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(54) Title: COMPOSITIONS AND METHODS FOR WELL COMPLETIONS

(57) Abstract: Incorporation of carbonaceous materials in a cement slurry increases the linear thermal-expansion coefficient of the set cement. When placed in a subterranean well having at least one casing string, cement sheaths with linear thermal-expansion coefficients similar to that of the casing will be subjected to lower compressive and tensile stresses during downhole-temperature changes. Such cement slurries are particularly advantageous in the context of thermal-recovery wells.

COMPOSITIONS AND METHODS FOR WELL COMPLETIONS

BACKGROUND OF THE INVENTION

[0001] The statements in this section merely provide background information related to the present disclosure and may not constitute prior art.

[0002] This invention relates to compositions and methods for treating subterranean formations, in particular, compositions and methods for cementing and completing thermal recovery wells.

[0003] During the construction of subterranean wells, it is common, during and after drilling, to place a tubular body in the wellbore. The tubular body may comprise drillpipe, casing, liner, coiled tubing or combinations thereof. The purpose of the tubular body is to act as a conduit through which desirable fluids from the well may travel and be collected. The tubular body is normally secured in the well by a cement sheath. The cement sheath provides mechanical support and hydraulic isolation between the zones or layers that the well penetrates. The latter function is important because it prevents hydraulic communication between zones that may result in contamination. For example, the cement sheath blocks fluids from oil or gas zones from entering the water table and polluting drinking water. In addition, to optimize a well's production efficiency, it may be desirable to isolate, for example, a gas-producing zone from an oil-producing zone.

[0004] The cement sheath achieves hydraulic isolation because of its low permeability. In addition, intimate bonding between the cement sheath and both the tubular body and borehole is necessary to prevent leaks. However, over time the cement sheath can deteriorate and become permeable. Alternatively, the bonding between the

cement sheath and the tubular body or borehole may become compromised. The principal causes of deterioration and debonding include physical stresses associated with tectonic movements, temperature changes and chemical deterioration of the cement.

[0005] Development of heavy oil reserves often involves applying heat to the producing reservoir. Such thermal-recovery wells frequently employ steam injection. Steam injection encompasses a number of techniques, including steam assisted gravity drainage (SAGD), cyclic steam stimulation (CSS) and steamflooding. During such operations, the resulting well temperature may vary from 150° to 700°C, subjecting the cement sheath to especially severe stresses and possibly leading to cement-sheath failure, formation of microannuli or both. Indeed, a significant percentage of thermal-recovery wells suffer from various forms of leaks including complete steam breakthrough to surface.

[0006] There have been several proposals to solve the problems of cement-sheath deterioration. One approach is to design the cement sheath to mechanically survive physical stresses that may be encountered during its lifetime (US 6,296,057). Another approach is to employ additives that improve the physical properties of the set cement. US 6,458,198 describes the addition amorphous metal fibers to improve the strength and impact resistance. EP 1129047 and WO 00/37387 describe the addition of flexible materials (rubber or polymers) to confer a degree of flexibility to the cement sheath. WO 01/70646 describes cement compositions that are formulated to be less sensitive to temperature fluctuations during the setting process. However, these solutions are not as effective in the context of thermal-recovery wells. The stresses may be too severe for the solutions to be effective, the active material may not be stable at such high

temperatures, or both.

[0007] Therefore, despite the valuable contributions of the prior art, a need still remains for improved cement formulations that can better withstand the thermal and mechanical stresses associated with thermal-recovery wells.

SUMMARY OF THE INVENTION

[0008] The present invention allows improvements by providing cement formulations that, when set, have linear thermal-expansion coefficients that are ideally equal to that of the casing in the subterranean well. When the cement sheath and casing expand similarly as heat is applied to the well, the resulting stresses on the cement sheath and the cement/casing bond are minimized, thereby helping to preserve zonal isolation in the well.

[0009] In an aspect, embodiments of the invention relate to methods for adjusting the thermal-expansion properties of a cement formulation for placement in a subterranean well.

[0010] In a further aspect, embodiments of the invention relate to methods for controlling thermal and mechanical stresses in a cement sheath in a subterranean well.

[0011] In yet a further aspect, embodiments of the invention aim at uses of at least one carbonaceous material to adjust the thermal-expansion properties of set cement placed in a subterranean well.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 presents two graphs that show how the maximum

compressive and tensile stresses in a cement sheath vary with the linear thermal-expansion coefficient of the set cement, when the well temperature is increased linearly from 10° to 250°C.

