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(54) **Önjavító cementek**

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Description

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to self-adaptive cements. In particular, the invention relates to set cements that are "self-healing," i.e., formulations that 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 wells, cement is used to secure and support casing inside the well and prevent fluid communication between the various underground fluid-containing layers or the production of unwanted fluids into the well.

[0003] Various approaches have been developed to prevent failure of the cement sheath. 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 for example in US 6,296,057. Another approach is to include, in the cement composition, materials that improve the physical properties of the set cement. US 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.

[0004] Nevertheless, the above-described approaches do not allow restoration of the zonal isolation once the cement sheath has actually failed due to the formation of cracks or microannuli.

[0005] A number of self-healing concretes are known for use in the construction industry. These are described for example in US 5,575,841, US 5,660,624, US 5,989,334, US 6,261,360 and US 6,527,849, and in the document entitled "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.

[0006] Nevertheless, none of these self-healing concretes are immediately applicable to well cementing operations because of the need for the material to be pumpable during placement.

[0007] "Self-healing" cements were eventually developed for oil and gas industry applications such as described in US 2007/0204765 A1, WO 2004/101951 and WO 2004/101952 A1. These formulations generally contain additives that react and/or swell upon contact with downhole fluids. When cement-sheath deterioration occurs, exposing the cement matrix or cement-sheath surfaces to downhole fluids, the additives respond and seal cracks or fissures, thereby restoring cement-matrix integrity and zonal isolation. Well cements are potentially exposed to several fluid types during service, including liquid and gaseous hydrocarbons, water, brines and/or carbon dioxide. Thus, depending on the anticipated wellbore environment, it would be desirable to incorporate additives that are able to respond to one or more types of downhole fluids.

[0008] Despite the many valuable contributions from the art, a particular need still exists for a self-healing set cement that responds to formation fluids that contain high concentrations of gaseous hydrocarbons.

SUMMARY OF THE INVENTION

[0009] The present invention allows improvements by providing set cements that are self-healing when exposed to hydrocarbons, and methods by which they may be prepared and applied in subterranean wells.

[0010] In an aspect, embodiments of the invention relate to methods for maintaining zonal isolation in a subterranean well that penetrates one or more hydrocarbon-containing formations.

[0011] In a further aspect, embodiments of the invention relate to uses of thermoplastic block-polymer particles to impart self-healing properties to a cement formulation that is placed in a subterranean well penetrating one or more hydrocarbon-containing formations, wherein the particles comprise styrene-isoprene-styrene polymer particles, styrene-butadiene-styrene polymer particles or both.

DESCRIPTION OF THE DRAWINGS

[0012]

Figure 1 is a plot showing the swelling characteristics of styrene-isoprene-styrene (SIS) and styrene-butadiene-styrene (SBS) particles in the presence of methane at various temperatures and pressures.

Figure 2 is a schematic diagram of an experimental apparatus for measuring the self-healing ability of fractured cement samples.

Figure 3 presents normalized flow-rate reductions for set cements containing SIS and SBS particles exposed to methane.

Figure 4 presents the effect of slurry density on normalized flow-rate reductions for set cements containing SIS and SBS particles exposed to methane.

Figure 5 presents normalized flow-rate reductions for set cements containing SIS and SBS particles exposed to methane at various pressures.

DETAILED DESCRIPTION OF THE INVENTION

[0013] At the outset, it should be noted that in the development of any such actual embodiment, numerous implementations-specific decisions must be made to achieve the developer's specific goals, such as compliance with system related and business related constraints, which will vary from one implementation to another. Moreover, it will be appreciated that such a development effort might be complex and time consuming but would nevertheless be a routine undertaking for those of ordinary skill in the art having the benefit of this disclosure. In addition, the composition used/disclosed herein can also comprise some components other than those cited.

[0014] This invention concerns compositions for cementing subterranean wells, comprising a settable material, water and at least one additive that swells in the event of structural failure of or damage to the set material (i.e., the cement sheath). Such behavior restores and maintains a physical and hydraulic barrier in the failure zone. As a result, zonal isolation in the subterranean well is preserved. Such set cements are said to be "self-healing" or "self-repairing." In this application, both terms are used indifferently, and are to be understood as the capacity of a cement sheath to restore hydraulic isolation after suffering a matrix-permeability increase, structural defects such as cracks or fissures, or debonding from casing or formation surfaces (i.e., microannuli).

[0015] Examples of settable materials include (but are not limited to) Portland cement, microcement, geopolymers, mixtures of cement and geopolymer, plaster, lime-silica mixtures, resins, phosphomagnesium cements or chemically bonded phosphate ceramics (CBPCs).

[0016] As stated earlier, there is a need for self-healing set cements that operate in an environment containing high concentrations of gaseous hydrocarbons, methane in particular. Surprisingly, the inventors have discovered that self-healing properties may be achieved in this environment by incorporating thermoplastic block-polymer particles in the cement formulation. Typical block polymers comprise alternating sections of one chemical compound separated by sections of a different chemical compound, or a coupling group of low molecular weight. For example, block polymers can have the structure (A-b-B-b-A), wherein A represents a block that is glassy or semi-crystalline and B is a block that is elastomeric. In principle, A can be any polymer that is normally regarded as thermoplastic (e.g., polystyrene, polymethylmethacrylate, isotactic polypropylene, polyurethane, etc.), and B can be any polymer that is normally regarded as elastomeric (e.g., polyisoprene, polybutadiene, polyethers, polyesters, etc.).

[0017] Further embodiments of the invention relate to methods for maintaining zonal isolation in a subterranean well having a borehole that penetrates one or more hydrocarbon-containing formations. The method comprises pumping a cement slurry comprising thermoplastic block-polymer particles into the well, and allowing the cement slurry to form a cement sheath. Those skilled in the art will recognize that a cement slurry is generally considered to be pumpable when its viscosity is less than or equal to 1000 mPa-s at a shear rate of 100 s^{-1}, throughout the temperature range the slurry will experience during placement in the well. The cement sheath may be located between the well casing and the borehole wall, or between the casing and another casing string. If microannuli, cracks or defects occur in the cement sheath, the casing-cement interface or the cement-borehole wall interface, the particles will be exposed to formation hydrocarbons, causing them to swell and enabling the cement sheath to have self-healing properties.

[0018] In further embodiments of the invention aim at uses of thermoplastic block-polymer particles to impart self-healing properties to a set cement sheath in a subterranean well that penetrates one or more hydrocarbon-containing formations. The particles swell when contacted by hydrocarbons from the formation, in particular gaseous hydrocarbons.

[0019] For all aspects of the invention, the tensile strength of the block polymer may be varied between (but is not limited to) about 1.5 MPa and 40 MPa, preferably between 3.4 to 34 MPa. Even more preferred tensile-strength may be between 2MPa and 3.45 MPa or between 28 MPa and 34 MPa.

[0020] Preferred thermoplastic block polymers include styrene-isoprene-styrene (SIS), styrene-butadiene-styrene (SBS) and mixtures thereof. The block-polymer-additive may be in one or more shapes, including (but not limited to) spherical, ovoid, fibrous, ribbon-like and in the form of a mesh.

