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(54) Titre : FORMULATION GEOPOLYMERIQUE POMPABLE ET APPLICATION POUR LE STOCKAGE DE DIOXYDE
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(54) Title: PUMPABLE GEOPOLYMER FORMULATION AND APPLICATION FOR CARBON DIOXIDE STORAGE

(57) **Abrégé/Abstract:**

The invention provides geopolymeric compositions intended for use in carbon dioxide injection or production wells or storage reservoirs and preferably in a supercritical carbon dioxide conditions. The geopolymeric composition is formed from a suspension comprising an aluminosilicate source, a carrier fluid, an activator taken from the list constituted by: a metal silicate, a metal aluminate, an alkali activator, or a combination thereof, and a retarder able to retard the thickening and/or the setting times of the suspension and/or an accelerator able to accelerate the thickening and/or the setting times of the suspension, wherein the metal is an alkali metal and the oxide molar ratio M_2O/SiO_2 is greater than 0.20 wherein M is the metal.



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(54) Title: PUMPABLE GEOPOLYMER FORMULATION AND APPLICATION FOR CARBON DIOXIDE STORAGE

(57) Abstract: The invention provides geopolymeric compositions intended for use in carbon dioxide injection or production wells or storage reservoirs and preferably in a supercritical carbon dioxide conditions. The geopolymeric composition is formed from a suspension comprising an aluminosilicate source, a carrier fluid, an activator taken from the list constituted by: a metal silicate, a metal aluminate, an alkali activator, or a combination thereof, and a retarder able to retard the thickening and/or the setting times of the suspension and/or an accelerator able to accelerate the thickening and/or the setting times of the suspension, wherein the metal is an alkali metal and the oxide molar ratio M₂O/SiO₂ is greater than 0.20 wherein M is the metal.

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Pumpable geopolymer formulation and application for carbon dioxide storage.

Field of the invention

[0001] The present invention broadly relates to well cementing. More particularly the invention relates to a geopolymer composition and related method of placing the geopolymer composition in carbon dioxide supercritical environment, such as for instance a reservoir for storage of carbon dioxide gas.

Description of the Prior Art

[0002] Earth's atmospheric carbon dioxide [CO₂] content increases as a result of both natural and man-made emissions. This CO₂ remains in the atmosphere for several decades, and is slowly removed by natural sinks (oceans, vegetation and soils) that store CO₂ for indefinite period of time. Nevertheless, it has become clear to many scientists that humans must work to diminish anthropogenic effects, primarily those derived from burning fossil fuels. Fossil fuels produce a large amount of CO₂ emission (40% in mass for coal). Innovative ways to reduce CO₂ emission and their impact on the climate and environment are under development, but actually most conceivable plans are solutions to capture and store CO₂ emissions – also called CO₂ sequestration –, but will require extensive investment in infrastructure and considerable measures to reduce its cost. The separation and compression of CO₂ from emission streams remain the most expensive part of the process and can occur before or after the combustion process. Currently, the most widely used process is based on chemical absorption to capture CO₂ from flue gas. For the storage part, there are several ways of storing CO₂: deep ocean, saline reservoirs, depleted oil reservoirs, depleted gas reservoir, coalbed reservoir. Ocean storage, represents the largest potential for carbon storage, but is thought to carry a higher level of environmental risk. The remaining four are geologic storage options, of which the largest capacity is estimated to be in saline reservoirs (10,000 billion metric tons carbon). The annual global emissions in the year 2000 were 6.2 billion metric tons.

[0003] Therefore given its vast experience in reservoir management and its extensive range of technologies, the oil and gas industry is poised to take a leading role in the storage of CO₂ in geological formations, such as depleted reservoirs, deep saline aquifers and coalbeds. Geological storage of CO₂ will be more efficient if it is in supercritical conditions. Carbon dioxide has a low critical temperature of 31° C and a moderate critical pressure of 73.8 bars. Generally, this means that storage depths of 600 m or deeper are required. The storage of CO₂ in the subsurface requires various technologies and type of expertise to characterize the storage zone and surrounding strata, to drill and accurately place wellbores, to design and construct surface facilities, to monitor wells and fields, and to optimize systems.

[0004] In the construction of wells, usually conventional 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. Long-term isolation and integrity of CO₂ injection wells clearly needs to be improved to ensure long-term environmental safety. Failure of the material used in the injection interval and above may create preferential channels for carbon dioxide migration to the surface. This may occur on a much faster timescale than geological leakage. CO₂ injection well construction starts with drilling followed by well completion before starting CO₂ injection operations. In the framework of well completion, the completion phase guarantees well isolation from the reservoir to the surface and isolation between geological formations. A crucial technical problem in CO₂ sequestration is the chemical resistance to CO₂ over time of the material used for completion. In CO₂ sequestration, carbon dioxide has to be kept in supercritical conditions at all times.

[0005] However, conventional cement used for completion, as Portland cement based systems, used during the well cementation phase, are known not to be stable in supercritical CO₂ environments. This type of cement tends to strongly degrade once exposed to such acid gases. Optimization of advanced systems allowing long-term well isolation is critical to allow safe and efficient underground storage sites for carbon dioxide and thus keep the greenhouse gas out of the atmosphere for long duration. Today, the cement durability over hundred years is not known. Prior art solutions have tended to

minimize the degradation process of the cement matrix under supercritical CO₂ environments or normal CO₂ environments; nevertheless no solution exists which will stop totally the degradation process of the cement matrix.

[0006] Hence, it remains the need of a material, comporting as cement in terms of handiness, pumpability and ability to set, intended for use in CO₂ injection wells or storage reservoirs and preferably in a supercritical CO₂ conditions.

[0007] Geopolymers are a novel class of materials that are formed by chemical dissolution and subsequent recondensation of various aluminosilicate oxides and silicates to form an amorphous three-dimensional framework structure. Therefore, a geopolymer is a three-dimensional aluminosilicate mineral polymer. The term *geopolymer* was proposed and first used by J. Davidovits (Synthesis of new high-temperature geopolymers for reinforced plastics/composites, SPE PACTEC' 79, *Society of Plastics Engineers*) in 1976 at the IUPAC International Symposium on Macromolecules held in Stockholm.

[0008] Geopolymers based on alumino-silicates are designated as poly(sialate), which is an abbreviation for poly(silicon-oxo-aluminate) or $(-\text{Si-O-Al-O-})_n$ (with n being the degree of polymerization). The sialate network consists of SiO₄ and AlO₄ tetrahedra linked alternately by sharing all the oxygens, with Al³⁺ and Si⁴⁺ in IV-fold coordination with oxygen. Positive ions (Na⁺, K⁺, Li⁺, Ca²⁺...) must be present in the framework cavities to balance the negative charge of Al³⁺ in IV-fold coordination.

[0009] The empirical formula of polysialates is: $M_n \{-(\text{SiO}_2)_z\text{-AlO}_2\}_n \cdot w \text{H}_2\text{O}$, wherein M is a cation such as potassium, sodium or calcium, n is a degree of polymerization and z is the atomic ratio Si/Al which may be 1, 2, 3 or more, until 35 as known today.

[0010] The three-dimensional network (3D) geopolymers are summarized in the table 1 below.

Si/Al ratio	Designation	Structure	Abbreviations
1	Poly(sialate)	$M_n(-Si-O-Al-O-)_n$	(M)-PS
2	Poly(sialate-siloxo)	$M_n(-Si-O-Al-O-Si-O)_n$	(M)-PSS
3	Poly(sialate-disiloxo)	$M_n(-Si-O-Al-O-Si-O-Si-O-)_n$	(M)-PSDS

Table 1 : Geopolymers chemical designation (wherein M is a cation such as potassium, sodium or calcium, and n is a degree of polymerization).

[0011] The properties and application fields of geopolymers will depend principally on their chemical structure, and more particularly on the atomic ratio of silicon versus aluminum.

Geopolymers have been investigated for use in a number of applications, including as cementing systems within the construction industry, as refractory materials and as encapsulants for hazardous and radioactive waste streams. Geopolymers are also referenced as rapid setting and hardening materials. They exhibit superior hardness and chemical stability.

[0012] The applicants have take advantage of their knowledge in geopolymeric compositions in terms of application in oilfield industry and more precisely in well in general to formulate particular geopolymeric composition intended for use in CO₂ injection wells or storage reservoirs and preferably in a supercritical CO₂ conditions.

Summary

[0012a] According to an aspect of the present invention, there is provided a geopolymeric composition for use in presence of carbon dioxide, resistant to carbon dioxide and formed from a suspension, comprising: an aluminosilicate source, a carrier fluid, an activator comprising a metal silicate, a metal aluminate, an alkali activator, or a combination thereof, and a retarder able to retard the thickening and/or the setting times of the suspension and/or an accelerator able to accelerate the thickening and/or the setting times of the suspension, wherein the metal is an alkali metal and the oxide molar ratio M_2O/SiO_2 is greater than 0.20 wherein M is the metal.

[0012b] According to another aspect of the present invention, there is provided a geopolymeric composition for use in presence of carbon dioxide and resistant to carbon dioxide formed from a

suspension comprising an aluminosilicate source, a metal silicate, an alkali activator, a retarder and/or an accelerator and a carrier fluid wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal, wherein the suspension has a viscosity lesser than or equal to 300 cP.