[0013] Figure 2 presents two graphs that show how the maximum compressive and tensile stresses in a cement sheath vary with the linear thermal-expansion coefficient of the set cement, when the well temperature is increased linearly from 10° to 700°C.

[0014] Figure 3 is a graph showing how the formation of a microannulus between casing and set cement is influenced by the Young's moduli of the formation and the cement sheath.

[0015] Figure 4 is a graph showing how the formation of a microannulus between casing and set cement is influenced by the linear thermal-expansion coefficient of the set cement, and the Young's moduli of the formation and the cement sheath.

DETAILED DESCRIPTION

[0016] The invention may be described in terms of treatment of vertical wells, but is equally applicable to wells of any orientation. The invention may be described for hydrocarbon production wells, but it is to be understood that the invention may be used for wells for production of other fluids, such as water or carbon dioxide, or, for example, for injection or storage wells. It should also be understood that throughout this specification, when a concentration or amount range is described as being useful, or suitable, or the like, it is intended that any and every concentration or amount within the range, including the end points, is to be considered as having been stated. Furthermore,

each numerical value should be read once as modified by the term “about” (unless already expressly so modified) and then read again as not to be so modified unless otherwise stated in context. For example, “a range of from 1 to 10” is to be read as indicating each and every possible number along the continuum between about 1 and about 10. In other words, when a certain range is expressed, even if only a few specific data points are explicitly identified or referred to within the range, or even when no data points are referred to within the range, it is to be understood that the inventors appreciate and understand that any and all data points within the range are to be considered to have been specified, and that the inventors have possession of the entire range and all points within the range.

[0017] Most materials expand when they are heated because, as the temperature increases, the distance between the atoms also increases. Thermal expansion may be expressed in various ways. The linear coefficient of thermal expansion (LCTE) describes the specific linear elongation of a material per unit value of temperature and at a constant pressure. The areal coefficient of thermal expansion (ACTE) relates the change in a material’s area dimensions as a function of temperature. The volumetric coefficient of thermal expansion (VCTE) describes the change in volume of a material per unit value of temperature. For exactly isotropic materials, the VCTE is three times the LCTE.

[0018] A typical LCTE for a conventional set Portland cement is about $8 \cdot 10^{-6}/^{\circ}\text{C}$, whereas the typical LCTE for carbon steel is about $13 \cdot 10^{-6}/^{\circ}\text{C}$. Thus, when a cement sheath around steel casing is subjected to a thermal load, the dimensions of the cement and casing will change and diverge from each other. In the presence of thermal

loads associated with thermal-recovery wells, the dimensional divergence may induce significant mechanical stresses on the cement sheath, leading to the formation of a microannulus, cement-sheath failure in both tensile and compressive modes, or both. The present invention minimizes the aforementioned stresses by providing set cements whose LCTEs are more compatible with the casing LCTE.

[0019] The influence of the LCTE on compressive and tensile stresses in a cement sheath is illustrated in Figs. 1 and 2. Two cement formulations with different Young's moduli were considered in the simulation. The properties of the casing and the formation are given in Table 1. The stresses were calculated for two scenarios: one during which the casing was linearly heated from 10° to 250°C; the other involving the linear heating of the casing from 10° to 700°C. The time period for both scenarios was 3 days.

Formation properties	
Density	2300 kg/m ³
Young Modulus	4000 and 9000 MPa
Poisson's Ratio	0.425
Thermal Conductivity	1.83 W/(m.°K)
Specific Heat Capacity	710 J/(kg.°K)
Linear Thermal Expansion Coefficient	13 • 10 ⁻⁶ /°C
Open hole	400.0 mm
Inner Casing	
Material Name	Steel
Density	8000 kg/m ³
Casing OD	298.45 mm
Casing ID	273.61 mm
Standoff	80%
Young Modulus	200,000 MPa
Poisson's Ratio	0.27

Weight	89.29 kg/m
Thermal Conductivity	15 W/(m.K)
Specific Heat Capacity	500 J/(kg.K)
Linear Thermal Expansion Coefficient	$13 \cdot 10^{-6}/^{\circ}\text{C}$

Table 1. Formation and casing properties for stress simulations presented in Figs. 1 and 2.

Figures 1 and 2 show that, for both cement systems, the compressive and tensile stresses decrease as the LCTE approaches that of the steel— $13 \cdot 10^{-6}/^{\circ}\text{C}$.