[0021] The concentration of the block-polymer particles is preferably between about 10% and 55% by volume of solids in the cement slurry, also known as percentage by volume of blend (BVOB). A more preferred particle concentration lies between about 20% and 50% BVOB. The particle-size range is preferably between about 100 μm and 900 μm, and more preferably between about 200 μm and 800 μm.

[0022] One of the current challenge that the industry is facing is the presence in some wells of high concentration of gaseous hydrocarbons such as methane, propane and/or ethane. Such gaseous hydrocarbons being much more volatile than hydrocarbons in liquid form have the tendency to penetrate the failures and/or microannuli that can be present and the cement sheath and thus modifying the pressure and safety conditions of the well as the integrity is diminished. The inventors have determined that the compositions according to the present invention can solve this problem up to very high concentration of gaseous hydrocarbon. In a preferred embodiment, the gaseous concentration of hydrocarbon fluid is greater than about 91 mol%, and more preferably above about 95 mol%. In addition, the hydrocarbon pressure to which the cement sheath is exposed is preferably above about 3.5 MPa, more preferably above about 6.9 MPa and most preferably above about 13.7 MPa.

[0023] The block-polymer particles may be further encapsulated by a protective layer. The layer may rupture or degrade upon exposure to one or more triggers, including (but not limited to) contact with a hydrocarbon, propagation of a crack within the set-cement matrix, time and/or temperature.

[0024] In addition to the block-polymer particles, the cement slurries may also comprise customary additives such as retarders, accelerators, extenders, fluid-loss-control additives, lost-circulation additives, gas-migration additives and antifoam agents. Furthermore, the cement slurries may contain additives that enhance the flexibility and/or toughness of the set cement. Such additives include (but are not limited to) flexible particles having a Young's modulus below about 5000 MPa and a Poisson's ratio above about 0.3. Preferably, such particles would have a Young's modulus below about 2000 MPa. Examples include (but are not limited to) polypropylene, polyethylene, acrylonitrile butadiene, styrene butadiene and polyamide. Such additives may also include fibers selected from the list comprising polyamide, polyethylene and polyvinyl alcohol. Metallic microribbons may also be included.

[0025] The block-polymer particles may also be used in engineered-particle-size cement formulations involving trimodal or quadrimodal blends of small, medium and coarse particles. Such as formulations exemplified in US 5,518,996 and/or CA 2,117,276.

[0026] The block-polymer particles may be further associated with one or more compounds from the list comprising: an aqueous inverse emulsion of polymer comprising a betaine group; poly-2, 2, 1-bicyclo heptene (polynorbornene); alkylstyrene polymer; crosslinked substituted vinyl acrylate copolymers; diatomaceous earth; natural rubber; vulcanized rubber; polyisoprene rubber; vinyl acetate rubber; polychloroprene rubber; acrylonitrile butadiene rubber; hydrogenated acrylonitrile butadiene rubber; ethylene propylene diene polymer rubber; ethylene propylene monomer rubber; styrene-butadiene rubber; styrene propylene diene polymer; brominated poly(isobutylene-co-4-methylstyrene); butyl rubber; chlorosulphonated polyethylenes; polyacrylate rubber; polyurethane; silicone rubber; brominated butyl rubber; chlorinated butyl rubber; chlorinated polyethylene; epichlorohydrin ethylene oxide copolymer; ethylene acrylate rubber; ethylene propylene diene terpolymer rubber; sulphonated polyethylene; fluoro silicone rubbers; fluoroelastomer; and substituted styrene acrylate copolymers.

[0027] Those skilled in the art will appreciate that the disclosed method and use may not necessarily be applied throughout the entire length of the subterranean interval being cemented. In such cases, more than one cement-slurry composition is placed sequentially. The first slurry is called the "lead," and the last slurry is called the "tail." Under these circumstances, it is preferred that the inventive slurry be placed such that it resides in regions where hydrocarbons exist. In most cases, this will be at or near the bottom of the well; therefore, the inventive method and use would preferably apply to the tail. Those skilled in the art will also appreciate that the disclosed method and use would not only be useful for primary cementing, but also for remedial cementing operations such as squeeze cementing and plug cementing.

[0028] Other and further objects, features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the examples which follows, taken in conjunction with the accompanying drawings.

EXAMPLES

[0029] The following examples serve to further illustrate the invention.

[0030] Table 1 lists the styrene-isoprene-styrene (SIS) polymers and styrene-butadiene-styrene (SBS) polymers that were used in the examples.

Table 1. Suppliers and Properties of SIS and SBS Polymers Employed in Examples.*

Property	**SIS #1**	**SIS #2**	**SBS #1**	**SBS #2**	**SBS #3**	**SBS #4**
Supplier	ICO Polymers	Kraton	ICO Polymers	ICO Polymers	ICO Polymers	Kraton
Product Name	ICO1	D1161 PTM	ICO 3	ICO 4	ICO 5	D1192 EM

(continued)

Property	SIS #1	SIS #2	SBS #1	SBS #2	SBS #3	SBS #4
Melt Index (200°C/5kg) (g/10min)	13	13.5	<1	23-37	<1	<1
Density (kg/m^3)	963	920	940	940	981	940
Tensile strength at break (MPa)	17	21	16	10	33	
Hardness, Shore A (30s)	24	32			72	70
Elongation at break (%)	1400	1300	680	900	880	
*Test methods: ISO 1133 (Melt Index measurement) ISO 37 (Tensile Strength at Break and Elongation at Break measurements) ISO 2781 (Density measurement) ISO 868 (ICO Polymers) and ASTM 2240 (Kraton) (Hardness measurement)						

EXAMPLE 1

[0031] Several polymer particles were placed inside a pressure cell equipped with a window that allows one to observe the behavior of materials within the cell. The cell supplier was Temco Inc., Houston, Texas (USA). The cell temperature was also adjustable. A camera captured images from inside the pressure cell, and image-analysis software was employed to interpret the behavior of materials inside the cell. For particle-size measurements, the software examined the cross-sectional area of the particles in the cell.

[0032] After the polymer particles were introduced into the cell, the cell was sealed. The cell was then heated to the desired temperature. The initial particle sizes were measured.

[0033] A methane-gas line was then connected to the cell, and the methane pressure was raised to 21 MPa over a 3-min period. The cell pressure was maintained for 2 hr, after which the particle sizes were measured again.

[0034] Tests were performed at 22°C and 42°C with an SIS polymer (SIS #1 from Table 1) and an SBS polymer (SBS #3). The results are presented in Fig. 1. At both temperatures, both SIS and SBS polymer demonstrated good performance.

EXAMPLE 2

[0035] The properties of cement slurries containing SIS or SBS particles were measured. The tests conformed to standard methods published by the International Organization for Standards (ISO): "Petroleum and natural gas industries-Cements and materials for well cementing-Part 2: Testing of well cements," International Organization for Standards Publication No. ISO 10426-2. Two cement slurries were tested-one containing SIS particles (SIS #1), and the other containing SBS particles (SBS #3). The test conditions were as follows-bottomhole static temperature: 53°C; bottomhole circulating temperature: 44°C; bottomhole pressure: 21 MPa (3000 psi).