[0012c] According to a further aspect of the present invention, there is provided a geopolymeric composition for use in presence of carbon dioxide and resistant to carbon dioxide formed from a suspension within water comprising an aluminosilicate source, a metal silicate, an alkali activator, and a retarder and/or an accelerator wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal, wherein the suspension has a viscosity lesser than or equal to 300 cP.

[0012d] According to yet another aspect of the present invention, there is provided a geopolymeric composition resistant to carbon dioxide formed from a suspension within water comprising an aluminosilicate source, a metal silicate, an alkali activator, and a retarder and/or an accelerator wherein the geopolymeric composition is in majority a poly(sialate-siloxo) geopolymer and wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal, wherein the suspension has a viscosity lesser than or equal to 300 cP.

[0012e] According to another aspect of the present invention, there is provided a method to place a geopolymeric composition in a part of a borehole in presence with carbon dioxide, the method comprising: (i) providing a suspension comprising an aluminosilicate source, a metal silicate, an alkali activator, a retarder and/or an accelerator and a carrier fluid wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal, (ii) pumping the suspension into the part of the borehole, and (iii) allowing the suspension to set and thereby form the geopolymeric composition into the part of the borehole wherein the suspension has a viscosity lesser than or equal to 300 cP.

[0012f] According to a further aspect of the present invention, there is provided a method to place a geopolymeric composition in a part of a borehole in presence with carbon dioxide, the method comprising: (i) providing a suspension comprising an aluminosilicate source, a metal

silicate, an alkali activator, a retarder and/or an accelerator and a carrier fluid wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal, (ii) pumping the suspension into the part of the borehole, (iii) allowing the suspension to set and thereby form the

geopolymeric composition into the part of the borehole, and (iv) exposing the geopolymeric composition to carbon dioxide, wherein the suspension has a viscosity lesser than or equal to 300 cP.

[0012g] According to an aspect of the present invention, there is provided a method to place a geopolymeric composition in a part of a borehole in presence with carbon dioxide, the method comprising: (i) providing a suspension within water comprising an aluminosilicate source, a metal silicate, an alkali activator, and a retarder and/or an accelerator wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal, (ii) pumping the suspension into the part of the borehole, and (iii) allowing the suspension to set and thereby form the geopolymeric composition into the part of the borehole, wherein the suspension has a viscosity lesser than or equal to 300 cP.

[0012h] According to yet another aspect of the present invention, there is provided a method to place a geopolymeric composition in a part of a borehole in presence with carbon dioxide, the method comprising: (i) providing a suspension within water comprising an aluminosilicate source, a metal silicate, an alkali activator, and a retarder and/or an accelerator wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal, (ii) pumping the suspension into the part of the borehole, (iii) allowing the suspension to set and thereby form the geopolymeric composition into the part of the borehole, and (iv) exposing the geopolymeric composition to carbon dioxide, wherein the suspension has a viscosity lesser than or equal to 300 cP.

[0013] In selected embodiments, the present disclosure also discloses a suspension comprising: an aluminosilicate source, a carrier fluid, an activator taken from the list constituted by: a metal silicate, a metal aluminate, an alkali activator, or a combination thereof, and a retarder able to retard the thickening and/or the setting times of the suspension and/or an accelerator able to accelerate the thickening and/or the setting times of the suspension, wherein the metal is an alkali metal and the oxide molar ratio M_2O/SiO_2 is greater than 0.20 wherein M is the metal. Preferably, the oxide molar ratio M_2O/SiO_2 is greater than or equal to 0.27. All the four components do not need necessarily to be added separately: for example the alkali activator can be already within a carrier fluid. So, the aluminosilicate source can be in the form of a solid

component; the metal silicate can be in the form of a solid or of a mix of metal silicate within a carrier fluid; the alkali activator can be in the form of a solid or of a mix of alkali activator within a carrier fluid. Importance is to have a carrier fluid to make suspension if aluminosilicate source, metal silicate and alkali activator are all in solid state. If aluminosilicate source, metal silicate are in solid state and alkali activator is in liquid state, alkali activator is considered to already have a carrier fluid within. Further, as it is understood, unicity of the carrier fluid is not required, two or more carrier fluids can be used. A geopolymeric composition having such rheological properties that a suspension of the geopolymeric composition has a good pumpability and stability may be provided. A pumpable composition in the oilfield industry has a rheology lesser than or equal to 300 cP, preferably in other embodiment lesser than or equal to 250 cP, more preferably in another embodiment lesser than or equal to 200 cP. Further, the suspension may be a stable suspension. The geopolymeric composition is mixable and pumpable; therefore applications in well in general are possible.

[0014] The geopolymeric composition may be such that the suspension is resistant to carbon dioxide and/or supercritical carbon dioxide and/or further to acid gas or corrosive components, as H₂S and also the set geopolymeric composition is resistant to carbon dioxide and/or supercritical carbon dioxide and/or further to acid gas or corrosive components, as H₂S.

[0015] In one embodiment, the retarder is selected from the group constituted of boron containing compound, lignosulfate, sodium gluconate, sodium glucoheptonate, tartaric acid and phosphorus containing compounds. Preferably, the retarder is an anhydrous or hydrated alkali metal borate or a pure oxide of boron. More preferably, the retarder is a sodium pentaborate decahydrate, a boric acid, or a borax. The control of the setting time is here efficient from 20°C to 120°C. Sodium pentaborate decahydrate and borax are able to control setting time from 20°C, preferably from 25°C. When the retarder is a boron containing compound, the suspension of said geopolymeric composition has an oxide molar ratio B₂O₃/H₂O of less than 0.03. More preferably, the geopolymeric composition has an oxide molar ratio B₂O₃H₂O of less than or equal to 0.02.

[0016] In another embodiment, the accelerator is an alkali metal containing compound as lithium. Preferably the accelerator is a salt of lithium. More preferably, the accelerator is a

chlorure of lithium. The control of the setting time is here efficient from 20°C to 120°C. When the accelerator is a lithium containing compound, the suspension of said geopolymeric composition has an oxide molar ratio $\text{Li}_2\text{O}/\text{H}_2\text{O}$ of less than 0.2. More preferably, the geopolymeric composition has an oxide molar ratio $\text{Li}_2\text{O}/\text{H}_2\text{O}$ of less than or equal to 0.1.

[0017] The geopolymeric composition may be poly(sialate), poly(sialate-siloxo) or poly(sialate-disiloxo). More preferably, the geopolymeric compositions are poly(sialate-siloxo) components and therefore the silicon on aluminum atomic ratio between 1.8 and 2.2, more preferably is substantially equal to two.

[0018] The geopolymeric composition may use aluminosilicate source which is selected from the group constituted of ASTM type C fly ash, ASTM type F fly ash, ground blast furnace slag, calcined clays, partially calcined clays (such as metakaolin), aluminium-containing silica fume, natural aluminosilicate, synthetic aluminosilicate glass powder, zeolite, scoria, allophone, bentonite and pumice. Preferably, the geopolymeric composition is made with metakaolin, ground granulated blast furnace slag and/or fly ash. Preferably, the geopolymeric composition is made with metakaolin, ground granulated blast furnace slag and/or fly ash. Mixtures of two or more aluminosilicate source may also be used if desired.

[0019] The geopolymeric composition may use a metal silicate, with the metal selected from the group constituted of lithium, sodium, potassium, rubidium and cesium. Preferably, the metal is sodium or potassium. In another embodiment, the metal silicates can be replaced by ammonium silicates. The metal silicate in another embodiment can be encapsulated.

[0020] The geopolymeric composition may use for the alkali activator, for example an alkali metal hydroxide. Preferably, the alkali metal hydroxide is sodium or potassium hydroxide. The alkali activator and/or the metal silicate and/or the carrier fluid may be encapsulated. Alkali carbonates can also be used as alkali activator. Also, the alkali activator in another embodiment can be encapsulated.

[0021] The geopolymeric composition may use for the carrier fluid an aqueous solution as water.

[0022] To control the density of the geopolymeric composition, a lightweight particle and/or a heavyweight material can be added. The lightweight particles also called fillers are selected from the group constituted of: cenospheres, sodium-calcium-borosilicate glass, and silica-alumina microspheres. The heavy particles also called the weighting agents are typically selected from the group constituted of: manganese tetroxide, iron oxide (hematite), barium sulfate (barite), silica and iron/titanium oxide (ilmenite). The geopolymeric compositions can also be foamed by foaming the suspension of said geopolymeric composition with a gas as for example air, nitrogen or carbon dioxide. The geopolymeric composition can further comprise a gas generating additive which will introduce the gas phase in the suspension. Preferably, the density of the suspension of said geopolymeric slurry compositions varies between 1 gram per cubic centimeter and 2.5 grams per cubic centimeter, more preferably between 1.2 grams per cubic centimeter and 1.8 grams per cubic centimeter.

[0023] In another embodiment, the geopolymeric composition further comprises an additive selected from the group constituted of: an activator, an antifoam, a defoamer, silica, a fluid loss control additive, a flow enhancing agent, a dispersant, a rheology modifier, a foaming agent, a surfactant and an anti-settling additive.

[0024] In another embodiment, when the geopolymeric composition comprise several particles of various type, as for example, different aluminosilicate source and/or lightweight particles and/or a heavy particles, the particle size of the components has been selected and the respective proportion of particles fractions has been optimized in order to have at the same time the highest Packing Volume Fraction (PVF) of the solid,

and obtaining mixable and pumpable slurry by using the minimum amount of water, i.e., at slurry Solid Volume Fraction (SVF) of 35-75% and preferably of 50-60%.