[0020] Figures 1 and 2 also show that compressive and tensile stresses in the cement sheath remain low when the set-cement LCTE exceeds that of the steel casing. Indeed, as shown in Fig. 3 and 4, the LCTE of the set cement may be significantly higher than that of the casing before deleterious effects occur—in the form of microannuli.

[0021] Certain properties of the casing, cement and formation are given in Table 2. All other parameters are the same as those described in Table 1.

Open Hole	216 mm (8.5 in.)	Formation	
		Poisson's ratio	0.3
Casing	178 mm (7.0 in.), 38.7 kg/m	Young's modulus	variable
Linear Thermal-Expansion Coefficient	$13 \cdot 10^{-6}/^{\circ}\text{C}$	Cement	
Standoff	100 %	Poisson's ratio	0.15
		Young's modulus	4500 or 8500 MPa
Temperature Ramp	20° to 260°C in 4 hours		

Table 2. Formation, cement and casing properties for stress simulations presented in Figs. 2 and 3.

[0022] Figure 3 is a plot of microannulus width versus rock Young's

modulus. The linear thermal-expansion coefficient is significantly higher than that of steel casing— $50 \cdot 10^{-6}/^{\circ}\text{C}$. Two cement Young's moduli were considered—4500 MPa and 8500 MPa. The results show that, as long as the rock Young's modulus is greater than about 33% of the cement Young's modulus, no microannulus will occur.

[0023] Figure 4 is a plot of microannulus width versus the cement linear thermal-expansion coefficient. Three Young's-modulus conditions are considered, whereby the cement and rock Young's moduli are varied. The results show that the microannulus width is not only a function of the cement thermal-expansion coefficient, but also of the ratio between the cement and rock Young's moduli. The results show that a cement thermal-expansion of $20 \cdot 10^{-6}/^{\circ}\text{C}$ is an upper limit beyond which exists a risk of forming a microannulus if there is a large difference between the cement and rock Young's moduli (e.g., a factor of 8 or 9).

[0024] The inventors have surprisingly discovered that the thermal-expansion properties of a cement system may be adjusted by incorporating at least one carbonaceous material in the slurry formulation. Preferred carbonaceous materials include (but are not limited to) one or more members of the list comprising delayed coke, fluid coke, calcined coke, asphalt, charcoal, coal, anthracite, graphite, flake coke, amorphous pitch coke, tar coke, anode coke, metallurgical coke, amorphous graphite, lignite, bituminous coal, sub-bituminous coal, exinite, vitrinite, inertinite, fine kolite, activated carbon and gilsonite. Delayed coke may occur in one or more forms, including (but not limited to) shot, sponge, needle, maze, calcined and green. Even more preferred carbonaceous materials are chosen from the list consisting of coke, kolite or coal and mixtures thereof. The most preferred carbonaceous compound to be used being coke.

[0025] Embodiments of the invention relate to methods for adjusting the thermal-expansion properties of a cement system for placement in a subterranean well having at least one casing string. The method comprises incorporating a carbonaceous material in the cement system, such that the linear thermal-expansion coefficient of the set cement is higher than that of a set cement not containing the carbonaceous material. Such linear coefficient of thermal expansion being preferably lower than or equal to about $50 \cdot 10^{-6}/^{\circ}\text{C}$. A more preferred linear thermal-expansion-coefficient range is between about $11 \cdot 10^{-6}/^{\circ}\text{C}$ and $20 \cdot 10^{-6}/^{\circ}\text{C}$, and an even more preferred linear thermal-expansion coefficient range is between about $11 \cdot 10^{-6}/^{\circ}\text{C}$ and $17 \cdot 10^{-6}/^{\circ}\text{C}$.

[0026] Further embodiments of the invention relate to methods for controlling thermal and mechanical stresses in a cement sheath in a subterranean well. The method comprises installing at least one casing string in the well whose linear thermal-expansion coefficient is known. A cement slurry comprising at least one carbonaceous material is formed such that, after setting, it has a linear thermal-expansion coefficient higher than that of set cement not containing the carbonaceous material. Such linear coefficient of thermal expansion being preferably lower than or equal to about $50 \cdot 10^{-6}/^{\circ}\text{C}$. A more preferred linear thermal-expansion-coefficient range is between about $11 \cdot 10^{-6}/^{\circ}\text{C}$ and $20 \cdot 10^{-6}/^{\circ}\text{C}$, and an even more preferred linear thermal-expansion coefficient range is between about $11 \cdot 10^{-6}/^{\circ}\text{C}$ and $17 \cdot 10^{-6}/^{\circ}\text{C}$. The cement slurry is pumpable and is placed in the well adjacent to the casing string and then allowed to set. Those skilled in the art will recognize that a pumpable cement slurry has a viscosity preferably below about 1000 mPa-s at a shear rate of 100 s^{-1} , throughout the temperature range the slurry will experience during placement in the well.