[0036] The composition of the slurry containing SBS is given in Table 2, and the test results are presented in Tables 3 and 4. The slurry density was 1606 kg/m^3, and the solid volume fraction (SVF) of the slurry was 51.8%.

Table 2. Composition of Test Cement Slurry Containing SBS as Self-Healing Particle.

Component	Type	Quantity (kg/m^3)
Cement	Class G Portland cement	696
Self-healing particle	SBS #3	214.5
Silica	200 mesh (74 μm)	200.5
Water	Fresh	395
Lightweight particle	Acrylonitrile-butadiene copolymer	5

(continued)

Component	Type	Quantity (kg/m^3)
Antifoam	Polypropylene Glycol	4
Dispersant	Polymelamine sulfonate	9
Antisettling	90% crystalline silica; 10% polysaccharide biopolymer	1
Fluid-loss additive	RHODOFLAC™, available from Rhodia Nederland	72
Retarder	Calcium Lignosulfonate	2.5

Table 3. Rheological Properties of Test Cement Slurry Containing SBS as Self-Healing Particle.

Mixing	20-min Conditioning
PV: 233 cP Ty: 4.32 N/m^2 (9.0 lbf/100ft^2)	PV: 219 cP Ty: 8.16 N/m^2 (17 lbf/100ft^2)

Table 4. Additional Properties of Test Cement Slurry Containing SBS as Self-Healing Particle.

Measurement	Results
Free fluid	0.8%
Fluid loss	13 mL
Thickening time	8:53 (to 70 Bc)
Compressive strength development	• 500 psi [3.4 MPa] (UCA) after 23:42 • 1000 psi [7 MPa] (UCA) after 72:58 • 783 psi [5.4 MPa] (crush); 512 psi [3.5 MPa] (UCA) after 24:00 • 1316 psi [9 MPa] crush (996 psi [6.9 MPa] UCA) after 72:00
Tensile strength*	1.9 MPa
*Cement was cured for 7 days at 53°C and 20 MPa before measuring tensile strength.	

[0037] The composition of the slurry containing SIS is given in Table 5, and the test results are presented in Tables 6 and 7. The slurry density was 1606 kg/m^3, and the solid volume fraction (SVF) of the slurry was 51.7%.

Table 5. Composition of Test Cement Slurry Containing SIS as Self-Healing Particle.

Component	Type	Quantity (kg/m^3)
Cement	Class G Portland cement	694
Self-healing additive	SIS #1	208
Antifoam	Polypropylene Glycol	5
Silica	200 mesh (74 μm)	219
Water	Fresh	393
Dispersant	Polymelamine Sulfonate	8
Antisettling	Biopolymer	1
Fluid loss	RHODOFLAC™, available from Rhodia Nederland	81

Table 6. Rheological Properties of Test Cement Slurry Containing SIS as Self-Healing Particle.

Mixing	20-min Conditioning
PV: 119 cP Tv: 6.72 N/m^2 (14 $lbf/100ft^2$)	PV: 107 cP Ty: 9.12 N/m^2 (19 $lbf/100ft^2$)

Table 7. Additional Properties of Test Cement Slurry Containing SIS as Self-Healing Particle.

Measurement	Results
Free water	0.3 %
Thickening time	4:13 (to 70 Bearden consistency)
Compressive strength development (measured by UCA)	500 psi [3.4 MPa] after 11:52 1000 psi [7 MPa] after 32:00 867 psi [5.5 MPa] after 24:00 1260 psi [8.82 MPa] after 72:00

EXAMPLE 3

[0038] Various cement formulations containing SIS or SBS were evaluated for their self-healing properties. The slurry compositions are presented in Table 8. The formulation that contains acrylonitrile-butadiene copolymer rubber (ABCR) was included as a control with no self-healing capability.

Table 8. Slurry Compositions for Self-Healing Tests.

Particle type	Unit	ABCR	SIS #1	SIS #12	SBS #1	SBS #2	SBS #3	SBS #4
Density	**(kg/m^3)**	*1571*	*1498*	*1606*	*1498*	*1498*	*1498*	*1606*
SVF	**(%)**	55	*50.3*	*52.3*	*50*	*50.6*	*50*	*52*
Particle		286	240	210	243	239	243	213
Cement		616	560	645	555	563	553	641
Silica		219	199	281	197	200	196	279
Water	**(kg/m^3)**	436	494	459	498	491	497	463
Antifoam*		3	4	3	4	4	6	3
Dispersant*		5	0	5	0	0	3	5
Antisettling*		1	1	1	1	1	1	1
Retarder*		5	0	0	0	0	0	0
*Antifoam Agent: polypropylene glycol; Dispersant: polymelamine sulfonate; Antisettling Agent: 90% crystalline silica, 10% polysaccharide biopolymer; Retarder: calcium lignosulfonate.								

[0039] Each cement slurry was prepared according to the method described in ISO Publication 10426-2, and samples were prepared in the manner required to perform a Brazilian tensile-strength test. This test is also described in ISO Publication 10426-2. The cement-core samples were 66 mm long and 22 mm in diameter. The samples were cured at room temperature and atmospheric pressure. The curing times are presented in Table 9. Columns with two numbers indicate that two tests were performed.

Table 9. Curing times.

Particle name	ABCR	SIS #1	SIS #2	SBS #1	SBS #2	SBS #3	SBS #4
Curing time (days)	40 / 121	48	104	101	79 / 77	78 / 105	100

[0040] The samples were fractured by the Brazilian method, then transferred to a steel tube and secured by a sealing cement. As shown in Fig. 2, the steel tube **101** is 180 mm long. There are two 90-mm sections-one with an internal diameter of 31.5 mm in diameter, the other with an internal diameter of 29.5 mm. The fractured cement sample **102** is placed inside the tube and the sealing cement **103** is applied around the sample. Midway along the cement sample, owing to the different tube diameters, there is an edge **104** to prevent the cement sample from sliding.

[0041] The composition of the sealing cement was a 1.88-kg/m^3 Portland cement slurry containing 2.7 mL/kg polynaphthalene sulfonate dispersant, 2.7 mL/kg polysiloxane antifoam agent, 178 mL/kg styrene butadiene latex and 2.1% by weight of cement calcium chloride accelerator.

[0042] Pure methane was then injected through the fractured samples for 24 hours at 21 MPa backpressure and at ambient temperature (20°-23°C). Flow-rate and pressure variations were recorded, and normalized flow rates were calculated. The results are shown in Fig. 3.

[0043] The cement matrices incorporating SIS particles demonstrated normalized flow-rate reductions greater than 98%. The performance of cement matrices incorporating SBS particles demonstrated flow-rate reductions between 49% and 97%. The control did not show a flow-rate reduction.

EXAMPLE 4

[0044] Using the methods described in Example 3, the effect of slurry density on the performance of set cements containing SIS#1 or SBS#3 was investigated. The slurry compositions are shown in Table 10.

