement to provide a physical barrier in the zone of failure. Examples of such material include particles of super-absorbent polymer. These additives have the effect of making the cement self-healing in the event of physical failure or damage such as micro-annuli. The self healing property is produced by the contact of the water itself, the potential repair mechanism is thus activated if and when needed in case of start of loss of zonal isolation. Several super-absorbent polymers have been identified such as polyacrylamide, modified crosslinked poly(meth)acrylate and non-solute acrylic polymers.

SELF-ADAPTIVE CEMENT SYSTEMS

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to adaptive cement systems. In particular, the invention relates to cement systems which are "self-healing", i.e. system which can adapt to compensate for changes or faults in the physical structure of the cement, or which adapt their structure after the setting phase of the cement in the cementing of oil, gas, water or geothermal wells, or the like.

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 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 gas. In order to fulfill this function, it is necessary that the cement be present as an impermeable continuous sheath. However, for various reasons, over time this sheath can deteriorate and become permeable. The deterioration can be due to physical stresses caused by tectonic movements of temperature effects, chemical degradation of the cement, or various other reasons.

[0003] There have been a number of proposals to deal with the problems of deterioration of the cement sheath over time. One approach is to design the cement sheath to take into account physical stresses that might be encountered during its lifetime. Such an approach is described in U.S. Pat. No. 6,296,057. Another approach is to include in the cement composition materials that improve the physical properties of the set cement. U.S. Pat. No. 6,458,198 describes the addition of amorphous metal fibers to the cement slurry to improve its strength and resistance to impact damage. EP 1129047 and WO 00/37387 describe the addition of flexible materials (rubber or polymers) to the cement to confer a degree of flexibility on the cement sheath. WO 01/70646 and PCT/EP03/01578 describe cement compositions that are formulated so as to be less sensitive to the effects of temperature on the cement when setting.

[0004] A number of proposals have been made for designs of self-healing concretes for use in the construction industry. These are described in U.S. Pat. No. 5,575,841, U.S. Pat. No. 5,660,624, U.S. Pat. No. 5,989,334, U.S. Pat. No. 6,261,360 and U.S. Pat. No. 6,527,849, and in "Three designs for the internal release of sealants, adhesives, and waterproofing chemicals into concrete to reduce permeability", Dry, C. M., Cement and Concrete Research 30 (2000) 1969-1977. None of these are immediately applicable to well cementing operations because of the need for the cement to be pumpable during placement and because of the pressure and temperature range.

[0005] 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 allow the cement sheath to adapt its structure in response to environmental conditions.

SUMMARY OF THE INVENTION

[0006] More precisely, the present invention aims at providing well cementing systems that include at least one additive that reacts and/or swells when the set cement is in contact with an aqueous fluid, such as formation waters. This behavior has the effect of making the cement self-healing in the event of physical failure or damage.

[0007] The additive is a material which reacts/expands in contact with water—for instance from the underground formation which enters a fault in the cement matrix. Examples of such materials include super-absorbent polymers. Super-absorbent polymers are crosslinked networks of flexible polymer chains. The most efficient water absorbers are polymer networks that carry dissociated, ionic functional groups. When super-absorbent polymers absorb liquids, an elastic gel forms. The gel is a soft, deformable solid composed of water and the expanded polymer chains.

[0008] The polymer particles can be of almost any shape and size: spherical, fiber-like, ovoid, mesh systems, ribbons, etc., which allows their easy incorporation in cement slurries of comprising solid materials in discrete particle size bands. In practice, polymer particles ranging from about 10 to about 1500 μ can be used.

[0009] The absorbent materials are preferably dry blended with the cement and any other solid components before transport to the well-site, mixing with water and placement in the well. The sizes and quantities will be selected to allow even dispersion through the cement matrix.

[0010] It has been found that though the super-absorbent polymers such as polyacrylamide and modified crosslinked polymethacrylate swell when incorporated in a cement slurry, they seem to release at least part of the absorbed water during the cement hydration and hence, have a reserve of absorbability that allow them to swell again if they are later exposed to water due to a crack of the matrix for instance. Since they are highly reactive with water, the concentration of super-absorbent added to the blend must remain relatively small, compositions with more than 3.2% of super-absorbent (by weight, of cement) may typically have a viscosity too high for pumping the slurry in favorable conditions. In fact the maximum SAP concentration depends on the slurry density and also on the nature of the Super Absorbent Polymer.