[0027] Yet further embodiments of the invention aim at uses of at least one carbonaceous material to adjust the linear thermal-expansion properties of set cement placed in a subterranean well having at least one casing string. The incorporation of the carbonaceous material allows one to control the thermal and mechanical stresses exerted upon the cement sheath in the well. The cement slurry is formulated such that, after setting, it has a linear thermal-expansion coefficient higher than that of a set cement not containing the carbonaceous material. Such linear coefficient of thermal expansion being preferably lower than or equal to about $50 \cdot 10^{-6}/^{\circ}\text{C}$. A more preferred linear thermal-expansion-coefficient range is between about $11 \cdot 10^{-6}/^{\circ}\text{C}$ and $20 \cdot 10^{-6}/^{\circ}\text{C}$, and an even more preferred linear thermal-expansion coefficient range is between about $11 \cdot 10^{-6}/^{\circ}\text{C}$ and $17 \cdot 10^{-6}/^{\circ}\text{C}$.

[0028] For all aspects of the invention, the preferred carbonaceous-material concentration may be between about 10% and about 60% by weight of cement, and preferably between about 11% and 50% by weight of cement, even more preferably between 15% and 40% by weight of cement. The particle-size range of the carbonaceous material may be between about 1 μm and 1200 μm , preferably between 40 μm and 1000 μm and more preferably between about 90 μm and 800 μm .

[0029] For all aspects of the invention, the cement may comprise one or more members of the list comprising Portland cement, calcium aluminate cement, fly ash, blast furnace slag, lime-silica blends, geopolymers, Sorel cements, chemically bonded phosphate ceramics, cement-kiln dust and zeolites. In a preferred embodiment, the cement is Portland cement.

[0030] The well may be a thermal-recovery well, preferably the well

temperature is comprised between 150°C and 700°C. If the cement slurry comprises Portland cement, silica may be added to prevent strength retrogression at the high temperatures associated with thermal-recovery wells. Depending on the ultimate temperature, the silica concentration may be adjusted such that the calcium oxide-to-silicon dioxide (CaO/SiO₂) ratio is between about 0.6 and 1.2. Such compositions may promote the formation of beneficial calcium-silicate-hydrate minerals such as xonotlite and truscottite. Under these circumstances, the silica concentration in the cement slurry may be between about 20% and 60% by weight of cement, and preferably between about 25% and 45% by weight of cement. The particle size of the silica may vary from 0.1 μm to 200 μm, preferably from 1 μm to 80 μm, even more preferably from 2 μm to 80 μm. In a preferred version, the silica used is silica sand.

[0031] The cement slurry may further comprise one or more members of the list comprising accelerators, retarders, dispersants, fluid-loss additives, extenders, swellable materials, pozzolans, fibers and antifoam agents. The cement-slurry density may be adjusted by adding extenders or weighting agents, which include (but are not limited to) glass microspheres, composite microsphere components (such as described in US7767629), ceramic microspheres, hematite, ilmenite, barite, sand, silica and manganese tetraoxide. The density of the cement slurry involved in the various embodiments as described above is preferably from 1100 kg/m³ to 2300 kg/m³, more preferably from 1400 kg/m³ to 1900 kg/m³ and even more preferably from 1500 kg/m³ to 1850 kg/m³.

EXAMPLES

[0032] The following examples are not limiting and serve to further illustrate the invention.

EXAMPLE 1

[0033] The influence of various carbonaceous materials on set-cement linear thermal-expansion properties was investigated. The cement-slurry compositions are given in Table 3.