Density	**(kg/m^3)**	**1606**	**1606**	**1498**	**1498**
SVF	**(%)**	52	51.5	50.3	50.7
Particle type		**SIS#1**	SBS#3	SIS#1	SBS#3
Particle	**(kg/m^3)**	213	216	240	242.5
Class G cement		641.5	635.5	560	554.3
Silica		280	277	199	196
Water		462.5	467.5	494	496.5
Antifoam		5	5	4	4
Dispersant		3	3	0	3
Antisettling		1	1	1	1

Table 10. Slurry Compositions for Self-Healing Tests

[0045] The cement slurries were cured for 7 days at 53°C and 20 MPa. The self-healing test results are presented in Fig. 4. For both cement matrices, density variation does not affect performance in terms of flow-rate reduction.

EXAMPLE 5

[0046] Using the methods described in Example 3, the effect of pressure on the performance of set cements containing SIS#1 or SBS#3 was investigated. The 1606-kg/m^3 formulations from Table 9 were tested.

[0047] The samples were cured for 7 days at 53°C and 20 MPa. Flow-rate-reduction measurements were performed at four methane pressures: 3.5 MPa, 7 MPa, 13.7 MPa and 20 MPa. The results, presented in Fig. 5, indicate that flow-rate reduction was achieved at 3.5 MPa for the set cement containing SIS, and at 7 MPa for the set cement containing SBS.

Claims

1. A method for maintaining zonal isolation in a subterranean well in which a borehole penetrates one or more hydrocarbon-containing formations, comprising:

   (i) pumping a cement slurry comprising thermoplastic triblock-polymer particles into the well, wherein the particles comprise styrene-isoprene-styrene polymer particles, styrene-butadiene-styrene polymer particles or both; and
   (ii) allowing the cement slurry to set to form a cement sheath;

wherein, should microannuli, cracks or defects occur in the cement sheath, allowing hydrocarbons from the formation to contact the particles, allowing the particles to swell, and enabling the cement sheath to have self-healing properties.

2. The method of claim 1, wherein the concentration of the particles is between 10% and 55% by volume of cement-slurry solids.

3. The method of claim 1 or claim 2, wherein the size of the particles is between 100 μm and 900 μm.

4. The method of any one of claims 1-3, wherein the slurry further comprises one or more members of the list comprising: an aqueous inverse emulsion of polymer comprising a betaine group; poly-2, 2, 1-bicyclo heptene (polynorbomene); alkylstyrene polymer; crosslinked substituted vinyl acrylate copolymers; diatomaceous earth; natural rubber; vulcanized rubber; polyisoprene rubber; vinyl acetate rubber; polychloroprene rubber; acrylonitrile butadiene rubber; hydrogenated acrylonitrile butadiene rubber; ethylene propylene diene polymer rubber; ethylene propylene monomer rubber; styrene-butadiene rubber; styrene propylene diene polymer; brominated poly(isobutylene-co-4-methylstyrene); butyl rubber; chlorosulfonated polyethylenes; polyacrylate rubber; polyurethane; silicone rubber; brominated butyl rubber; chlorinated butyl rubber; chlorinated polyethylene; epichlorohydrin ethylene oxide copolymer; ethylene acrylate rubber; ethylene propylene diene terpolymer rubber; sulfonated polyethylene; fluoro silicone rubbers; fluoroelastomer; and substituted styrene acrylate copolymers.

5. The method of any one of claims 1-4, wherein the hydrocarbon comprises at least 91 mol% methane.

6. The method of any one of claims 1-5, wherein the hydrocarbon pressure to which the set cement is exposed is higher than 3.5 MPa.

7. Use of thermoplastic triblock-polymer particles to impart self-healing properties to a cement formulation that is placed in a subterranean well penetrating one or more hydrocarbon-containing formations, wherein once set, the cement forms a cement sheath in which the particles swell when contacted by hydrocarbons from the formation, and wherein the particles comprise styrene-isoprene-styrene polymer particles, styrene-butadiene-styrene polymer particles or both.

8. The use of claim 7, wherein the concentration of the particles is between 10% and 55% by volume of cement-slurry solids.

9. The use of claim 7 or claim 8, wherein the size of the particles is between 100 μm and 900 μm.

10. The use of any one of claims 7-9, wherein the slurry further comprises one or more members of the list comprising: an aqueous inverse emulsion of particles comprising a betaine group; poly-2, 2, 1-bicyclo heptene (polynorbomene); alkylstyrene polymer; crosslinked substituted vinyl acrylate copolymers; diatomaceous earth; natural rubber; vulcanized rubber; polyisoprene rubber; vinyl acetate rubber; polychloroprene rubber; acrylonitrile butadiene rubber; hydrogenated acrylonitrile butadiene rubber; ethylene propylene diene polymer rubber; ethylene propylene monomer rubber; styrene-butadiene rubber; styrene propylene diene polymer; brominated poly(isobutylene-co-4-methylstyrene); butyl rubber; chlorosulphonated polyethylenes; polyacrylate rubber; polyurethane; silicone rubber; brominated butyl rubber; chlorinated butyl rubber; chlorinated polyethylene; epichlorohydrin ethylene oxide copolymer; ethylene acrylate rubber; ethylene propylene diene terpolymer rubber; sulphonated polyethylene; fluoro silicone rubbers; fluoroelastomer; and substituted styrene acrylate copolymers.

11. The use of any one of claims 7-10, wherein the hydrocarbon comprises at least 91 mol% methane.

12. The use of any one of claims 7-11, wherein the hydrocarbon pressure to which the set cement is exposed is higher than 3.5 MPa.

Patentansprüche

1. Verfahren zum Aufrechterhalten einer Zonenisolierung in einem unterirdischen Bohrloch, in dem ein Bohrloch eine oder mehrere kohlenwasserstoffhaltige Formationen durchdringt, das aufweist:

(i) Pumpen eines Zementschlamms, der thermoplastische Triblockpolymerteilchen aufweist, in das Bohrloch,

wobei die Teilchen Styrol-Isopren-Styrol-Polymerteilchen, Styrol-Butadien-Styrol-Polymerteilchen oder beide aufweisen; und
(ii) Ermöglichen, dass der Zementschlamm abbindet, um einen Zementmantel zu bilden;

wobei, sollten Mikroringe, Brüche oder Fehler im Zementmantel auftreten, Ermöglichen, dass Kohlenwasserstoffe aus der Formation mit den Teilchen in Kontakt kommen, Ermöglichen, dass die Teilchen aufquellen, und Ermöglichen, dass der Zementmantel Selbstheilungseigenschaften aufweist.

2. Verfahren nach Anspruch 1, wobei die Konzentration der Teilchen zwischen 10 Volumen-% und 55 Volumen-% der Zementschlammfeststoffe beträgt.