[0025] According to another aspect of the invention, a method to place a geopolymeric composition in a part of a borehole in presence with carbon dioxide is disclosed, the method comprising: (i) providing a suspension of the geopolymeric composition as described above, (ii) pumping the suspension into the part of the borehole, and (iii) allowing the suspension of said geopolymeric composition to set and thereby form the geopolymeric composition into said part of the borehole. Further, the step of allowing the geopolymeric composition to harden can be made in presence with carbon dioxide and further the method can comprise the step of exposing the geopolymeric composition to carbon dioxide. The method applies also to carbon dioxide which is in supercritical state, and also for temperature from 20°C to 100°C.

[0026] Preferably, the step of pumping the suspension of said geopolymeric composition is made with conventional well cementing equipment, familiar to those skilled in the art. The method applies as a primary cementing technique for cementing wells where the geopolymeric composition is pumped down a pipe until the shoe where it then flows up the annular space between the casing/liner and the borehole. A reverse circulation cementing technique can also be used for placing the geopolymer suspension at the desired depth in the borehole.

[0027] Further, the pumping and placement of geopolymer suspension below surface encompasses several other conventional cementing techniques such as the grouting of platform piles, skirts or the like, the squeeze operation for repair or plugging of an undesired leak, perforation, formation or the like, and the setting of a geopolymer composition plug for any purpose of a cement plug.

25 **Brief description of the drawings**

[0028] Further embodiments of the present invention can be understood with the appended drawings:

- Figure 1 shows a schematic view of the CO₂ supercritical vessel for test of CO₂ resistant cement.
- Figure 2 shows the impact of temperature on the thickening time of geopolymer formulations.
- 5 • Figure 3 shows the impact of accelerator addition on the thickening time of geopolymer formulations.

Detailed description

[0029] According to the invention, the geopolymer formulations involve use of an aluminosilicate source, a metal silicate and an alkali activator in a carrier fluid at near-ambient temperature. The carrier fluid is preferably a fresh water solution. As it has been
10 said previously, all the four components do not need necessarily to be added separately: for example the alkali activator can be already within water. So, the aluminosilicate source can be in the form of a solid component; the metal silicate can be in the form of a solid or of an aqueous solution of metal silicate; the alkali activator can be in the form of
15 a solid or of an aqueous solution of alkali activator.

[0030] Formation of the geopolymer concrete involves an aluminosilicate source, which is also called aluminosilicate binder. Examples of aluminosilicate source from which geopolymers may be formed include ASTM type C fly ash, ASTM type F fly ash, ground blast furnace slag, calcined clays, partially calcined clays (such as metakaolin),
20 aluminium-containing silica fume, natural aluminosilicate, synthetic aluminosilicate glass powder, zeolite, scoria, allophone, bentonite and pumice. These materials contain a significant proportion of amorphous aluminosilicate phase, which reacts in strong alkali solutions. The preferred aluminosilicates are fly ash, metakaolin and blast furnace slag. Mixtures of two or more aluminosilicate sources may also be used if desired. In another
25 embodiment, the aluminosilicate component comprises a first aluminosilicate binder and optionally one or more secondary binder components which may be chosen in the list: ground granulated blast furnace slag, Portland cement, kaolin, metakaolin or silica fume.

[0031] Formation of the geopolymer concrete involves also, an alkali activator. The alkali activator is generally an alkali metal hydroxide. Alkali metal hydroxides are generally preferred as sodium and potassium hydroxide. The metal hydroxide may be in the form of a solid or an aqueous mixture. Also, the alkali activator in another embodiment can be encapsulated. The alkali activator when in solid and/or liquid state can be trapped in a capsule that will break when subject for example, to stress on the capsule, to radiation on the capsule. Also, the alkali activator when in solid and/or liquid state can be trapped in a capsule that will naturally destroy due to the fact that for example, the capsule is made with biodegradable and/or self destructive material. Also, the alkali activator when in liquid state can be adsorbed onto a porous material and will be released after a certain time or due to a predefined event.

[0032] Formation of the geopolymer concrete involves also, a metal silicate. The metal silicate is generally an alkali metal silicate. Alkali metal silicates, particularly sodium silicate or potassium silicate, are preferred. Sodium silicates with a molar ratio of $\text{SiO}_2/\text{Na}_2\text{O}$ equal to or less than 3.2 are preferred. Potassium silicates with a molar ratio of $\text{SiO}_2/\text{K}_2\text{O}$ equal to or less than 3.2 are preferred. Also, the metal silicate in another embodiment can be encapsulated.

[0033] According to the invention, typical geopolymeric compositions in terms of oxide molar ratios, fall in the ranges:

20 $\text{SiO}_2 / \text{Al}_2\text{O}_3$ comprised between 2.3 and 6

$\text{M}_2\text{O} / \text{SiO}_2$ comprised between 0.2 and 0.50

$\text{M}_2\text{O} / \text{Al}_2\text{O}_3$ comprised between 0.8 and 1.2

$\text{H}_2\text{O} / \text{M}_2\text{O}$ comprised between 8 and 23

[0034] According to a preferred embodiment of the invention, typical geopolymeric compositions in terms of oxide molar ratios, falls within the ranges:

$\text{SiO}_2 / \text{Al}_2\text{O}_3$ comprised between 3.5 and 5

M_2O / SiO_2 comprised between 0.27 and 0.3

M_2O / Al_2O_3 comprised between 1 and 1.2

H_2O / M_2O comprised between 10 and 20

[0035] The method of the invention will be used for carbon dioxide application, preferably in completion of a well bore of a dioxide carbon storage reservoir or injection well. To be used in carbon dioxide application, a pumpable suspension has to be formed of the geopolymer blend mixed with the carrier fluid. Various additives can be added to the suspension and the suspension is then pumped into the well bore. The suspension is then allowed to set up in the well to provide zonal isolation in the well bore. Further, the set geopolymeric composition has to resist over time to the CO_2 .

Method of placement of the CO_2 resistant geopolymer

[0036] One property of the geopolymer composition is its ability to set rapidly, however if use for dioxide carbon storage reservoir or injection well is sought, mixable and pumpable geopolymer suspension is needed. For this reason, a way to retard the thickening of the geopolymer suspension or a way to control thickening times of the geopolymer should be found.

[0037] A large family of retarders allowing delay in the set of the geopolymer has been found. In table 2, the results of thickening time tests performed as per ISO 10426-2 Recommended Practice in a High Pressure High Temperature (HPHT) consistometer are reported. Such tests are performed to simulate the placement from surface to downhole of cement suspensions, at a defined Bottom Hole Circulating Temperature (BHCT). To realize such tests, a temperature heatup schedule is followed in order to mimic placement in a real well. For the tests performed at $57^\circ C$, the temperature is reached in 41 minutes and the final pressure is 33.8 MPa (4900 psi). For the tests performed at $85^\circ C$, the temperature is reached in 58 minutes and the final pressure is 55.1 MPa (8000 psi). For the tests performed at $110^\circ C$, the temperature is reached in 74 minutes and the final pressure is 75.9 MPa (11000 psi).

Temperature (°C)		57	85			110	
Sample		A2	A2	B 2	C2	D2	
Retarder		%bwob (by weight of blend):	Thickening time:				
	None	0	6:25	0: 53	0:37	5:45	1:40
	Na ₂ B ₁₀ O ₁₆ ,10H ₂ O	0.65				6:30	3:00
		1.3	23:52	6:08			
		1.6		7:30			
		1.8		10:39	9:51		
		2		13:05			
		2.6		28:23			
	H ₃ BO ₃	1.9		20:53			
	Phosphonate/sodium pentaborate	1.2			7:00		
	Phosphonate/phosphate salt	6.4	>15:00				
	Lignosulfonate	1.51		3:12			

Table 2 : Examples of ISO10426-2 thickening time measured with HPHT consistometer (hours:min) obtained with different retarders at different temperature.

- 5 ■ Sample A2 is made by dissolving the retarder amount in 358 g of water, adding the blend comprising 314 g of metakaolin and 227 g of sodium disilicate in the solution under mixing, adding 17.2 g of sodium hydroxide under ISO 1026-2 mixing, pouring the suspension in HPHT cell. Sample A2 is then tested by measuring the thickening time with the HPHT consistometer.
- 10 ■ Sample B2 is made by dissolving the retarder amount in 265 g of water, adding the blend comprising 232 g of metakaolin, 168 g of sodium disilicate and 414 g of silica particles as filler in the solution under mixing, adding 13 g of sodium hydroxide under ISO 10426-2 mixing, pouring the suspension in HPHT cell. Sample B2 is then tested by measuring the thickening time with the HPHT consistometer.
- 15 ■ Sample C2 is made by dissolving the retarder amount in 422 g of sodium hydroxide solution, adding the blend comprising 440 g of type F fly ash and 88 g of sodium disilicate in the solution under mixing following ISO 10426-2 mixing,

pouring the suspension in HPHT cell. Sample C2 is then tested by measuring the thickening time with the HPHT consistometer.

- Sample D2 is made by dissolving the retarder amount in 374 mL of water, adding the blend comprising 411 g of type F fly ash and 82 g of sodium disilicate under mixing at 4000 rpm, adding 75 g of sodium hydroxide under ISO 10426-2 mixing, pouring the suspension in HPHT cell. Sample D2 is then tested by measuring the thickening time with the HPHT consistometer.