Slurry #		1	2	3	4	5
Slurry Density (kg/m ³)		1900	1833	1660	1650	1780
Class G		100	100	100	100	100
Silica Flour (% BWOC)		–	40	35	35	35
Carbonaceous material (% BWOC)	Coke	–	–	42	–	–
	Coal	–	–	–	40	–
	Anthracite	–	–	–	–	56

Table 3: Compositions of Cement Slurries Containing Various Carbonaceous Materials

[0034] The concentrations by weight of the carbonaceous materials were chosen so that their respective volumetric concentrations in the cement matrix were equal—20%. The solids volume fractions (SVF) of the slurries were also equal—49%. The coke used was delayed petroleum coke having an average particle size of about 90 μm ; the coal material was fine kolite having an average particle size of about 200 μm ; the anthracite was having an average particle size of about 180 μm . Cement slurries were prepared and cured according to the standard methods given in the following publication:

“Petroleum and Natural Gas Industries—Cements and Materials for Well Cementing—Part 2: Testing of Well Cements,” International Organization for Standards Publication No. 10426-2. After preparation, the cement slurries were poured into molds with the following dimensions: 30 mm x 30 mm x 120 mm. The molds were then placed in curing chambers for one week at a temperature between 35° and 65°C and at 13.7 MPa pressure.

[0035] The LCTEs of the cement systems were then measured by the mechanical-dilatometry technique. The technique and apparatus are described in the following publication: Dargaud B and Boukelifa L: “Laboratory Testing, Evaluation, and Analysis of Well Cements,” in Nelson EB and Guillot D (eds.): *Well Cementing* (2nd Edition) Schlumberger, Houston, USA (2006) 627–658. The set-cement-sample temperature was increased from 20° to 80°C. The heating was performed in 10°C increments. The duration of each heating increment was one hour. After each heating increment, the sample temperature was held constant for a 3-hour period. The pressure was ambient. The results, presented in Table 4, show that a variety of carbonaceous materials effectively increase the LCTE compared to the control (Slurry #1).

Slurry #	1	2	3	4	5
Linear Thermal Expansion Coefficient ($\cdot 10^{-6}/^{\circ}\text{C}$)	9	10	13	13.5	11

Table 4. Linear thermal-expansion coefficients for set cements containing various carbonaceous materials.

EXAMPLE 2

[0036] Following the experimental protocol described in Example 1, the effect of carbonaceous-material concentration on the set-cement LCTE was studied. In this example, the carbonaceous material was delayed coke, and the cement-slurry compositions are presented in Table 5. The results, presented in Table 6, show that the LCTE increases with the coke concentration.

Slurry #	6	7	8	9	10	11
Slurry density (kg/m³)	1900	1833	1660	1660	1690	1670
Class G cement	100	100	100	100	100	100
Silica Flour (% BWOC)	-	40	35	40	35	40
Carbonaceous material (% BWOC)	-	-	42	43	15	53

Table 5. Compositions of cement slurries containing various coke concentrations.

Slurry #	6	7	8	9	10	11
Linear Thermal Expansion Coefficient ($\cdot 10^{-6}/\text{degC}$)	9	10	13	13	13	15

Table 6. Linear thermal-expansion coefficients for set cements containing various amounts of coke.

EXAMPLE 3

[0037] Following the experimental protocol of Example 1, the influence of metallurgical coke particle-size on the set-cement LCTE was studied. Using the composition of Slurry #8 in Example 2, the d_{50} of one coke powder was 160 μm , and the other was 450 μm . As shown in Table 7, the LCTE increased with the d_{50} of the coke powder.

Coke powder d_{50}	160 μm	450 μm
Linear Thermal Expansion Coefficient ($\cdot 10^{-6}/^{\circ}\text{C}$)	13	15

Table 7. Influence of coke particle size on linear set-cement thermal-expansion coefficient.

CLAIMS

1. A method for adjusting the linear thermal-expansion properties of a cement slurry for placement in a subterranean well having at least one casing string, comprising:

incorporating a carbonaceous material in the cement slurry, such that the linear thermal-expansion coefficient of the set cement is higher than that of a set cement not containing the carbonaceous material.
2. The method of claim 1, wherein the linear thermal-expansion coefficient of the set cement comprising the carbonaceous material is higher than that of a set cement not containing the carbonaceous material but lower or equal to $50 \cdot 10^{-6}/^{\circ}\text{C}$.
3. The method of claim 1 or 2, wherein the carbonaceous material is one or more members of the list comprising delayed coke, fluid coke, calcined coke, asphalt, charcoal, coal, anthracite, graphite, flake coke, amorphous pitch coke, anode coke, tar coke, metallurgical coke, amorphous graphite, lignite, bituminous coal, sub-bituminous coal, exinite, vitrinite, intertinite, gilsonite, fine kolite, needle coke and activated carbon.
4. The method of any one of claims 1–3, wherein the carbonaceous-material concentration is between about 10% and 60% by weight of cement.
5. The method of any one of claims 1–4, wherein the carbonaceous-material particle size is between about $1\mu\text{m}$ and $1200\mu\text{m}$.
6. The method of any one of claims 1–5, wherein the subterranean well is a thermal-recovery well.
7. The method of any one of claims 1–6, wherein the cement slurry further comprises silica in an amount of from 20% to 60% by weight of cement..
8. The method of any one of claims 1–7, wherein the cement slurry further comprises one or more members of the list comprising accelerators, retarders,