3. Verfahren nach Anspruch 1 oder Anspruch 2, wobei die Größe der Teilchen zwischen 100 μm und 900 μm beträgt.

4. Verfahren nach einem der Ansprüche 1-3, wobei der Schlamm ferner ein oder mehrere Elemente der Liste aufweist, die aufweist: eine wässrige inverse Emulsion eines Polymers, das eine Betaingruppe aufweist; Poly-2,2,1-bicyclohepten (Polynorbornen); Alkylstyrolpolymer; vernetzte substituierte Vinyl-Acrylat-Copolymere; Kieselgur; Naturkautschuk; Vulkanisat; Polyisoprenkautschuk; Vinylacetatkautschuk; Polychloroprenkautschuk; Butadien-Acrylnitril-Kautschuk; hydrierten Butadien-Acrylnitril-Kautschuk; Ethylen-Propylen-Dien-Kautschuk; Ethylen-Propylen-Monomer-Kautschuk; Styrol-Butadien-Kautschuk; Styrol-Propylen-Dien-Polymer; bromiertes Poly(isobutylen-co-4-methylstyrol); Butylkautschuk; chlorsulfonierte Polyethylene; Polyacrylatkautschuk; Polyurethan; Silikonkautschuk; bromierten Butylkautschuk; chlorierten Butylkautschuk; chloriertes Polyethylen; Epichlorhydrin-Ethylenoxid-Copolymer; Ethylen-Acrylat-Kautschuk; Ethylen-Propylen-Dien-Terpolymer-Kautschuk; sulfoniertes Polyethylen; Fluorsilikonkautschuke; Fluorelastomer; und substituierte Styrol-Acrylat-Copolymere.

5. Verfahren nach einem der Ansprüche 1-4, wobei der Kohlenwasserstoff mindestens 91 Mol-% Methan aufweist.

6. Verfahren nach einem der Ansprüche 1-5, wobei der Kohlenwasserstoffdruck, dem der abgebundene Zement ausgesetzt ist, höher als 3,5 MPa ist.

7. Verwendung von thermoplastischen Triblockpolymerteilchen, um einer Zementformulierung Selbstheilungseigenschaften zu verleihen, die in einem unterirdischen Bohrloch angeordnet ist, das eine oder mehrere kohlenwasserstoffhaltige Formationen durchdringt, wobei der Zement, sobald er abgebunden ist, einen Zementmantel bildet, in dem die Teilchen aufquellen, wenn sie mit Kohlenwasserstoffen aus der Formation in Kontakt kommen, und wobei die Teilchen Styrol-Isopren-Styrol-Polymerteilchen, Styrol-Butadien-Styrol-Polymerteilchen oder beide aufweisen.

8. Verwendung nach Anspruch 7, wobei die Konzentration der Teilchen zwischen 10 Volumen-% und 55 Volumen-% der Zementschlammfeststoffe beträgt.

9. Verwendung nach Anspruch 7 oder Anspruch 8, wobei die Größe der Teilchen zwischen 100 μm und 900 μm beträgt.

10. Verwendung nach einem der Ansprüche 7-9, wobei der Schlamm ferner ein oder mehrere Elemente der Liste aufweist, die aufweist: eine wässrige inverse Emulsion von Teilchen, die eine Betaingruppe aufweisen; Poly-2,2,1-bicyclohepten (Polynorbornen); Alkylstyrolpolymer; vernetzte substituierte Vinyl-Acrylat-Copolymere; Kieselgur; Naturkautschuk; Vulkanisat; Polyisoprenkautschuk; Vinylacetatkautschuk; Polychloroprenkautschuk; Butadien-Acrylnitril-Kautschuk; hydrierten Butadien-Acrylnitril-Kautschuk; Ethylen-Propylen-Dien-Kautschuk; Ethylen-Propylen-Monomer-Kautschuk; Styrol-Butadien-Kautschuk; Styrol-Propylen-Dien-Polymer; bromiertes Poly(isobutylen-co-4-methylstyrol); Butylkautschuk; chlorsulfonierte Polyethylene; Polyacrylatkautschuk; Polyurethan; Silikonkautschuk; bromierten Butylkautschuk; chlorierten Butylkautschuk; chloriertes Polyethylen; Epichlorhydrin-Ethylenoxid-Copolymer; Ethylen-Acrylat-Kautschuk; Ethylen-Propylen-Dien-Terpolymer-Kautschuk; sulfoniertes Polyethylen; Fluorsilikonkautschuke; Fluorelastomer; und substituierte Styrol-Acrylat-Copolymere.

11. Verwendung nach einem der Ansprüche 7-10, wobei der Kohlenwasserstoff mindestens 91 Mol-% Methan aufweist.

12. Verwendung nach einem der Ansprüche 7-11, wobei der Kohlenwasserstoffdruck, der der abgebundene Zement ausgesetzt ist, höher als 3,5 MPa ist.

Revendications

1. Procédé pour maintenir une isolation zonale dans un puits souterrain dans lequel un trou de forage pénètre une ou plusieurs formations contenant des hydrocarbures, comprenant :

   (i) le pompage d'un laitier de ciment comprenant des particules de polymère tribloc thermoplastique dans le puits, dans lequel les particules comprennent des particules de polymère styrène-isoprène-styrène, des particules de polymère styrène-butadiène-styrène ou les deux ; et
   (ii) le fait de laisser le laitier de ciment se figer pour former une gaine en ciment ;

   dans lequel, si des microcanules, fissures ou défauts se produisent dans la gaine en ciment, on laisse les hydrocarbures de la formation venir au contact des particules, on laisse les particules gonfler, et on permet à la gaine en ciment d'avoir des propriétés autoréparables.

2. Procédé selon la revendication 1, dans lequel la concentration des particules est entre 10 % et 55 % en volume de matières solides du laitier de ciment.

3. Procédé selon la revendication 1 ou la revendication 2, dans lequel la taille des particules est entre 100 μm et 900 μm.

4. Procédé selon l'une quelconque des revendications 1 à 3, dans lequel le laitier comprend en outre un ou plusieurs éléments de la liste comprenant : une émulsion inverse aqueuse de polymère comprenant un groupe bétaïne ; un poly-2,2,1-bicyclo heptène (polynorbornène) ; un polymère d'alkylstyrène ; des copolymères d'acrylate de vinyle substitués réticulés ; une terre à diatomées ; un caoutchouc naturel ; un caoutchouc vulcanisé ; un caoutchouc de polyisoprène ; un caoutchouc d'acétate de vinyle ; un caoutchouc de polychloroprène ; un caoutchouc d'acrylonitrile butadiène ; un caoutchouc d'acrylonitrile butadiène hydrogéné ; un caoutchouc de polymère d'éthylène-propylène-diène ; un caoutchouc d'éthylène-propylène-monomère ; un caoutchouc de styrène-butadiène ; un polymère styrène-propylène-diène : un poly(isobutylène-co-4-méthylstyrène) bromé ; un caoutchouc butyle ; des polyéthylènes chlorosulfonés ; un caoutchouc de polyacrylate ; un polyuréthane ; un caoutchouc de silicone ; un caoutchouc butyle bromé ; un caoutchouc butyle chloré ; un polyéthylène chloré ; un copolymère d'épichlorhydrine oxyde d'éthylène ; un caoutchouc d'acrylate d'éthylène ; un caoutchouc de terpolymère éthylène-propylène-diène ; un polyéthylène sulfoné ; des caoutchoucs de fluoro silicone ; un fluoroélastomère ; et des copolymères d'acrylate de styrène substitués.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel l'hydrocarbure comprend au moins 91 % en mol de méthane.

6. Procédé selon l'une quelconque des revendications 1 à 5, dans lequel la pression des hydrocarbures à laquelle le ciment figé est exposé est supérieure à 3,5 MPa.