[0011] It has been found that the addition of salts such as sodium chloride or calcium chloride for instance favors the rheology of the systems thereby enabling increasing the concentration of super-absorbent polymers. Cement slurries of lower density have also a greater acceptability of higher concentrations of super-absorbent polymers, even without salt.

[0012] In another aspect of the present invention, at least part of the super-absorbent polymers are encapsulated so that they are—for instance in the form of a resin or other material that releases the polymer in response to exposure to a downhole parameter (for instance such as temperature, a specific mineral system, pressure, shear etc). In yet another aspect, the rupture of the encapsulating means is actually induced by the failure of the cement matrix, in a way similar to the mechanism described by Dry for instance in U.S. Pat. No. 5,575,841, U.S. Pat. No. 5,660,624, U.S. Pat. No. 5,989,334, U.S. Pat. No. 6,261,360 and U.S. Pat. No. 6,527,849.

DETAILED DESCRIPTION

[0013] A screening has been carried out for identifying super-absorbent polymers suitable for self-healing cementing applications. The main issues were to check the ability to dry blend the polymers with cement and to optimize the rheology and thickening time.

Testing Procedure

[0014] Tests have been carrying out by incorporating powders of various types of polymers as solid additives in cement slurries. Properties of the slurry as well as properties of the set cement have been studied.

[0015] The slurries were optimized with the mere objective of obtaining stability. Focus was to get acceptable plastic viscosity (PV) and yield stress (TY) at mixing time and after 20 minutes of conditioning. Free water and sedimentation tests were also carried out. Mixing and test procedure was according to API Spec 10.

[0016] The same equipment and bob was used for all rheology measurements, whatever the tested design. Many tests were performed at one slurry density (15.8 lbm/gal) and one temperature (BHCT equal to 60° C.). Some examples were studied at 12 lbm/gal and at 14 lbm/gal. For lowest density, the temperature is equal 25° C. and 85° C. The design is based on tap water and black Dyckerhoff North cement. Unless otherwise mentioned, all designs include an antifoam agent based on polypropylene glycol at 0.03 gallon per US gallons per sack of 94 lbs of cement (in other words, 1 gps=88.78 cc/kg), polynapthalene sulfonate as dispersing agent at 0.04 gps and the superabsorbent polymer at concentration ranging form 0.1% BWOC (by weight of cement) to 0.9% BWOC for 15.8 lbm/gal. Decreasing the density allows to increase the concentration in Super Absorbent Polymer. For instance for a given SAP the maximum concentration at 15.8 lbm/gal is 1% bwoc without salt in the mixing water and can reach 3% bwoc at 12 lbm/gal.

[0017] Three types of superabsorbent polymers were tested:. S1, a polyacrylamide available form Lamberti, Italy. Three grades were tested, namely S1G-Lamseal® G, with particles ranging form 500 μ to 1500 μ (density 1.25 g/cm^3), S1GS-Lamseal® GS, with particles of about 200 μ (density 1.48 g/cm^3), and S1GM, Lamseal® GM, with particles of about 700μ(density 1.47 g/cm^3). S2, a modified polyacrylate available from Itochu, Japan, under the name Aqualic® CS-6HM, selected for its salt resistance, in particular its capacity to keep super absorbent capacity in high valent metal ions solutions. The average particle size is 100 μ and the density 1.46 g/cm^3. S3, a non soluble acrylic polymers , Norsocryl C200 from Atofina with particles of about 250 μ in average (density 1.6 g/cm^3).

[0018] In the examples, bwoc or BWOC stands for by weight of cement and bwow or BWOW for by weight of water.

EXPERIMENTAL RESULTS

Example 1

Addition Procedure

[0019] The first step was to define the best addition process. As shown in table 1 below, dry blending induces lower effects on rheology and free water and leads to an easy mixing

TABLE 1

Design	Reference	A1	A2	A3
S1G (% bwoc)		0.1	0.1	0.1
Note		prehydrated (static)	dry blended	prehydrated under agitation at 2000 RPM during 15 minutes.
		Mixing rheology		
Ty (lbf/100 ft^2)	2.3	2.8	1.4	3.2
PV (cP)	25.5	18.9	27.2	32.4
		BHCT rheology at 60° C.		
Ty (lbf/100 ft^2)	24.6	21.2	27.3	52.8
PV (cP)	20.9	18.4	26.6	33.3
10'/1'gel	25/16	14/9	19/11	15/13
Free Water mL	1	7	trace	2.5
Sedimentation ppg	1.14	1	0.4	0.7

Example 2

Influence of the Particle Sizes

[0020] For the S1 particles, the finer the particles, the higher the rheology and free water.