[0038] The retardation of geopolymeric formulations can be and is controlled at different BHCT by using either boron containing compounds as for example sodium pentaborate decahydrate, boric acid, borax, or lignosulphonate, or phosphorus containing compounds, or a mixture of them. Retardation of geopolymeric formulations will be sensitive to boron valence for boron containing compounds or phosphate valence for phosphorus containing compounds and/or to retarder concentration.

[0039] In table 3, the results obtained with Vicat apparatus with two boron-based retarders are presented. Vicat apparatus allows to measure when the setting of the material starts (IST) and ends (FST). It is based on the measurements of the penetration of a needle in a soft material. This apparatus is often used to realize pre-study at ambient temperature and atmospheric pressure.

Sample	A3	B3
No additive	1:45	12:00
Na ₂ B ₁₀ O ₁₆ 10H ₂ O		
2.6 %bwob	3:00	-
5.2 %bwob	4:10	>500:00
Borax		
4.2 %bwob	3:20	-

Table 3: Examples of initial setting time (hours:min) obtained with different retarders with Vicat apparatus at ambient temperature and atmospheric pressure.

- Sample A3 is made by dissolving the retarder amount in 139 g of sodium hydroxide solution, adding the blend comprising 105 g of metakaolin, 48 g of sodium metasilicate and 17 g of silica particles as filler in the solution under

mixing. Sample A3 is then tested by pouring the suspension in a Vicat cell to measure setting time at 25°C.

- Sample B3 is made by dissolving the retarder amount in 358 g of water, adding the blend comprising 314 g of metakaolin and 227 g of sodium disilicate in the solution under mixing, adding 17.2 g of sodium hydroxide under ISO 10426-2 mixing. Sample B3 is then tested by pouring the suspension in a Vicat cell to measure setting time at 25°C.

[0040] Retardation of geopolymeric formulations is sensitive to temperature. However, two boron-based retarders (sodium pentaborate decahydrate and borax) are able to strongly retard different types of geopolymer suspensions even at 25°C.

[0041] Figure 1 illustrates the impact of temperature on the thickening time for a geopolymer composition made by adding a blend comprising 411 g of type F fly ash and 82 g of sodium disilicate in 374 mL of water under mixing (retarder being predissolved in this water) and by adding 36.5 g of sodium hydroxide under ISO 10426-2 mixing. This way, retarders are efficient even at high temperature to control geopolymer suspension thickening time.

[0042] Control of the thickening time can also be realized by other means. As an example the nature of the alkali activator and its pH have an impact on the thickening time. Table 4 illustrates the influence of the alkali activator on the thickening time of geopolymeric suspensions. It demonstrates the ability to select the alkali activator source according to the downhole conditions.

Sample	A4	B4
100 Bc	0:53	>31:00

Table 4: Examples of ISO 10426-2 thickening time measured with HPHT consistometer (hours:min) with different alkali activators measured at 85°C.

- Sample A4 is made by adding the blend comprising 314 g of metakaolin and 227 g of sodium disilicate in 358 g of water under mixing, adding 17.2 g of sodium hydroxide under ISO10426-2 mixing, pouring the suspension in HPHT

cell. Sample A4 is then tested by measuring the thickening time with a HPHT consistometer.

- Sample B4 is made by adding the blend comprising 314 g of metakaolin and 227 g of sodium disilicate in 357 g of water under mixing, adding 23.4 g of sodium bicarbonate under ISO 10426-2 mixing, pouring the suspension in HPHT cell. Sample A4 is then tested by measuring the thickening time with a HPHT consistometer.

[0043] Control of the thickening and setting times by these methods of retardation can also be efficiently done with geopolymer having different silicon versus aluminum ratio.

[0044] Furthermore, depending on properties of the geopolymer, it can be suitable to accelerate thickening of the suspension. Table 5 illustrates the accelerating effect of lithium compounds on the thickening time of geopolymeric suspensions at temperature of 85°C. It demonstrates the ability of using lithium salts to control the thickening time of geopolymer suspensions.

Sample	A5	B5
No additive	22:57	5:21
LiCl		
3.5 %bwob	9:07	-
7 %bwob	4:07	
LiOH, H ₂ O		
2 %bwob	-	3:19

Table 5: Examples of ISO 10426-2 thickening time measured with HPHT consistometer (hours:min) obtained with typ eF fly ashes and accelerators.

- Sample A5 is made by adding the blend comprising 480 g of superfine typer F fly ash and 96 g of sodium disilicate in 406 g of the sodium hydroxide solution containing an accelerator following ISO 10426-2 mixing, pouring the suspension in HPHT cell. Sample A5 is then tested by measuring the thickening time with a HPHT consistometer.

- Sample B5 is made by adding the blend comprising 442 g of standard type F fly ash and 88 g of sodium disilicate in 423 g of the sodium hydroxide solution containing an accelerator following ISO 10426-2 mixing, pouring the suspension in HPHT cell. Sample B5 is then tested by measuring the thickening time with a HPHT consistometer.

[0045] Figure 2 illustrates the accelerating effect of lithium compounds on the thickening time for a geopolymer composition made by adding the blend comprising 480 g of superfine type F fly ash and 96 g of sodium disilicate in 406 g of the sodium hydroxide solution containing the accelerator following ISO 10426-2 mixing. The thickening time versus time of the suspension is then measured at temperature of 85°C. This way, accelerators such as lithium salts are shown to efficiently decrease the thickening time of geopolymer suspensions. The degree of acceleration of geopolymeric formulations is sensitive to accelerator type and/or concentration.

[0046] Depending on the properties of the geopolymer and on properties of the well, a real control of the thickening time of the suspension can be established. To increase the thickening time, nature of the retarder used can be changed, concentration of the retarder can be increased, nature of the alkali activator used can be changed, and nature of the aluminosilicate used can be changed.

[0047] Further, when use for dioxide carbon storage reservoir or injection well is sought, the geopolymer suspension has to be pumpable. Table 6 hereunder illustrates the rheological properties of geopolymer suspensions measured at a bottom hole circulating temperature (BHCT) of 60°C. Rheological values demonstrate the pumpability and the stability of geopolymeric suspensions for application in the oilfield industry.

Sample	A6	B6	C6
PV/TY after mixing	49/10	62/4	105/7
ISO 10426-2 PV/TY at BHCT cP/lbf/100ft ₂	48/7	53/2	85/7
ISO 10426-2 free fluid (mL)	0	0	0

Table 6: ISO 10426-2 Rheological and stability measurements obtained with different examples.

- 5 ▪ Sample A6 is made by adding the blend comprising 411 g of type F fly ash and 82 g of sodium disilicate in 374 mL of water under mixing, adding 75 g of sodium hydroxide under mixing. Sample A6 is then tested by measuring the rheological properties of the suspension after mixing and after conditioning at 60°C according to the ISO 1026-2 standard procedure.
- 10 ▪ Sample B6 is made by dissolving the 0.65 %bwob of sodiumpentaborate decahydrate in 422 g of sodium hydroxide solution, adding the blend comprising 440 g of type F fly ash and 88 g of sodium disilicate in the solution under ISO 10426-2 mixing, adding 36.5 g of sodium hydroxide under mixing. Sample B6 is then tested by measuring the rheological properties of the geopolymer suspension after mixing and after conditioning at 60°C according to the ISO 10426-2 standard procedure.
- 15 ▪ Sample C6 is made by adding the blend comprising 480 g of type F fly ash and 96 g of sodium disilicate in 406 g of the sodium hydroxide solution following ISO 10426-2 mixing conditions. Sample C6 is then tested by measuring the rheological properties of the suspension after mixing and after conditioning at 60°C according to the ISO 1-0426-2 standard procedure.

[0048] Also, when use for dioxide carbon storage reservoir or injection well is sought, the geopolymer suspension has to have a large range of densities. As presented in table 7, the tested geopolymer formulations propose a density range between 1.45 g/cm³ [12.1 lbm/gal] up to 1.84 g/cm³ [15.4 lbm/gal] either in reducing the water content, or in adding fillers.

Sample	A7	B7
Suspension density g/cm ³ (lbm/gal)	1.84 (15.4)	1.44 (12.06)

Table 7: Examples of suspension density obtained with some geopolymeric formulations.

- 25 ▪ Sample A7 is made by dissolving the retarder amount in 265 g of water, adding the blend comprising 232 g of metakaolin, 168 g of sodium disilicate and 414 g of

silica particles as filler in the solution under mixing, adding 13 g of sodium hydroxide under ISO 10426-2 mixing.

- Sample B7 is made by dissolving the retarder amount in 139 g of sodium hydroxide solution, adding the blend comprising 105 g of metakaolin, 48 g of sodium metasilicate and 17 g of silica particles as filler in the solution under mixing.

[0049] Further, to broaden the density range, either lightweight particles are added to reach lower densities or heavy particles to reach higher densities. The lightweight particles typically have density of less than 2 g/cm^3 , and generally less than 1.3 g/cm^3 . By way of example, it is possible to use hollow microspheres, in particular of silico-aluminate, known as cenospheres, a residue that is obtained from burning coal and having a mean diameter of about 150 micrometers. It is also possible to use synthetic materials such as hollow glass bubbles, and more particularly preferred are bubbles of sodium-calcium-borosilicate glass presenting high compression strength or indeed microspheres of a ceramic, e.g. of the silica-alumina type. The lightweight particles can also be particles of a plastics material such as beads of polypropylene. The heavy particles typically have density of more than 2 g/cm^3 , and generally more than 3 g/cm^3 . By way of example, it is possible to use hematite, barite, ilmenite, silica and also manganese tetroxide commercially available under the trade names of MicroMax™ and MicroMax FF.