7. Utilisation de particules de polymère tribloc thermoplastique pour conférer des propriétés autoréparables à une formulation de ciment qui est placée dans un puits souterrain pénétrant une ou plusieurs formations contenant des hydrocarbures, dans laquelle, une fois figé, le ciment forme une gaine en ciment dans laquelle les particules gonflent lorsqu'elles entrent en contact avec les hydrocarbures de la formation, et dans laquelle les particules comprennent des particules de polymère styrène-isoprène-styrène, des particules de styrène-butadiène-styrène ou les deux.

8. Utilisation selon la revendication 7, dans laquelle la concentration des particules est entre 10 % et 55 % en volume de matières solides du laitier de ciment.

9. Utilisation selon la revendication 7 ou la revendication 8, dans laquelle la taille des particules est entre 100 μm et 900 μm.

10. Utilisation selon l'une quelconque des revendications 7 à 9, dans laquelle le laitier comprend en outre un ou plusieurs éléments de la liste comprenant : une émulsion inverse aqueuse de particules comprenant un groupe bétaïne ; un poly-2,2,1-bicyclo heptène (polynorbornène) ; un polymère d'alkylstyrène ; des copolymères d'acrylate de vinyle substitués réticulés ; une terre à diatomées ; un caoutchouc naturel ; un caoutchouc vulcanisé ; un caoutchouc de polyisoprène ; un caoutchouc d'acétate de vinyle ; un caoutchouc de polychloroprène ; un caoutchouc d'acrylonitrile butadiène ; un caoutchouc d'acrylonitrile butadiène hydrogéné ; un caoutchouc de polymère d'éthylène-propylène-diène ; un caoutchouc d'éthylène-propylène-monomère ; un caoutchouc de styrène-butadiène ; un polymère de

styrène-propylène-diène : un poly(isobutylène-co-4-méthylstyrène) bromé ; un caoutchouc butyle ; des polyéthylènes chlorosulfonés ; un caoutchouc de polyacrylate ; un polyuréthane ; un caoutchouc de silicone ; un caoutchouc butyle bromé ; un caoutchouc butyle chloré ; un polyéthylène chloré ; un copolymère d'épichlorhydrine oxyde d'éthylène ; un caoutchouc d'acrylate d'éthylène ; un caoutchouc de terpolymère éthylène-propylène-diène ; un polyéthylène sulfoné ; des caoutchoucs de fluoro silicone ; un fluoroélastomère ; et des copolymères d'acrylate de styrène substitués.

11. Utilisation selon l'une quelconque des revendications 7 à 10, dans laquelle l'hydrocarbure comprend au moins 91 % en mol de méthane.

12. Utilisation selon l'une quelconque des revendications 7 à 11, dans laquelle la pression des hydrocarbures à laquelle le ciment figé est exposé est supérieure à 3,5 MPa.