TABLE 2

Design	Reference	S1 G	S1 GM	S1GS
S1 (% bwoc)		0.1	0.1	0.1
		Mixing rheology		
Ty (lbf/100 ft^2)	2.3	1.4	2.7	6.7
PV (cP)	25.5	27.2	29	41
		BHCT rheology at 60° C.		
Ty (lbf/100 ft^2)	24.6	27.3	24.4	38.7
PV (cP)	20.9	26.6	35.6	40.9
10'/1'gel	25/16	19/11	15/12	12/9
Free Water mL	1	trace	2	4
Sedimentation ppg	1.14	0.4	1	0.9

Example 3

[0021] This test shows that cement slurry with superabsorbent polymers S1 are compatible with conventional fluid loss control additive (flac). This shows that the composition of the present invention can still be optimized by the addition of conventional additives such as dispersing agent, fluid loss control agent, set retarder, set accelerator and anti-foaming agent.

TABLE 3

Design	X3.1	X3.2
S1G (% bwoc)	0.1	0.1
Flac		0.4
Mixing rheology		
Ty (lbf/100 ft^2)	1.4	7.9
PV (cP)	27.2	104.7

TABLE 3-continued

Design	X3.1	X3.2
BHCT rheology at 60° C.		
Ty (lbf/100 ft^2)	27.3	13.7
PV (cP)	26.6	125
10'/1'gel	19/11	13/7
Free Water mL	trace	trace

Example 4

[0022] Results with the polymethacrylate based superabsorbent polymer S2 show less sensitivity to the addition mode.

TABLE 4.1

Design	Reference	X4.1	X4.2	X4.3	X4.4
S2 (% bwoc)		0.05	0.1	0.1	0.15
	—	dry blended	dry blended	prehydrated	dry blended
Mixing rheology					
Ty (lbf/100 ft^2)	2.3	4.8	5.6	6.4	5.3
PV (cP)	25.5	31.9	35.9	37.9	64.8
BHCT rheology at 60° C.					
Ty (lbf/100 ft^2)	24.6	20.2	23.3	20.7	19.9
PV (cP)	20.9	24.3	22.4	30.3	57
10'/1'gel	25/16	17/9	15/9	12/7	12/10
Free Water mL	1		2.8	4.5	5.5
Sedimentation ppg	1.14	0.6	0.6	0.9	1

[0023] Polymer S2 can also be added in higher quantity, at least up to 0.45% BWOC as shown in the following table 4.2:

TABLE 4.2

Design	Reference	1	2	3	4
antifoam (gps)	0.03	0.03	0.03	0.03	0.03
Dispersing agent (gps)	0.04	0.04	0.04	0.04	0.04
S2 (% bwoc)	0	0.9 (exces)	0.2	0.45	0.45
S2 (% bwow)	0	2	0.44	1	1
Remarque		dry blended	dry blended	dry blended	prehydrated
Mixing rheology					
Ty (lbf/100 ft^2)	2.3	Too	8.3	19.7	24.9
PV (cP)	25.5	viscous	52.2	142.8	228.7
Comment					Difficult mixing
BHCT rheology at 60° C.					
Ty (lbf/100 ft^2)	24.6	Too viscous	14.3	25.8	11.6
PV (cP)	20.9		40.3	172.5	178.4
10'/1'gel	25/16		14/9	25/7	18/9
Free water mL	1	0	7	6	4.5
Sedim ppg	1.14	0.1	1.2	0.2	0.2

Example 5

[0024] This example shows that the setting properties and the rheological properties can be optimized, a key requirement for well cementing applications. In all cases, the super-absorbent polymer was dry blended with the cement.