[0050] Further, to broaden the density range, it is possible to foam the geopolymer composition. The gas utilized to foam the composition can be air or nitrogen, nitrogen being the most preferred. The amount of gas present in the cement composition is that amount which is sufficient to form a foam having a density in the range of from about 1 g.cm^{-3} to 1.7 g.cm^{-3} (9 to 14 lbm/gal).

[0051] In a further embodiment, other additives can be used with the geopolymer according to the present invention. Additives known to those of ordinary skill in the art may be included in the geopolymer compositions of the present embodiments. Additives are typically blended with a base mix or may be added to the geopolymer suspension. An additive may comprise an activator, an antifoam, a defoamer, silica, a fluid loss control

additive, a flow enhancing agent, a dispersant, an anti-settling additive or a combination thereof, for example. Selection of the type and amount of additive largely depends on the nature and composition of the set composition, and those of ordinary skill in the art will understand how to select a suitable type and amount of additive for compositions herein.

5 [0052] In another embodiment, when various components are used with or within the geopolymer formulation, the particle size of the components is selected and the respective proportion of particles fractions is optimized in order to have at the same time the highest Packing Volume Fraction (PVF) of the solid, and obtaining a mixable and pumpable slurry with the minimum amount of water, i.e., at slurry Solid Volume Fraction
10 (SVF) of 35-75% and preferably of 50-60%. More details can be found in European patent EP 0 621 247. The following examples do not constitute a limit of the invention but rather indicate to those skilled in the art possible combinations of the particle size of the various components of the geopolymer compositions of the invention to make a stable and pumpable suspension.

15 [0053] The geopolymeric composition can be a "trimodal" combination of particles: "large" for example sand or crushed wastes (average dimension 100-1000 micrometers), "medium" for example materials of the type of glass beads or fillers (average dimension 10-100 micrometers), "fines" like for example a micromaterial, or micro fly ashes or other micro slags (average dimension 0.2-10 micrometers). The geopolymeric
20 composition can also be a "tetramodal" combination of particles type: with "large" (average dimension about 200-350 micrometers), "medium" glass beads, or fillers (average dimension about 10 - 20 micrometers), "fine" (average dimension about 1 micrometer), "very fine" (average dimension about 0.1 - 0.15 micrometer). The geopolymeric composition can also be a further combinations between the further
25 categories: "very large", for example glass maker sand, crushed wastes (average dimension superior to 1 millimeter) and/or "large", for example sand or crushed wastes (average dimension about 100-1000 micrometers) and/or "medium" like glass beads, or fillers, or crushed wastes (average dimension 10-100 micrometers) and "fine" like, for example, micro fly ashes or other micro slags (average dimension 0.2-10 micrometer)
30 and/or "very fine" like, for example, a latex or pigments or polymer microgels like a

usual fluid loss control agent (average dimension 0.05-0.5 micrometer) and/or “ultra fine” like some colloidal silica or alumina (average dimension 7-50 nanometers).

Test on durability of CO₂ resistant geopolymer

[0054] Actually, there is no relevant test for durability of material intended for use in CO₂ injection wells in supercritical CO₂ conditions. For example, patent US 6,332,921 discloses a test for CO₂ durability: API Class G Portland Cement is mixed with 40% silica flour and water to form a cement slurry. The slurry is allowed to set for 24 hours at a temperature of 88° C (190° F). Thereafter, the set cement is placed in an aqueous 4% by weight sodium carbonate solution for 28 days at 315° C (600° F). However, this test has a major drawback, the solution contains only 4% of sodium carbonate (Na₂CO₃ or NaHCO₃). Effectively, this environment is less severe than CO₂ fluids met in CO₂ injection wells.

[0055] Therefore, a new test for CO₂ durability has been implemented. After mixing of geopolymeric composition is completed; the suspension is placed into cubic moulds and cured 3 days at 90° C (194° F). Then the cubic moulds are cored into cylinders (2.5 cm radius, 5 cm length) which are placed into a wet CO₂ supercritical vessel for degradation test during 15 days at 90° C (194° F) under 28 MPa (4 kPSI) of fluid pressure composed of 90 % by weight of CO₂ and 10 % by weight of water. Test conditions are always monitored to maintain CO₂ in supercritical state. Figure 1 is a schematic view of the CO₂ supercritical vessel. Two cores crowns, one at the bottom (1B), one at the middle (1A) of the reactor are isolated by viton slice or slices (15). The two cores crowns allow testing CO₂ resistance to two types of fluid, a first fluid (11) composed by CO₂ supercritical phase saturated by water, and a second fluid (10) composed by water phase saturated by CO₂.

[0056] The here mentioned test will be used below to test the CO₂ resistant geopolymer and will be called the test for CO₂ durability **Test 1** made in the first fluid and **Test 2** made in the second fluid.

[0057] The compressive mechanical properties were measured for the CO₂ resistant geopolymer compositions. The mechanical properties of the set geopolymer was studied using systems which had passed several days under high pressure and temperature.

Sample A8	Compressive Strength (CS) Mpa	Corrected Young modulus MPa
Before CO ₂ attack after 7 days of curing at 90°C/20.7MPa (3 kPSI)	14	2100
Before CO ₂ attack after 21 days of curing at 90deg.C/20.7MPa (3 kPSI)	18	1750
After 15 days of CO ₂ attack at 90°C/28MPa (4 kPSI)		
Test 1	14.5	1200
Test 2	12.3	1250

Table 8: Mechanical properties measured after 15 days in CO₂ fluids at 90°C – 27.6MPa (4000 PSI)

- 5 ▪ Sample A8 is made by dissolving the retarder amount (1.8 % bwob of sodium pentaborate decahydrated) in 358g of water, adding the blend comprising 314 g of metakaolin and 227 g of sodium disilicate in the solution under mixing, adding 17,2 g of sodium hydroxyde under API mixing, pouring the suspension in a curing chamber for 7 or 21 days at 90°C – 20.7MPa (3000 PSI), according to API
10 procedure. Samples cured 7 days are then tested 15 days in CO₂ fluids at 90°C under 28MPa (4000 PSI).

[0058] In conclusion, the mechanical properties of the set geopolymer are excellent in CO₂ supercritical phase or in water phase saturated by CO₂. Study of pictures of the set geopolymeric on SEM or AFM shows that there is no or practically no degradation of the
15 geopolymeric matrix in CO₂ supercritical phase or in water phase saturated by CO₂ (data not shown). The geopolymeric compositions of the invention can be used in long term application for dioxide carbon storage reservoir or injection well.

Applications of the CO₂ resistant geopolymer

[0059] As mentioned above, for wells containing carbon dioxide such as CO₂ injection wells generally require the use of well material compositions which do not deteriorate in the presence of carbon dioxide containing brines. The static bottom hole temperature for these wells is below 93° C (200° F). The geopolymeric compositions according to the invention have this property to be totally inert to all CO₂ environments and especially to supercritical CO₂ environments.

[0060] So, the methods of the present invention are useful in completing wells exposed to any significant carbon dioxide, such as for example CO₂ injection or production wells for storage, with concentrations of carbon dioxide dissolved in water up to 90% per weight. Placement of the geopolymeric composition in the portion of the wellbore to be completed is accomplished by means that are well known in the art of wellbore cementing. The geopolymer composition is typically placed in a wellbore surrounding a casing to prevent vertical communication through the annulus between the casing and the wellbore or the casing and a larger casing. The geopolymer suspension is typically placed in a wellbore by circulation of the suspension down the inside of the casing, followed by a wiper plug and a nonsetting displacement fluid. The wiper plug is usually displaced to a collar, located near the bottom of the casing. The collar catches the wiper plug to prevent overdisplacement of the geopolymer composition and also minimizes the amount of the geopolymer composition left in the casing. The geopolymer suspension is circulated up the annulus surrounding the casing, where it is allowed to harden. The annulus could be between the casing and a larger casing or could be between the casing and the borehole. As in regular well cementing operations, such cementing operation with a geopolymer suspension may cover only a portion of the open hole, or more typically up to inside the next larger casing or sometimes up to surface. This method has been described for completion between formation and a casing, but can be used in any type of completion, for example with a liner, a slotted liner, a perforated tubular, an expandable tubular, a permeable tube and/or tube or tubing.

[0061] In the same way, the methods of the present invention are useful in completing wells exposed to any significant carbon dioxide, wherein placement of the geopolymeric composition in the portion of the wellbore to be completed is accomplished

by means that are well known in the art of wellbore reverse circulation cementing technique.

[0062] The CO₂ resistant geopolymer can also be used in squeeze job and/or in remedial job. The geopolymer material is forced through perforations or openings in the casing, whether these perforations or openings are made intentionally or not, to the formation and wellbore surrounding the casing to be repaired. Geopolymer material is placed in this manner to repair and seal poorly isolated wells, for example, when either the original cement or geopolymer material fails, or was not initially placed acceptably, or when a producing interval has to be shut off.

[0063] The CO₂ resistant geopolymer can also be used in abandonment and/or plugging job. The geopolymer material is used as a plug to shut off partially or totally a zone of the well. Geopolymer material plug is placed inside the well by means that are well known in the art of wellbore plug cementing.