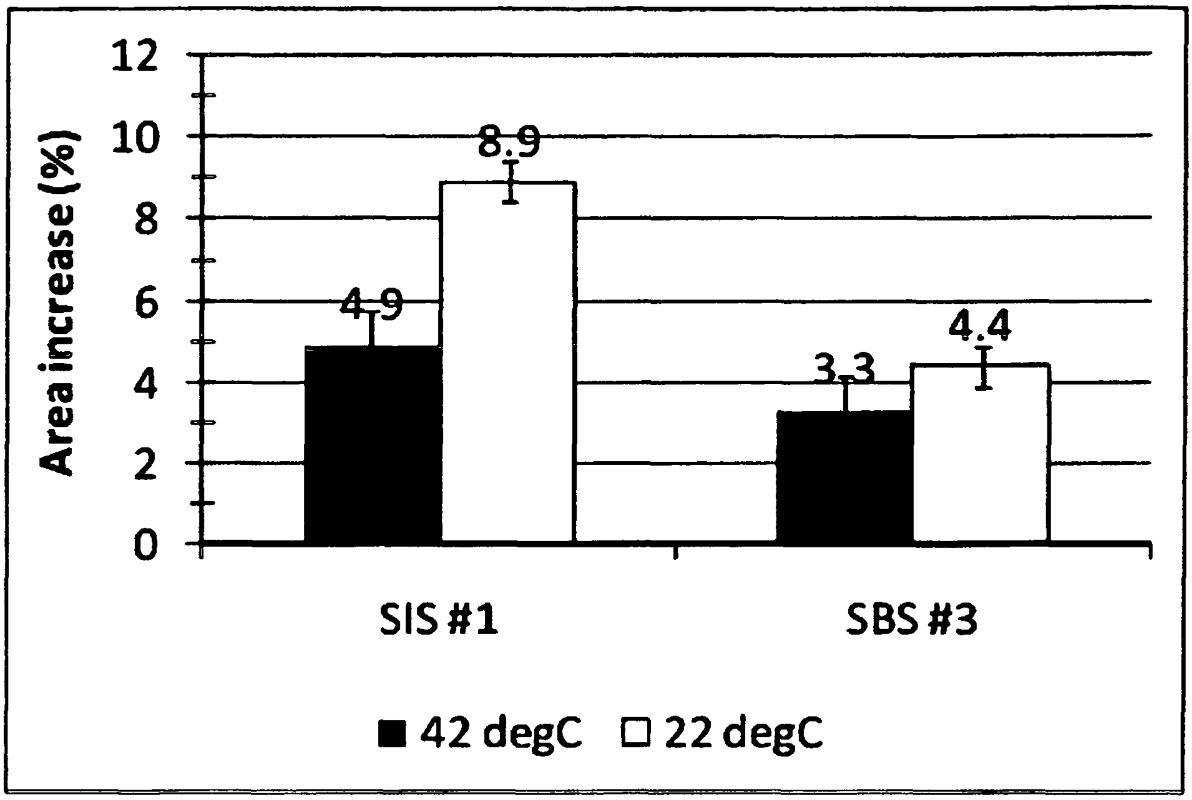


FIGURE 1

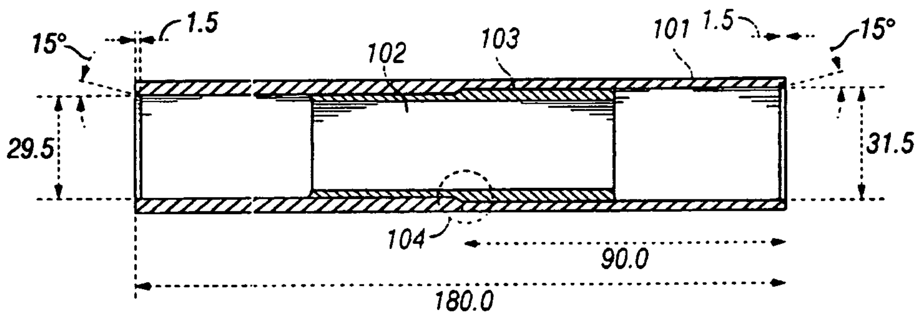


FIG. 2

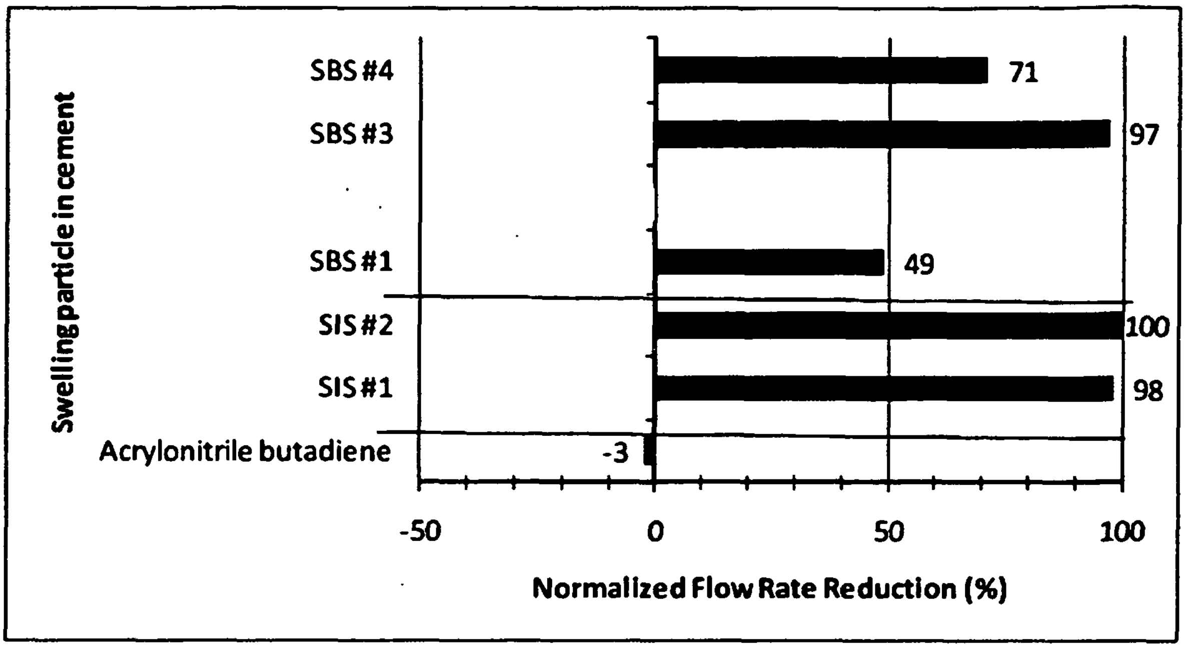
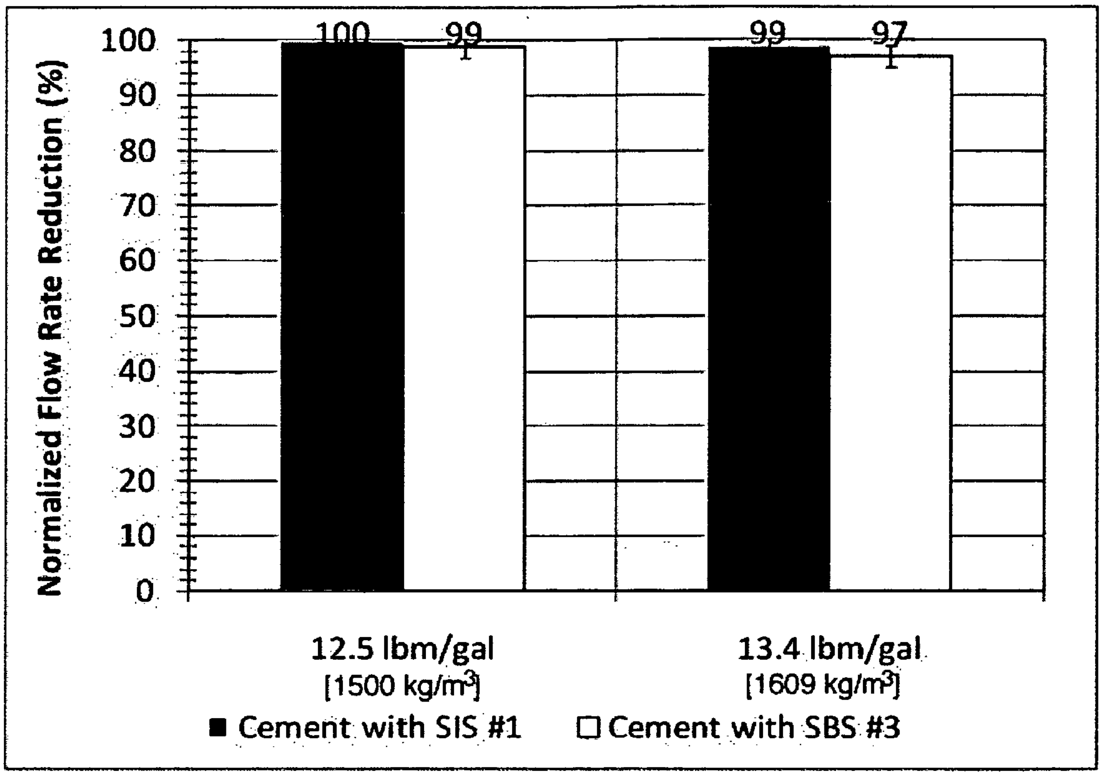

Swelling particle in cement
SBS #4
SBS #3
SBS #1
SIS #2
SIS #1
Acrylonitrile butadiene
71
97
49
100
98
-3
-50
0
50
100
Normalized Flow Rate Reduction (%)

FIGURE 3



Normalized Flow Rate Reduction (%)
100
90
80
70
60
50
40
30
20
10
0
100
99
99
97
12.5 lbm/gal
[1500 kg/m3]
13.4 lbm/gal
[1609 kg/m3]
Cement with SIS #1
Cement with SBS #3