dispersants, fluid-loss additives, extenders, swellable materials, pozzolans, fibers and antifoam agents.

9. The method of any one of claims 1–8, wherein the cement slurry density is adjusted by adding one or more members of the list comprising glass microspheres, ceramic microspheres, composite microsphere components hematite, ilmenite, barite and manganese tetraoxide.
10. Use of a carbonaceous material to adjust the linear thermal-expansion properties of a set cement placed in a subterranean well having at least one casing string, thereby controlling thermal and mechanical stresses exerted upon the cement sheath in the well.
11. The use of claim 10, wherein the linear thermal-expansion coefficient of the set cement is higher than that of a set cement not containing the carbonaceous material, and lower than or equal to about $50 \cdot 10^{-6}/^{\circ}\text{C}$.
12. The use of claim 10 or 11, wherein the carbonaceous material is one or more members of the list comprising delayed coke, fluid coke, calcined coke, asphalt, charcoal, coal, anthracite, graphite, flake coke, amorphous pitch coke, anode coke, metallurgical coke, amorphous graphite, lignite, bituminous coal, sub-bituminous coal, exinite, vitrinite, intertinite, gilsonite, fine kolite, needle coke and activated carbon.
13. The use of any one of claims 10–12, wherein the carbonaceous-material concentration is between about 10% and 60% by weight of cement.
14. The use of any one of claims 10–13, wherein the carbonaceous-material particle size is between about $1\mu\text{m}$ and $1200\mu\text{m}$.
15. The use of any one of claims 10–14, wherein the subterranean well is a thermal-recovery well.
16. The use of any one of claims 10–15, wherein the cement slurry further comprises

silica.

17. The use of claim 16, wherein the silica concentration is between about 20% and about 60% by weight of cement.
18. The use of any one of claims 10–17, wherein the cement slurry further comprises one or more members of the list comprising accelerators, retarders, dispersants, fluid-loss additives, extenders, swellable materials, pozzolans, fibers and antifoam agents.
19. The use of any one of claims 10–18, wherein the cement-slurry density is adjusted by adding one or more members of the list comprising glass microspheres, composite microsphere components, ceramic microspheres, hematite, ilmenite, barite and manganese tetraoxide.
20. A method for controlling thermal and mechanical stresses in a cement sheath in a subterreanean well, comprising:
 - i. installing at least one casing string in the well,
 - ii. forming a cement slurry containing at least one carbonaceous material in a quantity sufficient such that the set cement has a linear thermal-expansion coefficient higher than that of a set cement not containing the carbonaceous material, and lower than or equal to about $50 \cdot 10^{-6}/^{\circ}\text{C}$; and
 - iii. placing the cement slurry in the well, adjacent to the casing string, and allowing it to set.