[0064] The CO₂ resistant geopolymer can also be used in grouting job to complete a part of the annulus as described in Well Cementing from Erik B. Nelson. The geopolymer material is used to complete down this annulus. Geopolymer material is placed inside the well by means that are well known in the art of wellbore cementing.

[0065] The CO₂ resistant geopolymer can also be used for fast-setting operation, in-situ operation. Effectively, the geopolymer composition can have a setting time perfectly controlled, allowing an instant setting when desired. For example, a retarder/accelerator combination can be added to the geopolymeric composition to cause the system to be retarded for an extended period of time and then to set upon addition of an accelerator.

[0066] The CO₂ resistant geopolymer can also be a storable composition. As such, the suspension is over-retarder and is left intentionally in liquid phase. Said suspension is so, able to be stored and utilized in the well when needed.

[0067] According to other embodiments of the invention, the methods of completion described above can be used in combination with conventional cement completion.

Examples - CO₂ resistant geopolymer

[0068] The following examples will illustrate the practice of the present invention in its preferred embodiments.

Example 1

- 5 [0069] Geopolymeric composition is made in the amounts by weight of the total dry components as follows: 58.1% metakaolin and 41.9% sodium disilicate. Dry components are mixed with the appropriate amount of water, sodium hydroxide and additives. The specific gravity of the suspension is 1.53 g/cm³ (12.80 lbm/gal). The geopolymer has the following oxide molar ratios:

10 SiO₂/Al₂O₃=4.00

 Na₂O/SiO₂=0.27

 Na₂O/Al₂O₃=1.07

 H₂O/Na₂O=17.15

Example 2

- 15 [0070] Geopolymer composition is made in the amounts by weight of the total dry components as follows: 28.5% metakaolin, 20.6% sodium disilicate and 50.9% of a blend of silica particles. Dry components are mixed with the appropriate amount of water, sodium hydroxide and additives. The specific gravity of the suspension is 1.84 g/cm³ (15.40 lbm/gal). The geopolymer matrix has the following oxide molar ratios:

20 SiO₂/Al₂O₃=4.00

 Na₂O/SiO₂=0.27

 Na₂O/Al₂O₃=1.07

 H₂O/Na₂O=17.15

Example 3

[0071] Geopolymer composition is made in the amounts by weight of the total dry components as follows: 35.2% metakaolin and 64.2% potassium disilicate. Dry components are mixed with the appropriate amount of water, potassium hydroxide and
 5 additives. The specific gravity of the suspension is 1.78 g/cm³ (14.91 lbm/gal). The geopolymer matrix has the following oxide molar ratios:

$$\text{SiO}_2/\text{Al}_2\text{O}_3=4.00$$

$$\text{K}_2\text{O}/\text{SiO}_2=0.27$$

$$\text{K}_2\text{O}/\text{Al}_2\text{O}_3=1.07$$

$$10 \quad \text{H}_2\text{O}/\text{K}_2\text{O}=17.46$$

Example 4

[0072] Geopolymer composition is made in the amounts by weight of the total dry components as follows: 83.3% standard fly ash type F and 16.7% sodium disilicate. Dry components are mixed with the appropriate amount of water, sodium hydroxide and
 15 additives. The specific gravity of the suspension is 1.66 g/cm³ (13.83 lbm/gal). The geopolymer has the following oxide molar ratios:

$$\text{SiO}_2/\text{Al}_2\text{O}_3=5.60$$

$$\text{Na}_2\text{O}/\text{SiO}_2=0.3$$

$$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3=1.08$$

$$20 \quad \text{H}_2\text{O}/\text{Na}_2\text{O}=13.01$$

Claims

1. A geopolymeric composition for use in presence of carbon dioxide, resistant to carbon dioxide and formed from a suspension, comprising:

- an aluminosilicate source,
 - a carrier fluid,
 - an activator comprising a metal silicate, a metal aluminate, an alkali activator, or a combination thereof, and
 - a retarder able to retard the thickening and/or the setting times of the suspension and/or an accelerator able to accelerate the thickening and/or the setting times of the suspension,
- wherein the metal is an alkali metal and the oxide molar ratio M_2O/SiO_2 is greater than 0.20
wherein M is the metal.

2. The geopolymeric composition of claim 1, wherein the oxide molar ratio M_2O/SiO_2 is greater than or equal to 0.27.

3. The geopolymeric composition according to any one of claims 1 to 2, wherein the retarder is a boron containing compound and wherein the suspension of said geopolymeric composition has an oxide molar ratio B_2O_3/H_2O of less than 0.03.

4. The geopolymeric composition of claim 3, wherein the oxide molar ratio B_2O_3/H_2O is less than or equal to 0.02.

5. The geopolymeric composition according to any one of claims 1 to 4, wherein the retarder is efficient from 20°C to 120°C.

6. The geopolymeric composition according to any one of claims 1 to 5, wherein the accelerator is an alkali metal containing compound.

7. The geopolymeric composition of claim 6, wherein the accelerator is an lithium containing compound.

8. The geopolymeric composition according to any one of claims 1 to 7, wherein the accelerator is efficient from 20°C to 120°C.

9. The geopolymeric composition according to any one of claims 1 to 8, wherein the aluminosilicate source is selected from type C fly ash, type F fly ash, ground blast furnace slag, calcined clays, partially calcined clays, aluminium-containing silica fume, natural aluminosilicate as kaolin, synthetic aluminosilicate glass powder, zeolite, scoria, allophone, bentonite and pumice.
10. The geopolymeric composition according to any one of claims 1 to 9, wherein the geopolymeric composition is in majority a poly(sialate-siloxo) geopolymer.
11. The geopolymeric composition according to any one of claims 1 to 10, wherein the silicon on aluminum atomic ratio is between 1.8 and 2.2.
12. The geopolymeric composition according to any one of claims 1 to 11, wherein the metal is selected from lithium, sodium, potassium, rubidium, and cesium.
13. The geopolymeric composition according to any one of claims 1 to 12, wherein the alkali activator is an alkali metal hydroxide.
14. The geopolymeric composition according to any one of claims 1 to 13, wherein the alkali activator and/or the carrier fluid is encapsulated.
15. The geopolymeric composition according to any one of claims 1 to 14, wherein the metal silicate and/or the carrier fluid is encapsulated.
16. The geopolymeric composition according to any one of claims 1 to 15, wherein the geopolymeric composition is resistant to supercritical carbon dioxide.
17. The geopolymeric composition according to any one of claims 1 to 16, wherein the geopolymeric composition is resistant further to acid gas.
18. A method to place a geopolymeric composition in a part of a borehole in presence with carbon dioxide, the method comprising:
 - (i) providing a suspension according to any one of claims 1 to 16,
 - (ii) pumping the suspension into the part of the borehole, and

(iii) allowing the suspension to set and thereby form the geopolymeric composition into said part of the borehole.

19. The method of claim 18, wherein the step of allowing the suspension to set is made in presence with carbon dioxide.

20. The method of claim 18 or 19, further comprising the step of exposing the geopolymeric composition to carbon dioxide.

21. The method according to any one of claims 18 to 20, wherein the carbon dioxide is in supercritical state.

22. The method according to any one of claims 18 to 21, wherein the step of pumping the suspension is made with conventional tools of wellbore cementing.

23. The method according to any one of claims 18 to 22, wherein the method applies to placement of the geopolymeric composition in an annular space between a casing and the borehole.

24. The method according to any one of claims 18 to 23, wherein the method applies to the placement of the geopolymeric composition through a hole made in a casing.

25. The method according to any one of claims 18 to 24, wherein the method applies to the placement of the geopolymeric composition to plug a zone of the borehole.

26. A geopolymeric composition for use in presence of carbon dioxide and resistant to carbon dioxide formed from a suspension comprising an aluminosilicate source, a metal silicate, an alkali activator, a retarder and/or an accelerator and a carrier fluid wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal, wherein the suspension has a viscosity lesser than or equal to 300 cP.

27. The geopolymeric composition of claim 26, wherein the oxide molar ratio M_2O/SiO_2 is greater than or equal to 0.27.

28. The geopolymeric composition of claim 26, wherein the retarder is a boron containing

compound and wherein the suspension of said geopolymeric composition has an oxide molar ratio B_2O_3/H_2O of less than 0.03.

29. The geopolymeric composition of claim 28, wherein the oxide molar ratio B_2O_3/H_2O is less than or equal to 0.02.

30. The geopolymeric composition of claim 26, wherein the retarder is efficient from 20°C to 120°C.

31. The geopolymeric composition of claim 26, wherein the accelerator is a lithium containing compound.

32. The geopolymeric composition of claim 26, wherein the accelerator is efficient from 20°C to 120°C.

33. The geopolymeric composition of claim 26, wherein the aluminosilicate source is selected from type C fly ash, type F fly ash, ground blast furnace slag, calcined clays, partially calcined clays, aluminium-containing silica fume, natural aluminosilicate, synthetic aluminosilicate glass powder, zeolite, scoria, allophone, bentonite and pumice.

34. The geopolymeric composition of claim 26, wherein the geopolymeric composition is in majority a polysialate-siloxo geopolymer.

35. The geopolymeric composition of claim 34, wherein the silicon on aluminum atomic ratio is between 1.8 and 2.2.

36. The geopolymeric composition of claim 26, wherein the metal is selected from lithium, sodium, potassium, rubidium, and cesium.