FIGURE 4

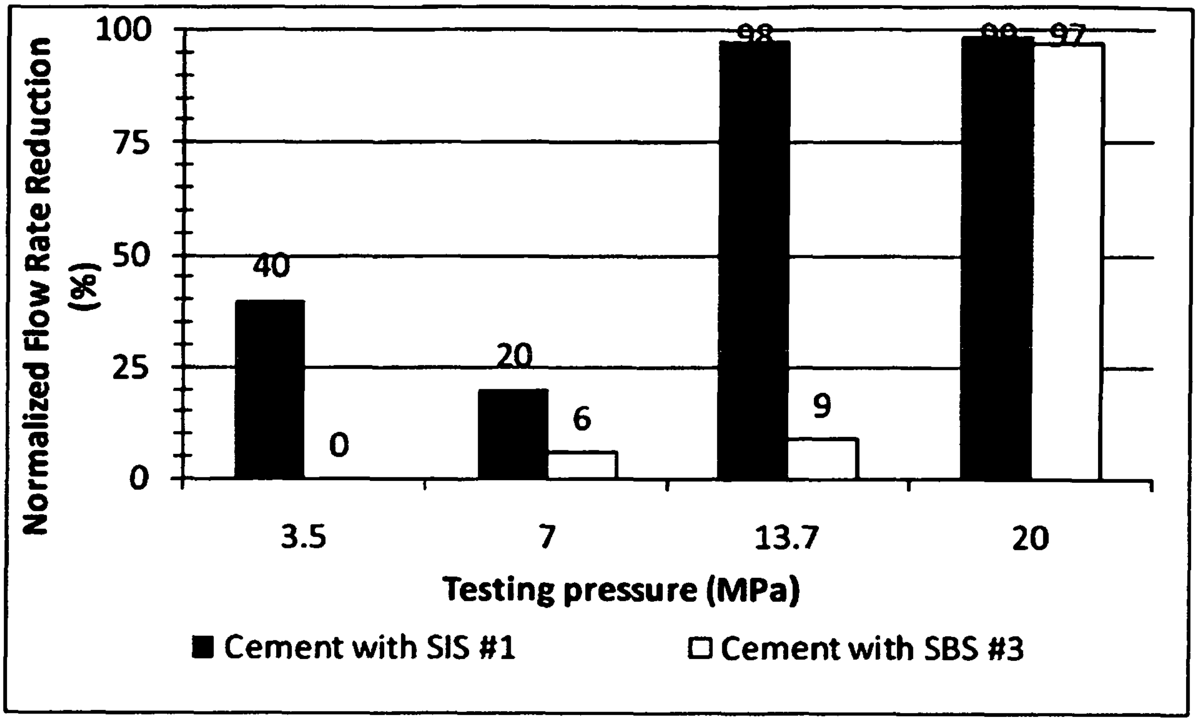

Normalized Flow Rate Reduction (%)
100
75
50
25
0
40
0
20
6
98
9
97
3.5
7
13.7
20
Testing pressure (MPa)
Cement with SIS #1
Cement with SBS #3

FIGURE 5

REFERENCES CITED IN THE DESCRIPTION

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715309/DO

ÖNJAVÍTÓ CEMENTEK

SZABADALMI IGÉNYPONTOK

1. Eljárás zonális szigetelés fenntartására egy föld alatti kútban, amelyben egy fúrólyuk áthatol egy vagy több szénhidrogén-tartalmú rétegen, amely eljárás magában foglalja, hogy:

(i) hőre lágyuló triblokk-polimer szemcséket tartalmazó cementiszapot szivattyúzunk a kútba, amely szemcsék sztirol-izoprén-sztirol polimer szemcséket, sztirol-butadién-sztirol polimer szemcséket vagy mindkettőt tartalmaznak; és

(ii) hagyjuk, hogy a cementtej megkössön, hogy cementköpenyt képezzen;

és amennyiben mikrogyűrűk, repedések vagy hibák keletkeznek a cementköpenyben, akkor hagyjuk, hogy a rétegekből származó szénhidrogének érintkezzenek a szemcsékkel, hagyjuk, hogy a szemcsék megduzzadjanak, és lehetővé tesszük, hogy a cementköpeny öngyógyító tulajdonságokkal rendelkezzen.

2. Az 1. igénypont szerinti eljárás, amelyben a szemcsekoncentráció a cementtej szilárdanyagára vonatkoztatva 10 és 55 térfogat% között van.

3. Az 1. vagy a 2. igénypont szerinti eljárás, amelyben a szemcseméret 100 µm és 900 µm között van.

4. Az 1-3. igénypontok bármelyike szerinti eljárás, amelyben a tej magában foglal továbbá a következő listában felsoroltak közül egyet vagy többet: egy betain-csoportot tartalmazó polimer vizes inverz emulziója; poli-2,2,1-bicikloheptén (polinorbornén); alkilsztirol polimer; térhálósított szubsztituált vinil-akrilát kopolimerek; kovaföld; természetes gumi; vulkanizált gumi; poliizoprén gumi; vinil-acetát gumi; polikloroprén gumi; akrilnitril-butadién gumi; hidrogénezett akrilnitril-butadién gumi; etilén-propilén-dién polimer gumi; etilén-propilén monomer gumi; sztirol-butadién gumi; sztirol-propilén-dién polimer; brómozott poli(izobutilén-ko-4-metil-sztirol); butil gumi; klórszulfonált polietilének; poliakrilát gumi; poliuretán; szilikon gumi; brómozott butil gumi; klórozott butil gumi; klórozott polietilén; epiklórhidrin etilén-oxid kopolimer; etilén-akrilát gumi; etilén-propilén-dién terpolimer gumi; szulfonált polietilén; fluorszilikon gumik; fluorelasztomer; valamint szubsztituált sztirol-akrilát kopolimerek.

5. Az 1-4. igénypontok bármelyike szerinti eljárás, amelyben a szénhidrogén legalább 91 mól% metánt tartalmaz.

6. Az 1-5. igénypontok bármelyike szerinti eljárás, amelyben a megkötött cementet terhelő szénhidrogén-nyomás nagyobb, mint 3,5 MPa.

7. Hőre lágyuló triblokk-polimer szemcsék alkalmazása olyan cementkészítmény öngyógyító tulajdonságokkal való felruházása céljából, amely egy, egy vagy több szénhidrogén-tartalmú rétegen áthatoló, föld alatti kútban van elhelyezve, amely cement – miután megkötött – egy cementköpenyt képez, amelyben a szemcsék megduzzadnak, amikor érintkeznek a rétegből származó szénhidrogénekkel, és amely szemcsék sztirol-izoprén-sztirol polimer szemcséket, sztirol-butadién-sztirol polimer szemcséket vagy mindkettőt tartalmaznak.

8. A 7. igénypont szerinti alkalmazás, amelyben a szemcsekoncentráció a cementtej szilárdanyagára vonatkoztatva 10 és 55 térfogat% között van.

9. A 7. vagy a 8. igénypont szerinti alkalmazás, amelyben a szemcseméret 100 μm és 900 μm között van.

10. A 7-9. igénypontok bármelyike szerinti alkalmazás, amelyben a tej magában foglal továbbá a következő listában felsoroltak közül egyet vagy többet: egy betain-csoportot tartalmazó szemcsék vizes inverz emulziója; poli-2,2,1-biciklopheptén (polinorbornén); alkilsztirol polimer; térhálósított szubsztituált vinil-akrilát kopolimerek; kovaföld; természetes gumi; vulkanizált gumi; poliizoprén gumi; vinil-acetát gumi; polikloroprén gumi; akrilnitril-butadién gumi; hidrogénezett akrilnitril-butadién gumi; etilén-propilén-dién polimer gumi; etilén-propilén monomer gumi; sztirol-butadién gumi; sztirol-propilén-dién polimer; brómozott poli(izobutilén-ko-4-metil-sztirol); butil gumi; klórszulfonált polietilének; poliakrilát gumi; poliuretán; szilikon gumi; brómozott butil gumi; klórozott butil gumi; klórozott polietilén; epiklórhidrin etilén-oxid kopolimer; etilén-akrilát gumi; etilén-propilén-dién terpolimer gumi; szulfonált polietilén; fluorszilikon gumik; fluorelasztomer; valamint szubsztituált sztirol-akrilát kopolimerek.

11. A 7-10. igénypontok bármelyike szerinti alkalmazás, amelyben a szénhidrogén legalább 91 mól% metánt tartalmaz.

12. A 7-11. igénypontok bármelyike szerinti alkalmazás, amelyben a megkötött cementet terhelő szénhidrogén-nyomás nagyobb, mint 3,5 MPa.

(A meghatalmazott)