TABLE 5.1

Design		8	9	10
S2 (% bwoc)		0.1	0.1	0.1
Antifoam (gps)		0.03	0.03	0.03
Lignosulfonate (gps)		0.05	—	0.025
Fluid loss control agent (gps)		0.4	0.4	0.4
Polynaphtalene (gps)		0.045	0.045	0.045
Mixing	Ty (lbf/100 ft^2)	10.4	11	10.6

TABLE 5.1-continued

Design		8	9	10
rheology	PV (cP)	121.9	134	125.8
BHCT	Ty (lbf/100 ft^2)	15.5	16.7	16
rheology	PV (cP)	132	132.4	129
at 60° C.	10'/1'gel	24/10	9/5	12/7
	Free water mL	0	0	0
	Sedimentation ppg	0.2	0.2	0.4
	Thickening test 100 Bc (hh:min)	13 h 30 min	3 h 03 min	8 h 49 min

[0025]

TABLE 5.2

Design	29	30	31	32
Antifoam (gps)	0.03	0.03	0.03	0.03
Lignosulfonate (gps)	0.025	0.025	0.025	0.025
Fluid loss control agent (gps)	0.4	0.4	—	0.2
Polynaphtalene (gps)	0.045	0.6	0.045	0.045
Mixing rheology				
Ty (lbf/100 ft^2)	46.8	41.9	23	32
PV(cP)	303	293	92	154
BHCT rheology at 60° C.				
Ty (lbf/100 ft^2)	32	35	6.6	19
PV(cP)	226	248	66	145
10'/1'gel	12/7	11/6	11/7	9/4
Free water mL	Trace	Trace	10	2.5

[0026] In the table 5.2, the designed slurries have a density of 15.8 lbm/gal, and the concentration of super-absorbent S2 is 0.3% bwoc (corresponding to 0.7% bwow).

TABLE 5.3

Design	33	34	35
Antifoam (gps)	0.03	0.03	0.03
Lignosulfonate (gps)	0.025	0.025	—
NaCl (by weight of water)			37
Fluid loss control agent (gps)	0.2	0.15	—
Polynaphtalene (gps)	0.045	0.045	0.9
Mixing rheology			
Ty (lbf/100 ft^2)	46.8	45	4.4
PV (cP)	223	208	61
BHCT rheology at 60° C.			
Ty (lbf/100 ft^2)	27	50	14
PV (cP)	217	240	51
10'/1'gel	10/5	10/7	20/9
Free water mL	1.5	1	—
API Fluid loss (ml)		170	

[0027] In the table 5.3, the designed slurries have a density of 15.8 lbm/gal, and the concentration of super-absorbent S2 is 0.4% bwoc (corresponding to 0.9% bwow).

Example 6

[0028] This example shows that the addition of a salt allows an increase of the concentration of superabsorbent polymer while keeping acceptable rheology properties. In table 6.1, tests have been carried out with sodium chloride as added salt. In table 6.2, the added salt is calcium chloride. In both tables, the cements have a density of 15.8 ppg.

TABLE 6.1

Design	1	36	37	38
S2 (% bwoc)	0.9	0.9	0.9	0.9
Antifoam (gps)	0.03	0.03	0.05	0.05
NaCl (by weight of water)	0	37	18.5	37
Polynaphtalene (gps)	0.04	0.9	0.9	1.5
Mixing rheology				
Ty (lbf/100 ft^2)	Too viscous	13.4	27.1	61.8
PV (cP)		119	207	352
BHCT rheology at 60° C.				
Ty (lbf/100 ft^2)		30.7	31.5	59
PV (cP)		107	1059	433
10'/1'gel		28/19	—	433
Free water mL		Trace		

[0029]

TABLE 6.2

Design	70	81
Antifoam (gps)	0.05	0.05
Flac (gps)	0.5	—
Lignosulfonate (gps)	0.05	—
Polynaphtalene (gps)	—	0.9
Sulfonated melamine-formaldehyde (gps)	0.12	—
Sodium chloride (% BWOW)	—	37
Calcium chloride (% BWOC)	2	—
S2 (% BWOC)	0.45	0.9
Mixing rheology		
Ty (lbf/100ft^2)	29	30
PV (cP)	244	173
BHCT tests at 60° C. Rheology		
Ty (lbf/100 ft^2)	34	22
PV(cP)	211	110
10'gel/1'stiring	17/9	23/10
Free water (mL)	0	0
Fluid loss (mL API)	78	18
Thickening time	5 h 17 min	—

Example 7

[0030] This example shows that if the slurry density is lower, higher concentration of super-absorbent polymers can be used, even without the addition of a salt.