37. The geopolymeric composition of claim 26, wherein the alkali activator is an alkali metal hydroxide.

38. The geopolymeric composition of claim 26, wherein the alkali activator and/or the carrier fluid is encapsulated.
39. The geopolymeric composition of claim 26, wherein the metal silicate and/or the carrier fluid is encapsulated.
40. The geopolymeric composition of claim 26, wherein the geopolymeric composition is resistant to supercritical carbon dioxide.
41. The geopolymeric composition of claim 26, wherein the geopolymeric composition is resistant further to acid gas.
42. A geopolymeric composition for use in presence of carbon dioxide and resistant to carbon dioxide formed from a suspension within water comprising an aluminosilicate source, a metal silicate, an alkali activator, and a retarder and/or an accelerator wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal, wherein the suspension has a viscosity lesser than or equal to 300 cP.
43. The geopolymeric composition of claim 42, wherein the retarder is a boron containing compound.
44. The geopolymeric composition of claim 42, wherein the accelerator is a lithium containing compound.
45. The geopolymeric composition of claim 42, wherein the aluminosilicate source is selected from type C fly ash, type F fly ash, ground blast furnace slag, calcined clays, partially calcined clays, aluminium-containing silica fume, natural aluminosilicate, synthetic aluminosilicate glass powder, zeolite, scoria, allophone, bentonite and pumice.
46. The geopolymeric composition of claim 42, wherein the geopolymeric composition is in

majority a poly(sialate-siloxo) geopolymer.

47. The geopolymeric composition of claim 46, wherein the silicon on aluminum atomic ratio is between 1.8 and 2.2.

48. The geopolymeric composition of claim 42, wherein the metal is selected from lithium, sodium, potassium, rubidium, and cesium.

49. The geopolymeric composition of claim 42, wherein the alkali activator is an alkali metal hydroxide.

50. The geopolymeric composition of claim 42, wherein the alkali activator and/or the alkali activator within water is encapsulated.

51. The geopolymeric composition of claim 42, wherein the metal silicate and/or the metal silicate within water is encapsulated.

52. A geopolymeric composition resistant to carbon dioxide formed from a suspension within water comprising an aluminosilicate source, a metal silicate, an alkali activator, and a retarder and/or an accelerator wherein the geopolymeric composition is in majority a poly(sialate-siloxo) geopolymer and wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal, wherein the suspension has a viscosity lesser than or equal to 300 cP.

53. The geopolymeric composition of claim 52, wherein the retarder is a boron containing compound.

54. The geopolymeric composition of claim 53, wherein the retarder is efficient from 20°C to 120°C.

55. The geopolymeric composition of claim 52, wherein the accelerator is a lithium containing compound.

56. The geopolymeric composition of claim 55, wherein the accelerator is efficient from 20°C to 120°C.

57. The geopolymeric composition of claim 52, wherein the metal is selected from lithium, sodium, potassium, rubidium, and cesium.

58. The geopolymeric composition of claim 52, wherein the alkali activator is an alkali metal hydroxide.

59. A method to place a geopolymeric composition in a part of a borehole in presence with carbon dioxide, the method comprising:

(i) providing a suspension comprising an aluminosilicate source, a metal silicate, an alkali activator, a retarder and/or an accelerator and a carrier fluid wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal,

(ii) pumping the suspension into the part of the borehole, and

(iii) allowing the suspension to set and thereby form the geopolymeric composition into said part of the borehole

wherein the suspension has a viscosity lesser than or equal to 300 cP.

60. The method of claim 59, wherein the step of allowing the suspension to set is made in presence with carbon dioxide.

61. The method of claim 59, wherein the carbon dioxide is in supercritical state.

62. The method of claim 59, wherein the step of pumping the suspension is made with conventional tools of wellbore cementing.

63. The method of claim 59, wherein the method applies to placement of the geopolymeric

composition in an annular space between a casing and the borehole.

64. The method of claim 59, wherein the method applies to the placement of the geopolymeric composition through a hole made in a casing.

65. The method of claim 59, wherein the method applies to the placement of the geopolymeric composition to plug a zone of the borehole.

66. A method to place a geopolymeric composition in a part of a borehole in presence with carbon dioxide, the method comprising:

(i) providing a suspension comprising an aluminosilicate source, a metal silicate, an alkali activator, a retarder and/or an accelerator and a carrier fluid wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal,

(ii) pumping the suspension into the part of the borehole,

(iii) allowing the suspension to set and thereby form the geopolymeric composition into said part of the borehole, and

(iv) exposing the geopolymeric composition to carbon dioxide,

wherein the suspension has a viscosity lesser than or equal to 300 cP.

67. The method of claim 66, wherein the step of allowing the suspension to set is made in presence with carbon dioxide.

68. The method of claim 66, wherein the carbon dioxide is in supercritical state.

69. The method of claim 66, wherein the step of pumping the suspension is made with conventional tools of wellbore cementing.

70. The method of claim 66, wherein the method applies to placement of the geopolymeric

composition in an annular space between a casing and the borehole.

71. The method of claim 66, wherein the method applies to the placement of the geopolymeric composition through a hole made in a casing.

72. The method of claim 66, wherein the method applies to the placement of the geopolymeric composition to plug a zone of the borehole.

73. A method to place a geopolymeric composition in a part of a borehole in presence with carbon dioxide, the method comprising:

- (i) providing a suspension within water comprising an aluminosilicate source, a metal silicate, an alkali activator, and a retarder and/or an accelerator wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal,
- (ii) pumping the suspension into the part of the borehole, and
- (iii) allowing the suspension to set and thereby form the geopolymeric composition into said part of the borehole,

wherein the suspension has a viscosity lesser than or equal to 300 cP.

74. The method of claim 73, wherein the step of allowing the suspension to set is made in presence with carbon dioxide.

75. The method of claim 73, wherein the carbon dioxide is in supercritical state.

76. The method of claim 73, wherein the step of pumping the suspension is made with conventional tools of wellbore cementing.

77. The method of claim 73, wherein the method applies to placement of the geopolymeric composition in an annular space between a casing and the borehole.

78. The method of claim 73, wherein the method applies to the placement of the geopolymeric composition through a hole made in a casing.

79. The method of claim 73, wherein the method applies to the placement of the geopolymeric composition to plug a zone of the borehole.

80. A method to place a geopolymeric composition in a part of a borehole in presence with carbon dioxide, the method comprising:

(i) providing a suspension within water comprising an aluminosilicate source, a metal silicate, an alkali activator, and a retarder and/or an accelerator wherein the oxide molar ratio M_2O/SiO_2 is greater than 0.20 with M being an alkali metal,

(ii) pumping the suspension into the part of the borehole,

(iii) allowing the suspension to set and thereby form the geopolymeric composition into said part of the borehole, and

(iv) exposing the geopolymeric composition to carbon dioxide,

wherein the suspension has a viscosity lesser than or equal to 300 cP.

81. The method of claim 80, wherein the step of allowing the suspension to set is made in presence with carbon dioxide.

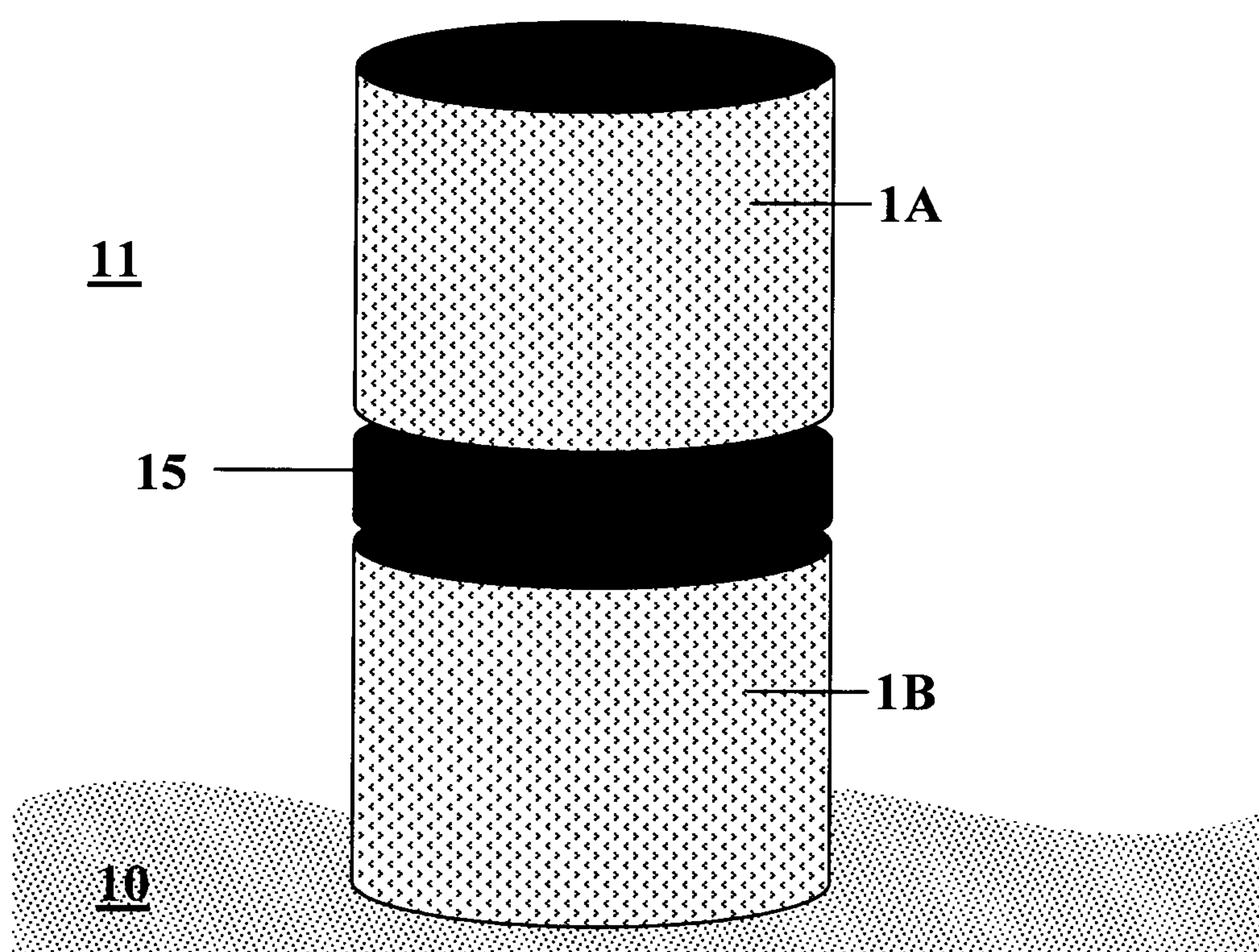
82. The method of claim 80, wherein the carbon dioxide is in supercritical state.