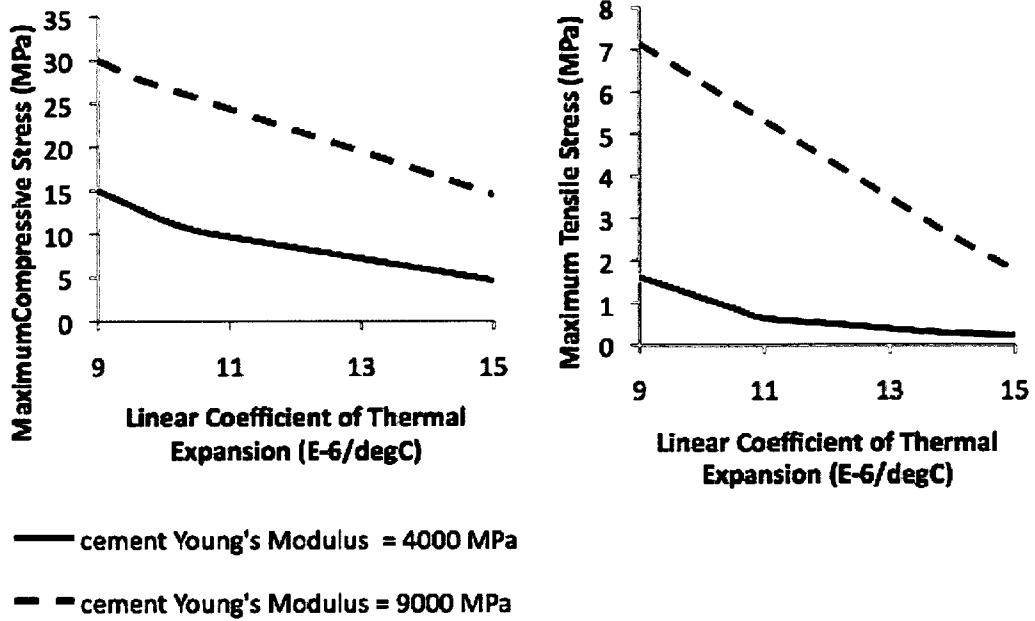


Figure 1

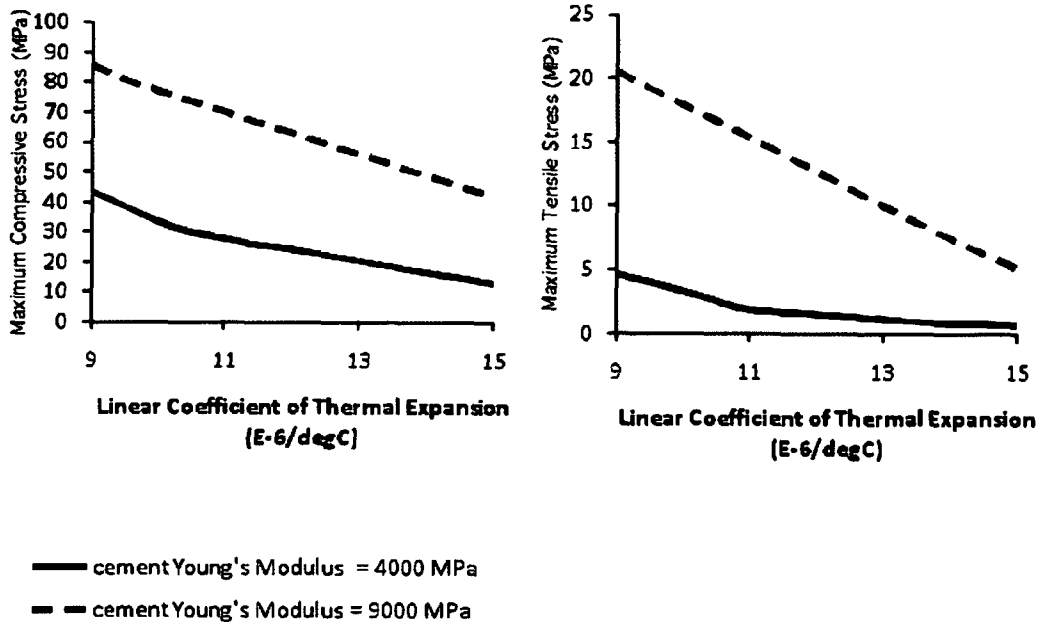


Figure 2

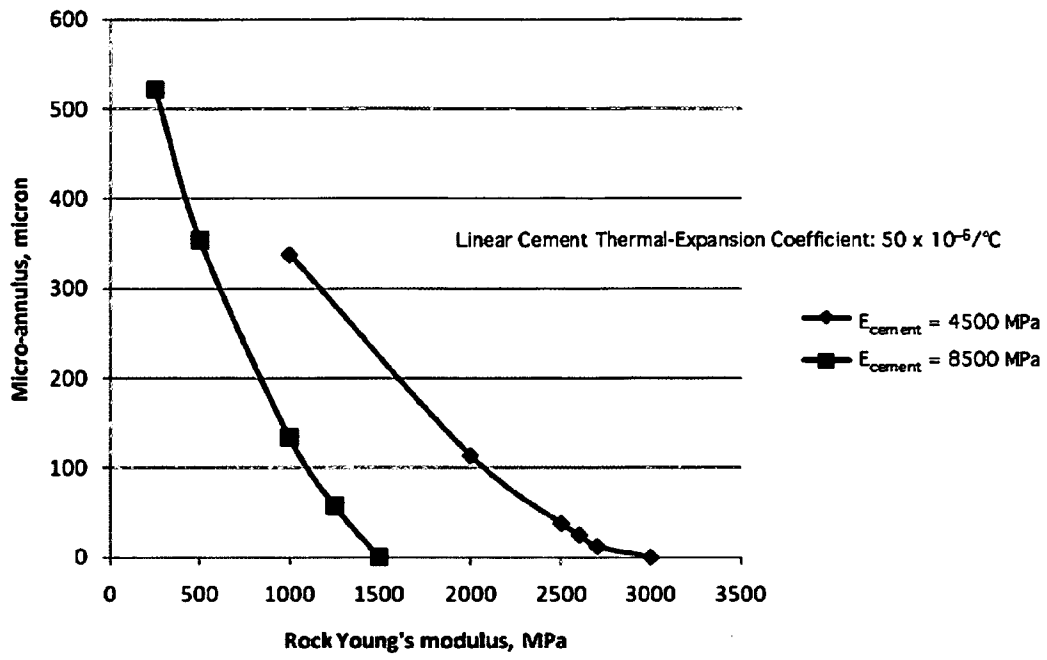


Figure 3

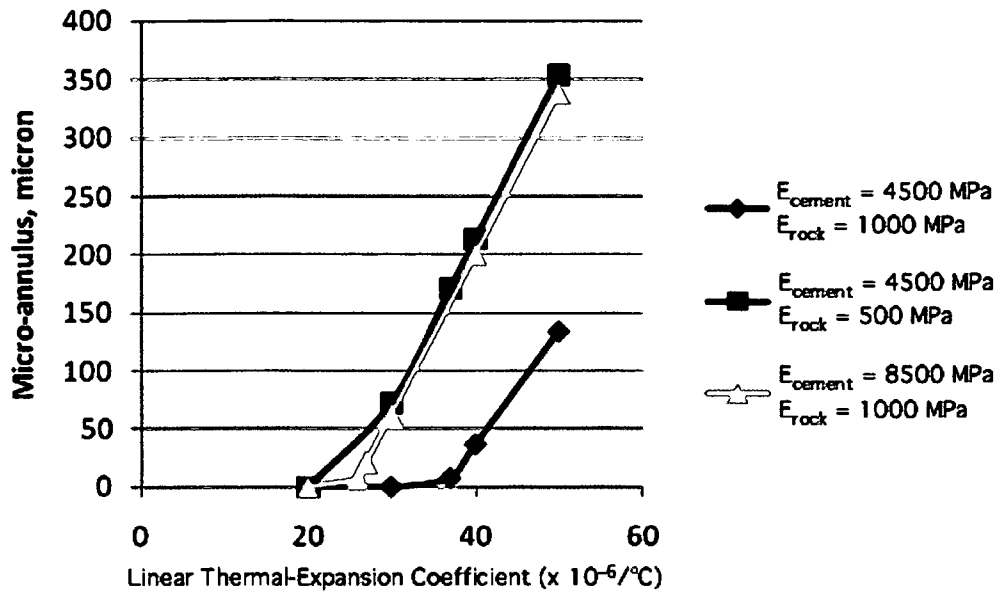


Figure 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/005167

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C04B28/02 C09K8/467 E21B33/13
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C04B C09K E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
 EPO-Internal, CHEM ABS Data, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/031736 A1 (HALLIBURTON ENERGY SERV INC [US]; CURTIS PHILIP ANTHONY [GB]; REDDY BA) 22 March 2007 (2007-03-22) claims 1-22; examples 1,2; tables 1-3 -----	1-20
A	EP 1 348 831 A1 (HALLIBURTON ENERGY SERV INC [US]) 1 October 2003 (2003-10-01) claims 1-10; example 1; tables 1,2 -----	1-20
A	US 4 721 160 A (PARCEVAUX PHILIPPE [FR] ET AL) 26 January 1988 (1988-01-26) claims 1-16 -----	1-20
A	US 5 226 961 A (NAHM JAMES J W [US] ET AL) 13 July 1993 (1993-07-13) example 1 -----	1-20

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
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Date of the actual completion of the international search 28 April 2011	Date of mailing of the international search report 09/05/2011
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Burtan, M
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2010/005167

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