Design	X7.1	X7.2	X7.3
Density (lbm/gal)	14	12	12
BHCT (deg C.)	60	25	85
Antifoam (gps)	0.03	0.02	0.02
Flac (gps)	0.4	—	—
Lignosulfonate (gps)	0.025	—	—
Polynaphtalene (gps)	0.045	0.03	0.03
S2 (% bwoc)	0.9	3	3
S2 (% bwow)	1.4	2.4	2.4
Mixing rheology			
Ty (lbf/100 ft^2)	21.18	19.2	19.63
PV (cP)	156.9	90.3	86.39

-continued

Design	X7.1	X7.2	X7.3
Rheology at BHCT			
Ty (lbf/100 ft^2)	49.31	27.5	4.92
PV (cP)	180.5	169.7	82.78
10'gel/1'stiring	32/22	28/12	11/6
Fluid loss (mL API)	—	149	240

Example 8

[0031] Cement samples comprising super-absorbent polymers were taken form the sedimentation column and additional water was added at the surface of broken pieces to simulate contact with formation water after a crack. Tests were performed at room temperature and at 60° C. In all cases, swelling was observed showing that the super-absorbent polymer particles remain effectively available to absorb additional water (even though the cement matrix always comprises residual water).

Example 9

[0032] This test was performed with super-absorbent S3. Good rheology is obtained.

TABLE 9

Design	5	13	19
Density (lbm/gal)	15.8	15.8	15.8
BHCT (deg C.)	60	60	60
Antifoam (gps)	0.05	0.03	0.05
Flac (gps)	0.5	0.4	—
Lignosulfonate (gps)	0.05	0.025	—
Polynaphtalene (gps)	—	0.05	0.9
Sulfonated melamine formaldehyde (gps)	0.12	—	—
Sodium chloride (% BWOW)	—	—	37
Calcium chloride (% BWOC)	2	—	—
S3 (% bwoc)	3	0.9	2
S3 (% bwow)	7.7	2.2	4.5
Mixing rheology			
Ty(lbf/100 ft^2)	26	19	4
PV (cP)	262	195	54
BHCT Rheology			
Ty (lbf/100 ft^2)	13	19	4
PV (cP)	154	145	30
10'gel/1'stiring	7/5	14/4	15/6
Free water (mL)	0	0	—
Fluid loss (mL API)	48	—	—

1. A composition for well cementing comprising:

i. a pumpable slurry of cement,

ii. water and

iii. a material having residual water-absorption properties after the setting of the cement, so that said material is susceptible to swell in contact with underground water in case of failure of the cement matrix.

2. The composition of claim 1, wherein said material is a super-absorbent polymer.

3. The cement system of claim 1, wherein the super-absorbent polymer is selected from the list consisting of polymethacrylate and polyacrylamide or a non-soluble acrylic polymers.

4. The cement system of claim 2, wherein the super-absorbent polymer is added to the slurry dry-blended with the cement.

5. The cement system of claim 2, wherein the super-absorbent polymer is added at a concentration between 0.05% and 3.2% by weight of cement.

6. The cement system of claim 2 further comprising a salt.

7. The cement system of claim 6, wherein said salt is sodium chloride or calcium chloride.

8. The cement slurry of claim 2, wherein the super-absorbent polymer is added under the form of particles ranging from 10 μm to 1500 μm.

9. The cement system of claim 1, whereby the material is provided in a capsule that releases the material in response to exposure of the cement to at least one downhole parameter.

10. The cement system of claim 1, whereby the material is provided in a capsule that releases the material when the cement matrix cracks.

11. The cement system of claim 1 further comprising at least one additive selected from the list consisting of dispersing agent, fluid loss control agent, set retarder, set accelerator and anti-foaming agent.

12. The cement system of claim 2 whereby the material is provided in a capsule that releases the material in response to exposure of the cement to at least one downhole parameter.

13. The cement system of claim 2 whereby the material is provided in a capsule that releases the material when the cement matrix cracks.

14. The cement system of claim 2 further comprising at least one additive selected from the list consisting of dispersing agent, fluid loss control agent, set retarder, set accelerator and anti-foaming agent.

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