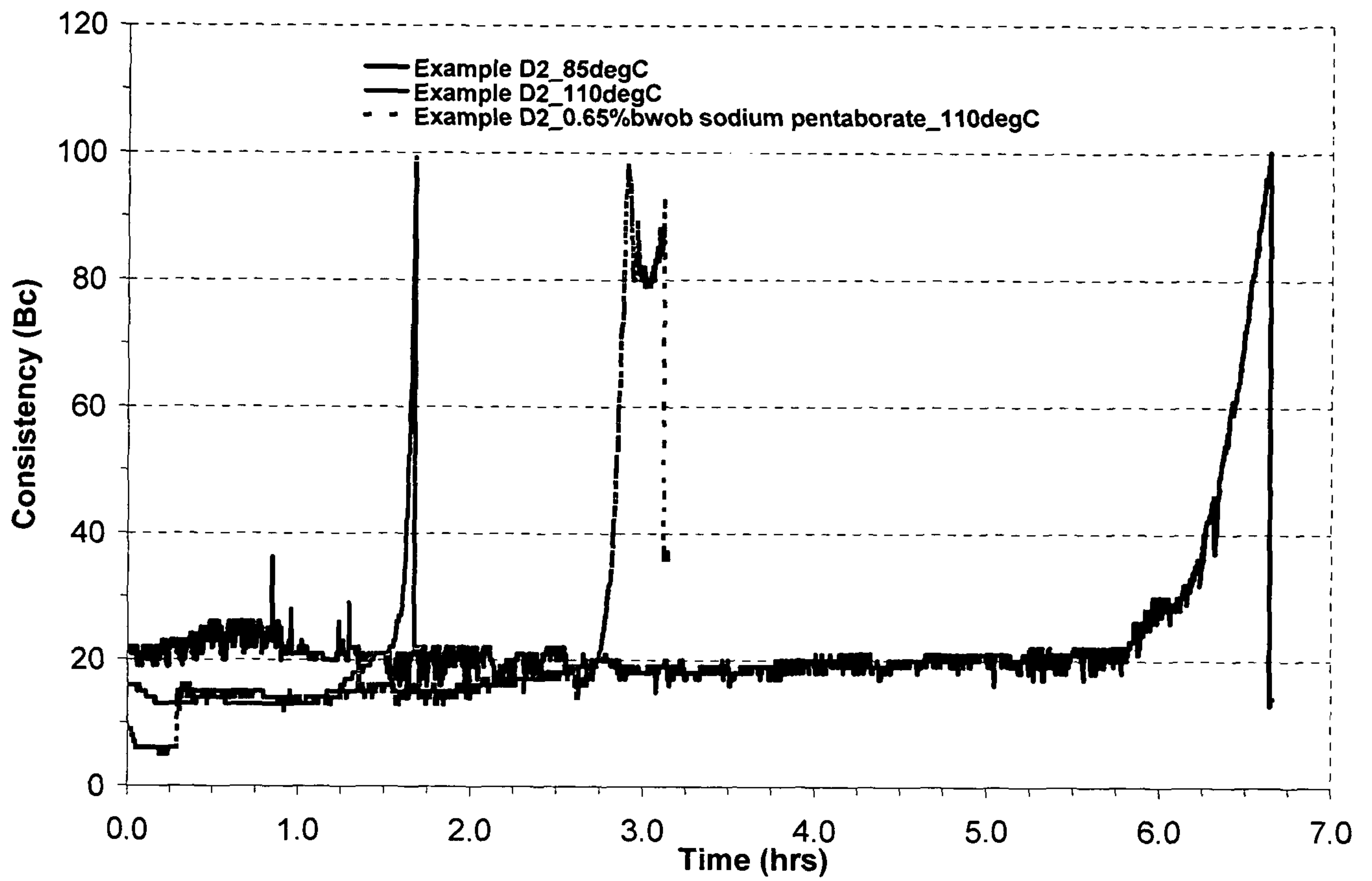
83. The method of claim 80, wherein the step of pumping the suspension is made with conventional tools of wellbore cementing.

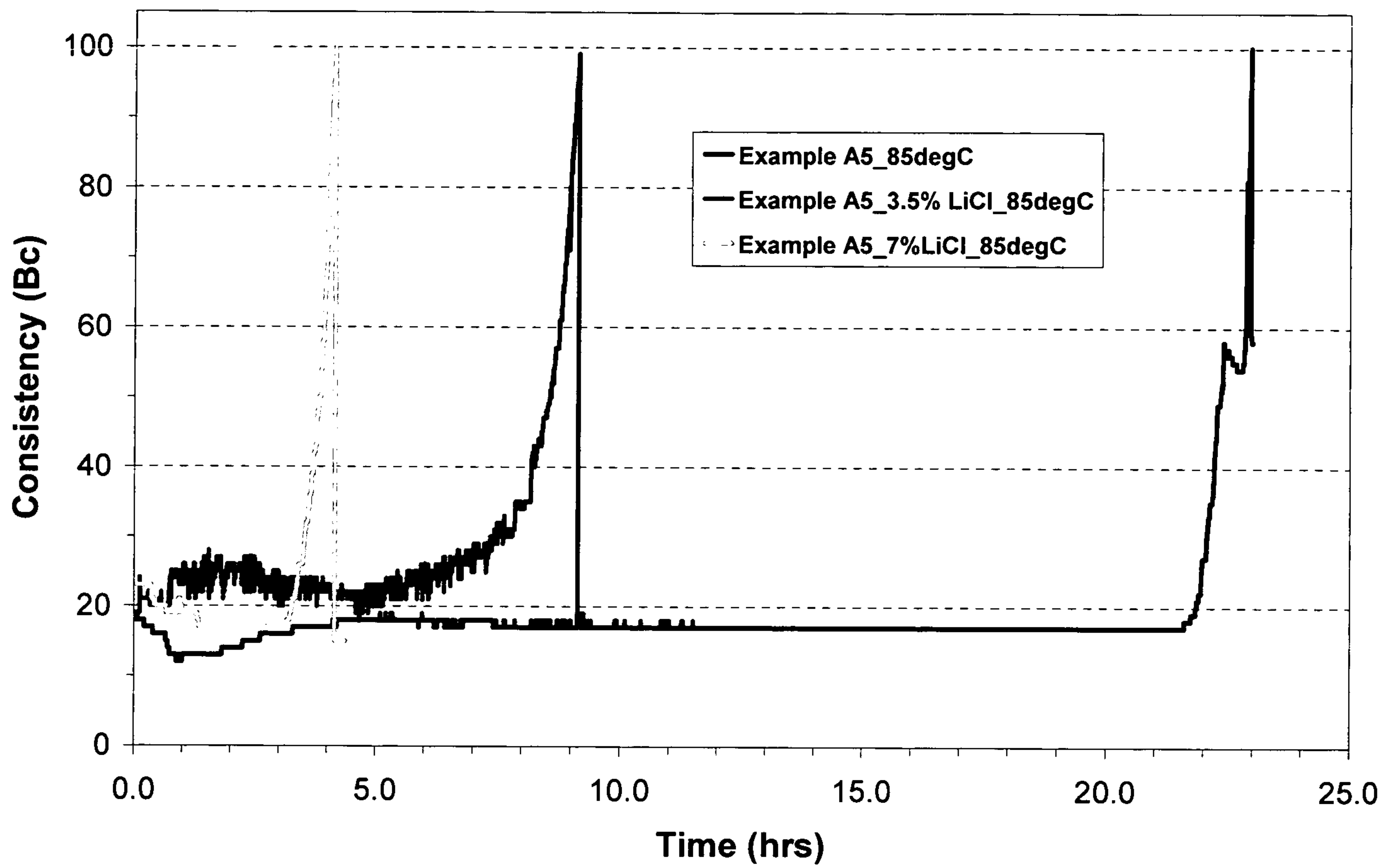
84. The method of claim 80, wherein the method applies to placement of the geopolymeric composition in an annular space between a casing and the borehole.

85. The method of claim 80, wherein the method applies to the placement of the geopolymeric composition through a hole made in a casing.

86. The method of claim 80, wherein the method applies to the placement of the geopolymeric composition to plug a zone of the borehole.

**FIGURE 1**

**FIGURE 2**

**FIGURE 3**